Crystallization Kinetics of Apatite-Biopolymer Nanocomposites

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Two kinds of nanocomposite microspheres consisting of carbonated hydroxyapatite (CHAp) nanospheres/poly(L-lactide) (PLLA), calcium phosphate (Ca-P) nanoparticles/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) have been fabricated for use in the construction of osetoconductive bone tissue engineering scaffolds by selective laser sintering (SLS). In SLS, individual microspheres are melted by laser beam to different degrees. Most microspheres comprise an un-melted core, surrounded by a melted and crystallized polymer that bonds with other microspheres. It is therefore necessary to study the crystallization kinetics of apatite-biopolymer nanocomposites since the mechanical properties of tissue engineering scaffolds are strongly related to the thermal properties of semi-crystalline biodegradable polymers.

The effects of 10 wt% CHAp nanospheres on the isothermal and nonisothermal crystallization behavior of PLLA matrix were studied, using neat PLLA for comparisons. The Avrami equation was successfully applied for the analysis of isothermal crystallization kinetics. Using the Lauritzen-Hoffman theory, the transition temperature from crystallization Regime II to Regime III was found to be around 120°C for both neat PLLA and PLLA/CHAp nanocomposite. The combined Avrami-Ozawa equation was used to analyze the nonisothermal crystallization process, and it was found that the Ozawa exponent was equal to the Avrami exponent for neat PLLA and PLLA/CHAp nanocomposites, respectively. The effective activation energy as a function of the relative crystallinity and temperature for neat PLLA and PLLA/CHAp nanocomposite under the nonisothermal crystallization condition was obtained by using the Friedman differential isoconversion method. The Lauritzen-Hoffman parameters were also determined from the nonisothermal crystallization data by using the Vyazovkin-Sbirrazzuoli equation.

The nonisothermal crystallization behavior of neat PHBV and Ca-P/PHBV nanocomposites containing 10, 15, and 20 wt% Ca-P was studied by DSC. The nonisothermal crystallization and melting behavior of PHBV and nanocomposites were significantly affected by the cooling rates and Ca-P content. At given cooling rate, the crystallization process was accelerated by increasing Ca-P content due to the increase of nucleation activity of the nanoparticles. Several models were applied to describe the nonisothermal crystallization. It was found that the effective activation energy decreased with increasing Ca-P content at low relative degree of crystallinity, showing that the Ca-P nanoparticles facilitated the crystallization of PHBV matrix.

CHAp or Ca-P nanoparticles in the composite acted as an efficient nucleating agent, enhancing the nucleation rate but at the same time reducing the spherulite growth rate. This investigation has provided significant insights into the crystallization behavior of PLLA/CHAp and PHBV/Ca-P nanocomposites, and the results obtained are very useful for making good quality scaffolds through SLS.