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ORIGINAL PAPERS

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DETERMINATION OF VISCOELASTIC PROPERTIES OF MINOR CONCENTRATIONS OF ZEIN SOLUTIONS WITH DYNAMIC LIGHT SCATTERING (DLS) MICRORHEOLOGY

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ABSTRACT

In the present study, it was aimed to determinate the rheological properties of zein solutions using DLS microrheology. For this purpose, zein solutions at different concentrations range between 0,08 and 0,32% were produced in aqueous ethanol and optimized. Rheological properties, namely G' (storage modulus), G'' (loss modulus), G* (complex modulus), η* (complex viscosity) and tan δ values, were determined. Regarding results of rheological measurements, both G' and G'' values were found to the highest at 0,08% zein sample. Except 0,16% zein, there was a crossover point between G' and G'' values of the other samples. Complex viscosity nonlinearly decreased at all angular velocity values analyzed. Additionally, K' values of 0,08% zein sample were found to higher than those of 0,32 and 0,16% zein samples. No significant differences was observed between n', K'' and n* values of all samples. The findings indicated that DLS microrheology could be used for the measurements of rheological properties of small amount-zein solutions.

KEYWORDS:
microrheology, dynamic light scattering (DLS), zein, viscoelastic properties

INTRODUCTION

Zein, the major (40% of total) storage protein of maize, is a water-insoluble protein consists of more than 12 amino acid signal peptides and extracted from corn endosperm cells [1;2-3]. Zein, is a mixture of lipophilic amino acids, dominantly alanine, glutamine, proline, leucine [4] and has four fractions, these are α- zein, β- zein, γ- zein, and δ-zein [5]. Out of all of fractions, α- zein, approximately 80% of total zein, is the most abundant one [5]. Zein, considered GRAS as food additive [6], can solve in 55-90% aqueous-alcohol solution, due to its special amino acid composition, which is more than 50% nonpolar. Regarding amphiphilic properties of zein, these molecules have the unique ability to self-assembly into nanoparticles upon reducing solubility using an anti-solvent like water [7]. Zein nanoparticles can increase the stability, functionality and controlled release of the ingredient by making core-shell formation with the encapsulated material [8]. Zein nanoparticles has been used for different purposes in many areas such as drug delivery [9;10], tissue engineering [11] and nutrient delivery [12]. In addition to food applications, there are some studies about using zein for formation of films and coatings [13]. Zein molecules exhibit high thermal resistance and are known for great oxygen barrier, which may allow for the encapsulation of sensitive materials that can be affected by temperature or oxidation [2]. In the recent years using zein as carriers have studied in different studies such as vitamin D3 [14], curcumin [15] and thymol [16]. In addition, some studies showed that zein nanoparticles as carrier increased the oral bioavailability of folic acid [5], resveratrol [17]. Many methods for manufacturing nanoparticles have been reported; these are emulsion/solvent evaporation, supercritical fluid technology, electrohydrodynamic atomization, nanoprecipitation etc. [18]. Zein nanoparticles are commonly manufactured by liquid-liquid anti-solvent precipitation technique and these nanoparticles are reported to take shape a solid internal core with the dimension of 200-300 nm [19]. Zein solutions produced can be directly used as coatings and are stable against gelation 90% of protein extracted [20].

Food Rheology is the response of flow or deformation characteristics of food materials against mechanical stress at a macroscopic scale, while microrheology measures local rheological properties of a material at a microscopic scale [21;22]. Microrheology is a number of approaches try to eliminate some limitations of traditional rheology [23] in many ways such as the sample size, the range of frequency, heterogeneity etc. [24]. In microrheology, an embedded micron sized probe is used to locally deform the material, which allows carrying out rheological measurement on small volumes [23]. When comparing microrheology to traditional rheology, micro-rheology has many advantages such as higher range of frequencies independent from time-temperature superposition

[25], fast thermal and chemical homogenization, which allows changing systems' transient rheology and the ability of measuring in-homogeneities of materials that are not accessible to traditional methods [26]. Microrheology can be subcategorized as passive microrheology (PM) and active microrheology (AM). The former one, measures mechanical properties of materials by associating the diffusive fluctuations of probe with the shear modulus of the matrix. The latter, measures the mechanical properties of the matrix from the movements of microscopic particles by dragged by external force [21]. Because of the lower thermal energy that required fluctuating the particles, passive microrheology is suitable for soft food materials. On the other hand, due to this technique does not need an external force, simple instruments can be used to measure motion of the particles such as dynamic light scattering (DLS), laser deflection tracking, direct visualization or diffusing wave spectroscopy (DWS) [21]. Out of four methods, DLS and DWS are considered the most common PM methods [27].

