

Contents lists available at ScienceDirect

### Materials Science & Engineering C



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

## Electrospun carboxyl multi-walled carbon nanotubes grafted polyhydroxybutyrate composite nanofibers membrane scaffolds: Preparation, characterization and cytocompatibility



Cai Zhijiang<sup>a,b,\*</sup>, Zhu Cong<sup>a</sup>, Guo Jie<sup>a</sup>, Zhang Qing<sup>a</sup>, Zhao Kongyin<sup>b</sup>

<sup>a</sup> School of Textiles, Tianjin Polytechnic University, No 399 BingShuiXi Street, XiQing District, Tianjin 300387, China
<sup>b</sup> State Key Laboratory of Separation Membranes and Membrane Processes, Tianjin Polytechnic University, No 399 BingShuiXi Street, XiQing District, Tianjin 300387, China

#### ARTICLE INFO

Keywords: Carbon nanotubes Polyhydroxybutyrate Electrospinning Composite nanofibers scaffold

#### ABSTRACT

Electrospun polyhydroxybutyrate (PHB)/carboxyl multi-walled carbon nanotubes grafted polyhydroxybutyrate (CMWCNT-g-PHB) composite nanofibers scaffolds were fabricated by electrospinning technology. The grafted product CMWCNT-g-PHB was prepared by condensation reactions between the carboxyl groups of CMWCNT and hydroxyl groups of PHB molecules and characterized by FTIR, XRD, XPS, TG and TEM measurements. The surface morphology, hydrophilicity and tensile mechanical properties of the electrospun PHB/CMWCNT-g-PHB composite nanofibers membrane scaffolds were investigated. The values of tensile strength, breaking elongation rate, initial modulus and fracture energy of the composite nanofibers scaffolds can reach to 4.64 MPa, 255.59%, 88 MPa and 109.73 kJ/m<sup>2</sup>, respectively. The biodegradability and cytocompatibility of the electrospun composite nanofibers scaffolds with the characteristics of large specific area, high porosity, good biodegradability and cytocompatibility as well as sufficient mechanical properties should be more promising in the field of tissue engineering scaffolds and biological medicine.

#### 1. Introduction

Scaffolds play the important roles by providing a suitable extracellular matrix (ECM) for new tissue formation. The desirable scaffolds should be highly porous, biocompatible and biodegradable which allow for the transportation of oxygen, nutrients, and non-toxic degradation products and facilitate cell metabolism, migration and proliferation [1–3]. Moreover, the scaffolds should withstand the mechanical stresses during tissue neogenesis [4,5]. Various types of processing techniques have been developed to fabricate porous tailored-scaffolds such as particulate leaching [6], template synthesis [7], phase separation [8], freeze drying [9], gas foaming [10], supercritical fluids assisted processes [11], self-assembly [12], and electrospinning [13]. By now, nanofibers and nanofibers scaffolds have attracted significant attention during recent years due to their structures with high similarity to the natural extracellular matrix, which has three-dimensional network structure composed of natural protein fibers with the diameter in the range of 50 to 500 nm. They have been widely studied for biomedical [14-17], shape memory [18], controlled release [19] and tissue engineering [20,21] applications.

Among these techniques, electrospinning is one of the most effective, lest expensive and simplest method for fabricating continuous nano-scale fibers with diameters in the range of tens nanometers to submicrometer by a high-voltage power supply than the conventional spinning process [13]. As we know, when the diameters of the polymer fibers are reduced from micrometer to nanometer levels, several desirable characteristics can be generated such as high specific surface area to volume ratio, flexibility in surface functionalities, three-dimensional network with completely interconnected pore structures, the qualitatively controlled pore size distribution from sub-micron levels to a few micrometers, and high porosity [22,23], compared to any other known forms of the material. Owing to these outstanding properties of the electrospun nanofibers, many synthetic and natural polymers, including single and blended polymers, have been prepared into electrospun nanofibers that can be employed as the optimal candidates for tissue engineering scaffolds [24-27]. Nevertheless, the electrospun nanofibers are randomly arranged due to the presence of an unstable state of "whipping" during the traditional electrospinning process [28], resulting in the poor mechanical properties that limits its application in tissue engineering scaffolds [29].

http://dx.doi.org/10.1016/j.msec.2017.08.005 Received 12 June 2017; Received in revised form 17 July 2017; Accepted 2 August 2017 Available online 04 August 2017 0928-4931/ © 2017 Elsevier B.V. All rights reserved.

