Supporting Information to manuscript

Hydrogels formed through regulated self-organization of gradually charging chitosan in solution of xanthan

Yury Shchipunov, Sergei Sarin, Il Kim, Chang-Sik Ha

The dynamic rheology was applied to study the mechanical properties of synthesized chitosan-xanthan materials. Rheometer was run in either an oscillation or creep regime. The oscillation measurements provided information about the material type. As examples, there are frequencies dependencies of shear moduli G^* and complex viscosity $|\eta^*|$ in Fig. 1. They present two main cases observed when chitosan was gradually charged in a xanthan solution by its progressive acidification.

The plot in Fig. 1A characterizes materials of which rheological features obeys a Maxwell model. This case can be described by a set of equations:[1]

$$G'(\omega) = G_0\omega^2\tau_t^2 \big/ (1+\omega^2\tau_t^2) \tag{1}$$

$$G''(\omega) = G_0\omega\tau_t \big/ (1+\omega^2\tau_t^2) \tag{2}$$

$$\eta^*(\omega) = (G'^2 + G''^2)^{1/2} \big/ \omega \tag{3}$$

where G' is the storage modulus, G'' the loss modulus, G_o the plateau modulus, τ_t the terminal relaxation time, ω the frequency in rad/s; $\omega = 2\,\pi f$, where f is the frequency expressed in Hz.

The plot may be conceived of consisting of two regions. The border, shown by the vertical dashed line in Fig. 1A, comes through point in which the curves corresponding to G' and G'' cross each other. The left low frequency region represents the case where $G' < G''$ and, furthermore, the storage modulus increases as the square of the frequency and the loss modulus, directly with f in accordance with Eqs. (1) and (2). The complex viscosity is almost constant. This value of $|\eta^*|$ is set equal to the zero-shear viscosity η_o. The storage modulus on the other side of the boundary becomes larger that the loss modulus. When the rheological behavior of material obeys the Maxwell model, this means that it is made up of a three-dimensional network of entangled entities being in physical contacts with each other.[2]

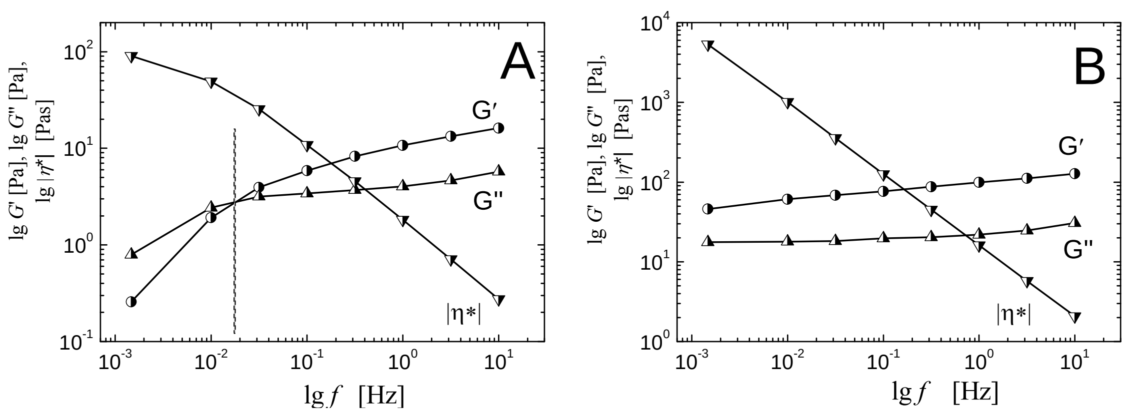

Fig. 1. The complex viscosity |η*|, storage modulus G’ and loss modulus G” vs oscillation frequency. The measurements were performed with samples containing 0.5 wt. % (A) and 1.5 wt.% (B) of xanthan dispersed in water. The temperature was 25.0 ± 0.1°C.

The second type of rheological behavior is seen in Fig. 1B. The distinctive feature is that the G' is higher in magnitude than G'' in the whole range of frequencies available for measurement. Furthermore, the shear moduli are almost independent of f, whereas the complex viscosity $|\eta^*|$ varies in inverse proportion to the oscillation frequency f. These properties are typical of gel or soft (semisolid) materials (see Ref. 3) to which the examined sample can be assigned.

The frequency dependencies of rheological parameters shown in Fig. 1A allow determining the type of material and also the zero-shear viscosity and plateau modulus that characterize the mechanical properties of materials. As mentioned above, the former is taken equal to the $|\eta^*|$ in the low-frequency region where the complex viscosity does not depend on the frequency. The G_o value was usually found by a fitting procedure by using the Eqs. (1) and (2).

The dependence in Fig. 1B, which refers to the gel-like materials, does not allow determining the zero-shear viscosity and plateau modulus. To find these parameters, one may perform a measurement carried out in the creep and recovery regime. An example is presented in Fig. 2 for a xanthan-chitosan hydrogel subjected to a constant shearing stress, σ_o.

The stress applied results in the development of strain, γ, in hydrogel with time. This can be described by the equation:[4]

$$\gamma(t) = \frac{\sigma_0}{G_0} + \frac{\sigma_0}{\eta_0} \cdot t \qquad (4)$$

where the first term relates to the elastic response of material, the second term, the viscous flow. This is the creep region.

The cessation of the stress causes a transition to a recovery region that is observed after the creep one. One may see only the elastic response in this region. Notes and constructions in Fig. 2 explain how the zero-shear viscosity and plateau modulus are determined from the creep and recovery measurements.

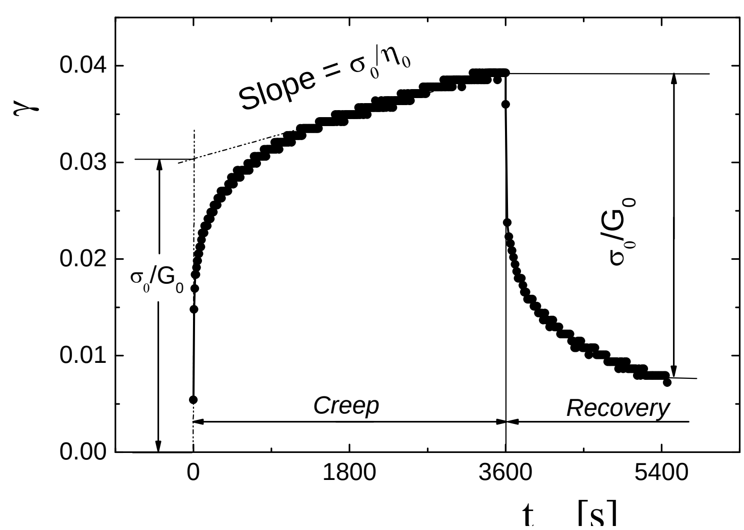

Fig. 2. Creep and recovery after application and cessation of a step stress *σo* of 50 Pa. The method used to determine the rheological parameters is explained by notes and constructions in the figure. The measurements were performed with a sample containing 1.5 wt. % xanthan, and 0.5 wt. % chitosan after its charging in the solution of anionic polysaccharide.

References

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