In the present work, it was aimed to determinate the mechanical properties of zein solutions by DLS, which is one of the most common microrheological methods that allows measuring small amount of samples in a short scale. For this purpose, zein solutions were prepared at different percentages ranged 0,02-0,32% by using 85% alcohol and optimized. Mechanical properties of optimized samples were measured by DLS.

MATERIAL AND METHOD

Material. Zein was purchased from Acros Organics. Carboxylated melamine with the diameter of 615 nm, used as a tracer for DLS microrheology measurements, was procured from Microparticle GmbH.

Methods. Preparation of Zein Nanoparticles. Zein solutions were prepared in aqueous ethanol and the preparation steps explained as follows. Briefly, zein was dissolved in 100 ml 85% ethanol and diluted to different concentrations ranged between 0,02 and 0,32%. After optimization of the formulations, 0,08, 0,16 and 0,32% zein solutions were found to be the most appropriate to perform microrheological experiments. All measurements were conducted at 25°C. Optimized zein samples at different concentrations were homogenized for 15 min at % 100 amplitude in ultrasonic water bath (VWR,50-60Hz, USA). 2 µl tracer was added into each 10-ml sample to ensure that the dominant scattering over zein. Tracer molecules is desired to have bigger size than zein molecules to monitor the rheological properties from the motions of tracer molecules. Firstly, zeta potential value of tracer particle was measured. Zeta potential was measured by adding sample onto tracer particles to figure out the concordance (chemically) between zein and the tracer. After no chemical interaction between zein and the probe was observed, microrheological measurements of zein samples was carried out.

Zeta potential measurements. DLS (Dynamic Light Scattering) measurements were carried out using a Phase Analysis Light Scattering (PALS) (Malvern Zeta Sizer, UK). Laser Doppler electrophorese) electrophorese, which measured mobility of particles was used in the present study. The zeta potential measurements were carried out by diffusion barrier technique Corbett et al. [28] reported. 10 ml previously prepared zein sample was put into a special cuvette and determined the rheological properties. Passive microrheology, which provides to measure rheological properties of samples by detecting motions of particles undergoing thermal fluctuations, was used. DLS records the correlation function of tracer particles, evaluate the means square replacement (MSR) of samples and calculates the rheological data of sample using Stokes-Einstein equation (1).

$$D = \frac{k_B \mathrm{T}}{3\pi\eta a} \quad (1)$$

Storage moduli (G') and loss (G") moduli and the other parameters calculated using these values, complex modulus (G*) and complex viscosity (η*) were obtained from a thermal energy balance and the measured mean square displacement of zeta potential measurements [29]. Following models (Equations 2-4) were fitted to the viscoelastic parameters mentioned above to calculate the model parameters which are intercepts (K′, K″ and K*), and slopes (n′, n″ and n*) according to the following equations [30;31]

$$G' = K'(\omega)n' \quad (2)$$

$$G'' = K''(\omega)n'' \quad (3)$$

$$\eta^* = K^*(\omega)^{n^*-1} \quad (a)$$

RESULTS AND DISCUSSION

Viscoelastic properties of the various zein samples were analyzed by DLS microrheology. Different rheological properties of the zein solutions of varying concentrations were shown in Table 1, Figure 1, 2 and 3. Viscoelastic parameters, namely, storage moduli (G'), loss moduli (G''), complex moduli (G*) and complex viscosity (η*) values as a function of angular velocity were presented. G' implies the solid-like (elastic) behavior of the material and G'' represents liquid-like (viscous) behavior [32].

