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Novel magneto-plasma processing for enhanced modification of electrospun biomaterials

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ABSTRACT

We report a method to increase the efficiency of radio-frequency (RF) generated plasma for surface modification of electrospun biomaterials by introducing magnetization. The x-ray photoelectron spectroscopy (XPS) reveals the oxygen/carbon ratio is consistently higher for various exposure times for magnetized plasma than non-magnetized plasma. The principle demonstrated here supports the use of magnetic fields as an additional controllable parameter in plasma processing of biomaterials and is extendable to other plasma sources. The surface activation and functionalization of biomaterials has impact in the broader arena of tissue engineering applications in that magneto-plasma processing (MPP) enables us to tune the shape of plasma plume for selective enhanced functionalization of surface of scaffolds, which in turn has wide applications for basic cell-patterning science and in applied regenerative medicine.

1. Introduction

The surfaces of biomaterials typically require either physical or chemical modification to produce functional bio-interfaces [1]. Surface activation and modification by plasma has been highly recommended as a functionalization approach for biomaterials. Specifically, plasma sources operating in the low-temperature regime (non-equilibrium plasma) which include radio-frequency (RF), dielectric-barrier discharge (DBD), and plasma-enhanced chemical-vapor deposition are described in literature for such applications [2–5].

The polymer poly(caprolactone) (PCL) have been extensively explored for fabricating electrospun scaffolds in applications ranging from bone tissue engineering to small-diameter vascular grafts and represents a model biomaterial [5–9]. For plasma surface modification of such biomaterials the typical process parameters include power, gas flow/composition, pressure, and exposure time [5]. An additional well-known controllable parameter is magnetization; however, this parameter has been unexplored for plasma surface processing of biomaterials. Magnetized plasmas, in general, are well explored and are described in other fields such as plasma diagnostics, plasma propulsion, and radio astronomy [10–14].

Herein we report a simple, yet, scalable method of using magnetized plasma to increase the rate of surface modification of electrospun PCL. The effects of the surface modification include enhanced hydrophilic character due to the rapid increase of oxygen-containing groups on the surface as evidenced by the contact angle measurements and surface elemental analysis. This methodology offers a convenient leading-edge approach to the surface activation of biomaterials intended for applications in tissue engineering.

2. Experimental

2.1. Preparation of electrospun constructs

Pellets of poly(ε-caprolactone) (PCL) (inherent viscosity 1.0–1.3 dL/g in $CHCl_3$) (Lactel Absorbable Polymers, Durect, Birmingham, AL) were dissolved in 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) (Oakwood Chemical, Estill, SC) at a concentration of 20 w/v%. Electrospinning was accomplished via a custom computer-controlled system described in our previous work [5]. Briefly, the parameters were 3 mL of working solution (rate 1.2 mL/h, 25 G) across a distance of 20 cm to a grounded aluminum cylindrical-mandrel (6 cm diameter × 20 cm length, rotation: 300 RPM). A potential of 16 kV was applied, and lateral displacement was 260 mm (rate of 40 mm/s). Fibers were degassed (vacuum, 48 h) to remove residual solvent.

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2.2. Plasma modification

A plasma cleaner (Harrick PDC-001, Ithaca, NY) was outfitted with a neodymium permanent magnet (200 mT ± 20 mT at the surface) by placing the magnet on the bottom of the quartz chamber (see Supplemental information for a diagram) and a glass microscope slide with samples of electrospun-PCL (2 cm × 2 cm). The slide was positioned in intimate contact with the magnet; the chamber was pumped down to working pressures of 500–600 mTorr, RF power was set to high (45 W), and ambient atmosphere was bled in at a rate of 25 sccm. Additional electrospun-PCL samples were modified with the same conditions without magnetized exposure and unmodified samples were retained as controls (polymer samples with no plasma exposure).

3. Results and discussion

Scanning electron microscopy (SEM) images show the porous nature (see Supplemental information) of the constructs. The random alignment of the fibers (diameters: 500 nm up to 3 μm) and their pristine nature without bead formation are due to the chosen electrospinning parameters. Fourier Transform Infrared Spectroscopy (FTIR) shows the expected peaks (Fig. 1a) for PCL. The aliphatic —CH— stretching modes are visible at2937 and 2921 cm^{-1} and the —C=O— stretching is visible at 1724 cm^{-1}. Plasma modification did not impact the peak positions, but a slight shift of baseline is noticed compared to control, however this is negligible and is likely the result of IR light scattering due to roughening of the surfaces from modification. This result is consistent with the fact that cold plasma modification is a surface technique as no change in bulk composition is observed [2–5].

