



Investigation of the hydrophobic recovery of various polymeric biomaterials after 172 nm UV treatment using contact angle, surface free energy and XPS measurements

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ABSTRACT

Surface modification as a route to improving the performance of polymeric biomaterials is an area of much topical interest. Ultraviolet (UV) light treatment has received much attention, but polymers so treated revert to their original surface condition over a period of time—an effect known as hydrophobic recovery. It is important to develop an understanding of the underlying processes contributing to the effect, since it has an impact on the applicability of UV treatment. In this work a number of polymeric biomaterials were surface-modified using 172 nm UV light from an excimer lamp. The modified polymers were characterised using contact angle, surface free energy (SFE) measurements and X-Ray Photoelectron Spectroscopy (XPS) techniques. The wettability, variation in surface free energy and chemical functionality changes were analysed on the surfaces immediately after UV treatment and subsequently over a period of 28 days. It was noted that hydrophobic recovery proceeds at a different rate for each polymer, is generally a two-phase process and that surfaces are still more hydrophilic after 28 days than the original untreated state. XPS analysis reveals that particular chemical configurations move from the surface at a faster rate than others which may contribute to the two-phase nature of the process.

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1. Introduction

Polymers are the largest class of biomaterials, with increased utilisation being driven by low cost and the ability to tailor the mechanical properties by means of adjusting composition, molecular weights, crosslinking, etc. [1]. The interaction of biomaterials with biological environments is the subject of much study, since the biocompatibility requirements of various materials differ depending on their specific application. If the device is designed for incorporation into the body tissue, it must allow for appropriate cell–substrate interactions. In contrast, if the biomaterial is not designed to be integrated into the body tissue, it must be bio-inert and cause minimal or no tissue response [2]. Since most polymers are chemically inert, polymer-based biomaterials

will typically need to be surface-modified if interaction with the in vivo environment is required. Previous work has made use of various surface modification techniques [3–5] to achieve the required increase in activity through increasing the surface free energy (SFE) of the polymer, and in turn, hydrophilicity [3]. Treatments that have been used to date to modify polymeric surface properties include plasma treatment [4,6,7] corona discharge treatments [5], and pressure glow discharge [8]. Laser and lamp methods have also been explored: polymers have been modified with excimer lasers [9–11], CO₂ and Nd:YAG lasers [10], ultraviolet (UV) lamps at 254 nm [12] and excimer UV lamps at 172 nm [3,13,14].

Hydrophobic recovery [15] is a phenomenon that is exhibited in many of the treatment methods listed above, whereby the water contact angle increases towards its original value after a period of time, with total recovery to the pre-treated state sometimes happening within a few hours [16]. This effect has an impact on the applicability of these techniques by determining the “shelf life” of the treatment. The exact natures of the mechanisms underlying hydrophobic recovery are not well understood.

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The use of UV lamp technology is interesting because it has the potential to be able to treat large areas on the substrate with a moderate light intensity [14] and to treat oddly shaped 3-D objects [17]. In principle, the cost of processing can be reduced in comparison to plasma treatment since high vacuum and the associated expensive apparatus is not necessary [14,18]. Of particular interest to this study are excimer lamps, which possess greater stability and extended lamp life compared to other UV lamps types [19]. The photon energy from the lamp used is high enough (>6.4 eV) to cause scission of covalent bonds at the surface. It creates high surface concentrations of energy rich species resulting in reactive groups and possible cross-linking between groups [1].

The materials chosen for this analysis include low-density polyethylene (LDPE), ultrahigh molecular weight polyethylene (UHMWPE), Sarlink, nylon 12 (N12) and polycaprolactone (PCL). These are important polymeric biomaterials and vary in their application. LDPE is used for tubing in catheters, UHMWPE is used for artificial joints, Sarlink has been proposed for use in total hip replacements [20], N12 is used as a suture material and PCL is used for bone and cartilage scaffolds. Two classes of polymers are represented in this selection: LDPE, UHMWPE and Sarlink are an example of polymers with non-polar characteristics and are therefore highly hydrophobic, while N12 and PCL are polar polymers due to the C–N and C–O groups present in their chemical structures. As such, we have included polymers which span a range of chemical characteristics and applications.

Contact angle measurements were used to determine wettability properties and to calculate the SFE properties of the various polymers [21]. XPS was used to complement SFE results by determining the type of chemical functional groups being added to the surface during UV treatment. We have sought to present additional SFE calculations and XPS measurements from materials during hydrophobic recovery to help further the understanding of the mechanisms of recovery.

2. Experimental

2.1. Materials

N12 (thickness 250 μm), UHMWPE (thickness 75 μm) and LDPE (thickness 1 mm) were obtained from Goodfellow Ltd., UK. These polymers were supplied in sheet and roll form and were cut into 1 cm \times 1 cm coupons for all experiments.

