Application of Rheological Modeling in Food Emulsions

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ABSTRACT: *Various scaling methods such as relative viscosity, Peclet and Reynolds scaling were used to find the best scaling law. Scaling and modeling of the flow curves of various model emulsions consist of Tragacanth Gum (TG) (0.5, 1 % wt), Oleic acid (5, 10% v/v) and WPI (2, 4 % wt) were investigated and the best models were selected. As these emulsions are non-Newtonian, they do not obey the usual, simple scaling laws. When the apparent viscosity is reduced to relative viscosity of the medium at zero shear rate, a distinct reduced flow curve is obtained, regardless of TG, oleic acid and WPI concentrations. This will lead to a technique of simplifying complex non-Newtonian flow curves and therefore predicting the rheological flow curves and fluid mechanics when different modifiers are added to food emulsions. The flow behavior of all samples was successfully modeled with Cross, power law and Ellis models and power law model was found as the better model to describe the flow behavior of dispersions. Results showed that both G' and G'' increased with TG, oleic acid and WPI concentrations with pronounce effect of TG content.*

KEYWORDS: *Modeling, Flow curves, Scaling, Tragacanth Gum (TG).*

INTRODUCTION

An emulsion is traditionally defined as a dispersion of droplets of one liquid in another, the two being immiscible [1]. Emulsions are metastable systems that tend to destabilize through a number of mechanisms (creaming, coalescence, flocculation, etc.). In order to increase emulsion stability, which is a key factor for its commercial applications, the use of emulsifiers such as proteins or surfactants is essential. The role of emulsifiers

in emulsion formation and stabilization has been extensively described in the literature of food colloids [2-5].

Whey proteins (β-lactoglobulin, α-lactalbumin, bovine serum albumin (BSA) and immuneglobulins) are characterized by well-defined three-dimensional structures held together by disulphide bridges [6]. It is known that both the major whey proteins, β-lactoglobulin and α-lactalbumin, adsorb to oil-water interfaces and are capable of stabilizing emulsions; the emulsions produced by these proteins are only slightly less stable than those made using caseins under the same conditions [7].

Besides emulsifiers, polysaccharides are often added to stabilize emulsions in an O/W emulsion [8, 9]. While proteins are recognized for adsorbing at the oil- water interface and forming interfacial films, polysaccharide usually impact the stability of the emulsions by modifying the physical properties of the continuous phase. In general, by adding polysaccharides to the emulsion, the viscosity of the continuous phase increases, the shelf life of the emulsion is extended, and flocculation, coalescence, and creaming are prevented [10-12].

Tragacanth Gum (TG) is a dried exudation obtained from the stems and branches of an Asiatic species of Astragalus (*A. rahensis*) [13]. TG is a branched, heterogeneous, and anionic polysaccharide consisting of two major fractions: tragacanthin (water-soluble) and bassorin (water-swellable). Tragacanth is one of the most acid-resistant gums, as well as one of the most efficient natural emulsifiers for acidic oil-in-water emulsions [13, 14]. It has been used as a stabiliser, emulsifier, and thickener in the food, pharmaceutical, and cosmetic industries. Several studies have been carried out mainly on the physical stability and rheological properties of beverage emulsions [15-22].

Rheological property is very important for several aspects such as the effect on mouth feeling, texture, structure and other characteristics of food products [23]. Scaling laws, determined by dimensional analysis, have been used as the basis from which experimental predictions of the constitutive shear-flow rheology, of a variety of particulate systems in shear flow, have been derived.

Various parameters affect the rheology of stable colloidal suspensions. In the limiting case of spheres without any interparticle interactions, only Brownian (thermal) forces and hydrodynamic forces affect the flow behavior. The case of "Brownian hard spheres" is quite well documented, experimentally and theoretically, at least for monodisperse particles [24, 25]. At sufficiently low shear rates Brownian motion will dominate the convective motion caused by the flow. Under these conditions the equilibrium structure of the particles that exist at rest is preserved during flow. As a result the viscosity does not change with shear rate and the contribution of the Brownian forces to the viscosity is at its maximum. When increasing the shear rate the Brownian motion will, at a certain stage, becomes lower than the convective motion. From this on the contribution of the Brownian motion to the viscosity will gradually decrease with increasing shear rate, whereas the hydrodynamic contribution remains relatively constant. This causes the viscosity to drop; a shear thinning region develops. At still higher shear rates the Brownian contribution levels off and becomes negligible, but an increase in hydrodynamic effects can either compensate the decrease, causing a Pseudo-Newtonian high shear plateau, or over compensate, producing a shear thickening zone [25, 26].

