Polymer Degradation and Stability 116 (2015) 1–13

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Effect of ageing and sterilization on plasma multilayer system

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ARTICLE INFO

Article history:
Received 8 October 2014
Received in revised form
3 February 2015
Accepted 16 February 2015
Available online 18 March 2015

Keywords:
Polymer coatings for biomaterial
Plasma polymer
Ageing
Sterilization

ABSTRACT

Single and coupled effects of sterilization (autoclaving and electron beam) and ageing of plasma polymer multilayer coating on polypropylene mesh are studied. The multilayer system consists in silver nanoparticles entrapped between two maleic anhydride plasma polymer layers and acts as a mechanosensitive antibacterial reservoir. Tensile strength generates cracks within the plasma polymer overlayer which might be used as diffusive channels for Ag^+ species. Changes in surface and bulk properties are followed by SEM, TEM, XPS and antibacterial assays. Whilst autoclave treatment influences surface structure unfavorably, electron beam irradiation with dose of 25 kGy does not induce surface physical or topographical changes. However, electron beam sterilization induces changes in chemistry of the surface causing a decrease in O/C elemental concentration ratio. The surface shows better antibacterial efficiency towards planktonic bacteria after electron beam sterilization and more surprisingly, the combination of electron beam sterilization and ageing has beneficial effect on final properties of the material under stretching.

1. Introduction

In recent years, considerable interest has emerged in plasma modified surfaces for biomedical applications [1–8]. In large part, this is due to the great ability of plasma polymerization to adapt to very diverse natures, morphologies and shapes of materials. The large variety of plasma polymerization approaches allowing the deposition of coatings onto polymers, metals as well as ceramics therefore gives the flexibility and reliability needed for the modification of biomedical devices and implants surfaces with the high level of security required in the biomedical field. In this context, special attention is mostly required regarding cleanliness and sterility of any medical devices, which must be kept up to their use. Therefore, processes leading to the sterilization of plasma polymer coatings constitute a crucial step of development of a new biomaterial coating. However, sterilization is commonly considered as a process of the production, without taking into account probable impacts on the final material properties. Additionally, the final properties of plasma polymer coatings may also be dramatically affected by the material ageing, potentially in combination with effects resulting from the sterilization step.

All the different methods available for sterilization of biomedical devices are likely to produce modifications of the surface properties. The use of heat (steam), radiation (β electrons or γ photons) or chemicals (mostly ethylene oxide) is known to affect the mechanical and optical properties of polymers [9,10]. Radiation, especially γ-rays, has been shown to induce chain scission leading to mechanical and thermal degradation effects [11]. Steam sterilization, carried out in a temperature range of 120–130 °C, probably does not affect the molecular structure of polymers, but it leads to post-crystallization and physical ageing effects [12]. Chemical sterilizing agents can potentially make medical grade plastics toxic [13] and can provide insufficient sterility on polymers [9,10]. Modern alternative sterilization processes such as electron irradiation, UV irradiation and the application of ozone are still not widespread, but all of the three methods are known to induce the formation of radicals in polymers, which might result in similar degradation effects as the γ –radiation [9].

In spite of this literature, few authors have specifically studied the influence of the sterilization step on plasma polymer coatings. Haddow et al. [14] demonstrated that plasma polymer modified surfaces containing carboxylic acid groups can function successfully after a standard ethylene oxide sterilization procedure. Study of Calderon et al. [15] performed on plasma-polymerized

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http://dx.doi.org/10.1016/j.polymdegradstab.2015.02.011
0141-3910/

allylamine films have shown good stability during autoclaving process. The influence of autoclaving, γ-irradiation, ethylene oxide exposure and Ar/H_2 low pressure plasma treatment have been also investigated on the surface chemistry of thin films of plasma polymerized diethylene glycol dimethyl ether [16]. This study revealed that all types of sterilization methods influenced the surface chemistry. In addition, plasma deposited films undergo certain chemical reactions during ageing, when exposed to atmosphere. For example, freshly deposited plasma polymers typically contain radicals, which rapidly react with in-diffusing oxygen during exposure to air. This ageing process, well known as auto-oxidation, consists in two steps [17]. During the primary ageing step, molecular oxygen reacts with C-radical sites, resulting in the formation of peroxy radicals (C–O–O•). During the secondary reaction step, decay of the peroxy radicals occurs, leading to the formation of different oxygen functionalities like C=O and COOH. These various reactions usually spontaneously occur, but may also be enhanced or prematurely triggered by sterilization processes. As far as we know, results of such potential combination (ageing and sterilization) have never been reported until now.

