Applied Surface Science xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Functionalization of biomedical materials using plasma and related technologies

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ARTICLE INFO

Article history:
Received 16 December 2013
Accepted 25 February 2014
Available online xxx

Keywords:
Magnesium alloys
Polymers
Biocompatibility
Plasma
Ion implantation

ABSTRACT

Plasma techniques are important to biomedical engineering and surface modification. By modifying selective surface characteristics, conventional materials can be designed with superior biological properties while the favorable bulk materials properties can be retained. In this mini-review, recent progress pertaining to surface modification of Mg-based and polymer-based biomaterials by plasma-based techniques such as gas or metal ion implantation, dual metal and gas ion implantation, as well as plasma immersion ion implantation and deposition is described. Plasma-based surface modification is promising in elevating the cell biocompatibility, blood compatibility, and antibacterial properties of Mg-based and polymer-based biomaterials and expected to be extensively applied to biomaterials.

1. Introduction

Mg-based materials were first introduced to orthopedic and trauma surgeries about one hundred years ago [1]. Compared to stainless steels, titanium, and titanium alloys, magnesium alloys have unique natural biodegradability in the physiological environment and stimulatory effects on new bone formation. Since Mg alloys have an elastic modulus similar to that of human bone, they produce less stress shielding and their natural degradability obviates the need for a second surgical process to remove the implants from patients thereby minimizing trauma and medical costs [2–4]. However, the major obstacle hampering their clinical use is rapid and uncontrolled degradation inside the physiological environment and local gas emission *in vivo* [5–7].

Medical polymers are used widely in biomedical implants such as bone substitutes, artificial heart valves, and artificial blood vessels because of their excellent mechanical properties and moderate biocompatibility [8,9]. However, common biopolymers such as polytetrafluoroethylen (PTFE) [10], polyetheretherketone (PEEK) [11,12], and poly(butylene succinate) [13] are bio-inert. These materials tend to induce the formation of soft tissues rather than direct bone integration, resulting in fibrous encapsulation of the implant surface. In addition, infection of medical devices can be a life threatening complication and lead to significant morbidity and mortality. Therefore, it is crucial to improve the biocompatibility and antibacterial properties of medical polymers.

In order to obtain optimal biological performance, it is usually necessary to apply surface treatment or coatings to biomaterials. Among the various surface treatment and coating techniques, plasma-based techniques such as plasma ion implantation and plasma immersion ion implantation and deposition (PIII&D) have been proven to be effective in improving the surface properties of materials while the favorable bulk materials attributes like mechanical strength, robustness, and inertness can be preserved [14–17]. By varying the implantation energy, excellent adhesion between the surface modified layer and substrate can be achieved as there is no distinct interface between the implanted layer and substrate. This process is controllable and reproducible and can be tailored to produce different types of surfaces in a desirable way [18]. In this mini-review, recent work conducted on plasma-based surface modification of biomaterials is described. Topics discussed include the cytocompatibility, hemocompatibility, and antimicrobial properties of plasma-treated magnesium alloys and medical polymers as well as corrosion resistance of plasma-treated biodegradable metals.

2. Gaseous plasma ion implantation

Different from conventional beamline ion implantation, plasma immersion ion implantation (PIII) circumvents the line-of-sight restriction and possesses a number of advantages such as simplicity, low cost, efficiency, large area, and batch processing [19]

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http://dx.doi.org/10.1016/j.apsusc.2014.02.168
0169-4332/

and has been applied to the improvement of surface mechanical properties and biocompatibility of biomedical polymers and metals [20]. The purpose of gaseous PIII into magnesium is to form a barrier layer on the surface to inhibit attack by aggressive ions in the physiological medium and decrease the degradation rate. Hydrogen [21], oxygen [22,23], nitrogen [24], and water [25] have been hitherto plasma implanted into magnesium alloys, as illustrated in Fig. 1 [26]. It has been found that nitrogen PIII can effectively improve the corrosion resistance of magnesium alloys if the implantation conditions are proper [24]. Different implantation parameters may produce adverse effects on the corrosion resistance. During lower energy ion implantation, the original oxide layer is eroded by ion bombardment thus reducing the natural blocking capability and consequently, the sample is prone to corrosion. High dose with high energy ion implantation may degrade the corrosion resistance due to the formation of a large amount of Mg_3N_2 which is sensitive to atmospheric moisture [27]. Hence, it is important to choose the proper implantation conditions in nitrogen PIII. Recently, oxygen PIII [22,23] and water PIII [22,23] have been reported. Although oxygen PIII and water PIII increase the thickness of the surface oxide film, effective protection cannot be provided because the Pilling-Bedworth ratio of magnesium oxide is less than 1 and no significant improvement in the surface corrosion resistance is observed [22]. In contrast, hydrogen ion implantation appears to be more effective due to the formation of corrosion resistant MgH_2 [21]. Although a variety of gas plasma treatment has been applied to magnesium alloys, the related biological properties and pertinent enhancement mechanisms are still not well known.