Scaling methods are also used with suspensions in non-Newtonian media. If, the viscosity data is plotted in reduced units, there is one general reduced flow curve for all concentrations of the non-Newtonian media; it will indicate that the flow curve obtained from one medium concentration can be used to predict the flow curves of the same particles in different non-Newtonian viscosities. This could have applications in predicting the fluid mechanics of industrial suspensions in food and chemicals [27].

There are two main scaling methods, Peclet and Reynolds methods, which are two alternative reduced shear rate scales. In colloid systems, the Peclet number is the ratio between the hydrodynamic forces due to shear and the forces of Brownian motion, and the Reynolds number is the ratio of the particle inertial forces (due to the velocity field on the particle) and resistive forces of the medium. Both of these require that the particle diameter be found and this was achieved using laser diffraction apparatus.

Fischer et al. (2009) concluded that to distinguish Brownian and non-Brownian systems, both the primary aggregate size, the thermal energy k_BT, and the imposed external stress matter [27]. A dimensionless group can be defined as peclet number that is the typical timescales for Brownian motion and for the flow process.

Table 1: The Composition of the formulas.

Sample No.	Conc. of WPI solution (%)	WPI (ML)	Conc. of TG solution (wt%)	TG (mL)	Oleic acid (mL)	Final composition in the emulsion		
						WPI conc. (wt%)	TG conc. (wt%)	Oleic acid (% v/v)
1	4.2	38	2.1	38	8	2	1	10
2	8.4	38	-	-	4	4	0	5
3	4.2	38	2.1	38	4	2	1	5
4	4.2	38	1.05	38	8	2	0.5	10
5	8.4	38	2.1	38	8	4	1	10
6	-	-	1.05	38	4	0	0.5	5

$$Pe = \frac{\gamma \eta_o \alpha^3}{k_B T} \qquad (1)$$

Where γ is shear rate, η_o is medium zero shear viscosity, α is droplet diameter, k_B is Boltzmann constant and T is temperature.

At Pe much smaller than unity, Brownian motion dominates while at higher Pe structure distortions by shear flow are more pronounced: Brownian motion can no longer restore the structure of the suspension to its equilibrium state and shear thinning and shear thickening will occur. Orientation effects of the aggregates may become important if Pe>>10 [28].

When the particles are sufficiently large, or the medium sufficiently viscous, Brownian motion is recessive and Reynolds scaling is suitable. Then the exact scaling law for a suspension of monodisperse frictionless spheres is Reynolds scaling [28].

$$Re = \frac{\gamma \rho_0 \alpha^2}{\eta_o} \qquad (2)$$

Where γ is shear rate, η_0 is medium zero shear viscosity, α is droplet diameter and ρ_0 is medium density.

In all scaling laws, the reduced viscosity depends only on the particle concentration and the shear rate in reduced form.

The objectives of this work were: (1) to evaluate the effect of tragacanth gum and WPI concentrations and oil-phase volume fraction on rheological properties of emulsions and (2) to investigate the rheological and scaling models in WPI- stabilized emulsions containing tragacanth gum.

EXPERIMENTAL SECTION
Materials

Tragacanth gum was obtained from Shahid Beheshti Medical Sciences University (Tehran, Iran). The gums were pulverized and sieved, and the collected powders (mesh size 200-500) were used. Oleic acid ($C_{18}H_{34}O_2$, purity 65-88% , ρ=0.889-0.895 kg/m^3) was purchased from the Merck Company (Merck, Hohenbrunn, Germany). WPI (protein, 90 wt %) was obtained from Davisco Foods International, Inc. (Eden Praire, MN).

Methods
Emulsion preparation

The continuous phase of emulsions were prepared by dissolving suitable amounts of WPI and TG powders separately into distilled water at 40ºC, followed by stirring for 30 min in 10000 rpm to ensure complete dispersion. Then, solutions were kept 24 h at room temperature to allow full hydration. The O/W emulsions were obtained by slowly mixing oleic acid into WPI solution, and then adding TG solution; the WPI solution/ oleic acid/ TG Solution mixture was finally emulsified with stirring by Ultra Turrax (IKA T25 Digital, Germany) in 15000 rpm for 10 min.

Six formulations of the above dispersions were randomly prepared by following the run order by fractional factorial design (Table 1). The final composition of these dispersions were 0–10% v/v oleic acid, 0– 4 wt % WPI, 0 - 1% wt XG, and pH= 6.7–7.