<sup>\*</sup> Corresponding author at: School of Textiles, Tianjin Polytechnic University, No 399 BingShuiXi Street, XiQing District, Tianjin 300387, China. *E-mail address*: xjfzfhcl@tjpu.edu.cn (C. Zhijiang).

Carbon nanotubes (CNTs) have attracted wide attention due to their unique structures, high aspect ratio, mechanical strength, high electrical and thermal conductivity and will enhance the overall performance of many CNTs based polymer composites [30,31]. Seo et al. [32] reported a hybrid scaffold composition of chitosan/silica (CS/Si) incorporated with functionalized-carbon nanotube (f-CNT). 2 wt% f-CNT based CS/Si scaffold showed the highest mechanical properties, including tensile strength and elastic modulus as well as significantly improved bioactivity and tissue reaction with respect to CS/Si free of f-CNT. Chen et al. [33] functionalized the CNTs with poly(L-lactic acid) (PLLA) with different molecular weights using a "grafting to" technique. Choi et al. [34] prepared carboxylic acid-terminated hyperbranched poly(ether-ketone)s (HPEKs) nano-composites with functionalized the CNTs via in situ polymerization and the resultant nanocomposites were homogeneously dispersed in various common polar aprotic solvents as well as in concentrated ammonium hydroxide. Thus, it is an effective method to improve the interfacial adhesive effect between CNTs and the polymer matrix through covalently grafting polymer chains on the surface of the carboxyl modified carbon nanotubes [35,36].

Polyhydroxybutyrate (PHB), one of the polyhydroxyalkanoates with good biocompatibility, biodegradability and a high degree of crystallinity, is produced by many species of microorganisms as their intracellular energy and carbon storage substance and widely used in the biomedical and other applications [37–41]. However, it is also characterized by high brittleness, poor processability and poor thermal stability [42,43]. The formation of nanofibers scaffolds using electrospinning technology can improve the properties of polymer matrix, specifically the addition of blending components or nano-particles in the polymer solution and expand its application in biomedicine [44–46]. A series of previous research work about electrospun PHB [47], PHBV [48] and their blend such as PHB/hydroxyapatite [49], PHB/chitosan [50], PHB/PCL [51], PHB/CA [52], PHBV/collagen [53], P(3HB-co-4HB)/Zein [54], etc., have been reported to be used as tissue engineering scaffolds.

In this paper, polyhydroxybutyrate was used as the polymer matrix to prepared carboxyl multi-walled carbon nanotubes grafted polyhydroxybutyrate (CMWCNT-g-PHB) composite through covalent functionalization and added into the PHB solution to fabricate PHB/ CMWCNT-g-PHB composite nanofibers via electrospinning technology. The CMWCNT-g-PHB composite was characterized by FTIR, XRD, XPS, TG and TEM. The surface morphology, hydrophilicity, tensile mechanical properties, biodegradability as well as cytocompatibility of the electrospun PHB/CMWCNT-g-PHB composite nanofibers scaffolds were also investigated.

#### 2. Experimental

#### 2.1. Materials

Polyhydroxybutyrate (PHB) was purchased from Tianjin Rhyme Biological Technology Co., Ltd. Carboxyl multi-walled carbon nanotubes (CMWCNT) were purchased from Nanjing XFNANO Materials Technology Co., Ltd. Chloroform, dimethylformamide (DMF) and ethanol were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Stannous octoate was purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd.

