



Plasma immersion ion implantation of a two-phase blend of polysulfone and polyvinylpyrrolidone



Elena Kosobrodova^{a,*}, Alexey Kondyurin^a, Wojciech Chrzanowski^b, David R. McKenzie^a, Marcela M.M. Bilek^a

^a School of Physics, The University of Sydney, NSW 2006, Australia

^b Faculty of Pharmacy, The University of Sydney, NSW 2006, Australia

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ABSTRACT

The blend of polysulfone (PSU) and polyvinylpyrrolidone (PVP) is widely used in a production of ultrafiltration membranes and hollow fiber membranes for hemodialysis and tissue engineering. Here we study the effect of plasma immersion ion implantation (PIII) treatment on a two-phase polymer blend. It was found that PIII treatment improves the compatibility between PSU and PVP in the blend in the modified surface layer and results in an increase of wettability and chemical resistance. A synergistic effect in cross-linking and oxidation of PIII treated PSU/PVP blend was observed. The morphology of dichloromethane washed PIII treated films depends on the ion fluence used in the treatment. The wavelength of the periodic wrinkles increases and their amplitude decreases with increasing PIII treatment time.

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1. Introduction

Polysulfone (PSU) and polyvinylpyrrolidone (PVP) blends are commonly used in the production of hollow fiber membranes for blood purification [1–3], tissue engineering [4–7] and the production of biochemicals such as vaccines, interferons, hormones, growth factors and monoclonal antibodies [8]. PSU has excellent thermal and mechanical properties and a high resistance to hydrolysis [9]. Besides hollow fiber membranes, PSU has found application in gas and humidity sensors [10], waste water recovery [11], biosensors [12], direct methanol fuel cells [9,13] and drug release systems [14]. PVP is a water-soluble polymer widely used for hydrophilizing biomaterials [15]. PVP improves wettability and biocompatibility of PSU membranes [16]. Unfortunately, PVP is washed away from PSU membrane over time under flow conditions [17] and the membrane becomes progressively more hydrophobic.

Plasma immersion ion implantation (PIII) significantly improves the wettability and the chemical resistance of polymers [18,19]. Also, a PIII treated polymer surface has a unique combination of high wettability with high protein binding capacity [20] that results in its high biocompatibility [21–23]. Radicals, produced in a polymer surface layer by PIII, form covalent bonds with protein molecules on contact and no chemical linkers are required for protein immobilization [20]. Protein remains on the PIII treated surface even after vigorous washing in a detergent at 70 °C [20]. Electron paramagnetic resonance spectroscopy shows that the concentration of radicals decreases with time after PIII

treatment. However, even after months of storage, the concentration of radicals is significantly higher in the PIII treated polymer than in an untreated polymer [24,25].

PIII treatment has a much greater effect on a polymer surface than UV- and γ -irradiation and conventional plasma treatment without application of pulsed bias [26,27]. During PIII treatment, bombarding ions are accelerated by a high bias potential applied to the sample holder. The depth of ion penetration is considerably larger in PIII than in conventional plasma treatment. The rate of thickness reduction, degree of oxidation and chemical resistance of PIII treated polymers are higher compared to plasma treated polymers [18]. At ion fluences higher than 10^{13} ions/cm², carbonized clusters are formed in the surface layer of PIII treated polymer [28,29]. The sizes and number of the clusters increase with increasing ion fluence, resulting in an increase of refractive index and extinction coefficient of the polymer [18]. At ion fluence higher than 10^{16} ions/cm², a carbonized quasi-layer is formed on the PIII treated surface. The carbonized layer is less susceptible to oxidation and has a high chemical resistance [18]. We expect that carbonization and cross-linking of the polymer surface layer will significantly reduce the PVP loss observed when PSU/PVP blends are placed in contact with water.

To gain a better understanding of the effect of PIII treatment on the PSU/PVP blend, we studied separately PSU and PVP films spin-coated on silicon as well as a PSU/PVP blend containing 9% PVP. This concentration of PVP roughly corresponds to the concentration of residual PVP in PSU hollow fiber membranes used for aforementioned applications. Although there are a number of publications on morphology and wettability of plasma treated polymer blends [30–32], to our knowledge, the effect of PIII treatment on the structure and properties of two-phase

* Corresponding author.

E-mail address: elena.kosobrodova@sydney.edu.au (E. Kosobrodova).

polymer blends has not yet been investigated. The morphology and miscibility of untreated PSU/PVP blends were well studied by Bhattacharya et al. [33] who demonstrated that the PSU/PVP blend is immiscible for most component ratios.

In this paper, optical properties, chemical structure, wettability and topography of PIII and radio frequency (RF) plasma treated films were investigated using ellipsometry, FTIR-ATR spectroscopy, water contact angle measurements and atomic force microscopy (AFM). Gel fraction formation in PIII and RF plasma treated PSU, PVP and PSU/PVP blends was studied by washing untreated and treated films in mQ-water and dichloromethane (DCM). The morphology of the DCM washed PIII treated films was analyzed using optical microscopy and AFM.

