



Preparation and characterization of conducting polycaprolactone/chitosan/polypyrrole composites

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ARTICLE INFO

Article history:

Received 6 February 2010

Received in revised form 26 June 2010

Accepted 30 June 2010

Keywords:

A: Polymer–matrix composites

B: Microstructures

B: Electrical properties

B: Mechanical properties

ABSTRACT

A novel processing method was developed to produce conducting polycaprolactone/chitosan/polypyrrole composite membranes. Results obtained from infrared and X-ray spectra as well as thermal dynamic measurements demonstrated that there were pronounced interactions between polycaprolactone and chitosan components, and composite membranes had partially miscible microstructures. It was found that some composite membranes showed conductivity transitions at a polypyrrole load of around 2 wt.%, and significantly enhanced conductivity for these composite membranes was already achieved in overall interval of polypyrrole loads compared to those membranes composed of a single component and polypyrrole particles. The tensile properties of composite membranes both in dry and wet state were examined, and the results revealed that the tensile mechanical properties of hydrated composite membranes could be well maintained if weight ratios of polycaprolactone to chitosan were selected as appropriate values.

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1. Introduction

Intrinsically conducting polymers have been used in various fields such as electrochromic displays, sensors, batteries, electrochromic windows and electromagnetic interference shielding for years [1,2]. Of different conducting polymers, polypyrrole (PPy) has been widely investigated. Except for its industrial applications, PPy has also been used for some biomedical purposes in the form of conducting composites or blends in which PPy component functions as a conductive ingredient, and some other polymers serve as matrices [3–11]. PPy has been favorably selected for these applications on account of its acceptable conductivity and relatively satisfactory biocompatibility with mammalian cells [12,13]. In considering biomedical applications of conducting polymer composites or blends, their polymer matrices should be biocompatible, biodegradable and meet many other biomedical requirements. Therefore, only limited polymers from synthetic or natural sources are available.

The main biodegradable polymers originated from synthetic sources are some polyesters, including polyglycolide, polylactide, polycaprolactone, and their copolymers. Despite their wide usability,

several obstacles are frequently encountered in the use of these materials due to a few common drawbacks [14]. One of the common strategies is to blend or incorporate these polyesters with some other natural biopolymers such as collagen, fibrin, elastin, polyglactin and polysaccharides [15]. Of naturally occurring biopolymers, chitosan has received great attention. Chitosan has many advantageous features [16], including biocompatibility, biodegradability, hydrophilicity, nontoxicity, nonantigenicity, and antimicrobial activity as well as bioadherence and cell affinity. Nevertheless, the less flexibility of chitosan in regulating mechanical properties and, especially, the mechanically weak feature in the wet state have sometimes limited the usage of chitosan.

Polycaprolactone (PCL) is a linear polyester with low melting point (ca. 60 °C), which enables itself to be easily processed. Although PCL has some drawbacks like other degradable polyesters its soft- and hard-tissue compatible properties and mechanical strong characteristics as well as much weak acidic degradation products make it useful for many applications [17]. In fact, chitosan and PCL have somewhat mutually complementary properties, and therefore, it is reasonable to expect that their individual deficiencies would be overcome if PCL and chitosan could be well incorporated together. In addition, by adding PPy component, the resultant PCL/chitosan/PPy composites will be endowed with new conducting functions. However, up to now, little is known about PCL/chitosan/PPy composites. It is thus worthy of investigating this new type of conducting composites for possible applications in nerve repairs.

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In the present study, PPy nanoparticles with high conductivity were first synthesized using our previously reported method [18]. These particles were then incorporated into the PCL/chitosan system to produce PCL/chitosan/PPy composite membranes using hexafluoro-2-propanol (HFIP) as the solvent since both PCL and chitosan can be dissolved in HFIP [19]. A two-step processing method involving pre-concentration and a controllable solvent-removed process was newly developed to mix well three components together and achieve desirable properties of the resultant composite membranes. Main results regarding the preparation and characterization of these new composite membranes were reported.

2. Experimental

2.1. Materials

Chitosan and PCL (PCL 1200D, molecular weight: 1.2×10^5) were supplied by Asahi Glass and Shenzhen Brightchina Industrial Ltd., respectively. The degree of deacetylation and viscosity average molecular weight of chitosan were measured as 82.4 (± 1.93)% and $2.43(\pm 0.21) \times 10^5$, respectively, according to a reported method [20]. HFIP was purchased from Alfa Aesar, and all other chemicals were obtained from Sigma–Aldrich (China) and used as received. PPy was synthesized following a known method [18]. These PPy particles had a size distribution ranging from 25 to 120 nm. The obtained PPy particles were either dispersed into HFIP as a suspension using ultrasonication or dried to constant weight for follow-up measurements.

