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A novel critical point for isotropic gel in rheological-fractal model

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ABSTRACT

The determination of critical point in rheological-fractal models for most of the food gel systems and polymer viscoelastic systems are based on the point of 95% or 90% value of the storage modulus in linear viscoelastic region. It is not a precise method because the modulus during linear-nonlinear viscoelastic transition region are not always monotonous decreasing. Therefore, there is an urgent need for a more stable and precise approach to determine the critical point, making the scaling behavior calculation closer to the physical truth. This research studied on a typical food system, acid-induced peanut protein isolate (PPI) gel, trying to put forward a new critical point for isotropy food gel and non-newton polymer systems. Result shows that when the increasing higher harmonic reaches a certain value, the corresponding strain could be regarded as a new critical strain point. The image of the microstructure captured by confocal laser scanning microscope (CLSM) was used to calculate the actual fractal dimension, which was 2.3517. It was demonstrated that the fractal dimension calculated from rheological fractal model using the new critical strain obtained from the Fourier transform analysis is closer to its actual value (2.3517).

1. Introduction

Fractal analysis is an effective method to connect the microstructure with the macro properties of gel. It can explain the macroscopic properties of matter from the microscopic point of view (Iannaccone and Khokha, 1996). Therefore, fractal analysis is often used to describe the complexity and chaos of branched chain or network structure as well as the type of branched chain (Wang et al., 2011).

Many scientists have put forward a number of scale theoretical models to study the fractal properties of protein and colloidal gels. It is believed that the rheological properties of the gel are closely related to the particle size, the volume fraction of the particles and the fractal dimension of the gel. At present, many researchers that are focusing on the fractal structure of gel are finding appropriate means to calculate the fractal dimension of different non-Newton viscoelastic system. Scientists have developed many methods which are divided into two categories, one is the direct methods of confocal scanning electron microscope (CLSM), small angle X-ray scattering (SAOS) and dynamic light scattering (DLS), the others are indirect methods based on the calculation by rheology or acoustic properties (Hagiwara et al., 1996; Hagiwara et al., 1997; Matsumoto et al., 1992; Wu et al., 2005). Within these methods, the rheological fractal model is a typical way to calculate the fractal dimension of a material by means of a scaling behavior of macroscopic parameters in rheological test. However, in previous models, the determination of critical point in rheological-fractal models for most of the food gel systems and polymer viscoelastic systems are based on the point of 95% value of the storage modulus in linear viscoelastic region (Shih et al., 1990; Wu and Morbidelli, 2001). It is not a precise method because, in most cases, the storage modulus between linear and non-linear viscoelastic region is not monotonous decreasing, therefore, there is an urgent need for a more stable and precise approach to determine the critical point.

In the field of food processing, the materials often go through a lot of short-term stress process, such as liquid delivery, mixing and so on (Wang et al., 2012). These processes require the measurement, characterization and quantification of non-linear rheological properties of complex fluid materials including molten polymers (Schlatter et al., 2005; Sugimoto et al., 2006; Vittorias and Wilhelm, 2007), mixed polymers (Carotenuto et al., 2008; Filipe et al., 2004; Filipe et al., 2006), dispersions (Kallus et al., 2001; Klein et al., 2007; Wilhelm,

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2002) and so on. This can be carried out by means of the combination of the large amplitude shear test and the Fourier transform analysis. Large amplitude oscillatory shear tests is often used to obtain and analyze some unconventional rheological parameters, such as the analysis of non-sinusoidal stress curve data, frequency domain spectral analysis and so on. A variety of oscillatory flow phenomena in food production, including processing and transportation, can be simulated and explained with large amplitude oscillatory shear tests.

This research studied on a typical food system, peanut protein isolate (PPI) gel, trying to put forward a new critical point using large amplitude shear test and Fourier transform analysis. It may provide a more stable and precisely way in calculating the fractal dimension. This method will expand the utilization of rheological-fractal method in analogous food gel and non-newton polymer systems.

2. Materials and methods

2.1. Materials

Peanut protein isolate (BR, > 90%) was obtained from Shanghai Yuanye Bio-Technology Co. Ltd. (Shanghai, China). Rhodamine B (BS) was obtained from Beijing Yinghai Fine Chemical Industry (Beijing, China). Glucono-δ-lactone (GDL) was purchased from Beijing Wohai Technology Ltd. (Beijing, China). The above materials used in experiments are without any treatment.

2.2. Sample preparation

PPI powder (22 g) was dissolved in 100 ml deionized water (pH = 7.0 ± 0.3) at 20 °C using a magnetic stirrer (85–2, Jiangsu Jintan Instrument) at 500 rpm for 2 h. This protein dispersion was heated at 95 °C for 30 min in a water bath to denature the protein completely and then cooled down to 4 °C. Denaturised PPI dispersion was diluted to the concentration of 14%,16%, 18%, 20% and 22% respectively. Those dispersions at different concentrations were stored at 4 °C overnight. Before testing, the overnight samples needed to be stirred for 5 min on magnetic stirrer to ensure the homogeneity of the samples.

