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Development of polymer synthetic systems able to undergo hardening via complex coacervation



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The aim of this project is to synthesize a bioadhesive for soft tissue repair and wound closure: the project is really challenging because a lot of requirements need to be fulfilled. The problem of achieving a strong bond under wet conditions has been solved by many marine organisms, which are able to bond dissimilar materials together under seawater with little if any surface preparation. Complex coacervation, that is the separation of a macromolecular solution composed of two oppositely charged macroions into two immiscible liquid phases, plays an important role in the formation of these adhesives. In particular, both the liquid phases contain huge amounts of water, but the complex coacervate phase contain most or all the charged macromolecules. Bio-inspired adhesives modelled after these examples have been developed: however, despite a good biocompatibility and biodegradability, they often lack the mechanical properties to maintain a strong bond in wet environments.

So, in order to get a more resistant material, some strengthening mechanisms have to be introduced, such as the introduction of a higher degree of chemical crosslinking. However, when a high degree of chemical crosslinking is achieved, it is hard to dissipate the energy of a crack present in the network, inducing the fracture of the whole material. On the other hand, cross-linking is desired because it could improve mechanical strength. Physical cross-linking, achieved using hydrophobic interactions, allows mechanical strength improvement and at the same time allows the dissipation of energy due to a crack.

In order to build an adhesive which can still display a tunable viscoelasticity and self-assembly, providing better mechanical properties, a new strategy is being developed in this project: complex coacervation between hydrophobically modified polyelectrolytes. In this way, hydrophobic domains are added to oppositely charged polymers which, upon mixing, can undergo complex coacervation leading to a new material with better mechanical properties.

The first step requires the synthesis of hydrophobically modified polyelectrolytes. The strategy used in this project is to build graft copolymers, which have a charged backbone and hydrophobic side chains. Two oppositely charged graft copolymers have been successfully synthesized: Poly acrylic acid-g-Poly N-isopropylacrylamide (PAA-g-PNIPAM) and Poly dimethylaminopropyl acrylamide-g-Poly N-isopropylacrylamide (PDMAPAA-g-PNIPAM). These copolymers have respectively a negatively charged and a positively charged backbone, bearing both PNIPAM side chains. PNIPAM is a thermoresponsive polymer which show an hydrophobic behaviour only above a certain temperature, called Lower Critical Solution Temperature (LCST). The LCST of PNIPAM is 32 °C which means that it can be able to self-assemble at 37 °C, the human body temperature, providing better mechanical properties to the adhesive when it is delivered into the human body.

The second step is the complex coacervation between the synthesized copolymers. Two water solutions of the two polyelectrolytes were mixed in order to have the same concentration of charged groups in the final material. Phase separation immediately took place and, after centrifugation, the polymer concentrated phase sedimented. So, the synthesized polymers have successfully been able to undergo complex coacervation.

The coacervate phase has been characterized by rheology to determine its mechanical properties, which are expected to improve when temperature is raised because of the LCST behavior of PNIPAM. As a matter of fact, at room temperature, the coacervate is a flowing material which has liquid-like properties at low frequencies and which exhibits a cross-over between the loss and the storage modulus at higher frequencies. However,

when the temperature is increased above the LCST of PNIPAM, the flowing behaviour is lost: the material displays a storage modulus higher than the loss modulus over the whole range of frequencies, exhibiting a gel-like behaviour. The value of the moduli at high temperatures are one order of magnitude higher than at low temperatures, that means that the material gets stronger when the temperature is increased. The flowing behaviour can be restored decreasing the temperature.

In conclusion, we were able to synthesize hydrophobically modified graft copolymers which are able to undergo complex coacervation. The strength of the coacervate phase can be tuned by varying the temperature: in particular, the material gets stronger when temperature is raised above 32 °C. Furthermore, this behavior is reversible. In the end, we were able to use complex coacervation to design a material which can display better mechanical properties at human body temperature. These results match our expectations and show that this material can be a promising candidate for the development of an underwater adhesive for soft tissue repair.