#### 2.2. Preparation of CMWCNT grafted PHB

The preparation of carboxyl multi-walled carbon nanotubes grafted polyhydroxybutyrate (CMWCNT-g-PHB) was carried out by the following procedures. 0.025 g of CMWCNT were added into the conical flask with 10 mL of chloroform, previously degassed with nitrogen, and used ultrasonic dispersion for 30 min. Then 0.5 g of PHB powder were dissolved in the dispersion and stirred for 2 h, which was kept at 20  $^{\circ}$ C under nitrogen. Simultaneously, the flask was placed in a thermostatic bath at 50 °C, and the catalyst, 0.005 g of stannous octoate were then dropped slowly and stirred for reaction for 6 h. The adequate amount of ethanol was added into the reaction product with stirring, which at this stage was in the form of a suspension, and then filtered under room condition and dried overnight under vacuum. The reaction products was dissolved in excess chloroform again and filtering to remove unreacted PHB homopolymer and stannous octoate through the PTFE membrane. The dissolution and filtration processes were repeated several times. The CMWCNT-g-PHB was finally obtained after drying overnight under vacuum.

## 2.3. Preparation of the electrospun PHB/CMWCNT-g-PHB composite nanofibers membrane scaffolds

The desired amount of diluted CMWCNT-g-PHB solution was firstly prepared by dissolving CMWCNT-g-PHB powder in the mixed solvent of chloroform/DMF (6/1, v/v) and then added PHB powder and stirred at 40 °C for 8 h to obtain 2.5 wt% homogeneous spinning solution. The mass ratios of CMWCNT-g-PHB and PHB powder were 0.5:9.5, 1:9, 1.5:8.5, 2:8, and 10:0, respectively. The nanofibers scaffolds were produced by an optimum electrospinning condition: an applied voltage of 16 kV, a polymer-flow-rate of 2 mL/h, a distance between the spinneret and the collector distance of 16 cm, and spinneret inner diameter of 0.6 mm. All experiments were done in an environmental chamber with constant temperature at 25 °C and the relative humidity at 35%.

#### 2.4. Characterization

Transmission electron microscopy (TEM, Hitachi-7650, Japan) was used to investigate the morphology of CMWCNT-g-PHB at an accelerating voltage of 100 kV. The Fourier Transform Infrared spectroscopy (FTIR, TENSOR37, Bruker, German) was used to analyze the changes of the internal molecular structure of the CMWCNT-g-PHB. For each spectrum, 32 scans were accumulated at  $4 \text{ cm}^{-1}$  resolution, in the scanning range of 4000–600 cm<sup>-1</sup>. The X-ray photoelectron spectroscopy (XPS, K-alpha, ThermoFisher, England) was used to analyze the chemical composition of the CMWCNT-g-PHB surface using an Al Ka Xray source (1486.6 eV). The energy scale was internally calibrated by referencing to the binding energy of the C1s peak of a carbon contaminant at 284.6 eV. The X-ray diffraction (XRD) analysis of the CMWCNT-g-PHB was carried out by Bruker AXS D8 discover small angle X-ray diffractometer, using Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å) with 20 ranging from 5 to 40°, and a scanning rate of  $0.02 \text{ s}^{-1}$ . The TG analysis (TG, STA409PC, NETZSCH, German) was performed under nitrogen in the temperature range of 40-800 °C with a heating rate of 10 °C/min. The grafting ratio was calculated by the thermal weightlessness of the sample using following equations:

$$G = \frac{W_C}{W_P} \times 100\% \tag{1}$$

where *G* is the grafting ratio (%),  $W_C$  and  $W_P$  are the weight of CMWCNT and PHB in grafted product, respectively. The scanning electron microscope (SEM, S-4800, HITACHI, Japan) were used to observe the surface morphology of the PHB/CMWCNT-g-PHB composite nanofibers scaffolds at an accelerating voltage of 10 kV after freezedried samples and sputter-coating with an ultrathin layer of gold. The average diameter of electrospun nanofiber was measured from the SEM image using Image-Pro Plus software. For each sample, 100 electrospun fibers were measured randomly in five SEM images. The tensile mechanical properties of the PHB/CMWCNT-g-PHB composite nanofibers scaffolds were examined by a tensile testing machine (LLY-06F, China) with stretching rate of 10 mm/min at room temperature. Before testing, the samples was tested by digital micrometer thickness gauge. Ten replicates were averaged for each sample. The water contact angle Download English Version:

# https://daneshyari.com/en/article/5434162

Download Persian Version:

https://daneshyari.com/article/5434162

Daneshyari.com