

Determination of Frequency Independent Critical Concentration of Xathan and Carob Mixed Gels

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Abstract The frequency independent critical concentration (Cc) of xanthan and carob (X/C) mixed gel was determined based on the Winter-Chambon's theory. X/C mixed (X/C=1:1 ratio) gels were prepared from 0.1 to 1% of concentration. The linear viscoelastic properties, i.e., storage and loss modulus, of X/C mixed gel at 20°C were measured by frequency sweep tests. The frequency independence of tangent function of phase angle ($\tan \delta$) of X/C mixed gels was graphically determined from the intersection of the plot of phase angle against concentration at varied frequencies. The intersection (C=0.43%) was considered to be Cc of X/C mixed gel.

Keywords: Winter-Chambon's theory, critical concentration, rheology, xanthan gum, locust bean gum

Introduction

Biopolymers, defined as macromolecules obtained from living organisms, are useful resources to control the functionality and quality of food and pharmaceutical products (1). Xathan (X) and carob gum (C) mixture is important for processed meat and dessert industry to control the texture and the cost of final products. It is well known that many polymers, including both synthetic and biopolymers, form a gel in moderately concentrated solution, whereas in dilute solutions thermo-reversible aggregates are formed (2). The gelation is a phase transition from liquid to solid at a critical extent of reaction of crosslinking polymers. In terms of rheology, the critical gel point (GP) is defined when its steady shear viscosity is infinite and its equilibrium modulus is zero (3).

The critical gel points are correlated with several gelation variables, such as temperature, time, and concentration. Theoretically, the gelation is described by the site-bond percolation process (4). Especially, for the thermoreversible sol-gel transition, thermodynamic variables to control this process are concentration (site process) and temperature (bond process). The elastic modulus, often used as the onset point of gelation, is described by the power-law form of these variables.

Time and temperature are readily accessible variables to control gelation process. Knowing the critical values is an important step for developing any gel product. To define the critical GP, 2 curing methods at constant frequency are usually used: 1) time sweep under an isothermal state, and 2) temperature sweep at constant heating/cooling rate. From the time sweep test, the gelation time (t_{gel}), defined as the time to reach the phase transition from sol to gel state under isothermal condition, is obtained. From the temperature sweep test, the gelation temperature (Tgel),

defined as the temperature required to form gel phase, is obtained. These 2 parameters (time and temperature) are very important for designing the process units and controlling manufacturing conditions. In addition, the critical concentration (Cc), defined as the minimum amount of concentration to form a gel, is another important gelation variable, and highly correlated with 2 other parameters to determine the critical gel point (5). One of the drawbacks of these time or temperature sweep test is the frequency dependence of critical values. Depending on the measuring frequency, the Tgel or t_{gel} may be varied. Since the critical values are material properties, they should not be varied with the measurement conditions.

Winter and Chambon (3) developed a gel equation to describe the linear viscoelastic behavior at critical gel, and it is widely acceptable (2, 3, 6). In the linear viscoelastic domain, the storage modulus (G') and loss modulus (G'') at the gel point show power-law dependence with the same exponent on the frequency of oscillation $2\pi/\omega$ and therefore, the phase angle δ does not depend on ω (6):

$$G'(\omega) \propto G''(\omega) \propto \omega^\Delta \quad (1)$$

then, the frequency independence at the critical gel point is expressed as:

$$\tan \delta = G''(\omega)/G'(\omega) = \text{constant} = \tan(\Delta\pi/2) \quad (2)$$

According to Eq. 2, the critical gelation parameters (Tgel, t_{gel} , or Cc) corresponding to the conditions can be determined from the experimental data. The empirical data for $\tan \delta$, i.e., $G''/G' = f(T)$, $f(t)$, or $f(C)$, obtained from gel curing tests repeated with several frequencies, can have an intersection at the gel point.

This theory has been applied for many synthetic polymer (7-10) and some biopolymers (11, 12). In these studies, the Tgel and t_{gel} were determined based on the frequency independence of $\tan \delta$ at gel point. However, the other gelation variable, i.e., concentration, has not been examined yet.

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The objective of this study is to determine the critical concentration of X/C mixed gels based on the frequency independence of $\tan \delta$.

Materials and Methods

Xanthan and carob mixed gel preparation To obtain the concentration dependence of tangent function of phase angle, different concentrations (0.1, 0.15, 0.25, 0.5, and 1%) of X/C mixed gels were prepared, and frequency sweep tests were performed under isothermal conditions. Then phase angle at different frequencies was collected, and replotted to find an intersection point.

Laboratory grade xanthan (X) and carob (C) were purchased and used (Sigma Chemical Co., St. Louis, MO, USA). The total polymer concentrations of 0.1, 0.15, 0.25, 0.5 and 1% (g/100 mL of 0.1 M NaCl solution) was used while the mixing ratio of X and C was maintained to be 1:1 for all mixtures. Deionized water was used to prepare the polymer solutions. The X and C were solubilized separately in water at 95°C by stirring for 30 min. The solutions were blended and mixed at 85°C for 30 min and used in the experiments. Small amplitude oscillatory shear (SAOS) tests were performed using the cone and plate geometry (angle=4° and diameter=40 cm) in a dynamic rheometer (CVO, Bohlin Instruments Inc., East Brunswick, NJ, USA). To prevent moisture loss during the experiment, mineral oil was applied around the sample edge. All gels are prepared by *in situ* cooling of the solution mixture from 80 to 20°C at a rate of -1°C/min.

Dynamic measurement Frequency sweep tests were conducted at wide range of frequencies (10⁻²-10¹ Hz). The $\tan \delta$ was calculated from the ratio of G'' and G' obtained from frequency sweep tests. All the experiments were performed in the linear viscoelastic region of gels (the applied strain <0.05).

