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Synthesis and characterization of gold nanotube/nanowire–polyurethane composite based on castor oil and polyethylene glycol

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ABSTRACT

Gold nanotubes/nanowires (GNT/NW) were synthesized by using the template-assisted electrodeposition technique and mixed with castor oil–polyethylene glycol based polyurethane (PU) to fabricate porous composite scaffolds for biomedical application. 100 and 50 ppm of GNT/NW were used to synthesize composites. The composite scaffolds were characterized by Fourier transform infrared spectroscopy, dynamic mechanical thermal analysis, differential scanning calorimetry, and scanning electron microscopy. Cell attachment on polyurethane–GNT/NW composites was investigated using fat-derived mesenchymal stem cells. Addition of 50 or 100 ppm GNT/NW had significant effects on thermal, mechanical, and cell attachment of polyurethane. Higher crosslink density and better cell attachment and proliferation were observed in polyurethane containing 50 ppm GNT/NW. The results revealed that GNT/NW formed hydrogen bonding with the polyurethane matrix and improved the thermomechanical properties of nanocomposites. Compared with pure PU, better cellular attachment on polyurethane–GNT/NW composites was observed resulting from the improved surface properties of composites.

1. Introduction

Polyurethanes (PUs) are an interesting class family of elastomers. These synthetic materials consist of repeated blocks of hard and soft segments. The arrangement of these segments provides unique properties and a wide range of application for polyurethanes [1]. Considering mechanical and chemical properties, controllable degradation and biostability, biocompatibility, and hemocompatibility makes PUs an outstanding material in medicine [2,3]. Poly (ether) urethanes are widely used for long term applications in tissues such as heart, liver, blood vessels, and urinary system due to their biostability [4,5]. However, poly (ester) urethanes are degradable and used as a matrix for engineered tissues [6,7].

Using vegetable oils as a polyol in PU synthesis leads to biodegradable polyurethanes with many medical applications such as cardiovascular system regeneration [8], peripheral nerve regeneration [9], cartilage and meniscus engineering [10], trabecular bone replacement [11], and controlled drug delivery systems [12]. Among all vegetable oils, castor oil (CO) is the most famous source of ricinoleic acid with three functional hydroxyl groups, which can be directly used in PU synthesis as the soft segment or chain extender without any further modification to functionalize it [13]. Castor oil has a very low toxicity as well as a low cost making it a valuable renewable agriculture resource [14].

In previous studies, it has been shown that castor oil based PUs are almost stable in a saline buffer for a time period of 95 days. However, adding polyethylene glycol (PEG) increased the degradation rate [13]. Polyethylene glycol as a hydrophilic polyol increases water permeability in bulk as well as surface and makes the material more susceptible to degradation with non-toxic degradation products [15]. Hydrolysis is the most common mechanism of in-vivo degradation in this kind of PUs [16]. Therefore, polyurethanes based on castor oil and polyethylene glycol are ideal materials for biomedical implants and tissue engineering applications due to their controllable degradation and wide range of mechanical properties.

Gold (Au) is chemically inert in many environments and has a very low toxicity. One dimensional gold nanostructures e.g., gold nanotubes (GNTs) or gold nanowires (GNWs) are the ideal candidate for sensors, optical devices, and nanoelectronic devices [17–19]. In previous studies, it has been shown that a small amount of gold nanoparticles induced morphological and structural changes in the hard and soft segments of waterborne polyurethanes [20]. An optimum amount of gold nanoparticles caused a significant improvement in the mechanical and thermal properties of polytetramethylene oxide-based waterborne polyurethane [21,22]. The improvement in these properties was related to the enhanced hydrogen bonding between hard segments. Naik et al. [23] reported the antimicrobial properties of polyurethane–gold nanoparticles

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used in catheters with the aim of avoiding infection. In their work, gold nanoparticles increased the bacterial kills when the polyurethane matrix was exposed to white light. An in vivo study on polyurethane–gold nanoparticle composites in porcine model showed better biostability and biocompatibility of composites compared with pure PU [2].

There have been many studies on the composition of the polymeric matrix with gold nanoparticles. However, just a few of these studies used gold as nanowires or nanotubes [24], and to the best of our knowledge there has been no study reporting the thermal and mechanical properties and biomedical application of polyurethane–gold nanowire/nanotube composites. In comparison with nanoparticles, the advantage of nanowires or nanotubes in porous polymeric structures is their ability to make a bridge between the pores of the polymeric matrix. As it has been suggested by Dvir et al. [24], this idea showed the benefit of cell communication and improvement in cell functionality via wires.

In the present work, aiming to develop a biodegradable biomaterial scaffold with an optimum initial mechanical integrity for implantation and better cell communication, we synthesized PU–GNT/NW composites including polyurethane based on castor oil and polyethylene glycol without any chain extender or additives. Different series of GNT/NW–polyurethane composites were fabricated and their mechanical, chemical, and structural properties were investigated. Cell behavior and cell attachment on these composites were also examined.

