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Structural and Rheological Properties of Gelatin-Carrageenan Mixtures

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Abstract: Rheological steady shear and dynamical measurement of gelatin-carragenan (G-CR) 1%, w/v mixtures at mixing ratios of 1:1 and 2:1at pH 7.0 were performed using stress controlled rheometer. The results reveal that Herschel-Bulkley (HB) rheological flow model gives the best fit (R^2=0.993) to capture the flow characteristics of highly yielding G-CR mixtures. Carrageenan improves the gel strength of the mixture due to moving towards more elastic modulus (order of G'≈10^3) as compared to gelatin elastic modulus (order of G'≈10). At 1.0 % of gum concentration, 2:1 of gum ratio, 13 ^oC of temperature, and pH of 7.0, the gel strength texture for G-CR mixtures were found to be as 4.71 N. Strengthening of gel network structures were also confirmed using SEM analysis of G-CR mixtures.

Keywords: Rheological measurements, Gelatin (G), Carrageenan (CR), G-CR gel network

Jelatin ve Karagenan Karışımlarının reolojik ve yapısal analizleri

Öz: Bu çalışmada, kütlece %1'lik jelatin-karagenan (G-CR) karışımının hacimce 1:1 ve 2:1 oranlarında pH 7.0 de stres kontrollü reometre ile reolojik yatışkın kayma ve dinamik ölçümleri yapılmıştır. Sonuçlar, gayet yüksek eşik stresine sahip G-CR karışımları için en yüksek tahmin katsayısı veren (R^2=0.993) Herschel-Bulkley (HB) reolojik akış modeline göre uyum göstermektedir. Karagenan, jelatine göre (G'≈10) daha yüksek mertebeli (G'≈10^3) elastik modüle sahip olduğundan, G-CR karışımına CR katkısının jel dayanımını arttırdığı gözlenmiştir. Karışımdaki , 2:1 karışım oranında 13 ^oC ve pH 7 de, jel dayanımı tekstür cihazı ile 4.71 N olarak bulunmuştur. Ayrıca, bu çalışmada jel ağlarındaki mukavemet artışı jellerin SEM analizleri ile desteklenmiştir.

Anahtar Kelimeler: Reolojik Ölçümler, Jelatin, Karagenan, Jelatin-Karagenan jel ağları

1. Introduction

Protein-polysaccharide mixtures are frequently used in food industry to control and process functional properties of food products [1, 2]. Gelatin due to its superior gelling and emulsifying properties is widely used especially in food industry. It is a protenious gel forming food material with a good film forming ability to coat fruit and vegetables because of its resistance to water vapour and protective effect for air diffusion. Gelatin (G) can be modified with other compatible polysaccharides used as stabilizer and thickener such as carrageenan (CR) a complex polysaccharide with a good compatibility to reinforce its mechanical strength and rheological properties CR in different food formulations [3, 4]. Gelatin can be modified with the chemical agents [5]. But, for food industry biocompatible polymers is necessary for the combination with gelatin [6]. Carrageenan is the one of the promising polymer owing to non-toxic and biodegradable properties to increase gel strength of the gelatin . Upon the addition of CR to gelatin, there occurs

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an interaction between G and CR molecules dependent on pH of the solution medium. At pH 7, CR and gelatin carries some negatively charges due to exceeding the isoelectronic point of gelatin (pI≈5 for this study). On the other hand, when pH of the system is lower than the pI, polyelectrolyte complexes occurs between the positively charged amine groups within the gelatin and the negatively charged sulphate and hydroxyl groups within the CR [7].

Rheological properties can be investigated to control or analyse the synergetic effect of G-CR mixtures. Numerous studies showed that the addition of polysaccharide into gelatin changes the rheological parameter such as viscosity, yield stress, elastic and viscous moduli of the gelling medium [8]. A possible modification of G-CR system is determined by concerning yield stress and elastic modulus levels before and after addition of CR into G as macroscopic rheological properties. Yield stress values can be captured by using steady shear measurements giving the shear stress and shear rate information [9]. There are several flow models such as Power Law, Herschel-Bulkley [10] and Casson [11] to characterize the yielding and flow behaviour of the solutions [12]. Viscoelastic characteristics are also another key parameter for defining elastic or viscous nature of mixings by using small amplitude oscillatory test. This testing serves the rigidity or strength of a material under applied low oscillatory stress or strain in the lineer viscoelastic region [13]. Gel strength can be directly predicted via textural measurements [14]. Thus, combined rheological and textural measurements could be better approach for the proper design of gel mixture systems [15]. Moreover, rheological studies are also related to microstructural changes with using Fourier Transform-Infrared (FT-IR) spectroscopy [16], SEM data exploring the structural basis rheological behaviour during gelling as a new perspective. Therefore, the aim of this study is to provide the comprehensive knowledge on the macro and micro-rheological changes of G- CR mixture.

