Supplementary Information to manuscript

Bionanocomposites formed by in situ charged chitosan with clay

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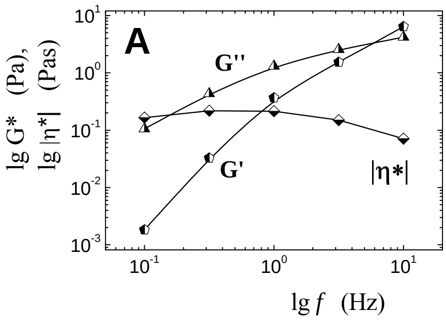
The mechanical properties of synthesized bionanocomposites were examined by means of rheological measurements. Rheometer was run in either an oscillation or creep regime. The former was used first to decide on the material type. As examples, there are frequencies dependencies of shear moduli G* and complex viscosity in Fig. 1 that present two main cases. One may be seen in Fig. 1A. Characteristic features of rheological properties of saponite dispersion are described in the framework of a Maxwell model by a set of equations:[1]

$$G'(\omega) = G_o\,\omega^2\tau_t^2 / (1 + \omega^2\tau_t^2) \qquad (1)$$

$$G''(\omega) = G_o\,\omega\tau_t / (1 + \omega^2\tau_t^2) \qquad (2)$$

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

where G' is the storage modulus, G" the loss modulus, $|\eta^*|$ the complex viscosity, G_o the plateau modulus, τ_t the terminal relaxation time, ω the frequency in rad/s; $\omega = 2\,\pi$ f. In the low frequency region until curves corresponding to G' and G'' meet each other, the storage modulus increases as the square of the frequency and the loss modulus, directly with f, whereas the complex viscosity is almost constant. This value of $|\eta^*|$ is set equal to the zero shear viscosity η_o. When the rheological behaviour obeys the Maxwell model, this means that the system is made up of a three-dimensional network of entangled entities being in physical contacts with each other.[2]



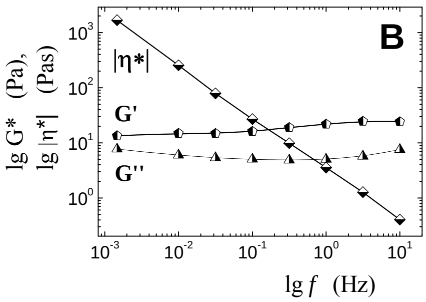


FIG. 1. The complex viscosity |η*|, storage modulus G' and loss modulus G" vs oscillation frequency. The measurements were performed with samples containing 1.45 (A) and 1.75 wt.% (B) of saponite dispersed in water. The temperature was 25.0 ± 0.1°C.

The second case is represented by Fig. 1B. The complex viscosity |η* | varies in inverse proportion to the oscillation frequency f, whereas G′ is higher in magnitude than G′′ and they both are almost independent of 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 zero shear viscosity and plateau modulus that characterize the mechanical properties of materials. The former is equal to the |η* | in the low-frequency region, in which this parameter does not depend on the frequency, whereas G_o value can found by a fitting procedure using the equations (1) and (2).

The plot in Fig. 1B, which presents the case of gel-like materials, cannot be used to determine the zero shear viscosity and plateau modulus. They may found with the help of a measurement carried out in the creep and recovery regime. Figure 2 gives an example of a saponite-chitosan hydrogel subjected to a constant shearing stress, σ_o.

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

$$\gamma(t) = \frac{\sigma_o}{G_o} + \frac{\sigma_o}{\eta_o} t \ , \tag{4}$$

where the first term is associated with an elastic response of material, the second term with the viscous flow.

The creep region is followed by a recovery region that is observed after the cessation of the stress. In the recovery region, one may see only the elastic response. To explain how the zero-shear viscosity and plateau modulus are determined from the creep and recovery measurements, there are notes and constructions in Fig. 2.

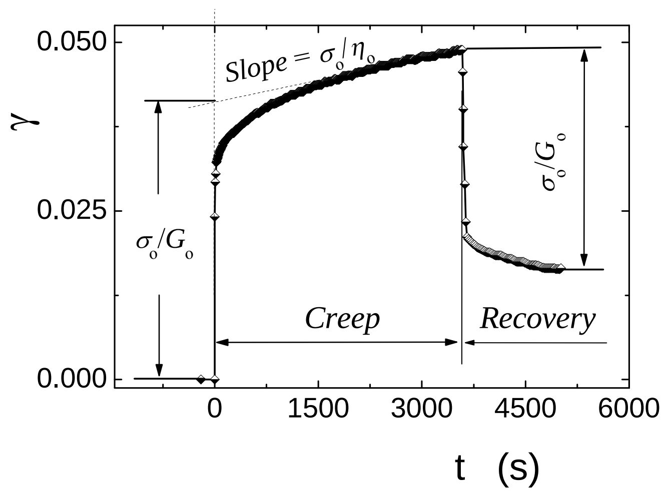


FIG. 2. Creep and recovery after application and cessation of a step stress σ_o of 50 Pa. The method used to determine the rheological parameters is explained by notes and constructions in the figure. The measurements were performed with a sample containing 1.7 wt. % saponite, and 0.1 wt. % chitosane after its solubilization.

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References

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