X-ray photoelectron spectroscopy (XPS) analysis (Fig. 1b, Fig. 2a) of the PCL surfaces revealed the efficacy of the magnetized RF plasma treatment. During much experimentation, it was observed that for various time exposures the magnetized plasma consistently resulted in higher yields of oxygenated functional groups. Surface treatment by air plasma is known to introduce new functional groups by a variety of active species including ozone, hydroxyl radical, excited molecular oxygen, NO_x species, and free electrons [2–5]. These, in turn, can react with the PCL chains resulting in the oxygen enrichment shown by XPS with the increase in oxygen/carbon ratios. These changes increase the surface polarity, thus, accounting for the decrease in measured contact-angles (Fig. 2b) (5 μL glycerol drop captured by video contact-angle measurements).

Magnetized plasma exhibits enhanced rates of modification when compared to non-magnetized plasma for surface processing at shorter exposure times (<5 min). The exact mechanism is unknown at this time and the effects of both plasma types are similar tending toward an equilibrium at longer exposure times (>5 min).

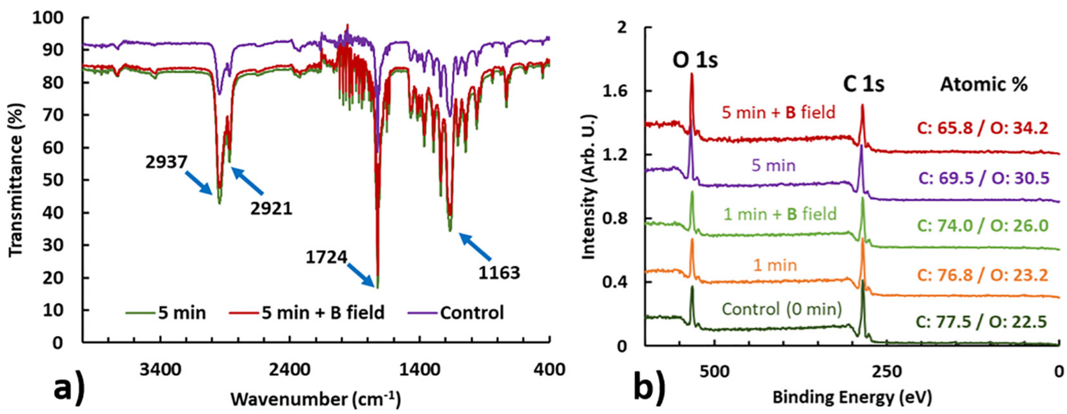

Fig. 1. FTIR (a) and representative XPS survey scans (b) of PCL modified with both magnetized and non-magnetized plasma. The control for each are unmodified neat PCL.

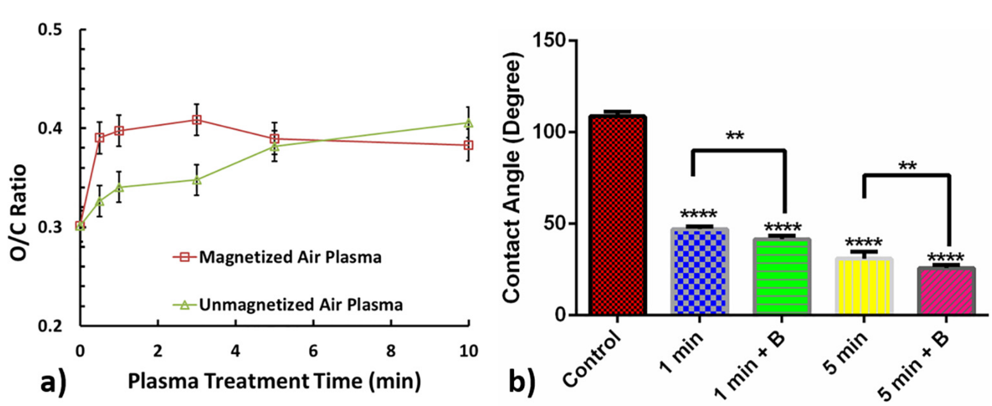

Fig. 2. XPS analysis (a) reveals consistently higher oxygen/carbon ratios as a function of exposure time (bars = standard error, n = 3 for each time point). Contact angle measurements (b) indicate a significant difference (P < 0.0001) for each treatment compared to control (unmodified PCL). For each subgroup (1 min and 5 min) there is also a significant difference (P < 0.01) between magnetized and non-magnetized exposure (n = 6 for each). Statistics generated in GraphPad (one-way ANOVA).

4. Conclusions

The report details a technique for increasing the efficiency of RF plasma modification of electrospun biomaterials using magnetic fields. The increase in surface oxygen and decrease of contact angle are evidence of the merit of this methodology. Our continuing research interest seeks to exploit this effect for additional plasma sources.

Conflict of interests

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2019.04.118.

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