2. Materials and Methods

2.1. Preparation of Carragenan (CR)-Gelatin (G) Mixtures

Samples of CR and gelatin (G) powders were provided from Benosen Food and Chemical Company(Istanbul, Turkey). The stock solutions were prepared 1.0 g of dry sample of carrageenan and gelatin with distilled water while continuously overnight mixing at 40 ^{o}C. The mixing solutions at ratios of G:CR as 1:1, 2:1(v/v) at pH 7.0 were also stirred with a magnetic stirrer for 2 h at 25 ^{o}C. The solutions were refrigerated over night (16 h) to completely hydrate the mixtures.

2.2. Rheological Measurements

Rheological measurements were carried out in a controlled stress rheometer (Kinexsus, Malvern Pro, USA) at the temperatures of 13 ^{o}C. Dynamic tests were performed in a frequency range between 0.1 and 10 rad/s using a cone-and-plate geometry with a cone angle of 4^{o} (40 mm diameter and 1.5 mm gap) in a duplicate. Plot of shear stress versus shear rate for solutions shows non-Newtonian behavior due to non-linearity relation between shear stress and shear rate. Several models have been used to characterize the flow behavior of solutions and among them Power law model (Eqn.1) has been frequently used for the determination of rheological properties of the non-Newtonian fluids. Also, Casson (Eqn.2) and Herschel-Bulkley (Eqn.3) models have been used for the characterization of non-Newtonian fluid flows.

$$\tau = K\gamma^{n} \quad (1)$$

$$\tau^{0.5} = K\gamma^{0.5} + \tau_0^{0.5} \quad (2)$$

$$\tau = K\gamma^{n} + \tau_0 \quad (3)$$

Where τ is shear stress (Pa), γ is shear rate (1/s), n is flow index (dimensionless), K is consistency index ($Pa.s^n$), τ_0 is dynamic yield stress value.

2.3. Textural measurements

Solutions were also analyzed using a texture analyzer (T.A. HD Plus Texture Analyzer, ABB, Ankara, Turkey) at 13 ^oC. A 5 kg load and aluminum cylindrical 36 mm probe was used to determine the gel strength. The test speed and rupture distance were 1 mm/s during the measurements. The gel strength (Newton) of formed gels was measured in a duplicate manner.

2.4. Characterization by scanning electron microscopy (SEM)

SEM images of solutions were observed using the following sample preparation: After swelling in deionized water at 25 ^oC for 48h, the solutions were freeze-dried under vacuum until all water was sublimed. The samples were placed on aluminum nails and coated with gold using Ion-coater KIC-IA COXEM (Daejeon, South Korea) with 4 mA for 220 sec. SEM analysis was performed at Bolu Abant Izzet Baysal University, Faculty of Arts and Science SEM laboratory. SEM images of the swollen solutions were obtained by using JSM 6480 LV-JEOL scanning electron microscope (Tokyo, Japan) operating at 15 kV.

3. Results and Discussion

Dynamic shear measurements were carried out using stress controlled rheometer using shear rate ramp measurements. Figure 1 depicts rheological data (shear stress and shear rate) to capture flow behavior of solutions over a shear rate range 0.1-100 s^{-1} at 13 ^oC. After preliminary experimental study, this temperature was chosen to get viscous form of G-CR mixture. Model constants were given in Table 1 under steady shear measurements and rheological parameters. All of samples show perfectly fitted to three models due to reasonable high coefficient of determination value (R^2=0.82-0.99).

