

Research Article

Fabrication of Hybrid Composites Consists of Poly Methyl Methacrylate and Polyvinyl Alcohol and Hydroxyapatite

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Abstract The weakness of bone plate made up from metal alloys and almost ceramics as well as thermosetting polymers is non biodegradable or very slow biodegradable. Thermoplastic and elastomeric polymers are degradable with various rates. A composite consisted of these polymers could be adjusted for required biodegradable rate. Beside, the composites would overcome mechanical behavior requirements to become promising device in tissue engineering. To support this point, fine hydroxyapatite (HAp) particles were penetrated in the composite. A hybrid composite with polymer mixture with HAp was fabricated by electrospinning method. Poly methyl methacrylate (PMMA) is a thermoplastic polymer, it was demonstrated good biocompatibility. However, PMMA inhibited inappropriate degradable rate in prosthetic treatment. Polyvinyl alcohol (PVA) is an elastomeric polymer; it has good biocompatibility, and rapidly bioabsorbable. These polymers were sprayed by electrospinning machine to form mats. HAp, was synthesized by microwave assisted process, and the contents in the composites were 0%, 2%, 4% and 6% by weight. Warm-pressing process was applied to form bone plate from mats. In MTT assay, the composites were non-toxic and showed good biocompatibility.

Keywords hydroxyapatite; PMMA; PVA; electrospinning; warm-pressing; bone plate

1 Introduction

Plate and screw fixation is the most popular method for rigid internal fixation of the fractured bone [6]. The first generation of bone fixation was made up stainless steel, Cr-Co and Ti alloys. Their strength stood very high pressure through the implantation. However, they were so rigid that arose some big drawbacks, such as stress shielding effect and required post-operative removal. Ceramics were not potential materials for bone fixation, because they were broken under bending stresses that the fixation plates were

often suffered throughout the healing treatment. Therefore, polymer emerged as promising materials for bone fixation applications.

Polymer composite materials offered desired high strength and bone like elastic properties. For decades, a variety of polymers was proposed for bone plate application. First of all were composites constituted of carbon fiber (CF), graphite fiber (GF) and thermosetting polymer (i.e. epoxy) or thermoplastic polymers (i.e. PP, PS, PE, nylon, PEEK) [6]. Thermoplastic polymer composites can be bent and contoured at the time of surgery and implantation. Among of them, CF/PEEK composite is reportedly biocompatible [6]. Recently, Ramakishna et al. [1,3,6] developed braided CF/PEEK composite bone plate using new technique to fabricate good quality continuous bulk. However, these composites were non-resorbable materials in physiological milieu. Hence, they would not decrease stress with time of implantation. Therefore, the stress-shielding effect can not be avoided perfectly. Moreover, removal operation still was need.

To overcome this disadvantage, Tormala et al. proposed a bio-resorbable polymeric composites by reinforcing matrices with resorbable fibers (PLLA) and calcium phosphate based glass fibers [6,7]. The maximum mechanical property of resorbable materials continued to be a limitation and hence they were limited to applications where the loads are moderate (i.e. fixed rods and screws) [7].

A new hybrid composite was proposed to fabricate bone plates. PMMA and PVA were sprayed by electrospinning to fibrous mats. Fine HAp powder was dispersed in PVA mats. Subsequently, mechanical deformation of hybrid composite was manufactured by die drawing method at temperature $T_m > T > T_g$, where T_g is the glass transition temperature and T_m is the melting point of PMMA [7]. Concurrently, pressing was performed formation of the composites.