We recently developed a new generation of bioactive coating, dedicated to soft medical implants and able to adjust the release of a bioactive agent under mechanical stimuli [18]. A plasma multilayer coating was deposited on the surface of polypropylene made surgical mesh. Silver nanoparticles were trapped between two plasma polymer layers and acted as an antibacterial reservoir (see Fig. 1a). Owing to the differences between mechanical properties of the plasma polymer thin films and the polypropylene fiber, tensile strength generates cracks within the plasma polymer overlayer which might be used as diffusive channels for Ag^+ species (see Fig. 1b).

In the present paper, the new coating is considered as a model to study single and coupled effects of sterilization and ageing on the coating properties. The study focuses on the stability of the plasma polymer multilayer coating on polypropylene mesh when undergoing ageing and standard sterilization procedures. We examine the effects of *i)* ageing and *ii)* autoclaving and electron beam sterilization on surface properties of our system made of plasma polymerized layers of maleic anhydride.

2. Materials and methods

2.1. Plasma multilayer systems

Preparation and characterization of the plasma multilayer system are fully described in Kulaga et al. [18]. Briefly, PP substrates were placed in the center of the plasma reactor chamber followed by evacuation back down to the initial pressure (~5×10^{-4} mbar). They were first activated by argon plasma during 1 min at 60 W (*PP/Ar*). Subsequently, maleic anhydride vapor was introduced into the reaction chamber (pressure of 0.2 mbar) with a flow rate of approximately 1.6×10^{-9} kg s^{-1}. At this stage, the plasma was ignited and run for 30 min. The deposition conditions corresponded to: power output = 20 W, duty cycle = 2% and frequency = 816 Hz. Upon completion of deposition, the R.F. generator was switched off and the flow of monomer was maintained in the system for a further 2 min period prior to venting up to atmospheric pressure. Prior to use, plasma polymer modified substrates were immersed in deionised water to promote the hydrolysis of maleic anhydride groups into dicarboxylic acid groups (*PP/Ar/MAPP*). Then, silver was loaded directly on the *PP/Ar/MAPP* surface by immersion of the coated substrate into a 1.0 mM silver nitrate solution for 30 min. Silver cations diffused into the reservoir and formed electrostatic pairs with carboxylate groups. Ag^+ ions bound to carboxylate were reduced to zero-valent Ag nanoparticles using an aqueous solution of $NaBH_4$ (2.0 mM). Then, the *PP/Ar/MAPP/Ag* material was placed in the chamber of the plasma reactor and the system was pumped down to base pressure. Maleic anhydride vapor was introduced into the reaction chamber at a constant pressure of 0.2 mbar. The plasma was ignited and run for 10 min according to the following conditions: power output = 20 W, duty cycle = 50% and frequency = 816 Hz. Upon completion of deposition, the R.F. generator was switched off and the flow of monomer was maintained in the system for a further 2 min period prior to

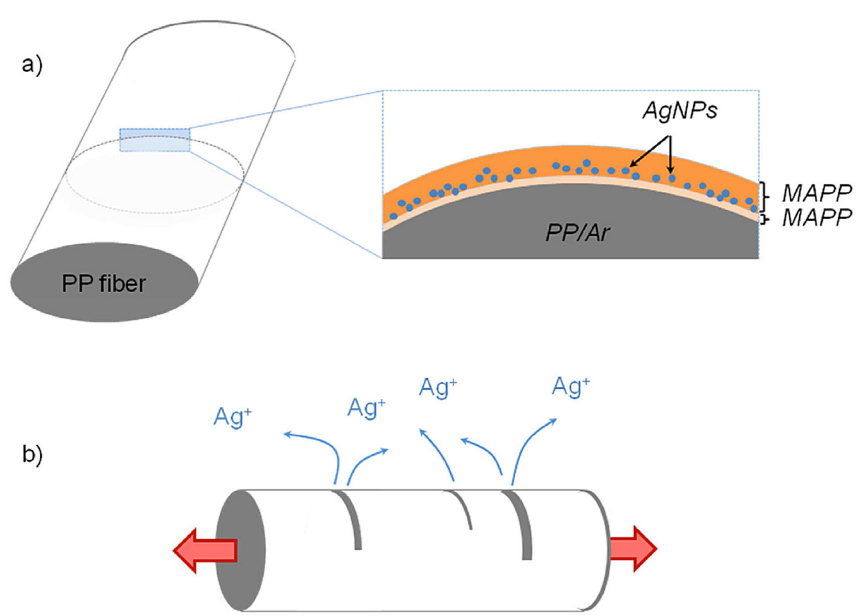

Fig. 1. Schematic view of the plasma multilayer coating that is deposited on the surface of polypropylene made surgical mesh. Silver nanoparticles are trapped between two plasma polymer layers and acted as an antibacterial reservoir (a). Ag^+ species are released through the cracks created within the plasma polymer overlayer under elongation (b).