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RHEOLOGICAL BEHAVIOUR OF SOME GELS BASED ON GELATIN

BY

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Abstract. Gelatin is used as an ingredient in many foods and pharmaceuticals as a gelling and thickening agent. The rheological properties are very important in the study of gelatin solutions. The change in the rheological behavior of three gels with different gelatin concentration is investigated. Adding different amount of gelatin in the solution causes a variation of storage modulus (G'), loss modulus (G") and apparent viscosity when measured as a function of strain or frequency. The results show that rheological techniques can be used to determine gel strength.

Keywords: viscoelastic properties; structural stability; gel strength; gelatin; rheology.

1. Introduction

Gelatin derived from collagen, is a long-chain polymer composed of amino acids (proline or hydroxylproline, glycine, arginine, alanine, etc.) with a complex three-dimensional structure. The compound is water diluted in small quantities and used in food production, cosmetics and pharmaceutics to enhance

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texture, avoid undesirable flow behavior, and optimize product stability. In solution, gelatin form a continuous network with a behavior between fluid (sol-like) state and solid (gel-like) state. In the fluid state, gelatin solution contains the disentangle triple helices, whereas in the gel state, the triple helices are entangled providing a three-dimensional network. The gelation process is influenced by temperature (fluid state at 40-80^{o}C and gel state at 4-40^{o}C), composition, concentration, and applied strain. Usually, gelatin materials show viscoelastic behavior when a strain is applied (Di Giuseppe *et al.*, 2009; Choi *et al.*, 2004).

Gelatin can be obtained from the skins and bones of animals (pigskin, beef bones, chicken and fish skin) and its source can affect its properties. The most important properties of gelatin based materials are the gel strength and the viscosity. Rheological measurements are a very useful tools to determine the quality of this type of materials. Three parameters must be carefully selected when doing rheological measurements on gelatin based materials: the time before beginning the experiment, the testing and preparation temperature, and the shear stress value (to be within the linear viscoelastic region) (Boran *et al.*, 2010; Gilsenan and Ross-Murphy, 2001).

In this study, oscillatory sweep measurements were used to determine the rheological properties of gels prepared with gelatin.

2. Materials and Methods

2.1. Materials

Gelatin solutions (2, 3, and 4% w/w) were prepared by mixing gelatin type A (gelatin from porcine skin) from Aldrich with distilled water. The gelatin solution was moderately stirred for 1 h at room temperature and was then heated at 40^{o}C in a water-bath for 30 min with mild agitation provided by a magnetic stirrer. At the end of the heating period, the sample was immediately transferred into a small plastic jar and covered with a polyethylene sheet to avoid sample sticking. The caps were tightly closed and stored at room temperature for 24 h for maturation. After maturation, the rheometer plate was loaded with the gel samples (G2% - gelatin solution 2%, G3% - gelatin solution 3%, and G4% - gelatin solution 4%). The excess sample was trimmed to fit the size of plate (50 mm in diameter). The outer gel surface was covered with a thin layer of mineral oil to prevent moisture loss during the measurements. Each sample was prepared in duplicate.

2.2. Methods of Analysis

Rheological tests have been performed on a Physica MCR 501 modular rheometer (Anton Paar, Austria) equipped with an electronically commutated synchronous motor allowing rheological testing both in controlled stress and control strain modes. Parallel-plate geometry with a diameter of 50 mm was selected as measuring system. The samples were heated using a Peltier system. All rheological characteristics were determined in dynamic oscillation mode (Ibănescu *et al.*, 2010; Danu *et al.*, 2012).

The **amplitude sweep** is used to determine the limit of the linear viscoelastic range. Here, the oscillation frequency is kept constant (ω = 10 rad/s), while the oscillation amplitude (γ) is varied (between 0.01 and 100%). The limit of the linear viscoelastic range permits the determination of the maximum deformation tolerated by the sample before the structure is destroyed.