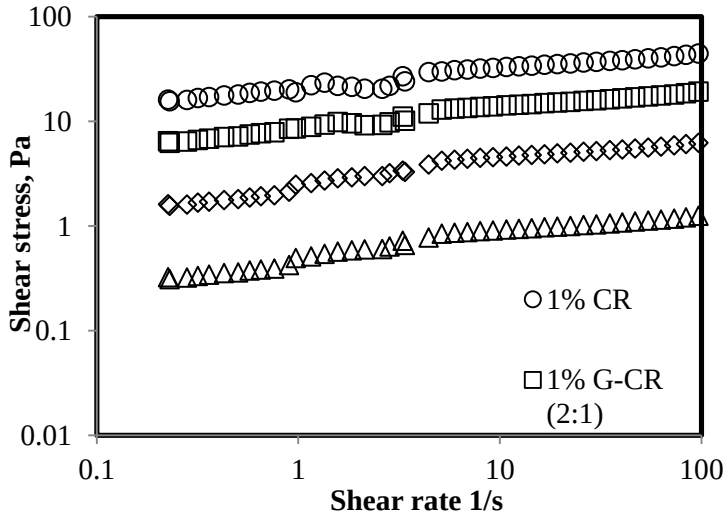


Figure 1. Shear stress v.s Shear rate of samples

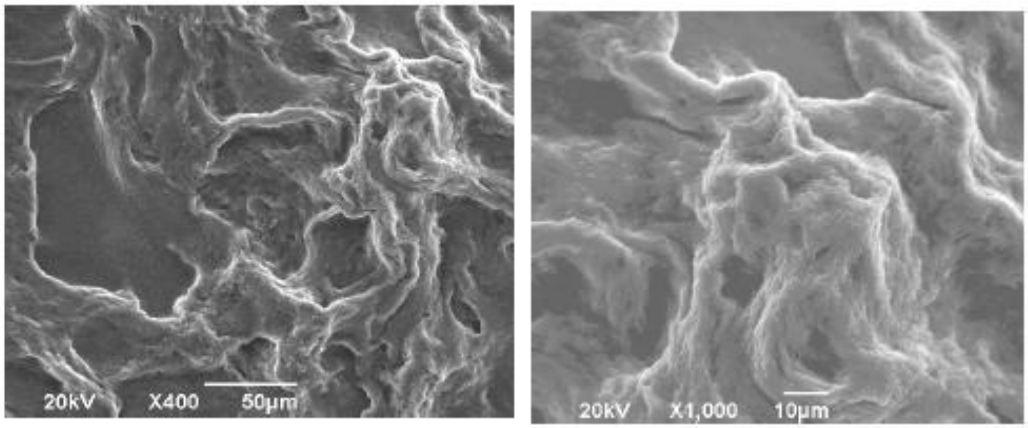
Herschel-Bulkley model was found to be a suitable model to explain the rheological behavior of G-CR mixture (R^2=0.985–0.995). For Herschel-Bulkley model, flow behavior index (*n*) of samples ranged from 0.276 to 0.320. The ratio of gelatin to CR ranges at 2:1, flow behavior index (*n*) of samples showed high values than 1% CR (Table 1). Sample containing 1% gelatin had the lowest consistency index (K=0.381). The lowest Herschel-Bulkley yield stress was found for 1% gelatin containing sample.

Table 1. Rheological parameters of the Casson, Power-law and Herschel-Bulkley models for description of rheological behavior of G, CR and their mixtures

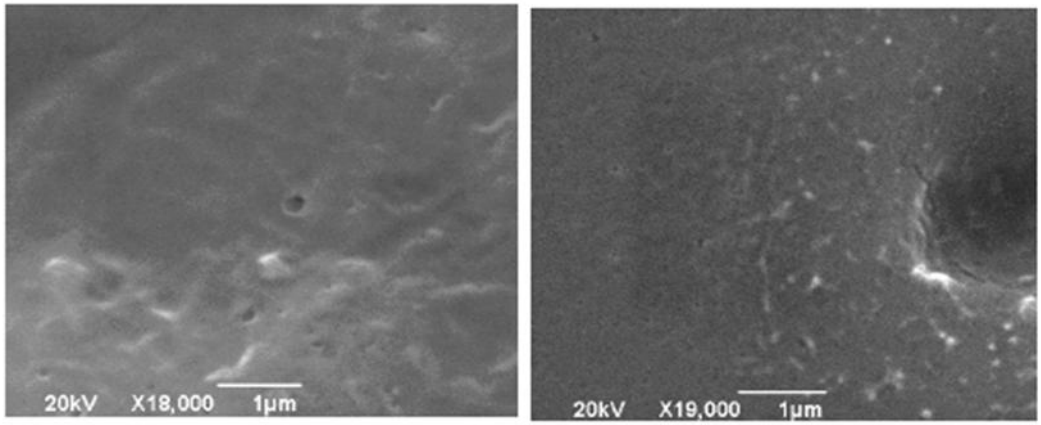
Sample(w/v%)	Casson Model	Power Law Model	Herschel-Bulkley Model	
1% G	K= 0.352 τ0=0.432 R^2 =0.887	K= 0.381 n= 0.343 R^2 =0.882	K=0.376 τ0=0.520	n=0.320 R^2 =0.985
1% CR	K= 14.248 τ0=18.234 R^2 =0.981	K=16.29 n= 0.283 R^2 =0.821	K=15.230 τ0=20.821	n= 0.276 R^2 =0.995
1% G-CR (2:1)	K=5.543 τ0= 7.656 R^2 =0.967	K=5.821 n= 0.312 R^2 =0.873	K=5.721 τ0=8.456	n= 0.302 R^2 =0.992
1% G-CR (1:1)	K=1.782 τ0= 2.025 R^2 =0.984	K=1.763 n= 0.291 R^2 =0.842	K=1.875 τ0=2.234	n= 0.283 R^2 =0.993

