Rheological properties of the gellan/water system

Abstract  Rheological properties of the gellan/water system were investigated. Frequency dispersion curves of dynamic storage and loss moduli ($G'$ and $G''$, respectively) for gellan/water at 5 wt% showed solidlike behavior at low temperatures. The values of $G'$ and $G''$ appeared to decrease with increasing time after gelation. The temperature dispersion curve of $G'$ on heating showed a shoulder in the transition region, while no shoulder was observed on the cooling curve. This indicated that the effect of aging on the rheological properties of the gels becomes larger at low temperatures. At 2 wt%, where the system remains liquid, little effect of aging on the rheological properties was observed. The activation energy of flow was estimated to be 30 kJ/mol for the gellan/water system in the random-coil conformation from the temperature dependence of the zero-shear viscosity. Two types of concentration dependence have been observed for the gellan/water system: one corresponds to the curve for gellan in the random-coil form at high temperatures, and the other is for the curve in the helical conformation at low temperatures. The dependence curves at the intermediate temperatures show the transition behavior.

Key words  Gellan · Sol · Rheology · Zero-shear viscosity · Temperature dependence

Introduction

Gellan gum is widely used in the food industry because concentrated solutions of gellan form transparent and strong gels [1]. Aqueous solutions of gellan at high concentrations form gels at low temperatures, and the aggregates of double helices as well as the double-helical strands are believed to act as cross-links in the gels, whereas the molecules are in the random-coil conformation at high temperatures [2, 3]. At very low polymer concentrations, the system cannot form the gel even at low temperatures, but forms a sol where cross-links exist. The sol may contain the aggregates of the helical domains at higher concentrations. Although the sol is not a homogeneous solution, the system is still a liquid. Many studies have been made to clarify the structure and properties of the gellan/water system [4]. Among the properties, rheological properties of the system have been investigated extensively because of scientific interest as well as industrial importance; however, the studies have focused mainly on the properties of the gels, and the rheological properties of the sols still remain unclear at present. The main aim of this study is to examine the rheological properties of gellan in the liquid state in terms of the zero-shear viscosity.

Experimental

The gellan used was of the third distribution of the common sample supplied by San-Ei Gen F. F. I., Japan. Details of the characteristics of the sample are described in the papers by other research groups [5, 6]. No further purification was made for the gellan sample. Solutions of gellan were prepared by dissolving the powder in distilled water at 90 °C for 1 h. The polymer concentration ($c$)
ranged from 0.5 to 5 wt%. The dynamic storage modulus ($G'$) and the loss modulus ($G''$) of 0.5 wt% solutions were measured using a Vilastic 3 (Vilastic Scientific, USA) using a capillary of diameter 0.3 mm in angular-frequency-($\omega$)-sweep mode. Dynamic viscoelastic functions for the specimens at $c > 0.5$ wt% were measured using a DynAlyser (Reologica, Sweden). The geometry employed was a combination of bob and cup. In the temperature-sweep experiments, the dynamic viscoelasticity on heating was measured first and then the measurement on cooling was made at $\omega = 1$ s$^{-1}$. The cooling and heating rates were both 2 °C/min. A series of frequency-sweep experiments were initiated at the highest temperature ($60$ °C) and the temperature was lowered by $10$ °C after finishing a sweep. The experiment was terminated with the measurement at $10$ °C. The maximum strain amplitude applied to the system was 0.3 for both rheometers. The zero-shear viscosity ($\eta_0$) was calculated by [6].

$$\eta_0 = \lim_{\omega \to 0} \frac{G'(\omega)}{\omega}.$$  \hspace{1cm} (1)

**Results and discussion**

The temperature dispersion curves of $G'$ and $G''$ for the gellan/water system at 5 wt% are shown in Fig. 1. As can be seen from Fig. 1a (the dispersion curves on heating), $G'$ and $G''$ at low temperatures are almost constant, and both moduli show a steep change around 40 °C. The steep decrease with increasing temperature is induced by the conformational transition of the gellan molecules from helix to random-coil. When the temperature is raised further, the $G'$ curve continues to decrease but a shoulder appears at about 45 °C, while $G''$ decreases monotonically. The shoulder corresponds to the melting of large aggregates formed in the system at low temperatures. In the dispersions on cooling (Fig. 1b), $G'$ and $G''$ increase gradually at high temperatures as the temperature is lowered, and the steep change occurs around 40 °C for both curves. The $G'$ curve on cooling does not show a shoulder in the transition region, in contrast to the curve on heating, indicating that a large hysteresis exists in the $G'$ curve at the transition. After the steep change, the $G'$ and $G''$ curves leveled off in the low-temperature region. It is clear by comparing both figures that there is a large difference in the leveled-off values of $G'$ and $G'' \cdot G'$ and $G''$ on heating are lower than on cooling. The difference originates from the effect of aging, as discussed later.

Similar plots for the 2 wt% gellan/water system are shown in Fig. 2. The steep change in $G'$ and $G''$, originating from the conformational transition of the molecules, is observed at 30–35 °C in both heating and cooling curves. For this specimen, the shoulder is not observed in the $G''$ curve on heating. The $G'$ curves on heating at 3 and 4 wt% also did not show the shoulder, although we do not show the curves here. This suggests that large aggregates composed of the helical domains are not formed at $c$ lower than 5 wt%. Similar results have been obtained by Miyoshi and Nishinari [6, 8].

As can be seen from the figure, the $G''$ curve on cooling coincides well with that on heating at low temperatures, but the $G'$ curve on cooling is slightly different from that on heating.

Plots of $G'$ and $G''$ versus $\omega$ for the 5 wt% gellan system are shown in Fig. 3. It is clear from Fig. 3a that at 50 and 60 °C $G'$ is proportional to $\omega^2$ in the wide range of $\omega$. In the temperature range of 10–30 °C, the $G'$ curve depends weakly on $\omega$ but still keeps high values. This is because the system at these temperatures is in the solid (gel) state, as reported by Miyoshi and Nishinari [8]. The dispersion curve moves downwards with decreasing temperature. According to the theory of rubber elasticity [9], the modulus is proportional to the absolute temperature; however, the difference in the $G'$ values for the three curves is rather large compared with the difference in the absolute temperature. This means...