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Antibacterial ciprofloxacin HCl incorporated polyurethane composite nanofibers via electrospinning for biomedical applications

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Abstract

We report on the preparation and characterization of polyurethane (PU) composite nanofibers by electrospinning. Two different approaches were adopted to obtain the PU composite nanofibers. In the first approach, a homogeneous solution of 10 wt% PU containing ciprofloxacin HCl (CipHCl) drug was electrospun to obtain PU/Drug composite nanofibers. And in the second approach, the PU with ciprofloxacin HCl drug and ceramic hydroxyapatite (HA) particles were electrospun to obtain the PU/Drug and PU/Drug/HA composite nanofibers. The surface morphology, structure, bonding configuration, optical and thermal properties of the resultant products were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and UV–vis spectroscopy. The antibacterial activity was tested against common food borne pathogenic bacteria, namely, *Staphylococcus aureus*, *Escherichia coli* by the minimum inhibitory concentration (MIC) method. Our result results demonstrate that these composite nanofibers possess superior characteristics which can utilized for variety of applications.

Keywords: Antibacterial activity; Composite nanofibers; Eletrospinning; Polyurethane

1. Introduction

Polyurethane (PU) polymer has a broad spectrum of commercial applications in many market areas because of their excellent chemical and physical properties [1]. These polymers are synthesized from poly addition reactions of isocyanate and hydroxyl groups [2]. PU dispersions have found diverse applications in different industries like textile, adhesives, gloves, wood finishing, glass fiber sizing, automotive top coating films for packaging and other applications [3]. PU is frequently used in wound dressings because of its good barrier properties and oxygen permeability. PU foam and elastomer have been used as cushion insole material in footwear [4]. Recently, the design and synthesis of new polymer/nanosized inorganic composite materials have been widely investigated in order to combine the properties of inorganic fillers and polymer matrices which can be utilized for many technological applications [5–9]. In this connection, wound dressing from electrospun nanofibers potentially offers many advantages over conventional processes [10]. Immediate care of skin wounds is important for prevention of microbial infection and trans-epidermal water loss leading to acceleration of wound regeneration [11]. Electrospinning has attracted much attention as a simple and versatile technique capable of generating continuous nanofibers with novel properties including high surface-to-volume ratio, good mechanical properties and high aspect ratio [12,13]. Generally, the ultimate goal of the nanofiber design is to provide an ideal structure that can replace the natural extra cellular matrix until the host cells can grow and synthesize a new natural cellular matrix [6].

Extensive studies have been conducted to develop biocompatible electrospun nanofibrous scaffolds for wound dressing

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applications. An electrospun nanofiber membrane containing antibiotic agents has been used as a barrier to prevent the post-wound infections. The combination of both of these properties can result in a perfect wound dressing material. Among them, ciprofloxacin HCl (CipHCl), a fluoroquinolone antibiotic, is one of the most widely used antibiotics for wound healing because of its low minimal inhibitory concentration for both Gram-positive and Gram-negative bacteria that cause wound infections [14] and the frequency of spontaneous resistance to ciprofloxacin is very low [15]. On the other hand, hydroxyapatite (HA) is chemically similar to the inorganic component of bone matrix—a very complex tissue with general formula $Ca_{10}(OH)_2(PO_4)_6$. The close chemical similarity of HA to natural bone has led to extensive research efforts to use synthetic HA as a bone substitute and/or replacement in biomedical applications [16,17]. Recently, HA has been used for a variety of biomedical applications, including matrices for drug release control and bone tissue engineering materials [18,19]. HA exhibits excellent biocompatibility with soft tissues such as skin, muscle and gums. Such capabilities have made HA an ideal candidate for orthopedic and dental implants or components of implants [20]. HA nano-and microcrystals with multiform morphologies (separated nanowires, nanorods, microspheres, microflowers and microsheets) have been successfully synthesized by many powder processing techniques, including sol–gel synthesis [21–25], solid state reactions [26], co-precipitation [27], hydrothermal reactions [28], micro-emulsion syntheses [29] and mechanochemical synthesis [30]. So in this work, we utilize both cipHCl and HA to prepare the composite nanofibrous wound dressing material via the electrospinning technique. Blending of Drug and Drug/HA into PU nanofibers has attracted a great deal of attention in biomedical applications because the resulting nanofibers have very strong antimicrobial activity. The resultant composite materials can be utilized for many technological applications such as wound dressing, food packaging and other biomedical uses. This study involves the characterization of these nanofibers and biocompatibility of these scaffolds along with the simultaneous antibacterial activity of CipHCl. Such kinds of materials can have much improved properties in terms of thermal stability, flexibility and solubility with that of the pristine PU. Additionally, to our best of knowledge, there have been no reports based on these composite nanofibers.