Flow behavior index, *n* implies the tendency of shear viscosity changing ratio with respect to shear rate. Lower *n* values indicate highly more non-Newtonian and shear thinning behavior of solutions and it is observed for 1% CR solutions. The magnitude of K value leads the measure of viscosity of solutions. When G-CR is mixed in equal ratio (1:1), yielding behavior of gelatin and viscosity of gelling medium are enhanced. Higher presence of G in the mixture (2:1) also becomes the higher yield stresses of gel medium. Quantitatively, CR effect on rheological characteristics of gelatin can be connected with higher elastic modulus and higher yield stress of carrageenan compared as to gelatin. Table 1 clearly show that maximum, τ0 of 20.821 Pa value is observed for 1% CR solutions as the result of more hardening and more rigid micro molecular structure as seen in Figure 2a. CR solution exhibits more three dimensional network than that of 1% G solution, thus 1% G has lower apparent yield stress. This non-helical gel structure can be clearly seen in Figure 2b. As it can be also seen from the micrographs in Figure 2c, the microstructure of G-CR mixture is differed greatly from both Figure 2a and 2b. The morphological pattern of 1% CR and 1% G mixture shows transformations into helix and globular hydrogel form due to hydrogen bond interactions between G-CR molecules as in Figure 2c.

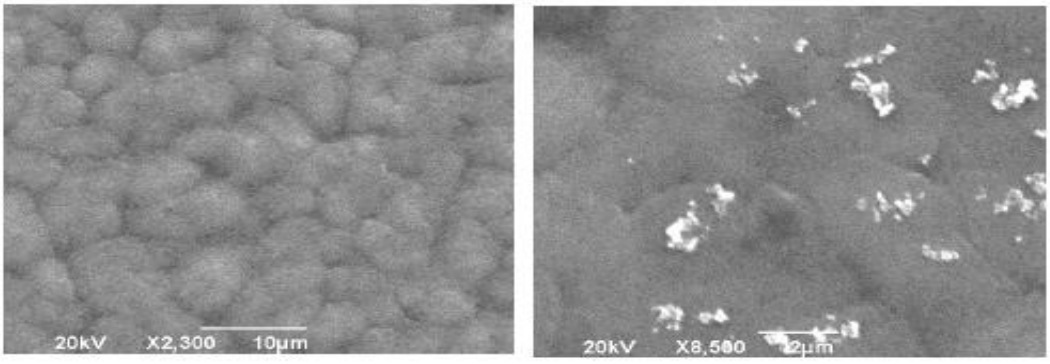
In pH=7, gelatin has negatively charged because of isoelectronic point of gelatin pI≈5 < pH (pI of gelatin 4.6 and 5.3 for this study). Only, hydroxyl groups (OH^-) in CR molecules () interacts with amide groups (NH^-) in G molecules via hydrogen bonding as secondary molecular interactions. An increase in intermolecular contacts might be due to the changes in the viscoelastic nature of mixing structure. As a common property, all elastic modulus (G') are bigger than the viscous modulus (G'') of the samples in Figure 3. However, there is large difference between elastic and viscous counterparts for 1% CR solution. Elastic and viscous moduli are nearly constant especially at low frequencies for 1% CR and 1% G: CR (2:1) mixtures. They have similar trends for G' and G'' and they can be characterized as strong gel due to more solid-like state of material. But, linearity relation exists between viscoelastic properties of G' and G" for 1% G. It is not significant discrepancy between G', G'' moduli.



(a) 1.0% CR



(b)1.0% G



(c) 1.0% G: CR (1:1)

Figure 2. Sem images for (a) 1.0% G (1 µm) B) %1 CR(50 ve 10 µm) C) %1 G:CR (10 ve 2 µm)

They are attributed to more viscous gel response for native G compared to C-CR mixtures. Pranoto et al. (2007) [17] and Derkach et al. (2015) [18] also reported that an increase in CR content into G accelerated the formation of gelling medium and provided the more elastic nature of gel with a higher yield stress and G' value.

