Silk-PLA Bio-composite Materials for Medical Applications

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Statement of Purpose: A large number of studies have illustrated that new soft composite materials based on proteins and synthetic polymers are promising, as the backbones of these two molecules can be significantly different, so that the advantages of each component can be tunable, i.e., their selectivity, specificity, precise chemical structure, diverse functionalities, as well as their corrosion resistance and the stability or processability of materials could be manipulated [1-3]. In this study, we blended SF with PLA systematically in solvent to fabricate SF/PLA composite films at different ratio using a physical method. The ratios of SF range from 0% to 100%. Besides, the molecular interactions between SF and PLA were investigated by DSC and FTIR techniques, and the morphology of composites was observed by SEM. Finally the thermal stability of composites was evaluated by TG analysis, and the enzymatic degradation behaviors as well as cell response to samples were also observed. This study not only provided comprehensively phase information and structural properties of SF/PLA blend films, but also theoretically proved that a fully miscible blending system of protein (SF) and synthetic polymer (PDLA) is achievable. Simultaneously, this study will help for tailor-making novel SF composites in the further, i.e. films, gels, microspheres, nanofibers, sponges, which have broad applications in biomedical science, such as for tissue regeneration, tissue fixation, wound closure, wound dressing, and anti-cancer drug delivery, etc. [2, 4, 5].

Methods: The surface morphologies of the samples were observed by SEM (LEO 1530 VP, ZEISS Corporation, Japan). Fourier Transform Infrared spectroscopy (FTIR) analysis of silk/PDLA films was performed using a FTIR spectrophotometer (TENSOR 27, BRUKR Co. Ltd, German), equipped with a deuterated triglycine sulfate detector and a multiple reflection, horizontal MIRacle ATR attachment (using a Ge crystal, from Pike Tech). In addition, the dried silk/PLA blends (each about 5 mg) were encapsulated into Al pans and heated in a TA Instruments (Q100, TA Instruments Co. Ltd, USA) DSC, with purged dry nitrogen gas flow (50 ml·min^{-1}), and equipped with a refrigerated cooling system. Thermal gravimetric Analysis (Hi-Res TGA 2950, TA Instruments Co., USA) was also used to measure weight changes of SF/PLDA samples with increasing temperatures. The enzyme degradation study of film samples were performed at 37 °C in 3.1UmL^{-1} protease XIV (Sigma-Aldrich, St. Louis, MO) PBS (phosphate buffered saline) solutions.

Results: The IR results indicated that a new conformation (Silk II structure, 1625 cm^{-1},1540 cm^{-1} and 1267 cm^{-1}) appeared after mixing [6,7]. Some structure contents, such as alpha helix (1652 cm^{-1}), have also increased, and the Tyr side chains (1514 cm^{-1}) [7] were enhanced after SF blending with PLA. Besides, to quantify the percentage of the secondary structures in the SF/PLA samples, a deconvolution method based on curve fitting FSD spectra was performed in the Amide I region. The standard DSC and temperature modulated DSC (TMDSC) was used to prove that the formed SF/PLA systems were fully miscible with different ratios of these two components. [8] The TGA results demonstrated that the SF and PLA components were well blended in the film systems, and did not follow their original individual thermal stability profiles [9]. SEM showed that the morphologies of blend films are uniform in macroscopic scale, but with interesting micro-phase separation patterns. The enzymatic degradation showed that the in-vitro biodegradation of the SF/PLA films are increased with the increase of SF contents.

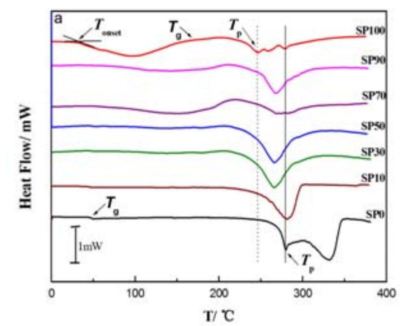

Figure 1. Standard DSC scans of the SF/PLA blend films (SP100 (silk), SP90, SP70, SP50, SP30, SP10 and SP0 (PLA)). The samples were heated at 2 ℃•min^{-1}.

Conclusions: This study provided comprehensive information about miscibility, stability, structure, morphology and biodegradation properties of SF/PLA blend films. The SF/PLA composites can be further fabricated into various forms such as nanosphere, sponges, gels and fibers. Therefore, this study provided an important platform for the fabrication of different SF composites with various biomedical, green chemistry and engineering applications in the future.

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