The **frequency sweep** is a widely used standard test in gel rheology. In this test a sinusoidal strain with a constant amplitude (γ = 1-5%) is applied and the oscillation frequency is varied (between 0.05 and 500 rad/s). All measurements were carried out at a constant temperature of 25^{o}C.

3. Results and Discussions

Rheological parameters can be used to describe textural behavior of materials. If the material shape is restored when the external forces are removed, the elastic behavior is observed, whereas if the material shape does not take back its original shape, the viscous or plastic behavior is detected (El-Hefian and Yahaya, 2010).

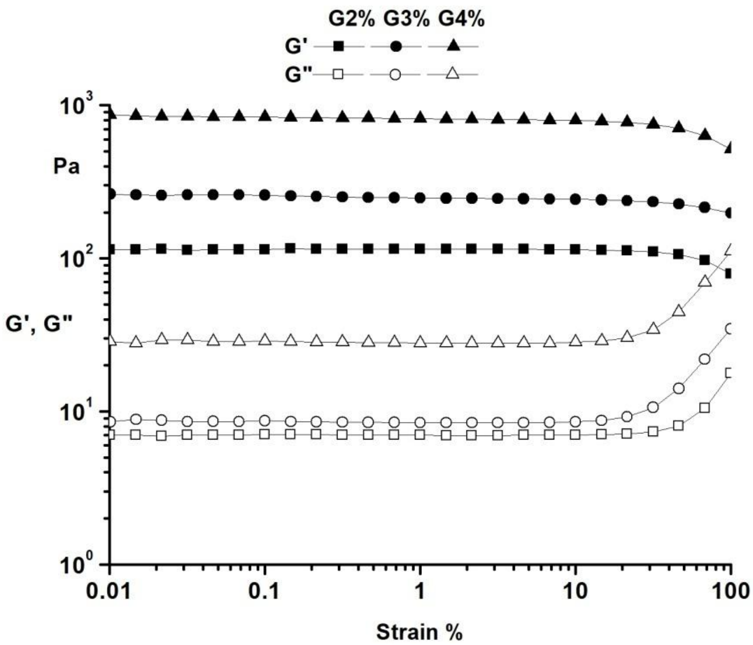

Fig. 1 – Amplitude sweep for gelatin samples.

A **strain sweep** test (Fig. 1) at frequency of 10 rad/s was performed to determine the linear viscoelastic region, from which an appropriate strain was selected for the next oscillatory tests. Viscoelastic properties of the network were evaluated by recording the evolution of the dynamic moduli, G' and G". The evolution of the storage modulus (G') gives information about the solid-like (elastic) behavior of the sample while the loss modulus (G") offers information about the liquid-like (viscous) behavior (Danu *et al.*, 2012; Simionescu *et al.*, 2013). The deformation limit resulting from the amplitude sweep data for samples is between 1-5%.

In **frequency sweep** tests, storage modulus (G') and loss modulus (G") were measured at a constant strain over a frequency range of 0.1-100 rad/s.