As seen in Fig. 1, both elastic and the viscos moduli of 0,32% zein-samples were in the range between 0,39 Pa and 1,5 Pa. Viscoelastic results demonstrated that while G'' values tended to monotonically increase, G' values increased until a certain point and then started to decrease with the steadily increasing angular frequency. On the other hand, a crossover point of G' and G'' values was observed at a certain point. At this particular point, zein solution started to lose its gel strength and become more viscous. The gel point can be identified as the crossover point where the elastic moduli and viscous moduli are equal (G'=G") [33].

In a cross-linking polymerization, when the material is in the liquid form, which means viscous behavior is dominant and less energy is stored than dissipated (G''>G') [34]. Another parameter of rheological properties, complex viscosity, exhibited a drastically decreasing at all angular frequency values performed.

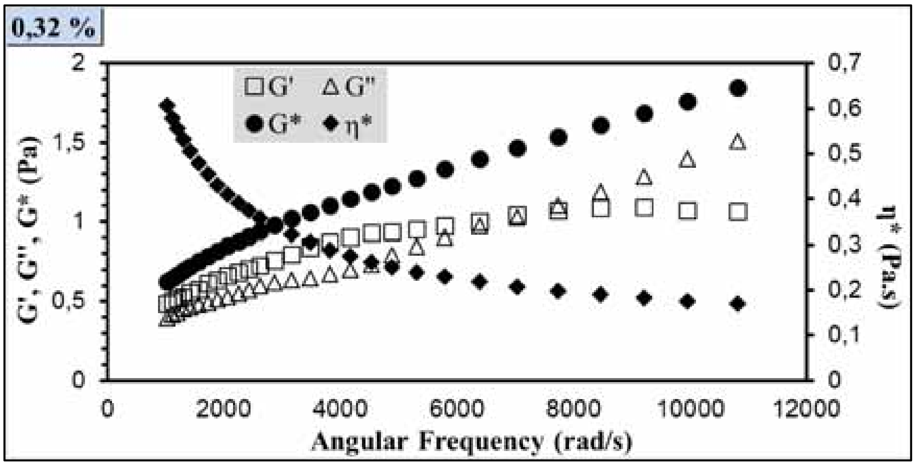

FIGURE 1
Viscoelastic Properties of 0,32% zein solutions

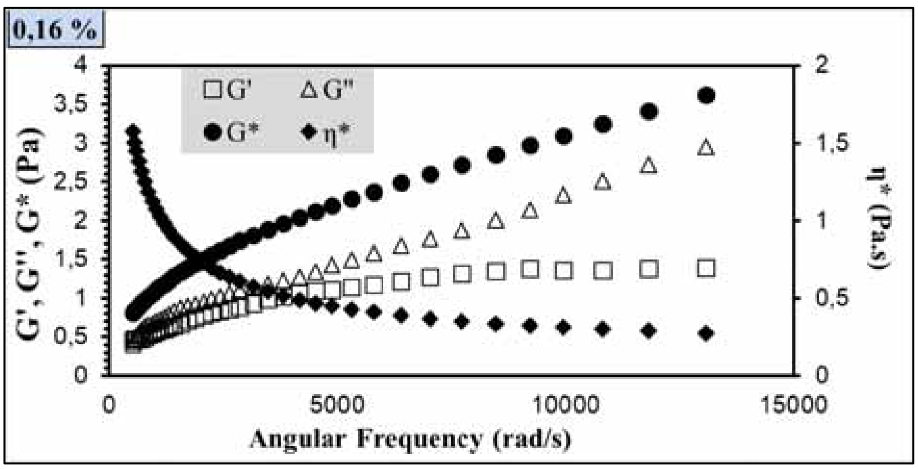

FIGURE 2
Viscoelastic Properties of 0,16% zein solutions

TABLE 1
Viscoelastic Properties of Zein Nanoparticles

	Dynamic Parameters									
	G' = K'(ω)n'				*G'' = K''(ω)n''*			*η* = K*(ω)n*–1*		
Samples	*K'* (Pa)	*n'*	*R2*		*K''* (Pa)	*n''*	*R2*	*K** (Pa)	*n**	*R2*
0.32	0.049 ± 0.000b	0.342 ± 0.002a	0.980 0.003	±	0.005 ± 0.000a	0.626 ± 0.029a	0.985± 0.000	29,0901± 1,1009b	0,442± 0,0024 a	0,999± 0.001
0.16	0.071 ± 0.003b	0.364 ± 0.035a	0.989 0.003	±	0.012 ± 0.006a	0.577 ± 0.009b	0.989 ± 0.004	50,814±7, 9475ab	0,441± 0,0262 a	0,999± 0,0001
0.08	0.138 ± 0.028a	0.326 ± 0.006a	0.990 0.002	±	0.016 ± 0.006a	0.565 ± 0.020b	0.985 ± 0.0001	102,737± 25,978a	0,392± 0,004a	0,999± 0,0001

*Different letters show significant differences between the zein samples (*P*<0.05)