For the confocal laser scanning microscopic (CLSM) test, the PPI dispersion samples was stained with an aqueous solution of Rhodamine B (0.05 ml of 0.01% (w/w) Rhodamine B + 5 ml stock solution of PPI dispersion). Then, 0.1 g glucono-δ-lactone was added into these samples. The stained stock solution was added onto a concave slide and sealed, then, the gel was formed at 60 °C for 30 min (exact the same time-temperature treatment as the gels suffering in the rheological studies) (Bi et al., 2014).

2.3. Rheological tests

2.3.1. Gel formation

AR2000ex rheometer (TA Instruments Ltd., Crawley, UK) equipped with aluminum parallel plate geometry (40 mm diameter, 1000 mm gap) was used for all the rheological tests including SAOS and large amplitude oscillatory shear (LAOS). Acid-induced PPI gel was formed in situ on a Peltier plate, which was connected to a water circulation pump to control the temperature (standby temperature of Peltier is 5 °C when sample loaded). Samples containing GDL were transferred (inject) between the geometry and Peltier and the gel was formed when the temperature of Peltier raise and hold at 60 °C. At this temperature, GDL can reduce the pH of the dispersion very soon. When the pH decreased to the isoelectric point of PPI (pH = 4.5), the network structure was formed among the PPI molecules and PPI dispersion was turned into a gel. During the gel formation process, a small oscillatory strain of 1% was applied on the sample (ω = 0.628 rad/s) and the storage (G') and loss (G'') moduli were monitored and recorded at every 15s. Gel formation step was terminated when the increment of 5 continuous G' values changes less than 3%. A thin layer of silicone oil was applied at the edges of the samples to minimize the evaporation of water. Once the formation of gel was completed, the temperature of Peltier was decreased to 20 °C for 10 min to prevent the pH values from decreasing further. Each test was performed in triplicate and the averaged values were reported.

2.3.2. Large amplitude oscillatory shear test

LAOS test was applied in oscillatory model in which the strain varies from 0.01% to 10%, at a fixed angular frequency of 6.28 rad/s. The strain and stress data points were recorded at a rate of 10 points per decade. The temperature is controlled at 20 °C. With the increase of strain, the trends of storage modulus (G') and loss modulus (G'') of acid-induced PPI gels were measured and recorded.

At lower strains (typically < 1%), the stress response waveform is sinusoidal. However, the waveform becomes distorted and the signal becomes non-sinusoidal when the strain amplitude increases beyond the linear viscoelastic regime (Le Grand and Petekidis, 2008). Fourier transform analysis is a mature method to acquire the entire frequency spectra covering the non-linear stress response (Wilhelm et al., 1998). The data of odd harmonics (i.e. I_1, I_3, I_5 …, frequency of harmonics is odd times of fundamental wave) obtained from LAOS and Fourier transform analysis were used to explain the non-linear behavior of acid-induced PPI gels. In large amplitude region, the stress waveform not only becomes non-sinusoidal but also goes out of phase. For simplicity, we focused on the odd harmonics (1, 3, 5 …) in Fourier transformation rather than covering the entire complex waveform.

The time domain non-sinusoidal stress response was transferred into frequency domain spectra using the Fourier transformation and the stress was decomposed into a series of higher harmonics as given by equation (1).

$$\sigma = Asin(\omega_1 t + \delta_1) + Bsin(\omega_2 t + \delta_2) + Csin(\omega_3 t + \delta_3) + \cdots \quad (1)$$

where, σ *is* the non-sinusoidal stress wave (Pa), $\omega_{1,2,3\ \ldots}$ and $\delta_{1,2,3\ \ldots}$ are the angular frequency (rad/s) and phase angle (degree) of each harmonic, respectively.

Lissajous loop was used here for auxiliary analysis and to interpret the non-linear viscoelastic properties of PPI gel system. The two limiting cases of the Lissajous loop are the Hooke elastic solid and the Newton fluid. For the Hooke elastic solid, the Lissajous loop is a straight line with a slope of G. For the fluid, the Lissajous loop is an elliptic curve with respect to the axis of symmetry (Ewoldt et al., 2008). The ratio of the viscosity and elasticity of the material is determined by the shape of the Lissajous loop. The line inside the Lissajous loop indicates the effect of a high order harmonics on the stress response curve. Furthermore, the integral area of the Lissajous loop shows the energy consumption of a single cycle per unit volume, given as equation (2) (Ewoldt et al., 2008).

$$E_d = \pi \gamma_0 G_1'' \quad (2)$$

2.3.3. Confocal laser scanning microscope (CLSM) test and fractal analysis

CLSM image capture: Samples for these tests were prepared as indicated in Section 3.1. The microscopic image of acid-induced PPI gels was collected by LEICA TCS SP5 confocal laser scanning microscope (LEICA instruments, Germany). The CLSM comprises an inverted microscope (Leica DMI6000, an objective lens of 40 × 0.85(NA)) and He-Ne/visible light laser source (Leica Microsystems (CMS) GmbH., Mannheim, Germany). The CLSM confocal principle can realize confocal tomography imaging of the sample, which is of much advantage for fractal dimension calculation.

CLSM image processing: First, the RGB (Red Green Blue) images were transformed to 8-bit grey images with a scale of 1024x1024 pixels. A black-white binarization was performed using the mid-value of the grey level histogram of each image as a threshold (Bi et al., 2014). Box-counting method (Vicsek, 1989) was applied to calculate the fractal dimension (D_f) of acid-induced PPI gel samples. This method is based