



**Fig. 2.** Schematic drawing that shows the typical reversible behavior of a material with thixotropic properties under a mechanical stress, then after a period of rest (Adapted from Barbucci 2013).

point where the seemingly solid material is made by particles linked among them by the other liquid component of the mixture, i.e., water. Then if the shear rate is applied progressively and sufficient time is allowed for a high enough shear rates to develop; the particles are separated from each other by the breaking of weak interactions of the mixture. In other cases where the thixotropic material is a flocculated suspension, the shear rate determines a floc size decreasing, until at a determined shear stress value the flocs disintegrate completely into their constituent primary particles and become liquid. The capability of polysaccharide-based hydrogels to absorb a large amount of water makes them similar to highly viscous solutions and is the basis of the thixotropic behavior that characterizes some of them. When an appropriate stress is applied (by a rheometer or by squeezing the hydrogel through a syringe), some of the interactions present in the hydrogel break, generating flocs that slide on the water that connects them, with a laminar flux. The system undergoes a reversible gel–sol isothermal transition. Once the stress is removed, the gel structure slowly recovers as a consequence of the Brownian motion of particles (Frendlich and Juliiusberg 1935) and the three-dimensional form of the material is restored. The same phenomenon is observed by squeezing the hydrogel through a syringe (Fig. 3). Figure 4 shows the typical trend of a stress sweep test performed on a polysaccharide-based hydrogel. For low values of oscillation stress, the storage modulus ( $G'$ ) is higher than the viscous one ( $G''$ ), indicating the gel-like nature of the material. Over the cross-point (i.e., the oscillation stress at which  $G'$  and  $G''$  have the same value)  $G''$  becomes higher than  $G'$ , which is a characteristic behavior of a liquid. This implies a gel–sol transition of the material. The thixotropic nature of the hydrogel is demonstrated by a double rheological graph, obtained by putting together an increasing and decreasing shear curve. The two curves do not overlap, meaning that the material morphology has changed after the stress sweep test for the breaking of some interactions and the formation of gel flocs. The area within the two curves is called the hysteresis loop and it represents the energy dissipated in the sol–gel transition. Its presence confirms the thixotropic nature of a hydrogel. By increasing and decreasing the applied stress cyclically on the same sample we observe that at the end of the second step the  $G'$  and  $G''$  values are lower than those at the first step. The same curves and  $G'$  and  $G''$  values remain in the subsequent stress cycles (Fig. 5). These processes determinate a change in the overall structure of the hydrogel without affecting its chemistry, as demonstrated by NMR and