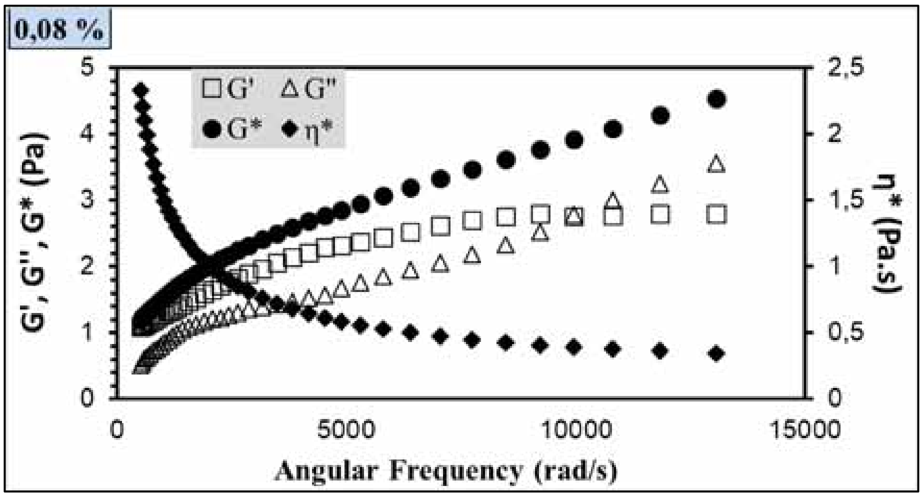

FIGURE 3
Viscoelastic properties of zein 0,08% zein solutions

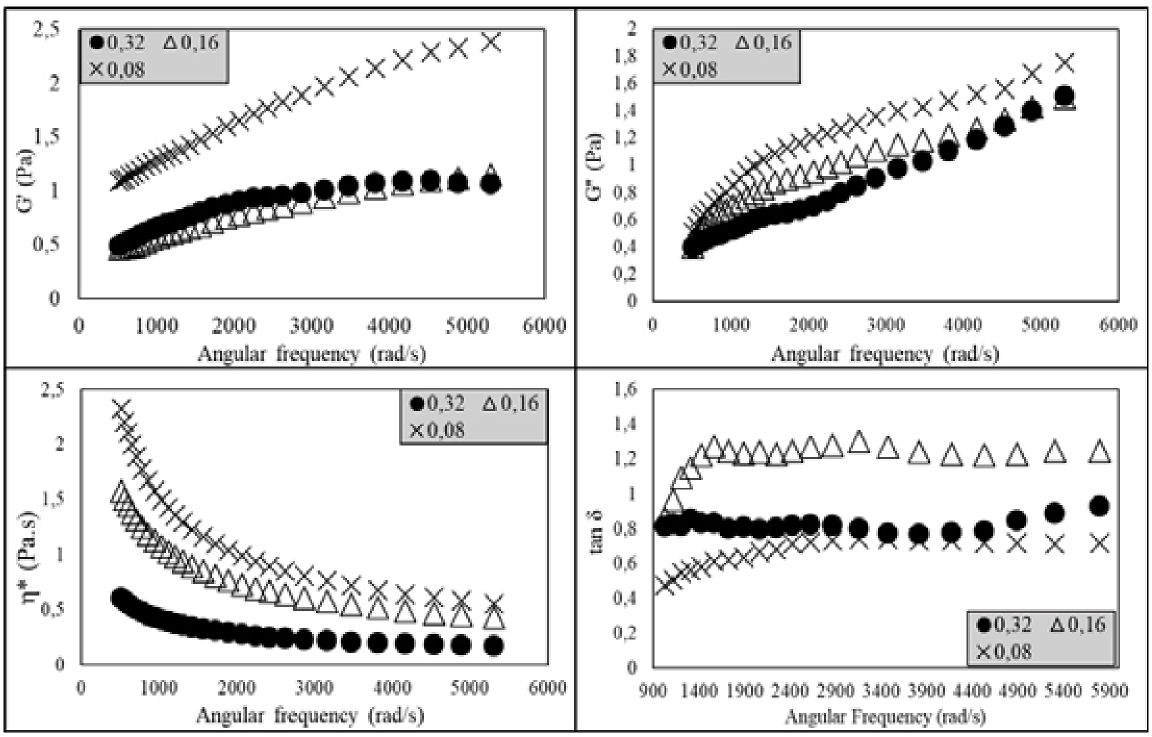

FIGURE 4
Comparison of different rheological properties of zein samples

As clearly seen in Fig. 2, while G’ values tended to increase non-linearly, G’’ values showed an increase constantly. Regarding viscoelastic properties of 0,16% zein solution, there was no crossover point at any angular frequency values. Complex viscosity displayed a decreasing tendency at all angular frequency values like 0,32% zein solution.

As seen in Fig. 3, both elastic and the viscos moduli of 0,32% zein-samples were in the range between 0,51 Pa and 3,6 Pa. Viscoelastic results exhibited that while G’’ values tended to increase non-linearly, G’ values increased until a specific point and then started to decrease. The decrease in the elastic moduli occurs from the connection loss between particles caused by shear rate [35]. Like 0,32% zein, crossover point was observed and complex viscosity decreased at all angular frequency applied. Slightly increase in G' and G" values versus to angular velocity, representing characteristics of solid-like gels [36]. When compared G’ values of all samples, 008% zein solution had the higher G’ than those of 0,32 and 0,16 zein samples. Decreasing amount of zein in solution resulted an increase at the G’ value. Similarly, 0,08% zein sample had the highest G’’ values among all samples analyzed. Madeka & Kokini [37] reported that n value of zein at 50ºC was 0,59, both G’ and G’’ values increased and there was no cross over point. In another study, Zhang et al. [38] found that viscosity of 10% zein solution decreased and samples had weak shear thinning behavior.