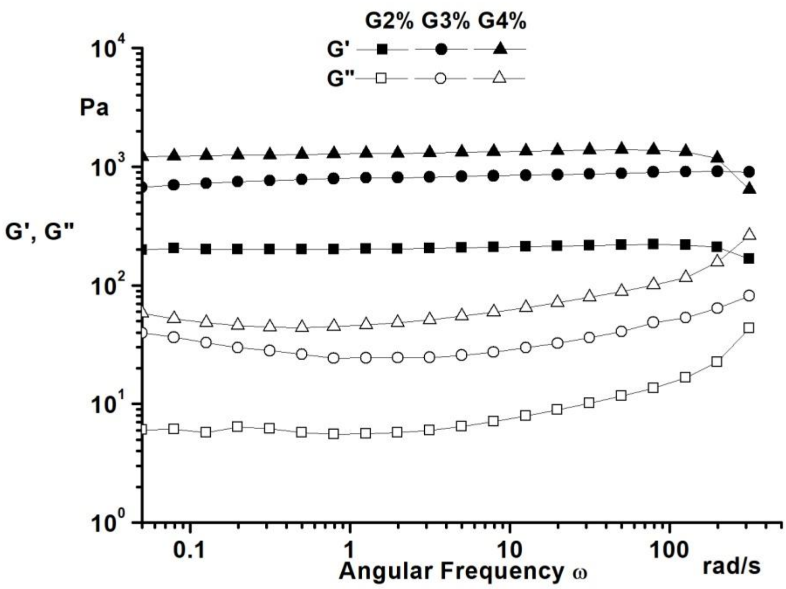

Fig. 2 – Frequency dependence of G' and G" for gelatin samples.

Fig. 2 show the frequency dependence of G' and G", at 25°C, for gelatin gels. The storage modulus was higher than the loss modulus suggesting a greater contribution from the elasticity than the viscosity. Rheological measurements indicate a nearly frequency independent G', while G" increased slightly with the frequency as is characteristic for gel materials (Clark *et al.*, 1983; Nishinari, 1997). The gel strength can be appreciated by the magnitude of G' and by the great difference between G' and G", also indicating a strong gel in the present case with G' > G" (Chenite *et al.*, 2001).

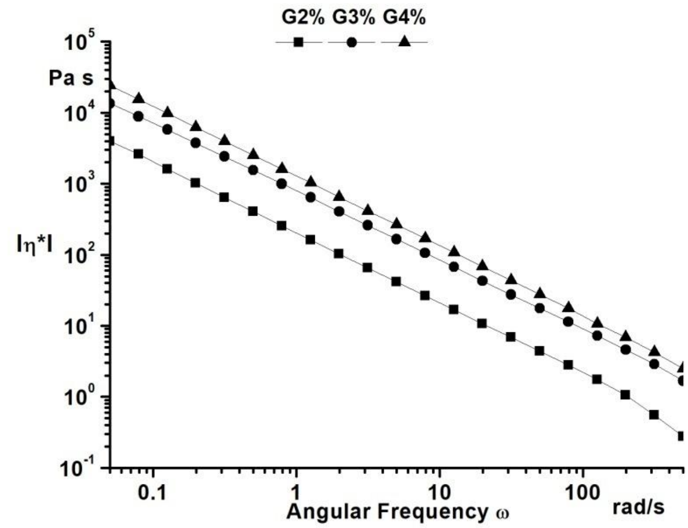

Fig. 3 – Frequency dependence of complex viscosity for gelatin samples.

Fig. 3 present the results of gel samples at different frequency. All samples showed a shear thinning behavior as complex viscosity decreased with rising frequency (Lai *et al.*, 2007).

4. Conclusions

In gelatin solution, the dynamic rheological data of storage (G') and loss (G'') moduli, as a function of strain and frequency showed that the gelatin samples displayed strong gel-like behavior (depending on concentration of gelatin solution). Magnitudes of storage moduli (G') for gelatin materials is a measure of the gel strength. Owing to the importance of rheology in several fields and products including gelatin gels, this article has attempted to describe the rheological behavior of gels. It is anticipated that rheology will be an indispensable tool for gel research in the future.

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COMPORTAMENTUL REOLOGIC AL UNOR GELURI PE BAZĂ DE GELATINĂ

(Rezumat)

Gelatina este un ingredient foarte utilizat în multe produse alimentare şi farmaceutice ca agent de gelifiere sau de îngroșare. Proprietățile reologice sunt foarte importante în studiul soluțiilor de gelatină. Modificări ale comportamentul reologic se observă atunci când prin adăugarea de cantități diferite de gelatină în soluție se determină variația modulilor dinamici G' (modulul de acumulare) și G" (modulul de pierdere) și a vâscozității aparente în funcție de deformație și de frecvență. Rezultatele obținute în acest studiu sugerează faptul că măsurătorile reologice pot fi utilizate pentru a estima tăria structurală a gelurilor.