Production of Porous Poly(ε-caprolactone)/Silica Hybrid Membranes with Patterned Surface Pores

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Introduction: Poly(ε-caprolactone) (PCL), as one of the most widely used biodegradable polymers, has been extensively evaluated for potential applications in tissue engineering and drug delivery owing to its outstanding mechanical properties, flexibility, good biocompatibility and biodegradability. However, pure PCL has limited cell affinity and relatively low stiffness, as is often the case with other synthetic biodegradable polymers [1]. More recently, sol-gel derived silica with outstanding biocompatibility, biodegradation and a porous structure [2,3] was hybridized with biodegradable polymers, such as chitosan and PCL, at room temperature. Therefore, in this study, we propose a novel, simple way of producing porous poly(ε-caprolactone)/silica hybrid membranes with patterned surface pores by casting a mixture of a PCL solution and sol-gel derived silica sol. The porous structure of the hybrid membranes prepared at various initial TEOS contents in relation to the PCL content (0, 20, 30, and 40 vol%) in the mixture was observed by scanning electron microscopy (SEM). The chemical composition was also characterized by energy dispersive X-ray spectroscopy (EDS).

Method: First, a poly(ε-caprolactone) solution was prepared by dissolving 8 g PCL (PCL, M_n =80,000) in a mixture containing 30 mL of dichloroethane (DCE) and 10 mL of N, N-dimethylformamide (DMF) as the solvent and non-solvent, respectively. In a separate preparation, the silica sol was synthesized using a sol gel process at room temperature by mixing tetraethyl orthosilicate ($Si(OC_2H_5)_4$;TEOS), distilled water, and ethanol at a molar ratio of 1:1:1 with 1N HCl as a catalyst using a magnetic stirrer for 2 h. Subsequently, predetermined amounts of the silica sol, namely, initial TEOS contents of 0, 20, 30, and 40 vol% in relation to the PCL content, were added to the PCL solutions, followed by magnetic stirring for 12 h at room temperature. The mixtures were then cast into glass Petri dishes and dried at room temperature for more than 12 h.

Results: The porous structure of the hybrid membranes was strongly affected by the initial silica sol content in the mixture, as shown in Figs. 1 (A)-(C). A pure PCL membrane without a silica sol showed a relatively dense structure with very small pores only on the top and bottom surfaces. However, interestingly, a highly porous structure with patterned pores on the top surface appeared with increasing initial TEOS content to 20 vol%. The formation of patterned surface pores became more obvious with increasing initial TEOS content to 40 vol% and the walls between pores became thicker. The presence of a silica phase in the hybrid membrane prepared at an initial TEOS content of 40 vol% was confirmed by EDS attached to a SEM, as shown in Fig. 2 (A) and (B). Strong peaks only associated with Si and O elements were observed (Fig. 2 (A)). In addition, Si element was observed to be distributed uniformly throughout the hybrid membrane, as characterized by EDS mapping (Fig. 2 (B)).

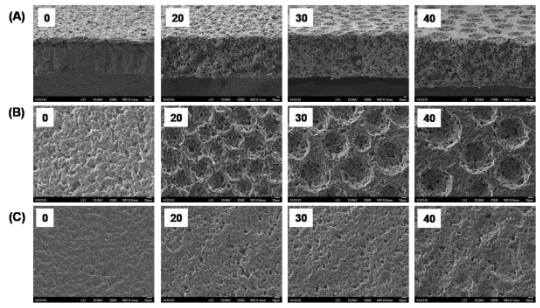

Fig. 1. SEM micrographs of (A) cross-sections, (B) top surfaces, and (C) bottom surfaces of the PCL/silica hybrid membranes produced at various initial TEOS contents in relation to the PCL content contents (0, 20, 30, and 40 vol%) in the mixture.

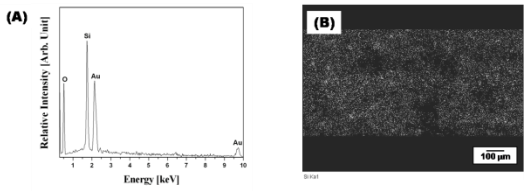

Fig. 2. (A) EDS spectrum of the PCL/silica hybrid membrane produced at an initial TEOS content of 40 vol% and (B) EDS mapping of Si element throughout the cross-section of the sample.

Conclusions: Porous PCL/silica hybrid membranes were produced by casting a mixture containing a PCL solution and sol-gel derived silica sol. The porous structure of the PCL/silica hybrid membranes was affected significantly by the initial silica sol content in the mixture. Without adding the silica sol, a pure PCL membrane showed a relatively dense structure. However, when the initial TEOS content was ≥ 20 vol%, the hybrid membranes showed a highly porous structure with patterned surface pores.

References:

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