Particle size distribution

Droplet size of emulsions was determined by integrated light scattering using a Mastersizer 2000 (Malvern Instruments Ltd., Malvern, UK). The samples were analyzed immediately after preparation in duplicate. The instrument used the principle of Fraunhofer diffraction where a parallel, monochromatic beam of laser light (red light = 633 nm) illuminates the emulsions.

The light diffracted by the dispersion droplets gives a stationary diffraction pattern regardless of the particle movement. As particles enter and leave the illuminated area, the diffraction pattern changes, always reflecting the instantaneous size distribution in the illuminated area [29]. The particle diameter range, specific surface measurements were performed at room temperature (20°C). A 45 mm focal lens was used for the measurements. The average droplet size was characterized by the mean diameter d_{32} defined by *Dickinson*; (1998)[30]:

$$d_{32} = \sum_i n_i d_i^3 / \sum_i n_i d_i^2 \tag{3}$$

And

$$d_{43} = \sum_i n_i d_i^4 / \sum_i n_i d_i^3 \tag{4}$$

Where n_i is the number of droplets of diameter d_i. The d_{43} and d_{32} values were used to monitor changes in the droplet-size distribution of freshly made solutions with different compositions. These measurements were used to calculate peclet and Reynolds numbers [2].

Rheological measurements

The apparent viscosity of dispersions were measured using of oscillatory rheometer(MCR 301, Anton Para Co, Germany) at 0.1- 500 1/s. Couette geometry with a cup (33.93mm diameter) and a bob system (32.05mm diameter, 33.29 mm length) was used. All measurements were performed in 20° C. The relative viscosity, η_r , was calculated by following equation:

$$\eta_r = \eta/\eta_o \tag{5}$$

Where η_o is medium viscosity at zero shear rate.

The well-known rheological models such as Power law, Ellis and Cross models were used to describe the flow behavior of suspensions [31, 32].

Power-law model

$$\eta = k\gamma^{n-1} \tag{6}$$

Cross model

$$\eta = \eta_\infty + \frac{\eta_{o-\eta_\infty}}{1+(c\gamma)^m} \tag{7}$$

Ellis model

$$\eta = \eta_\infty + \frac{\eta_{o-\eta_\infty}}{1+\left(\sigma/\sigma_c\right)^m} \tag{8}$$

where γ is Shear rate, k is consistency coefficient, n is flow behavior index, m is exponent constant value, η is viscosity, η_o is zero shear viscosity, η_∞ isinfinite shear viscosity, C is characteristic time, m is exponent constant value, σ is shear stress, σ_c is critical stress or yield stress and could be defined as the stress above which the structure of the system is broken down [33].

Amplitude sweep tests were done at shear stress 0.00001- 1 Pa, strain 0.1-20 and fixed frequency of 1Hz to determination the linear region of viscoelasticity. Frequency sweep tests were carried out at frequency 0.1- 20 HZ and constant shear stress 0.001 to evaluate the dynamic rheological properties such as G', G" and phase tangent. All measurements were performed in 20°C.

Frequency (ω) dependence of G' and G" was modeled with the power law parameters a, b, x and y described by the Eqs. (1) and (2) [34].

$$G' = a\omega^x \tag{9}$$

$$G'' = b\omega^y \tag{10}$$

The densities of the all samples were determined with a standardized 25-mL pycnometer. The mass of the solution was calculated from the weight difference between the empty and the filled pycnometer. The pycnometer filled with each gum solution was incubated at 20°C for 1h in order to equilibrate the sample before density determinations. These measurements were used to calculate volumetric fractions and peclet number.

Statistical analysis

SAS software (SAS, 9.1, Inc., USA) was used to evaluate the experiments data. Analysis of variance (ANOVA) was used to determine if the means of responses were significant (P 0.05) (Microsoft Excel 2007). All experiments were performed in triplicate.

