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Fabrication of Porous 3-D Structure from Poly(L-lactide)-based Nano-composite Foams

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Abstract – We have examined the enzymatic degradation of a poly(L-lactide) (PLLA)-based nano-composite foam having different cell density (microcellular and nanocellular), using proteinase-K as a degrading agent at 37 °C. The surface and cross sectional morphologies of the foam recovered after enzymatic hydrolysis for different intervals were investigated by using scanning electron microscopic and mercury porosimetric analyses. The fabrication of porous three-dimensional structure for tissue engineering scaffolds and the degradation performance in nano-composite foams were discussed.

In enzymatic degradation, Williams [1] reported the hydrolysis of PLLA in the presence of proteinase-K, which was successfully extracted from protease in a fungus called *Tritirachium album* in 1974. This enzyme has a molecular weight of 18,500±500, an isoelectric point of 8.9 and a pH optimum activity range between 7.5 and 12.0. Proteinase-K preferentially degrades PLLA over poly(D-lactide). The degradation rate significantly increases with reducing % L content from 100 to 92% in PLLA, suggesting the crystalline order dominates enzymatic degradation.

Figure 1 shows the results of the linear degradation rate. The linear degradation rate of the nanocellular is about two times higher than that of microcellular with same crystallinity. The accelerated enzymatic degradation in the foam is caused by the large surface area inside the nanocellular structure. The calculated value of the specific surface area (3.3×10^5 mm^2) is two times higher than that of microcellular (1.7×10^5 mm^2). Obviously, both the difference of the degradation rate and the difference of the surface area inside the cell structure are almost same level for both cellular structures. This trend reflects the relative importance of the surface erosion in the enzymatic degradation of matrix PLLA .

Figure 2 presents the morphological change of the cross section in the nanocellular after enzymatic degradation for 240 h (corresponding to 48 wt% degradation). The interesting feature is the formation of some flower-like structure as a remaining scaffold in the core part, reflecting the spherulite of the crystallized PLLA. After the restricted amorphous region has been degraded, the porous 3-D scaffold left the core part in the nano-foam. This morphology of the PLLA crystals is enhanced with degradation up to 240 h. The structure size with a diameter of 10 μm observed by SEM is in good agreement with the average diameter of the spherulite developed in the sample by annealing at 100 °C before degradation. The generation of the porous 3-D structure is completely different from the enzymatic degradation of bulk sample, where the morphology of the core parts remain unchanged during degradation because of the surface erosion mechanism (photo not shown). Thus, the degraded nanocellular provides the porous 3-D scaffold and the pore size is determined by controlling the degradation time using proteinase-K as an effective degrading agent [2].

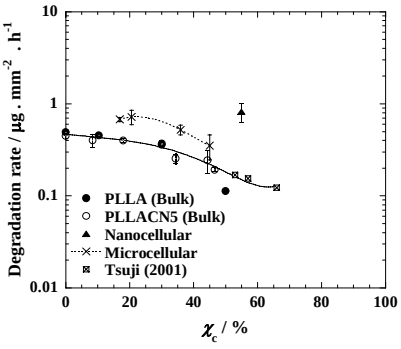

Figure 1: Semi-logarithmic plots of linear degradation rates (μg/mm^2 h) of neat PLLA bulk, nano-composite bulk, microcellular and nanocelluar versus initial χ_c.

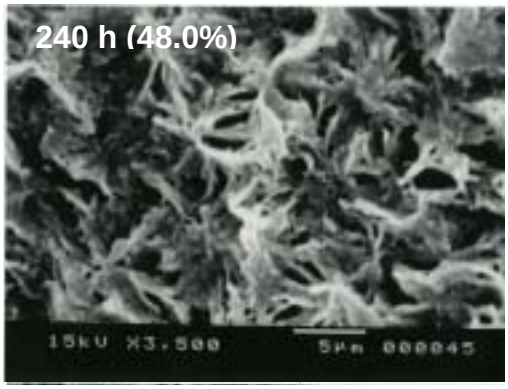

Figure 2: Typical results of SEM images of the cross section and the surface of nanocellular after enzymatic degradation for 240 h.

Refs: [1] DF Williams, Eng. Med. 10 (1981) 5-7. [2] M Bitou, M Okamoto, Polym. Degrad. Stab. 93 (2008) 1081-1087.