Gaseous PIII can be conducted on polymers to improve the cytocompatibility, blood compatibility, and/or antibacterial properties. Precise control of the processing parameters can modulate the surface characteristics of polymers such as surface topography, chemical composition, and surface hydrophilicity thereby enabling the polymer to meet the requirements for particular applications.

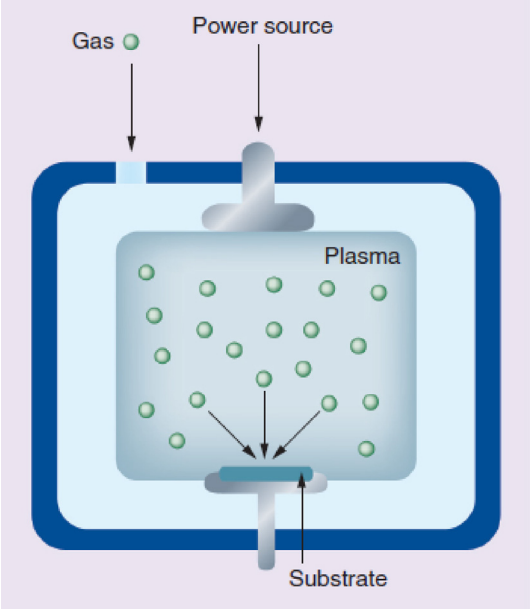

Fig. 1. Schematic illustrating the process of plasma surface modification. A gas is introduced into the evacuated chamber and then ionized by a plasma source. The charged species then impact the substrate to modify the surface in the immersion configuration [26].

Up to now, nitrogen [28–31], oxygen [10,32], hydrogen [33], argon [30,34,35], and helium [36,37] have been implanted into polymers to enhance the biological properties. Nitrogen PIII produces nitrogen-containing functional groups on the polymer surface. For example, the modified polyethylene (PE) surface has antibacterial properties and the ability to enhance osteoblast differentiation [28]. The enhanced biocompatibility may be related to the new

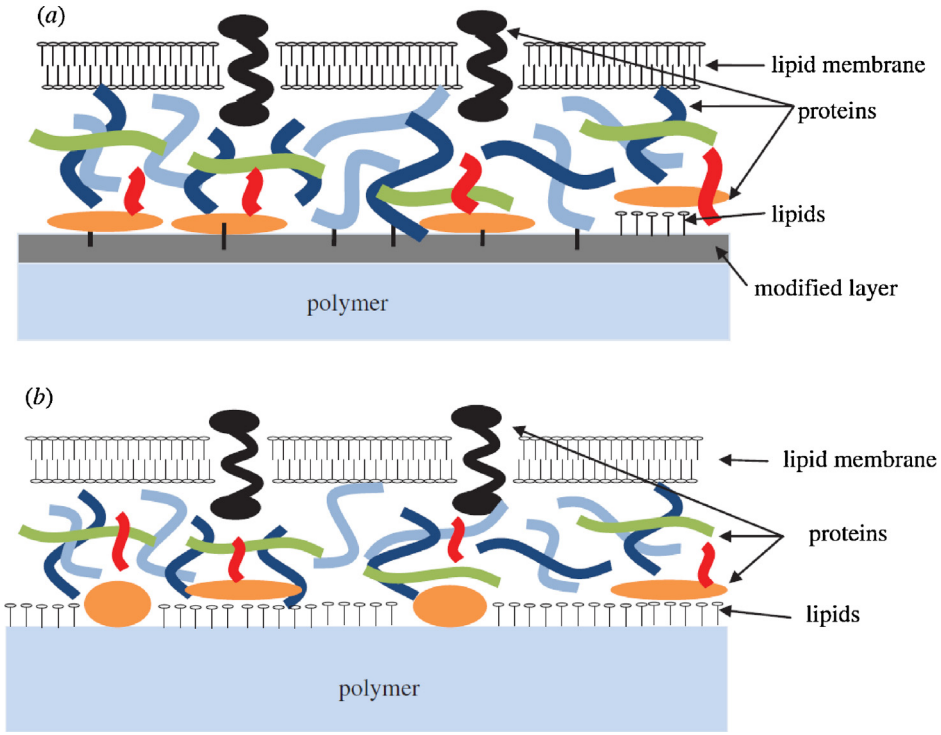

Fig. 2. (a) Schematic of a yeast cell wall attached to a PIII-treated surface. The proteins from the cell wall are covalently bound to the modified surface (covalent bonds are indicated by solid line segments). (b) Schematic of a rehydrated yeast cell wall attached to an untreated surface. The lipids and proteins are physisorbed on the hydrophobic surface [29].

Please cite this article in press as: Y. Zhao, et al., Functionalization of biomedical materials using plasma and related technologies, Appl. Surf. Sci. (2014), http://dx.doi.org/10.1016/j.apsusc.2014.02.168