2. Materials and methods

Castor oil (Sigma-Aldrich, Germany), polyethylene glycol 2000 (Merck, Germany), 1, 6-hexa-methylene diisocyanate (HDI, Merck, Germany), and $HAuCl_4$ solution (Sigma-Aldrich, Germany) were used for PU–GNT/NWs synthesis. All the materials were used as received without any further modification. The $HAuCl_4$ solution was dissolved in double distilled water. High glucose DMEM culture medium (Biosera, UK), fetal bovine serum (Sigma, Germany), and penicillin/streptomycin (Gibco, Germany) were used as received for cell culture. Acid hematoxylin solution (Sigma, Germany) and eosin B (Sigma, Germany) were used for cell staining.

2.1. Gold nanotube/nanowire synthesis

Firstly, one face of polycarbonate templates (Whatman Inc., UK) was sputter-coated with a very thin Au layer of about 20 nm and afterward it was ultrasonically immersed in double distilled water for about 15 min. The sputtered side of the template was placed on a platinum sheet in a sample holder and served as working electrode. The potentiostatic deposition of GNT/NWs was performed at a constant over-potential of −0.4 V vs. saturated calomel electrode (SCE) in a 40 mM $HAuCl_4$ solution by a similar approach according to the literature [17]. Electrodeposition of GNT/NWs was carried out in a conventional three-electrode cell with a platinum plate as an auxiliary electrode by using a potentiostat/galvanostat Autolab model PGSTAT302N [17].

2.2. Polyurethane–GNT/NW composite synthesis

HDI, 20 wt.% aqueous solutions of PEG, and castor oil with molar ratios of 4:1:3 (PU1) were mechanically mixed for 150 min at 70 °C under N2 atmosphere. The mixture was casted in a Teflon mold and dried at room temperature for 2 days. Another solution of HDI and castor oil with the molar ratio of 3:2 (PU2) was mechanically mixed for 2 h at 70 °C under N2 atmosphere. A 30 wt.% solution of PU1 in chloroform was added to PU2 and mixed for an extra 30 min to obtain a homogenous solution (PU3).

A dispersion of GNT/NW in chloroform was added to the solution of PU3 and mixed for 30 min under N2 atmosphere to reach 50 and 100 ppm of dried PU3 content. A part of the solution was casted on a Teflon sheet with the thickness of 1 mm. For fabrication of porous scaffolds, 355–600 μm sieved table salt was added to the remaining solution, and the mixture of polymer and salt was casted in the Teflon mold having a 10 mm diameter and 4 mm thickness. Afterwards, all the samples were dried at room temperature for 48 h, and the porous scaffolds were placed in water for 2 more days to remove the salt. Fig. 1 shows a schematic of the scaffold preparation as described above.

2.3. Characterization

A BOMEM Fourier transform infrared (FTIR) spectrophotometer was used to observe the chemical composition of samples within the wave numbers of 600 to 4000 cm^{-1}.

Dynamic mechanical thermal analysis (DMTA) of samples was performed in a Triton DMTA machine (TTDMA model, UK), within a temperature range of −120 to 100 °C, a heating rate of 5 °C/min, and a frequency of 1 Hz, in tensile mode. The loading amplitude was set at 20 μm. The sample size was 5 × 20 × 1 mm.

Enthalpy changes of samples indicating glass temperature (T_g), crystallinity temperature (T_c), and heat of fusion (ΔH_f) were examined using a Mettler Toledo differential scanning calorimetry (DSC) machine in a temperature range of −60 to 200 °C at a heating rate of 10 °C/min.

KRUSS-K14 digital surface tension measuring system (Kruss, Germany) was used to determine polar and disperse surface energies as well as contact angle according to Owens–Wendt–Rabel–Kaeble method [25]. The measurements were performed at room temperature with two different liquids of water and formamide.

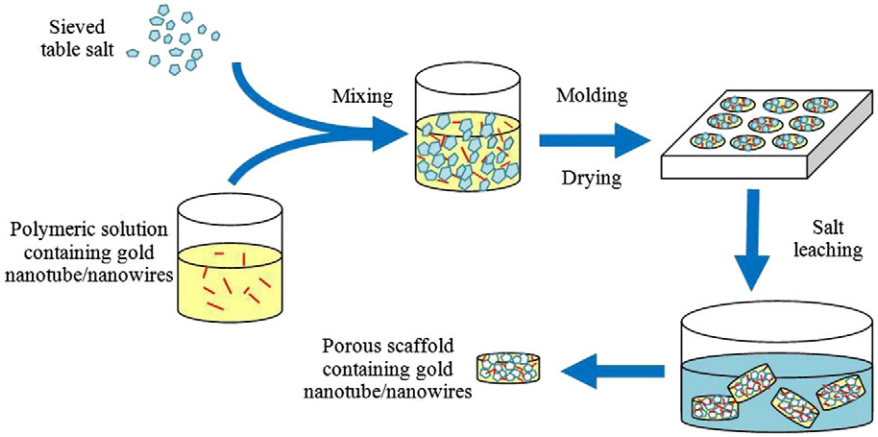

Fig. 1. Schematic of the scaffold preparation.