Results and Discussions

Frequency spectrum of X/C mixture (0.5%) at 80°C shows a strong frequency dependence of G' and G'', however at room temperature (20°C) there is a frequency independent plateau region (Fig. 1). The equilibrium G' and G'' indicates approximately 10 and 1 Pa, respectively. This is clear evidence that X/C mixture solution is gelled at 20°C.

The frequency spectra of X/C mixed gels of each

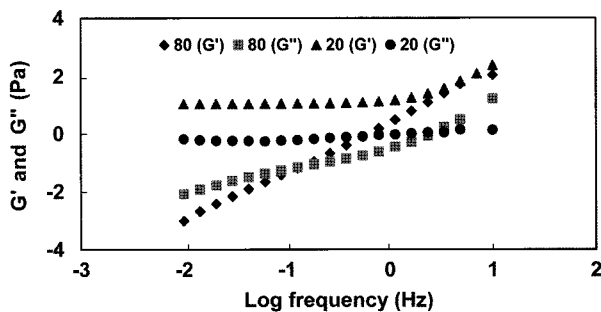


Fig. 1. Frequency spectrum for storage (G') and loss (G'') modulus of X/C mixed gels (0.5%) at 80 and 20°C.

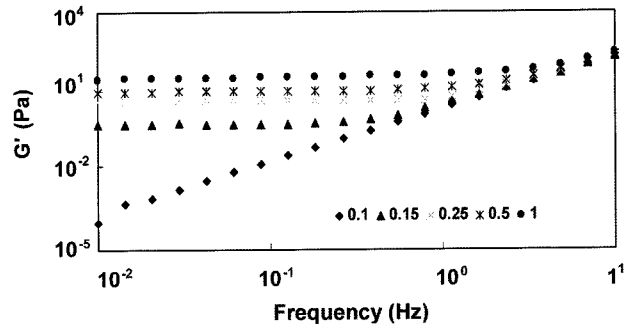


Fig. 2. Frequency spectrum of X/C mixed gels at different concentrations (0.1, 0.15, 0.25, 0.5, and 1%).

concentration are shown in Fig. 2. The existence of plateau regions of G' in frequency spectrum is a widely used criterion to determine Cc. However, as shown in Fig. 2, the plateau regions also show frequency dependency. As the concentration is lower, the frequency dependence became significant. In case of some biopolymer gels, there exists a transition region due to the molecular rearrangements, which is not a thermodynamic transition, but totally frequency dependent, at high frequency region (13). Although 0.15% of gel shows a short plateau region at low frequency region (<0.8 Hz), the modulus is highly frequency dependent at high frequency region. This frequency dependence of modulus may give rise a doubt to use this criteria to determine Cc.

The $\tan \delta (=G''/G')$ of each concentration was calculated

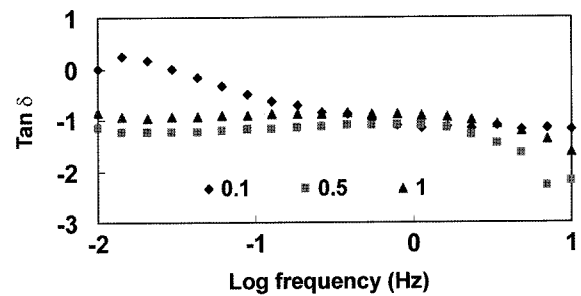


Fig. 3. The tangent function of phase angle ($\tan \delta$) at different concentrations.

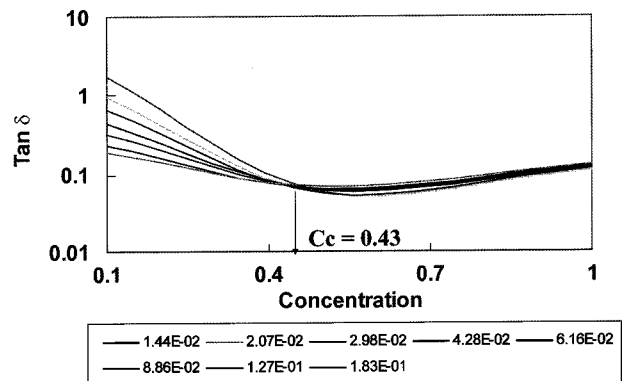


Fig. 4. Concentration dependence of $\tan \delta$ at varied frequencies. The $\tan \delta$ are collected from Fig. 3. Legends indicate frequencies (Hz) used for frequency spectrum.

from frequency sweep results (Fig. 3), and collected at each frequency, then replotted (Fig. 4). There is an intersection of different curves at $C=0.43$ in Fig. 4. Since this intersection is the only point independent of frequency, it enables us to determine the C_c of X/C mixed gel as a given relation by Eq. 2 derived based on the Winter-Chambon's theory. It has to be noticed here that only high frequencies (>0.02 Hz) were used for data collection. When lower frequencies are used, it is difficult to observe the clear intersection. The Winter-Chambon's theory implies that when the gelation variables are lower than their critical values, the state is remained as sol. Based on their theory, when the X/C concentration is lower than 0.43 g/100 mL, the X/C can not form a gel at 20°C .

In this study, to determine the critical concentration of X/C mixed gel, Winter-Chambon's theory was applied. The frequency independent of phase angle was found from the plot of phase angle against concentration. The intersection found at $C=0.43$ may include the nature of gel point: the phase angle, which can be a function of critical parameters corresponding to the conditions of an incipient continuous network, is constant at varied frequencies. Therefore, the intersection point at $C=0.43$ can be considered a critical concentration of X/C mixed gel. This study will be useful for gelation applications in many food industries (14-16).

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