The biodegradable polymer PCL (10 kDa) was obtained from Sigma Aldrich Ireland Ltd. The PCL samples were prepared by dissolution in chloroform to form a 5% solution, which was then spin-coated onto a 5-inch silicon wafer (spin speed of 1000 rpm and spin time of 60 s). A film thickness of 4 μm was obtained. The PCL coated wafer was then diced into 2 cm \times 2 cm coupons.

SarlinkTM 3280, a product of DSM (NL), is a thermoplastic elastomer (TPE), and was supplied in injection moulded sheets (12 cm \times 12 cm). The exact composition of the TPE is a trade secret, but it is known that it consists of a rubber phase, the terpolymer ethylene-propylene-diene (EPDM; approximately 50%) dispersed in a polypropylene (PP; approximately 25%) matrix, with the third phase being a mineral oil (approximately 12%). The mineral oil is thought to be encapsulated within the material [22] and is not expected to contribute to surface behaviour. Coupons of 1 cm \times 1 cm were cut from the injection moulded sheets and dipped in hexane for 5 s to remove any mineral oil that may emerge as a result of cutting.

2.2. UV treatment (UV lamp and treatment details)

The polymers were cleaned ultrasonically in ethanol before UV treatment. The samples were then treated with a Heraeus

BlueLight 172 excimer lamp. The lamp is based on the Xe₂^{*} excited dimer which emits vacuum ultraviolet (VUV) light at a wavelength of 172 nm with a measured intensity of 21 mW cm⁻¹.

It is well known that the excimer lamp treatment utilised in this study creates active sites on the polymer surface to which chemical species from the surrounding air can attach, resulting in surface chemical modification [3]. It is also well established that 172 nm radiation is strongly absorbed by air. Okabe noted that 90% of the 172 nm radiation is absorbed within 8 mm of air at normal atmospheric pressure [23]. Since our apparatus features a minimum lamp-sample separation of 3 cm, we worked at reduced air pressure to increase the extinction length. We experimentally determined that 200 mbar was the optimum pressure to facilitate exposure of the surface by UV photons while maintaining sufficient air in the immediate vicinity of the surface to exhibit true “air” processing characteristics.

Experiments were also performed to determine the variation of water contact angle with exposure time. For all materials used in the study maximum wettability was achieved after 20 min of exposure to this lamp. This interval was therefore used for all experiments.

2.3. Contact angle and total surface free energy measurements

Static contact angles were measured using the sessile drop method [24]. This consisted of placing a 3 μl liquid drop on the polymeric surface using a microsyringe. The drop was viewed from the side using an imaging telescope and digital camera. Images were recorded approximately 30 s after depositing the drop. Imaging software with a calibrated field-of-view was used to measure the height and width of the base of the drop and the contact angle was determined using the relation $\tan(\theta/2) = 2h/w$, where θ is the contact angle, h is the height of the drop and w is the width of the base of the drop [25].

The Young equation is the most widely used method for determining the interaction energy between a liquid (L) and a solid (S) in an ambient atmosphere (V). When a liquid drop is placed on a solid, the energies of cohesion between the molecules of liquid and the forces of adhesion between the liquid and solid are related by [26]:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (1)$$

where the surface tension of the liquid–vapour interface is designated by γ_{LV} , contact angle is represented by θ and γ_{SV} and γ_{SL} are the solid surface–vapour tension and the solid–liquid tension, respectively. As the interactions with vapour are considered to be low, γ_{LV} is regarded as the liquid surface tension γ_L and γ_{SV} is regarded as γ_S , the SFE of the analysed solid [27].

Obtaining contact angles for a number of different fluids enables one to calculate the total SFE of a solid γ_S^{TOT} consisting of apolar and polar contributions using the van Oss–Chaudhury–Good (vOCG) approach [28]. According to van Oss and colleagues, non-covalent surface and interfacial interactions give rise to Lifshitz-van der Waals (LW) apolar component and electron donor/electron-acceptor (Lewis acid/base) (AB) polar component, which include hydrogen donor–hydrogen acceptors interactions. Therefore the total SFE of solids, γ_S^{TOT} , is the sum of the apolar, γ_S^{LW} , and polar, γ_S^{AB} , components [29]:

Van Oss expanded the Young equation to give Eq. (2):

$$(1 + \cos \theta) \gamma_L = 2(\sqrt{\gamma_S^{\text{LW}} \gamma_L^{\text{LW}}} + \sqrt{\gamma_S^+ \gamma_L^+} + \sqrt{\gamma_S^- \gamma_L^-}) \quad (2)$$

where γ_S^{LW} and γ_L^{LW} are the total apolar components of the solid and liquid, respectively. γ_S^+ , γ_S^- are the electron acceptor and electron donor contributions to the polar component of the solid, while γ_L^+ , γ_L^- are similar quantities for the liquid.

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