2. Methods and materials

Polysulfone (PSU) films were purchased from Goodfellow (Cambridge Limited, UK). Polyvinylpyrrolidone (PVP) was obtained

from (Sigma-Aldrich, Australia). 2% w/v solutions of PSU and PVP were prepared in dichloromethane. The solutions of PSU and PVP and their blend containing 9% PVP were spin-coated on (100) silicon wafers using an SCS G3P-8 Spincoater with a speed of 2000 rpm. The silicon wafers were purchased from Topsisil, USA. The wafers were P-doped (10^4 – $2 \cdot 10^4 \Omega \cdot \text{cm}$) and had one side polished. Their thickness was 0.610–0.640 mm. Before spin-coating, the silicon wafers were washed for 20 s in mQ-water with ultrasound and air dried.

Inductively coupled radio-frequency (RF) nitrogen plasma, powered at 13.56 MHz, was used as a source for PIII. The base pressure of the vacuum system was 10^{-5} Torr (10^{-3} Pa) and the pressure of nitrogen during the implantation was $2 \cdot 10^{-3}$ Torr ($4.4 \cdot 10^{-2}$ Pa). The forward power was 100 W with reverse power of 12 W when matched.

The samples were placed on a stainless steel holder with a mesh made of the same material. The mesh was electrically connected to the holder and held in front of the sample parallel to its surface. The distance between the sample and the mesh was 5 cm. Plasma ions

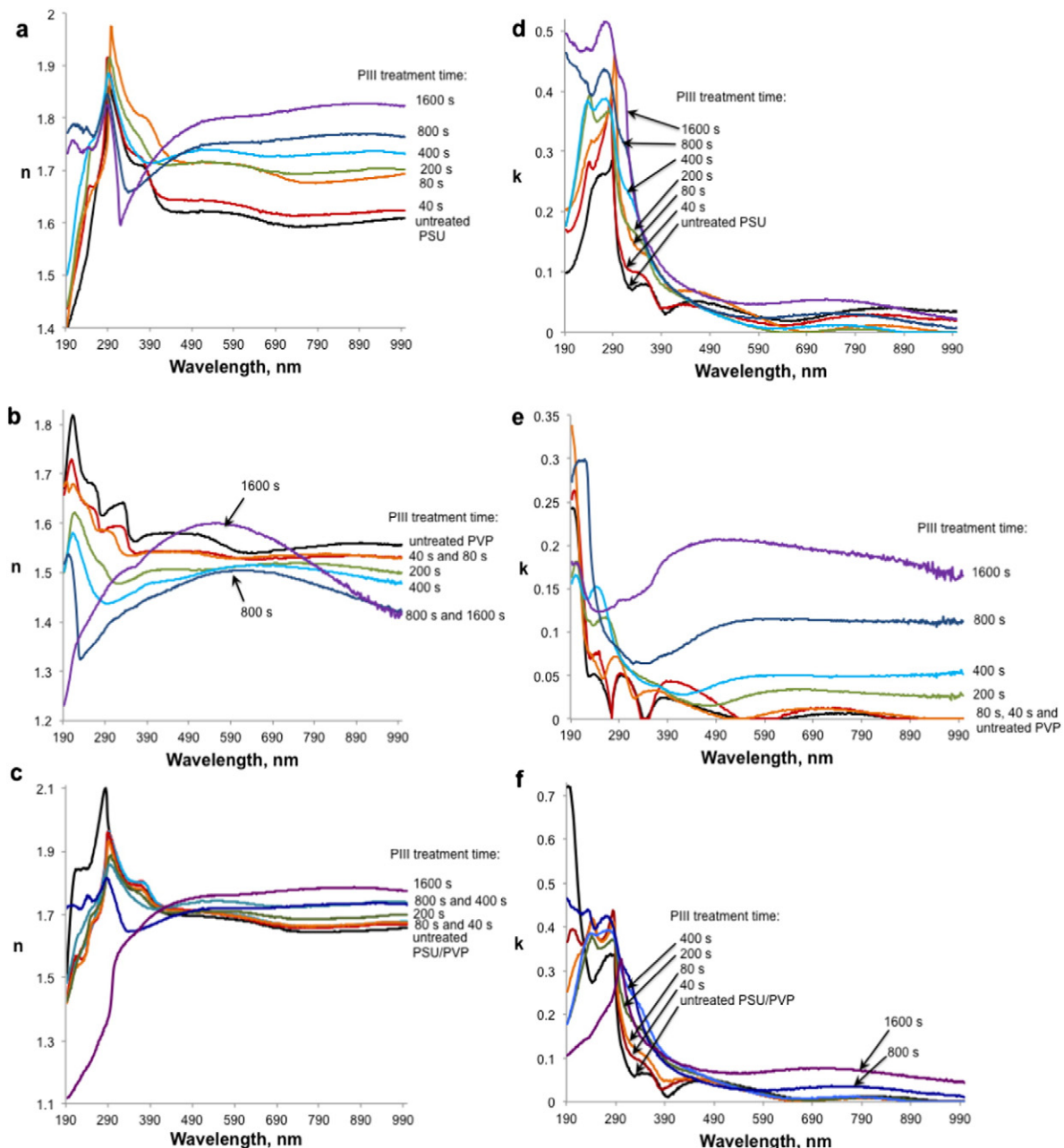


Fig. 1. Refractive index (n) and extinction coefficient (k) of PIII treated PSU (a and d), PVP (b and e) and their blend (c and f) at different PIII treatment times.

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