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Functionally graded polymeric materials: A brif review of current fabrication methods and introduction of a novel fabrication method

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ABSTRACT

The present work reviews the current fabrication methods of the functionally graded polymeric material (FGPM) and introduces a novel fabrication method that is versatile in applications as compared to those of existing used methods. For the first time electrophoresis was used to control the distribution of the tetracycline hydrochloride (TC) in a film made of polylactic acid (PLA), aiming to induce antimicrobial effect on the film prepared. The elemental analysis on the film surface showed that by employing electrophoresis force, higher amount of TC was detected near the top surface of the film. Results also showed that the FGPM samples with higher percentage of the TC on the film surface were highly effective to minimize the growth of *Escherichia coli*. These findings are useful and important to improve dispersion quality of the particles in the composite material and further enhance its antibacterial property.

1. Introduction

In the modern life living without polymers is almost impossible. Compounding polymers with different additives for various purposes, namely enhancement of antimicrobial property [1], improved bioactivity [2] and mechanical properties [3] as well as precise drug delivery [4] have widen the applications of the polymeric devices.

Functionally graded materials (FGMs) are one category of the composite materials in which their composition, phases and porosity can be systematically controlled to achieve desired properties [5]. The idea of gradient in polymeric materials can be traced to 1980s [6,7], before the birth of FGMs [8]. Recently, there are several studies reported the use of functionally graded polymeric material (FGPM) for different applications, namely biomedical applications [9,10] and membranes for water purification [11–14]. Controlling the distribution of the additives is of importance as it can ensure the positive features of them to be appeared on the FGPM. For instance, the distribution of the loaded drug in the polymeric matrix could precisely control the drug release rate [15] and the use of surface modifying macromolecules (SMMs) played a main role to alter membrane surface hydrophobicity [11,16]. Furthermore, depositing photocatalysts on the membrane surface could induce photocatalytic effect for organic pollutants degradation under UV irradiation [17].

Table 1 shows the methods that have been used for the fabrication of FGPM. These fabrication methods can be generally classified in two main groups. In the first group, FGPM is produced using homogeneous suspension or polymer blend solution that normally contains components of different density [18,19] or hydrophobicity [11,20,12–14]. The second group of the fabrication methods is based on the layer-by-layer (LbL) deposition of the components [21,22]. However, none of these methods are versatile as they are limited to specific characteristics of components used. For instance, SMM is only compatible with several types of polymeric dope solutions. For this method, SMM (either hydrophilic or hydrophobic) is driving to the surface of the membrane using the tendency of the polymer itself to reach the lowest system's interfacial tension [23]. One of the major disadvantages of using SMM is the long air exposure time needed for the migration of this macromolecule to the membrane surface. Also, it is not effective in the case where thick membrane film is produced [16]. The complicated SMM synthesis is another issue that limits its practical application. In view of this, using a low cost and versatile method that is able to drive a wide range of the entrapped particles to the polymeric film surface is urgently needed in order to overcome the technical issues of existing methods.

The effects of electric field on the distribution of materials have been previously studied by several researchers [30,15,31,32]. Reuss [31] discovered the electro kinetic phenomenon of the particles in the solution in the early 19th century. Based on the findings, theoretical analysis of electrophoresis was established for separation of macromolecules with different sizes [33]. The mobility study of the rigid particles

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Table 1
Overview of the fabrication methods of FGPM and their potential areas of applications.

Fabrication method	Materials	Application	Results	Ref.
Centrifugation method	Collagen-glycosaminoglycan	Tubular scaffolds radial pore size gradient	Potential as bone scaffold	[18,19]
Blending	SMM	Separation	Enhancement of membrane surface hydrophobicity	[11,20,12–14]
Magnetron co-sputtering	Poly(tetrafluoroethylene) and AISI 316L stainless steel	Vascular stents coating	Improved wettability and better adhesion	[9,24]
Selective laser sintering	Nylon-11/glass beads	–	Improved mechanical properties	[25]
Laser materials processing	Polycaprolactone with different molecular weight	Biomedical trigger capsule	Production of FGM with different mechanical properties	[21]
Spark plasma sintering	Ti/NaCl, poly lactic acid	Implant	Reduction of the elastic modulus of the Ti implant	[26]
Control the proportion of the salt crystals as porogens	Polyglycolide/NaCl	Scaffold with gradually change of the pore size	Potential as bone substituting material	[27]
3D printing process	Calcium phosphate tribasic, PLGA/PLA	Articular cartilage scaffold	Desirable mechanical properties (full joint replacement)	[22]
Supercritical CO_2 foaming	Polymethyl methacrylate	Devices with gradually changing the pore size	Desirable mechanical properties	[28]
Fused deposition process	Polypropylene/tricalcium phosphate	Porous scaffolds with gradient change of pore size	Suitable for bone scaffold	[29]