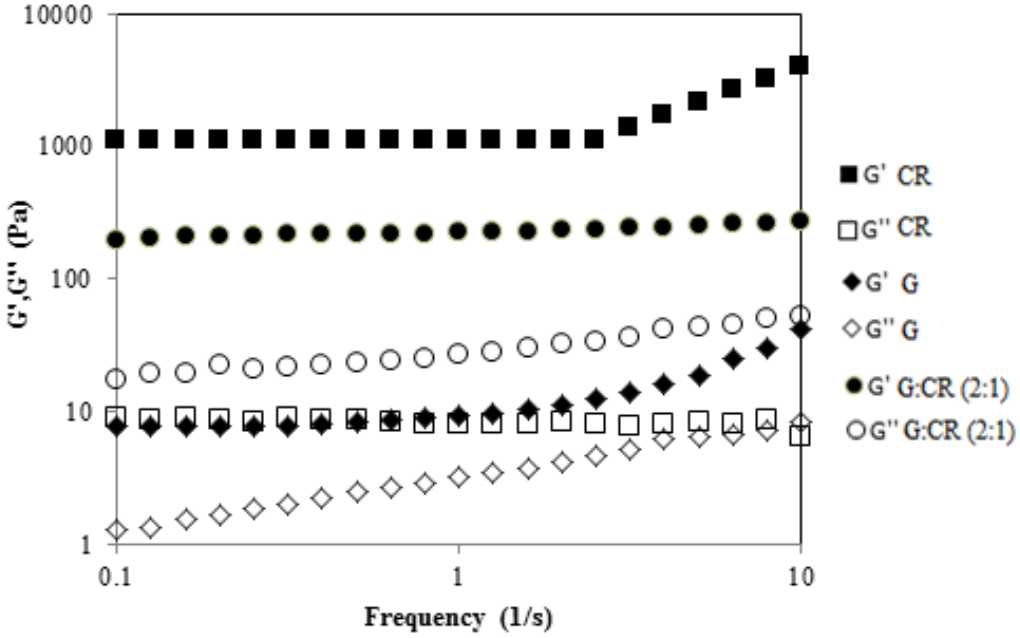


Figure 3. Elastic and viscous modulus changing of samples

The strength of gels is obtained from using textural measurements as listed in Table 2. While 1% G has lower mechanical gel strength as expected. Gel strength is improved by the addition 1% CR into G solutions due to the increase in the viscoelastic character of gel network, for mixed gel system. It is also interesting to note that at even C-CR ratio of 2:1, G gel improved by CR to increase the gel strength due to the increase of hydrogen bonding of gel network. This similar founding was reported by Sow et al. (2018) [19] in which mixing of fish gelatin and CR at a ratio of 96:4 (w:w) in a 0.5% (w/v) resulted in that showed significant modification of gel strength of G by increasing stiff structure capable of resisting deformation of G.

Table 2. Textural gel strength measurement of G, CR and their mixtures

Sample(w/v%)	Gel Strength (N)
1% G	1.28
1% CR	5.86
1% G-CR (1:1)	3.82
1% G-CR (2:1)	4.71

4. Conclusion

The rheological and structural analyses on 1% w/v of G-CR gel systems depicting effect of mixing ratios as 1:1 and 2:1 at pH 7.0 was given in this study. Based on experimental data, following conclusions can be drawn:

- The rheological flow parameters such as yield stress, behavior and consistency index were determined by Herschel-Bulkley model due to giving highest regression coefficient with the experimental data of 1% G, 1% CR, and their mixtures.
- Yield stress value of G-CR mixtures increases with the addition of CR to G solutions because of more hardening and rigidity of the micro molecular structure of CR compared to G solutions.
- SEM micrographs of G-CR mixture show that morphological pattern transforms into helix and globular hydrogel form. This might be due to the hydrogen bonding interactions between G-CR molecules of gelling network.
- Oscillatory test reveals that 1% G, 1% CR and their mixtures have also exceeding elastic modulus over viscous modulus. Especially 1% CR solution has the highest elastic modulus.
- For the mixed gel system, gel strength is improved by the addition 1% CR into G solutions due to increase in the viscoelastic character of gel network. It is interesting to note that at even C-CR ratio of 2:1, G gel improved by CR also leads to increase the gel strength due to the increase in elastisity of gel network.
- This mixture can be used as a coating material especially in fruit preservation industry.

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