Alteration of Physicochemical Properties of Sericin by Chemical Modification with Isocyanates

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Sericin of silk protein, working to glue fibroin filaments, has the characteristic amino acid composition, that is, it contains over 70% of hydrophilic amino acids including about 30% of serine residues. The abundance of hydroxylated and charged amino acids provides sericin with high reactivity, and hence sericin may be useful as reactive substrate to develop various functional materials.

In this study, the reactivity of sericin was investigated with some isocyanate compounds, which is highly reactive toward hydroxyl and amino groups. Since isocyanates also react with water, the reactions were carried out in dehydrated dimethyl sulfoxide (DMSO) with 1 M LiCl, which was added to solubilize sericin into DMSO to make the reaction system homogeneous. First, 4-cyanophenylisocyanate was subjected to the reaction. After the reaction at 60 °C for 5 hours, the solution was poured into ethanol to precipitate sericin. The precipitate was collected by centrifugation and washed with ethanol, and then lyophilized. FT-IR analysis of the reaction products showed that the reaction had proceeded smoothly under this condition. Absorption peaks in the IR spectra around 1730 and 2226 cm⁻¹ correspond to C=O stretching of urethane bonds and C≡N stretching of 4-cyanophenyl groups, respectively. This analysis demonstrated that hydroxyl groups of sericin reacted with isocyanates to form urethane linkages and 4-cyanophenyl groups became incorporated into sericin molecules. The ability of sericin to absorb ultraviolet light increased considerably by the modification. The reaction with other isocyanate compounds, phenyl isocyanate and hexyl isocyanate, also proceeded smoothly under the same condition. By incorporation of these new functional groups, sericin became more hydrophobic, and the solubility increased into organic solvents such as DMSO or hexafluoro- isopropanol (HFIP).