2.2. Preparation of PCL/chitosan/PPy composite membranes

PCL and chitosan were dissolved in HFIP to prepare a 1.5 wt.% PCL solution and a 0.5 wt.% chitosan solution, respectively. Two types of solutions were mixed at various weight ratios to produce different mixtures. To each mixture, 5 mL of PPy suspension was introduced dropwise at a slow rate during 30 min using microsyringes with stirring. The resultant mixtures were then concentrated by heating at ca. 40 °C with stirring for various periods until the mixtures became a fluid with a high concentration. Each mixture was degassed and cast onto a Teflon mould, and membranes were slowly dried for at least 4 days at ambient temperature in a chamber equipped with several small and adjustable windows. After that, the membranes were dried again at 40 °C under vacuum until constant weight was reached. A series of PCL/chitosan/PPy composite membranes was prepared with varied weight ratios of PCL to chitosan at 60/40, 40/60 and 20/80 (referred to as PCL/ch40/PPy, PCL/ch60/PPy and PCL/ch80/PPy, respectively). Some pure PCL or chitosan membranes, PCL/PPy and chitosan/PPy membranes were also prepared using the same method and they were used as controls. PPy content in different composite membranes was determined by the amount of pyrrole monomer used in the synthesis of PPy. In most cases, PPy content in composite membranes was set 8 wt.%, unless otherwise specified.

2.3. Characterization

Small pieces of composite membranes were cryogenically milled into powder. Infrared (IR) spectra of powder samples were recorded on a spectrometer (IR Prestige-21, Shimadzu) in a transmission mode.

Differential scanning calorimetric (DSC) measurements of membranes were carried out on DSC Q20 (TA Instruments) under a nitrogen atmosphere by setting a heating rate at 10 °C/min. Dynamic mechanical analysis (DMA) of membranes was performed

using a dynamic mechanical analyzer (DMA 242C, Netzsch) from –80 to 200 °C at a frequency of 1 Hz and a heating rate of 3 °C/min under a nitrogen atmosphere.

An X-ray diffractometer (ADX-2500, Angstrom Advanced) was used to record the diffractograms of membranes. Dry membranes were scanned at a speed of 2°/min from 5° to 40° (2θ). The relative crystallinity (X_c , %) of membranes was calculated with a known method [20].

Some composites were cut into rectangle strips, coated with gold–palladium, and the surface and cross-section area of specimens were examined using an FEI Quanta 200 scanning electron microscope.

2.4. Tensile test

Tensile parameters of membranes both in the dry and wet states were measured using an Instron universal testing machine (model 5865). Dry samples were cut into rectangular strips with dimensions of 70 mm \times 25 mm and strained to failure using a gauge length of 30 mm at a crosshead speed of 2 mm/min at ambient temperature. In the case of hydrated samples, after being immersed in water for 2 h, the samples were taken out and surface water was removed using blotting paper. The hydrated samples were also cut into strips with the same size mentioned above and tested under the same conditions.

2.5. Measurement of conductivity

All membrane samples were dried until their weight reached constant prior to measurements. Conductivity of membranes was measured using a standard four-point probe technique at ambient temperature. The conductivity of pure PPy disc was determined as $1.98 (\pm 0.14) \text{ S cm}^{-1}$.

3. Results and discussion

3.1. Processing method and morphology of membranes

Of three components in PCL/chitosan/PPy membranes, PCL has its melting point of around 60 °C, and hence, composite membranes would not be able to endure a higher environmental temperature (upper limit of temperature: 200 °C) during some crucial measurements if the thickness of membranes was too thin and/or the weight ratio of PCL was too high. Based on many trials, it was found that (1) the membranes with a PCL load higher than 60 wt.% were usually not strong enough for the required DMA measurements even though they had a right thickness; and (2) the membranes having a thickness thinner than 700 μm were sometimes melted and broken before 200 °C during DMA examinations even if the PCL load was less than 60 wt.%. Weight ratio of PCL in composite membranes was thus selected not higher than 60 wt.%, and the thickness of the membranes was chosen thicker than 700 μm .

It is known that PPy is insoluble, infusible, and non-biodegradable and therefore, PPy load inside the composite membranes should be maintained as low as possible if these PCL/chitosan/PPy composites would be finally used *in vivo*. In the present study, a PPy load of 8 wt.% for composite membranes was selected to examine the basic structures and properties of membranes. However, results presented in a follow-up subsection will provide some optimize values for PPy loads.

Except for choosing proper weight ratios of components for these ternary composite membranes, the processing method was found to play a very crucial role for obtaining thicker and dense membranes with desirable properties. Although many different

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