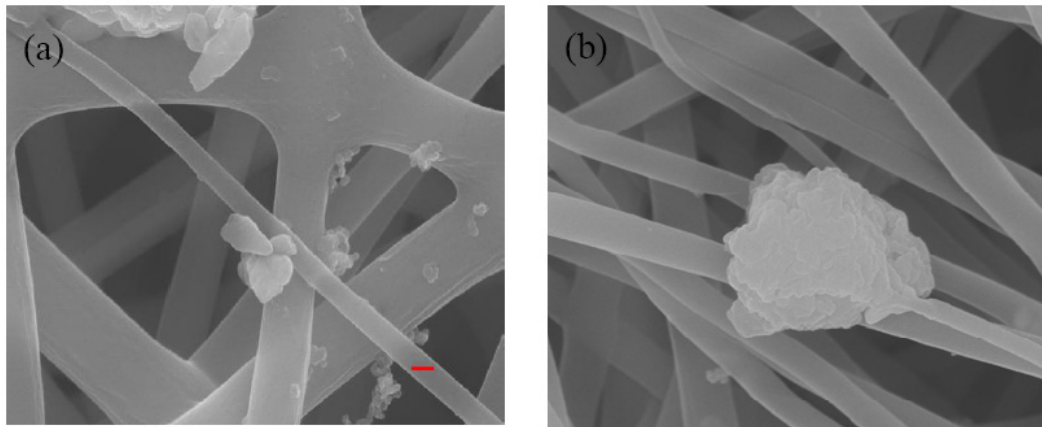


Figure 1: Electrospun HAp-contained PVA (the dash ruler represents 200 nm).

2 Materials and methods

PVA with a % hydrolyzation > 98% was purchased from Sigma-Aldrich Company. PMMA ($M_w > 110,000$ g/mol) was obtained from LG Chemical Company. Nitromethane (CH_3NO_2 , Duksan Pure Chemical Co. Ltd) and distilled water were used as solvents for dissolution of PMMA and PVA, respectively. HAp nano powder was synthesized by hydrothermal-microwave assistant method [4].

PMMA fibers, were obtained by electrospinning method, formed easily when was dissolved in nitromethane [5]. Therefore, PMMA powder was dissolved in nitromethane with 20 wt% by ultrasonic process. HAp was measured from 2 wt% to 6 wt% of PVA content. PVA and HAp powder were stirred in D. I. water simultaneously at 80 °C [2].

Single electrospun spraying was applied to form mats. The PMMA and HAp-contained PVA mats were sprayed in turn. The masses of PVA and PMMA in each electrospun layer were measured the same amount. Then, amount of multilayer electrospun mats were overlapped and were heated to temperature ($T, T_m > T > T_g$). When the mats and moulds reached desired temperature, they were pressed immediately and cooled in air to room temperature. PVA composites and PMMA composites were fabricated as the same method to elucidate biocompatibility.

The morphology of mats and fracture surface of composites were observed by scanning electron microscopy. MTT assays were performed with 3 composites.

3 Results and discussion

Nano HAp powder was penetrated successfully in PVA electrospun mats.

In this literature, HAp content was maximized at 6 wt% in PVA. HAp particle sizes were not homogeneous. Therefore, HAp particles, that these average diameter were smaller than average diameter of PVA fibers, were

entered the inner of PVA fibers (Figure 1(a)). Conversely, the big HAp particles connected to the outer of PVA fibers. Specially, several HAp particles, whose diameters were sub-micron, also connected to PVA fibers (Figure 1(b)). These results demonstrated the ability to increase HAp contents in PVA electrospun mats.

Separated electrospun spraying of PMMA and PVA might make a questionable problem about the association between adjacent layers. Figure 2 showed morphology of multilayer electrospun mat. PMMA fibers were micron ones and PVA fibers were sub-micro ones. The PMMA fibers and PVA fibers made up separated layers. However, the border between PMMA and PVA layers were not observed.

Because electrospinning method could not fabricate enough mass of mats for each time of warm-pressing, mats were overlapped to desired shape (Figure 3(a)). Morphology of fracture surface of hybrid composite exhibited multiple layers clearly (Figure 3(b)). It emerged an interrogative problem about the association of each layers. However, amount of borders in each volume of composite pattern influenced on the infiltrated rate of human fluid when it was applied on clinical operation. Hence, it became a parameter to control biodegradability of hybrid composite.

Before going on further on in vitro and in vivo studies, MTT assays were performed 3 types of composites, such as PVA, PMMA and multilayer. The cytotoxicity of PVA, PMMA and multilayer electrospun were evaluated on fibroblast culture by MTT assay method using ELISA reading at 560 nm wave length. Figure 4 shows the cytotoxicity of electrospun patterns from dilute medium with 0%, 12.5%, 25%, 50% and 100% dilute extracted solution. According to cytotoxicity comparison of each electrospun patterns, we found that 3 types of mat show good biocompatibility, in there PVA was the best one, and then PMMA and multilayer were the similar at 100% dilute extracted solution after 3 days incubation.

