

FORMULATION OF MIXED MOLECULAR/MACROMOLECULAR HYDROGELS BASED ON MODIFIED AMINOACIDS AND POLYSACCHARIDE

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Hydrogels find numerous applications in formulated products. Their rheological properties leading to liquid-like or solid-like mechanical behaviour according to external stress are key aspects for reaching targeted performances in operating conditions. Physical hydrogels rely on molecules or/and macromolecules interacting through low energy interactions (e.g. hydrogen bonds) and on physical entanglements between supra- or macromolecular species. Improving the control of the rheological properties requires more insight about the links between the molecular/supramolecular scale and the macroscopic physical properties. Thus it is of primary interest to characterize such hydrogels by combining spectroscopic and rheological techniques. In that work, a natural aminoacid, lysine, has been chemically modified for synthesizing three gelating compounds with similar structures and differing from each other by one or two functional groups. All three molecules were fully soluble in dimethylsulfoxide (DMSO) and gelled DMSO/H₂O mixtures with various compositions. Hydrogels could be produced by following a specific formulation procedure involving dialysis of DMSO/H₂O gels. Mechanical strength of the gels, thermal/mechanical reversibility, temperature of gel-sol transition as well as kinetics of gel formation were correlated to the chemical structure of the gelators as well as to the composition of solvent. The results of visual observation, rheological measurements and Raman spectra were compared (Figure 1). We demonstrated that subtle variations in the chemical structure of the gelator dramatically modified some properties like the time for gel formation (which varied between 10 and 5000 s) or thermal reversibility. The formulation pathway must be adapted to the gelling behaviour of each molecule. In addition a specific geometry was designed for rheological measurements. A non-ionic polysaccharide (dextran, $M_w \approx 400,000 \text{ g}\cdot\text{mol}^{-1}$) was added and the resulting modification of gel properties was investigated below and above its critical overlap concentration. According to the formulation of gels, their macroscopic properties could be adapted to specific applications.

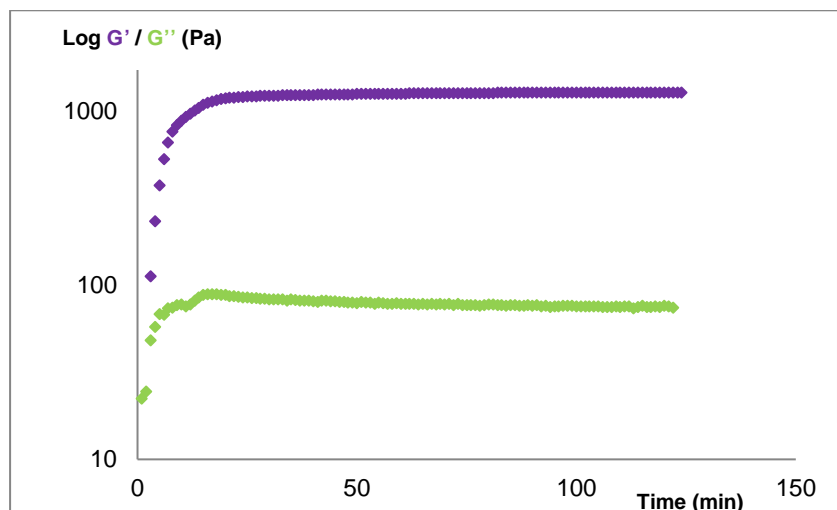


Figure 1: Left. Storage and loss modulus vs time for the gel formed by one lysine derivative (5 mg) in a mixture of DMSO (0.6 mL) and water (1.4 mL) at room temperature (stress : 1 Pa, ω : 10 rad/s). Right. Visual aspect of the gel after 1 day.