Progress in Organic Coatings 123 (2018) 282–291

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Structure and antibacterial activity of PLA-based biodegradable nanocomposite coatings by electron beam deposition from active gas phase

Chun He[a], Qi Chen[a], M.A. Yarmolenko[a,b,*], A.A. Rogachev[a,b], D.G. Piliptsou[a,b], Xiaohong Jiang[a,**], A.V. Rogachev[a,b]

[a] International Chinese-Belorussian Scientific Laboratory on Vacuum-Plasma Technology, College of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
[b] Francisk Skorina Gomel State University, 104, Sovetskaya Street, Gomel 246019, Belarus

ARTICLE INFO

Keywords:
Electron-beam deposition
PLA
AgNPs
Norfloxacin
Antibacterial activity

ABSTRACT

The synthesized poly(lactic acid)-based (PLA-based) biodegradable nanocomposite coatings with antibacterial properties were prepared from active gas phase generated by low-energy electron beam dispersion of the powder mixture of PLA and antibacterial components (Norfloxacin and silver nitrate, respectively) in vacuum. The molecular structure, morphology, optical property and chemical states of PLA-based coatings were investigated by ATR-FTIR, Uv–Vis, TEM and XPS. The analyses of ATR-FTIR spectra confirm the formation of polymer and the doped antibacterial components and show the interaction between them. XPS data show that the Ag nanoparticles are of metallic nature in the case of PLA-based nanocomposite coatings containing silver. The antibacterial activity of PLA-based coatings deposited on different substrates was tested against *E. coli* ATCC 25922 and *S. aureus* ATCC 12600 using the agar diffusion method on the solid LB agar medium. The influence of substrates on their antimicrobial behavior was stated.

1. Introduction

Advanced implant associated biomedical technologies for open fracture treatments including biomedical implants and devices have experienced a stage of rapid boom and found their practical implementations in improving the quality of human and animal lives within the last few decades. While building up health conditions of patients, possible subsequent implant related postoperative infections have become critical health concerns and perhaps the trickiest infections to conduct [1–4]. The treatment of postsurgical infections always requests prolonged therapy of antibiotics and might even lead to a possible removal of the placed internal devices through orthopedic surgeries [5]. In severe cases, an amputation may be needed which can lead to the death of patients in the worst cases. In the process of infection formation, the initial crucial step is the adhesion and anchorage of bacteria on the surface of implants and biomaterials. Bacterial adhesion occurs due to the attachment of them to the surface of biomedical devices followed by a slow colonisation of the bacteria and subsequently leads to the formation of a bacterial biofilm which is fatal for the development of infection. Therefore, the suppression of biofilm formation is a significant challenge towards prophylaxis and reduction of implant related infections. Concerning the bacterial adhesion, which is determined by the properties of implant surface, much effort has been attributed to modify it with biodegradable materials, since they will be used in biomedical industry.

Biodegradable polymeric materials which are blood compatible have been applied not only confined to biomedical implants and devices [1,6], release of drugs [7–9], food packagings [10,11], but also extended to wound dressings [12], bone cements [13] and tissue engineering scaffolds [14–16] due to their environment friendly nature and outstanding physicochemical features. One key reason that makes them attractive and interesting is their capacity of total biodegradability. The most well-known and important aliphatic poly(lactic acid) (PLA) and poly(glycolic acid) (PGA) of polymer family or their copolymers have been the most investigated biodegradable materials which are widely occupied as surgical products and biodegradable implants [17,18]. They have played a predominant role as biodegradable materials in orthopedic and medical applications, and among them the renewable biodegradable PLA has drawn the most attention and interest owing to its remarkable properties that make its commercial and

* Corresponding author at: International Chinese-Belorussian Scientific laboratory on Vacuum-Plasma Technology, College of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China.
** Corresponding author.
E-mail addresses: simmak79@mail.ru (M.A. Yarmolenko), jxh0668@sina.com (X. Jiang).

https://doi.org/10.1016/j.porgcoat.2018.02.030
Received 17 September 2017; Received in revised form 9 January 2018; Accepted 27 February 2018

large-scale production suitable for a large range of utilizations [19,20].

The modification of implant surfaces aiming at preventing infections can be conveniently achieved by coating the implant with nanocomposite antibacterial thin coatings loaded with antibiotics or other antimicrobial agents. The application of antibiotics constitutes a key point for the prophylaxis of implant related infections. It is well known that Norfloxacin is one of the most efficient antibiotics for preventing infections in hospitalized patients due to its excellent antimicrobial performance. The presence of antibiotics has a vital influence on bacterial adhesion and proliferation on the implant surface. Therefore, polymer-antibiotic coatings have been considered as one of the most promising and appealing options for treatment of implant related infections as these coatings will release antibiotics from implant surface to the internal environment, and as a result the production of medical implants coated with polymer-antibiotic coatings is highly demanded [6].

Silver nanoparticles (AgNPs) have been suggested to be the most promising inorganic nanoscale antimicrobial agents and broadly employed in precaution of implant related infections in medical sector due to their powerful antibacterial capacity against a great number of microorganisms. Hence, the antibacterial property of AgNPs has aroused a great interest of researchers and been considerably discussed [21,22]. It has been substantiated that the high surface area to contact of AgNPs is responsible for the enhanced inhibitory activity of nanomaterials. However, on the other hand, the high surface free energy of AgNPs also endows them with a tendency to be aggregated and oxidized when they are in contact with environment which may result in the decrease or even loss of some of their particular features. One commendable way to solve these problems is to introduce nano-sized Ag particles into stable polymer matrix materials to protect them from undergoing aggregation and oxidization which may retain their antibacterial property to some extent [15,23].