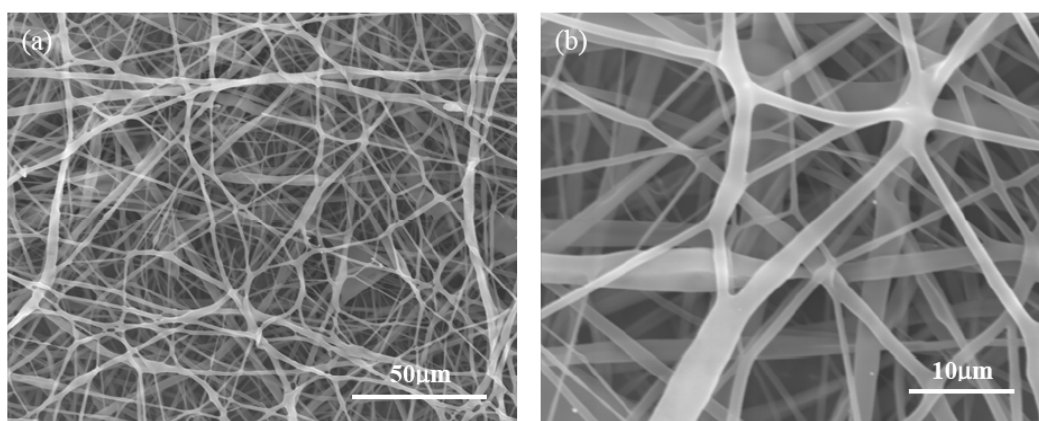


Figure 2: Morphology of electrospun multi-mat.

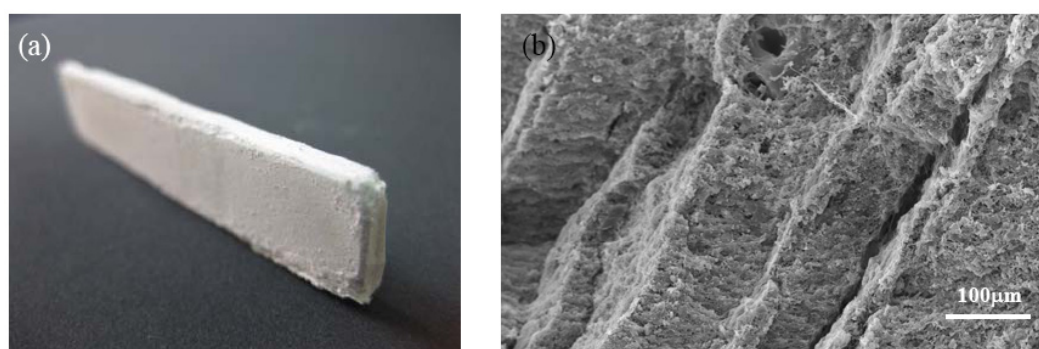


Figure 3: Photograph and cross-section morphology of hybrid composite.

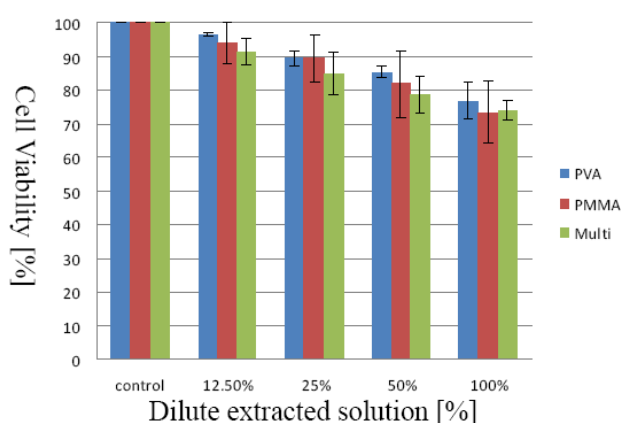


Figure 4: Cytotoxicity of electrospun PVA, electrospun PMMA and multilayer.

4 Conclusions

We provoked a new design for bone fixation. The fabrication of hybrid composites was successfully. Macrostructure and microstructure of composites were investigated. MTT assays demonstrated good biocompatibility of all

constituents of composites. From this, the new design was potential as bone fixed implantations. Furthermore, mechanical characteristics need to investigate more detail and adequately, such as compressive strength, bending strength, elastic modulus. Concurrently, in vitro and in vivo works would be performed.

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