RESULTS AND DISCUSSION
Scaling Methods

The apparent viscosity of all samples was plotted as function of shear rate. All samples showed a shear-thinning behavior in a wide range of shear rates (Fig. 1). The apparent viscosity decreased by increasing the shear rate, which indicative of progressive disruption of the flocs when the shear rate was increased. Increase in apparent viscosity of dispersion has been related to droplet flocculation because
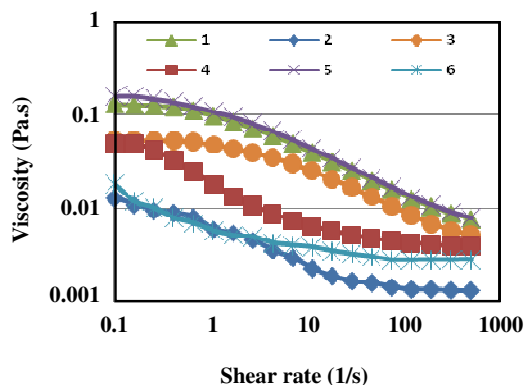
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Fig. 1: Viscosity of emulsion containing TG and WPI as function of shear rate (Numbers refer to formulations in Table 1).
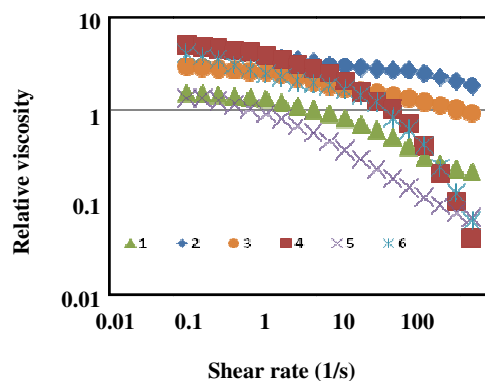

Fig. 3: Relative viscosity of emulsion containing TG and WPI as function of shear rate (Numbers refer to formulations in Table 1).
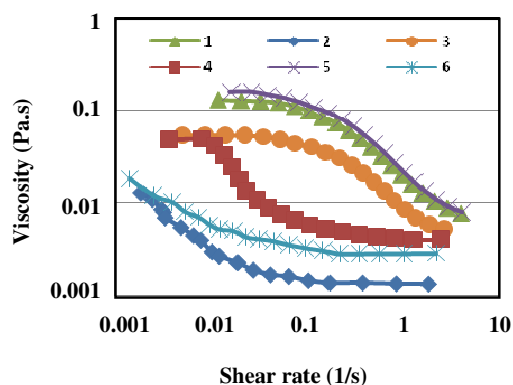

Fig. 2: Viscosity of emulsion containing TG and WPI as function of shear stress (Numbers refer to formulations in Table 1).
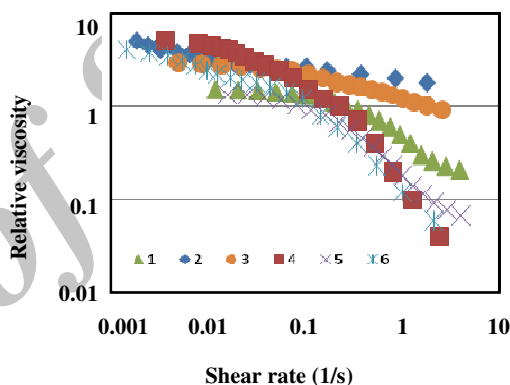

Fig. 4: Viscosity of emulsions containing of TG and WPI plotted as relative viscosity as function of shear stress (Numbers refer to formulations in Table 1).

the effective volume fraction of the particles in the system is increased due to the presence of the continuous phase trapped between the droplets in the flocs [1, 20, 35].

It was observed that the apparent viscosity increased with TG content and the aqueous dispersions were less susceptible to break down by shear since more cross linked positions were formed.

It was observed that plotting of apparent viscosity as function of shear stress instead of shear rate is more discriminating with a better quality of the results [36] (Fig. 2).

The data in Figs. 1 and 2 was plotted again (Figs. 3 and 4) in reduced units of relative shear apparent viscosity, η_r against shear rate and shear stress. The medium apparent viscosity at zero shear rate, η_o was found from data of various concentrations of TG in distilled water.

Fig. 3 showed the reduction is good at low shear rates.

The scaling resulted in overshooting, i.e. inversion of the results occurred. Similar results reported by some authors [29]. In contrast, plotting of the reduction form as function of shear stress is better and indicates that there is a general reduced flow curve for emulsions in non-Newtonian media, with a rheology modifier such as TG especially at low shear rates (Fig. 4).

