

Rheological properties of regenerated silk fibroin (RSF):glycerol solutions

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Regenerated silk fibroin (RSF) solutions have been used to prepare biomaterials such as gels, films and scaffolds, for medical and pharmaceutical applications. Some studies of the RSF aqueous solutions have been reported, but without glycerol addition. Glycerol seems to control transitions of silk fibroin chains and the mechanical properties of silk-based biomaterials. The aim of this study was to evaluate glycerol effects on the rheological properties of 2% (w/w) RSF aqueous solutions with glycerol at weight ratios varying from 0 to 20% (w/w). Rheology tests on oscillation mode were performed on a stress-controlled rheometer using stainless steel cone/plate geometry (30° cone angle, 60 mm cone diameter and gap of 15 μ m). An amplitude test was carried out first at a frequency of 1.0 Hz and 25°C with a strain range from 0.002 to 100 Pa. Frequency sweeps were performed from 0.1 to 100 rad s⁻¹ at 25°C and a constant strain of 1%. Dynamic temperature sweep tests were performed from 25 to 85°C at a rate of 5°C min⁻¹ with constant frequency (1.0 Hz) and strain (1%). Viscoelastic region was determined for all samples and the strain value selected for this work was 1%. All the subsequent measurements were conducted within the linear viscoelastic region. Elastic modulus (G') and viscous modulus (G'') variation as a function of angular frequency showed a predominantly elastic behaviour, i.e., G' dominance over G'' , with a low dependence of the frequency. In addition, an increase on G' and G'' moduli with glycerol addition was observed. Complex viscosity (η^*) dependence of strain indicated an increase in glycerol concentration promotes an increase in η^* up to 300% strain. Above this strain value, occurred fibers formation. Dynamic temperature sweep tests exhibited an abrupt increase in G' and G'' with temperature increment, occurring a plateau formation without a sol-gel transition ($G' > G''$). Therefore, for all glycerol concentration, a small difference between G' and G'' values was observed above 60°C, with a magnitude lower than 1 decade. Both G' and G'' moduli have less variation in temperature function up to 60°C with the increasing glycerol concentration, thus suggesting the presence of a limiting concentration. Likely, glycerol must achieve a critical concentration and appears to prevent the unstable α -helices toward β -sheet structure by replacing water in silk fibroin chain.

Keywords: fibroin, glycerol, rheological properties.

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