showed that dielectric constant of the solution, zeta potential/size of the particles as well as electric field have direct effect on the velocity of the migrating particles [34]. Recently, studies have demonstrated the effect of charge components such as alginate and Naproxen on their dispersion in polymeric solution [30,15,32]. It was found that the electrostatic charge tended to affect radial distribution of the electronegative atoms [32], charged group of the molecules [30] and ions [15] in the electrospun nanofibers. In addition, alternative current power supply was used for alignment of the multi-walled carbon nanotube in the composite membrane to enhance the membrane performance [35]. However, to our best knowledge, fabrication of FGPM using electric field has not been reported so far.

In general, most of the additives have electric charge in the polymeric solution. Thus, electrophoresis can be potentially employed to control their distribution in FGPM. Ions for instance have fixed charge (positive or negative) in the solution while the charge of nanoparticles can be varied by controlling the pH [36]. Some of the commonly used charged polymeric additives and inorganic nanomaterials are chitosan [37–39], sulfonated poly (ether ether ketone) [40,41], Naproxen [15], carbon nanotubes [42,43], silica nanoparticle [44,45], titanium dioxide nanoparticle [46,36], clays [47], zinc oxide [48], silver salts [49,50], etc. These additives were introduced in the polymeric composites for different applications such as water purification [37,39], fuel cell [40,41] and biomedical applications [51].

In this study, for the first time electrophoresis was used to fabricate functionally graded polymeric composite film that consisted of tetracycline hydrochloride (TC) and polylactic acid (PLA). TC and PLA were selected because of their vast usage in drug delivery and food packaging fields [52–55].

2. Materials and methods

Polylactic acid (PLA; Mw: 220 kDa; Mn: 101 kDa) was obtained from Biomer, Krailing, Germany (Biomer L9000). Tetracycline hydrochloride (CALBIOCHEM, EMD Chemical Inc.), chloroform (AR, 99.5%, QREC, C3059) and methanol (Merck, Germany) were used in this study as received without purification.

2.1. Sample preparation

10 wt% solution of PLA/chloroform was prepared by dissolving PLA in the chloroform using magnetic stirrer at room temperature for 4 h. TC that is insoluble in chloroform was dissolved separately in methanol with its concentration fixed at 10 wt%. The solution was continuously stirred for 1 h at room temperature. The TC solution was then added to the PLA solution at 1:10 TC/PLA weight ratio. The prepared solution was left at room temperature for 1 h to remove air bubbles from the solution. The final solution was yellow but clear, which indicated the polymer and drug was homogeneously mixed. 15 mL of the prepared solution was poured in the conductive container that attached to 4 kV positive, direct current (DC) power supply. Power was continuously supplied to the container until complete evaporation of the solvent, leading to solidification of the PLA/TC film. A control sample was also prepared without implying electrophoresis. This control sample is important to study the effect of unwanted parameters such as gravity and system's interfacial tension on the distribution of the TC in the composite film. Fig. 1 schematically shows the preparation setup of the composite film.

2.2. Characterization

FTIR characterization was conducted to study the existence of TC in the FGPM PLA/TC film. The attenuated total reflectance (ATR) was used during IR spectroscopy of the sample surface. Thermo Scientific iD5 Diamond ATR and the Nicolet iS5 FTIR Spectrometer was used for this analysis. The component distribution analysis was conducted on the cross section of the prepared film via Energy Dispersive X-ray (EDX) spectroscope. Three measurements were conducted on each section (top, middle and bottom section) to yield the average result.

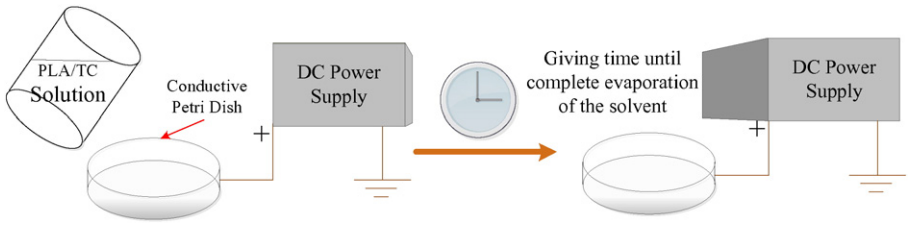

Fig. 1. Schematic of the preparation of FGPM PLA/TC film using electrophoresis.