In most traditional preparation methods of polymer-based nanocomposite coatings with low-molecular compounds or metallic nanoparticles as doped components, there always are liquid media or solvents. As a result, these methods usually have restrictions to the range of polymer matrixes and dispersed substances, the rate of deposition and the thickness of the synthesized coatings. One possible way to effectively overcome these drawbacks and get rid of solvents is the solvent-free low-energy electron beam coating deposition method in vacuum. The electron beam deposition method allows combining the advantages of both physical vapor deposition (PVD) methods and chemical vapor deposition (CVD) methods [24–26]. Specifically, the polymer-based nanocomposite thin coatings are deposited from the active gas phase generated as the products of electron beam dispersion of the solid target consisting of composite polymer based substances. In our case, the low-energy electron beam flux can effectively evaporate and further disperse the powder mixture of polymer and doped components and give rise to the formation of even and dense nanocomposite coatings in company with the uniform distribution of dispersed low-molecular compounds or metallic nanoparticles in polymer matrix volume. The deposition of coatings based on many high-molecular compounds: polytetrafluoroethylene, polyethylene, polyurethane, polyaniline, silicone resins, etc. and nanocomposite coatings on their basis are possible by electron beam dispersion. The deposition of these coatings, in particular, PU-PTFE, PE-PTFE by other methods is difficult or impossible [27]. Electron beam dispersion cannot be used for coatings based on compounds containing benzene rings (polystyrene, polyethylene terephthalate). Benzene rings are easily split off and removed by a vacuum pumping system. Electron beam dispersion is not effective in the formation of layers based on antibiotics, characterized by molecular mass of more than 800: polymyxins, vancomycin, and a number of other antibiotics – gentamycin, etc. The electron-beam coating method is most effective in the formation of layers based on ciprofloxacin. The impact of a low-energy electron flux is not accompanied by the destruction of an antibacterial drug [28,29]. Electron-beam dispersion of high-molecular compounds is accompanied by the deposition of layers with significantly lower molecular mass, which facilitates their relatively rapid decomposition in the human body. This also applies to polylactide-based coatings. In [30] it is noted that the amorphous structure of polylactide-based coatings, combined with a low molecular weight ($9.6\,10^4$ g/mol for the initial polymer and $1.5\,10^4$ g/mol for the coating), promotes the accelerated release of biocidal additives. As is known, one of the disadvantages of polylactide materials is the low rate of biodegradation, which requires the implementation of additional techniques. In particular, the introduction of a magnesium polymer [31]. Antibacterial coatings based on polylactide are free from this disadvantage.

It should be noted then the effectiveness of using antibacterial coatings is in some cases determined by the rate (character) of the medicinal component release from the thin layer. The release of silver nanoparticles is only possible at the decomposition of the polymer layer [32]. Consequently, these coatings will have a high surface bacterial activity. Using an antibacterial chemical might expect its more intense diffusion from the coating to the biological medium. In this regard, it was interesting to compare such coatings with various release kinetics.

The aim of this study is the investigation of the antibacterial activity of PLA-based biodegradable nanocomposite coatings due to the changes in structure and morphology of the coatings under the influence of the doped antibacterial components of different nature.

2. Experiment

2.1. Characterization of methods and instruments

The nanocomposite coatings were formed by the electron beam deposition method (EBD). The mechanical mixture of powders of the polymer (poly(lactic acid), Purac) and antibacterial components (Norfloxacin, Zhejiang Medicine Co., Ltd., silver nitrate ($AgNO_3$), 98%, Aldrich) was taken as the initial target.

The nanocomposite coating deposition was performed from active gas phase generated in vacuum as the product of electron-beam dispersion of powder mixture of PLA and antibacterial components in the mass ratio of 1:1. The scheme of electron beam deposition device is shown in Fig. 1.

The process of nanocomposite coating deposition was carried out at the initial pressure of residual gases in the vacuum chamber at 4×10^{-3} Pa. The electron gun with a filamentary cathode which is able to form low-energy electron beams with current density $j = 0.01–0.03$ A/cm^2 and energy E = 1000–2000 eV is used as the

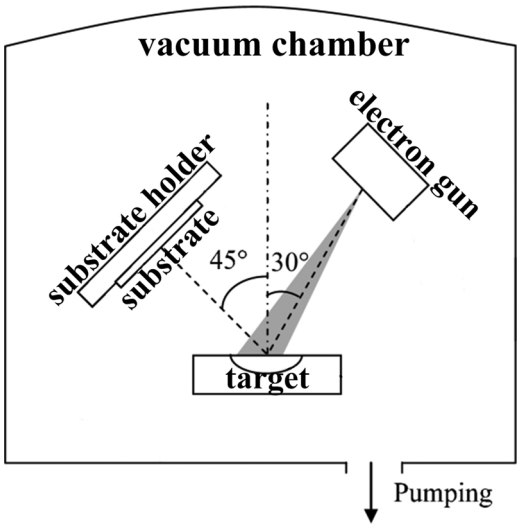

Fig. 1. Scheme of electron beam deposition device.