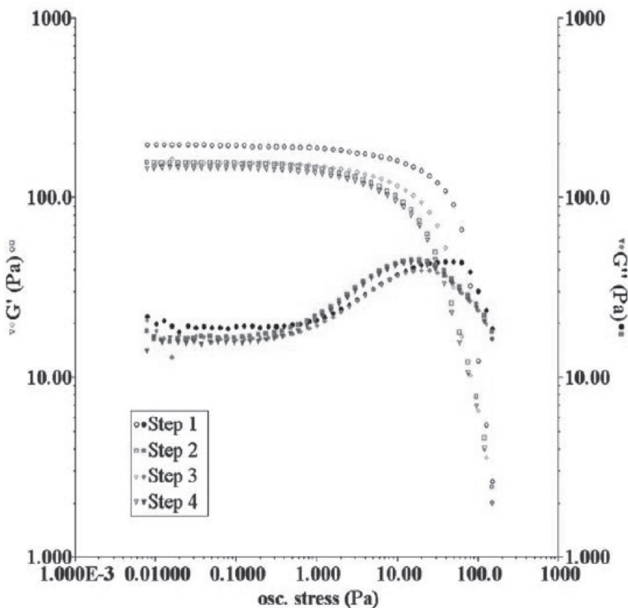


that the sample maintained gel-like characteristics even if both moduli are lower than those of the native hydrogel (Fig. 16). Furthermore, the stress sweep measurements obtained increasing (step 1 and step 3) and decreasing (step 2 and step 4) the applied oscillation stress showed for low values of oscillation stress (between 15 mPa and 400 mPa) the storage modulus is higher than the viscous one ( $G' > G''$ ). For step 1 a crosspoint (i.e., the oscillation stress at which  $G'$  and  $G''$  assume the same value) of 70 Pa was found. Above this value the viscous modulus is higher than the storage modulus, a characteristic trend of a liquid. By decreasing the oscillation stress (step 2),  $G'$  and  $G''$  show lower values than those found during the increase in oscillation stress. At the end of step 2, the  $G'$  value is slightly lower than that of the hybrid hydrogel at the beginning of the test. By repeating several times the same sequence of steps (that is increasing and decreasing in the oscillation stress) on the same sample,  $G'$  and  $G''$  values always follow the same trend of step 2.

Since the chemical structure was not changed by mechanical stress the observed rheological thixotropic behavior was attributed to the movement of water molecules bound to the polymer chains (Barbucci et al. 2011). In particular, the presence of water molecules organized near the polymeric chains (bound water) influences the rheological properties of the hydrogels, making the materials tougher. Under mechanical stress, a partial removal of bound water molecules occurs, making the hydrogel softer (Fig. 6).

In order to verify whether the hybrid hydrogel is capable of working as a drug carrier and depot, some samples were immersed in a water solution containing toluidine blue as a drug model. Once the hydrogel had become blue, it was washed several times with water until no release of dye was observed in the washing water.



**Fig. 16.** Stress sweep test performed on CMC–NP hydrogels after being squeezed by a syringe. The figure reports the  $G'$  and  $G''$  value vs. oscillation stress for each step of the test (Barbucci et al. 2011).