Experimental viscoelastic parameters versus ω (angular frequency) were fitted to power law, which describes the relation between ω and the corresponding parameter. R^2 values calculated for K', K'' and K* values were found to between 0.980-9.990, 0.985-0.989 and 0,99-0,99 respectively.

As seen in Table 1, K' values were higher than those of K'' values in all samples analyzed implying that zein samples had solid-like behavior rather than viscous character. K' values increased by lowering the amount of zein in solution. While the K' value of 0,08 zein sample was the highest (0,138), 0,32% zein had the lowest (0,049) and was equal to that of 0,16% zein statistically. Regarding flow behavior index (n), 0,16 zein sample was found to be higher than the other zein samples. At K'' values, there was no significant differences between all samples analyzed. Another parameter, K*, was found to the higher at 0,08% zein than those of other samples.

CONCLUSION

In the present study, rheological properties of different concentrations of zein solutions in aqueous ethanol were determined by DLS microrheolgy. A new method for measuring mechanical properties of materials was successfully performed. Both G' and G'' values of all samples increased at all angular frequency. 0,08% zein sample had the highest G' and G'' values among all three samples. On the other hand, except 0,16 zein sample; two cross over point were observed at a certain point. K' values of all samples were found to higher than those of K'' values representing that the elastic character was dominant over viscous character.

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