Viscoelastic properties of \( \kappa \)-carrageenan gels

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With 10 figures

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\( \kappa \)-carrageenan, a sulphated polysaccharide, extracted from Chondrus crispus, is well known for its capacity to form thermoreversible gels in aqueous solutions in the presence of potassium ions. Rees et al. (1) have established that the gelation is associated with macromolecular helix formation.

The creep behaviour of 1.5% gels of \( \kappa \)-carrageenan has been studied by Sawayama et al. (2). It has been shown that they can be strained both reversibly and irreversibly, the effective activation energy of the viscous flow in the temperature interval 11.5–37.0 °C being 24.5 kJ/mole. It should be noted that the method adopted by the above authors to determine the largest Newtonian viscosity, from the terminal slope of the creep curves, is not sufficiently reliable, as this portion can be rectilinear only seemingly, if the relaxation times are large enough.

It is the purpose of the present work to study the viscoelastic, particularly, thermostress properties of \( \kappa \)-carrageenan gels. The work uses a method of separating the reversible and irreversible compliance components based on the determination of the residual strain at elastic aftereffect (3). The creep behaviour was studied in the linear viscoelasticity region of the gels concentrated to 1.0–2.5% in the temperature interval 9–50 °C.

Materials and methods

The \( \kappa \)-carrageenan used in this study was extracted from a commercial carrageenan preparation manufactured by Sigma (tape 1, No. C. 1013). The extraction procedure and characteristics of the purified samples are given in ref. (4).

The gel samples for rheological tests were prepared by the following method: the freeze-dried sample of \( \kappa \)-carrageenan was dissolved in a bidistillate at 80 °C, and then to the hot solution of polysaccharide was added a solution of KCl at constant rate. In all the tests \( [\text{K}^+] = 3.0 \) where \( c_{\text{K}} \) is the mole concentration of \( \kappa \)-carrageenan per disaccharide unit.

Preparations of the samples and creep measurements are performed in the ref. (5). The measuring method consisted in the observation of the simple shear strain, of the sample placed between two corrugated parallel plates.

To attain an equilibrium residual strain at elastic aftereffect, the samples were kept at 40 °C up to the constant value of the residual strain (for about 6 h). The samples were aged for 24 h at 6.0 ± 1.5 °C at 100% humidity.

The fit of the experimental conditions to the region of the linear viscoelasticity and applicability of the Newton law to the description of the gel flow were also established by the methods reported in the ref. (5).

The fusion temperature of the gel was determined by the method described in the ref. (6), consisting in the observation of the melt being displaced by a heavier liquid predeposited onto the sample. Used as such a liquid was perfluorodecalin (\( \rho \) = 1.78 g/cm³). The heating rate was 2.5 deg/min.

The optical rotation of the gels was measured at \( \lambda = 436 \) nm in a thermostated cuvette 0.05 dm thick in the Jouan-Roussel polarimeter (France). The samples were aged in the same conditions as during creep studies. The temperature variation rate was 0.3 deg/min.

Results and discussion

Reversible strain

Shown in figure 1 is the temperature dependence of the shear modulus corresponding to reversible strain after 3 h of loading for a 1.5%–\( \kappa \)-carrageenan gel. The decrease in the shear modulus with temperature is typical of thermostress gels near the fusion temperature when the number of the network junction zones becomes fewer with temperature (7).
Studies in the effect of the temperature on the viscoelastic properties of \( \alpha \)-carrageenan gels indicate that the experimental data can be reduced in the temperature interval \( 9-41 \) °C. The temperature-invariant curve (fig. 2) was constructed by a simultaneous shift of the experimental curves along the time and compliance axes; the reduction temperature \( T_0 = 298.2 \) °K.

The reduction parameters \( \alpha_T \) and \( b_T \) are proportional to \( \exp(-E_A^s/R) \) (figs. 3 and 4). The activation energy of the relaxation processes \( (E_A^s) \), as calculated from the temperature dependence of \( \alpha_T \), is \( 86 \pm 2 \) kJ/mole. For \( b_T \), the angular coefficient \( (-\Delta H_{b_T}/R) \) controls a variation in the number of the gel junction zones. The breakdown enthalpy for these zones \( \Delta H_{b_T} = 27 \pm 4.5 \) kJ/mole.

The shape of the temperature-invariant curve for the relaxation of the reversible strain (fig. 2) is typical of the viscoelastic systems located in the transition and plateau zones. To determine the equilibrium compliance value from the temperature-invariant curve, use was made of a modified extrapolation Thirion-Chasset equation proposed for the description of the creep curves in ref. (8):

\[
J(\alpha_T) \cdot \left( \frac{T}{T_0} \right) \cdot b_T = J_{e,T} \cdot \left( \frac{T}{T_0} \right) \cdot b_T \left[ 1 + \left( \frac{\tau_T}{\tau_m} \right)^{-m} \right]^{-1},
\]

where \( J_{e,T} \) is the equilibrium compliance; \( m \) and \( \tau_m \) are the empirical constants.

This equation is applicable to the terminal portion of the transition zone. Consequently, the experimental points on the temperature-invariant curve, lying to the righthand side of the bending point, were taken for the calculation purposes. The equation describes this portion of the curve for the 1.5%-gel with a dispersion of \( \pm 0.5\% \) at \( 25 \) °C, \( J_{e,T} = 4.8 \cdot 10^{-5} \) Pa\(^{-1}\), \( \tau_m = 3.2 \cdot 10^{-2} \) and \( m = 0.43 \).

Shown in figure 5 is the concentration-invariant curve for the relaxation of the reversible strain. The superposition was attained by shif-