In this study, we prepared pristine PU nanofibers, PU/Drug and PU/Drug/HA composite nanofibers by using electrospinning process. The resultant composite nanofibers PU, PU/Drug and PU/Drug/HA were characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD), Fourier transform (FT-IR), differential scanning calorimeter (DSC), thermogravimetric analysis (TGA) and UV–vis spectroscopy. The antibacterial activity of the PU composite nanofibers were tested against common food borne pathogenic bacteria namely, *Staphylococcus aureus*, *Escherichia coli*, by the minimum inhibitory concentration (MIC) method.

2. Experimental

2.1. Materials

Polyurethane (PU, MW = 110,000) purchased from Cardio Tech, CipHCl (drug) was supplied from LKT laboratories, Inc., USA. Tetrahydro furan (THF) and N,N-dimethylformamide (DMF) (analytical grade, Showa, Japan) were used as solvents without further purification. Biomimetic hydroxyapatite is gifted by Professor Hak Yong Kim and the detailed synthesis procedure has been reported in [31] and the references therein. *S. aureus* (KCCM 29231), *E. coli* (KCCM 52922), were purchased from Korean Culture Center of Microorganisms (KCCM). These pathogenic microorganisms were used as the model bacteria for the disc diffusion susceptibility test. For the bactericidal activity measurement Mueller-Hinton broth (MHB) & Mueller-Hinton agar (MHA) (Difco, Sparks, MD, USA) were used.

2.2. Electrospinning

Two different approaches were adopted to incorporate the drug and the HA particles in to PU nanofibers. In the first method, PU solution with 10 wt% was prepared by dissolving in THF and DMF with the ratio of 1:1. HA 2%: Drug 1.5% solution was prepared and then added to the PU with 10 wt% of the polymer solution. The final homogenous mixture was used to electrospinning. Herein, the resultant composite nanofibers are named as PU, PU/Drug and PU/Drug/HA. A high voltage power supply (CPS-60 K02V1, Chungpa EMT, South Korea) of 15 kV to the syringe micro-tip was supplied to electrospin the nanofibers, whereas a ground iron drum covered by blue paper served as counter electrode. In our study, we used the conventional electrospinning setup, where the syringe has been kept inclined to flow the spinning solution. The tip-to-collector distance was kept at 15 cm. Polymer solution was fed to the 5 mL syringe with plastic micro-tip. All the experiments were conducted at room temperature. These experimental parameters were chosen from an optimization of a series experiments. The developed nanofiber mats formed were collected on the rotating drum covered with the collecting blue paper.

2.3. Characterizations

The morphology of the PU, PU/Drug and PU/Drug/HA composite nanofibers was observed by using scanning electron microscopy (SEM, Hitachi S-7400, Hitachi, Japan). Elemental composition analyses of the thin films were carried out by using a SEM equipped with an energy dispersive X-ray (EDX) spectrometer. Structural characterization was carried out by X-ray diffraction (XRD) in a Rigaku X-ray diffractometer operated with Cu Kα radiation ($\lambda = 1.540$ Å), The bonding configurations of the samples were characterized by means of Fourier transform