Metallophilic Hydrogels: A New Family of Injectable and Self-Healing Materials

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Abstract

In-situ forming hydrogel systems have attracted considerable interest as injectable scaffolds for tissue engineering and drug delivery due to their easy applications and minimally invasive injection procedure.[1,2] Our research group has recently developed a new generation of injectable supramolecular hydrogels based on low molecular-weight Au (I) and Ag (I) thiolates.[3,4] Here we present a new family of polymeric hydrogel with self-healing properties and adjustable mechanical properties.[5]

Supramolecular polymeric hydrogels were obtained by mixing an aqueous solution of salt metals ($AgNO_3$ or $HAuCl_4$) with an aqueous solution of thiolated polymer at physiological pH. The instantaneous gel formation allows its application as injectable scaffold for tissue engineering, e.g. bone or cartilage replacement. Interestingly the supramolecular polymeric hydrogel exhibits self-healing properties (Figure 1) due to the reversible supramolecular interaction of thiolates metal (I).

Moreover, the mechanical properties of these supramolecular hydrogels could be tuned on demand by varying the amount of metal ions incorporated into the hydrogel. For example, hydrogels with high amount of added gold exhibit a shear-thickening behavior similar to synovial liquid (Figure 2). Furthermore supramolecular hydrogels with lower gold concentration show more toughness but their self-healing properties are kept in (Figure 3). Also a judicious selection of the metal allows the hydrogel to be an excellent cell proliferation scaffold or to have antibacterial properties when gold and silver are used, respectively.

In summary, this new family of polymeric supramolecular hydrogels offers advantageous properties for a wide range of application from tissue engineering as injectable scaffolds, synovial liquid replacement due its shear-thickening behavior to material for wound healing.

References

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[2] Klouda, L. *et al.* EUR. J. PHARM. BIOPHARM. **68** (2008) 34-45
[3] Casuso, P. *et al.* ORG. BIOMOL. CHEM. **8** (2010) 5455-5458
[4] Odriozola, I. *et al.* ORG. BIOMOL. CHEM. **9** (2011) 5059-5061
[5] Patent number EP11382365

Figures

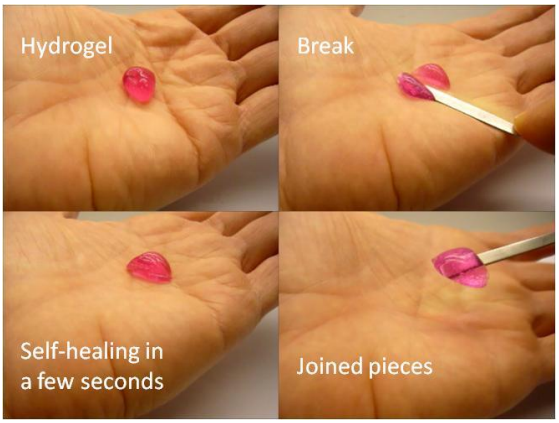

Figure 1. Self-healing behavior of the supramolecular hydrogel.

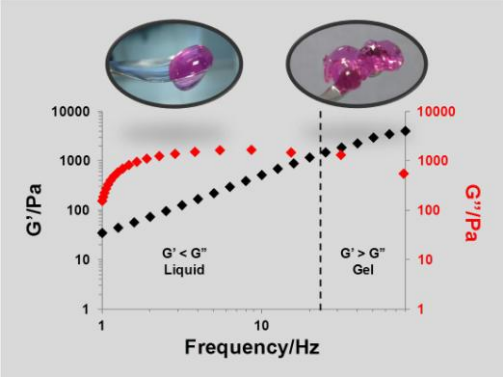

Figure 2. Variation of G' (solid behavior) and G'' (liquid behavior) with frequency.

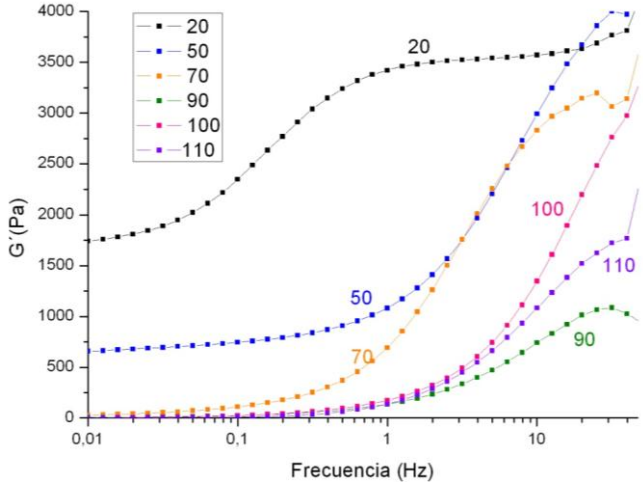

Figure 3. Variation of the storage modulus (G') with different amount of metallophilic interactions ranging from 20 to 110 mol % based on the initial quantity of thiols.