Figs. 3 and 4 illustrated that all flow curves reduced to approximately the same flow curve at low shear rates, which was independent of the TG concentration and droplet size. The data was plotted in reduced units in Figs. 5 and 6 according to Peclet scaling, apparent and relative viscosities. As shown in fig. 5 the Peclet scaling with apparent apparent viscosity made scaling results to be unsuitable. Peclet scaling with relative apparent viscosity reduces the data with more success, especially at higher
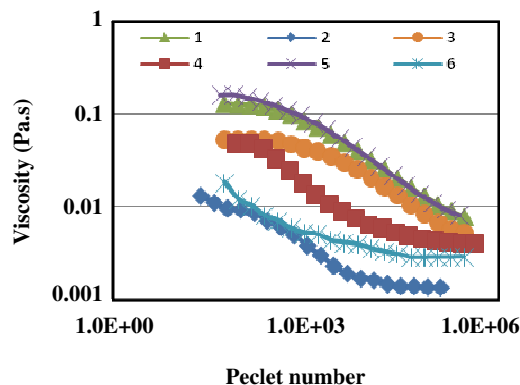
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Fig. 5: Viscosity of emulsions containing of TG and WPI plotted as relative viscosity as function of Reynolds number (Numbers refer to formulations in Table 1).
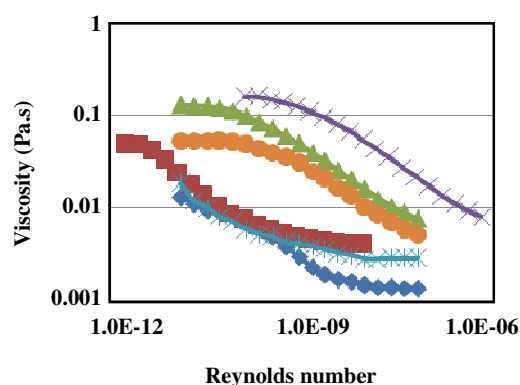

Fig. 7: Viscosity of emulsions containing of TG and WPI plotted as relative viscosity as function of Reynolds number (Numbers refer to formulations in Table 1).
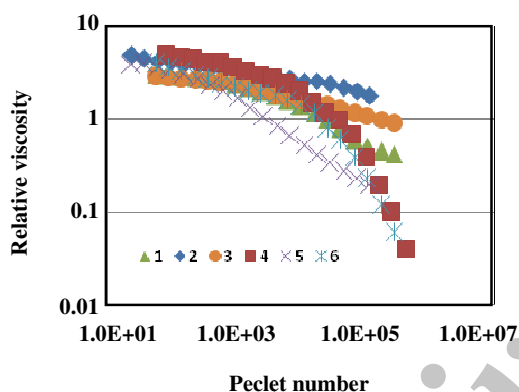

Fig. 6: Relative viscosity of emulsions containing of TG and WPI plotted as relative viscosity as function of peclet number (Numbers refer to formulations in Table 1).
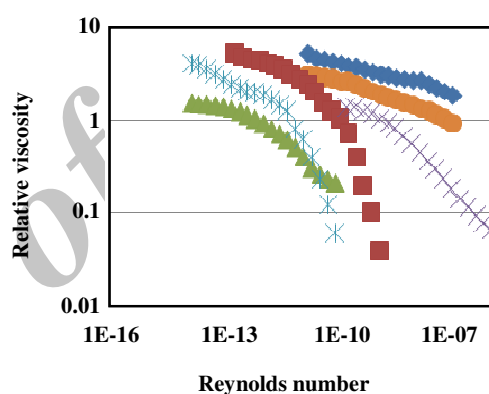

Fig. 8: Relative viscosity of emulsions containing of TG and WPI plotted as relative viscosity as function of Reynolds number (Numbers refer to formulations in Table 1).

concentrations of TG and low shear rates (Fig. 6). In this case also inversion of the results was observed. When Peclet scaling causes the results to super impose it demonstrates that only Brownian motion and viscous forces affect the mechanics of the system [25]. A similar result was reported by *savage* (2000) [27].

Reynolds scaling does not reduce the data, Figs. 7 and 8, and in some cases inverts the results. *Savage* (2000), investigated various scaling methods on system consists of the rheology modifier xanthan, glucose syrup and acid-thinned maize starch and concluded that Relative scaling and Reynolds scaling do not reduce the data in fact in most cases it is spread more by these methods, especially for higher starch concentrations and in nearly all cases, Peclet scaling works well [27].

Rheological Models

The flow curves of various formulations have been plotted as a function of shear stress (Fig. 2). Aqueous gum and WPI dispersions showed high apparent viscosity at low shear stresses and a shear-thinning behavior also appeared in a wide range of shear stresses for all formulations. Flow curves corresponded to a structured fluid, with three well-defined regions: at low shear stresses (γ), apparent viscosity reached a limiting value, namely zero-shear apparent viscosity (η_o); as the shear stress increased an abrupt decay in the apparent viscosity was observed until the development of a new flocculated system, where droplets form a structural network [38] (*Guerrero et al.*, (1998,1999); *Quintana et al.*, (2002a, 2002b)); and a plateau region (η_∞), which is high shear-limiting

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Table 2: Cross, Power law and Ellis models parameters of each sample flow curves.

Samples	Model											
No.	Power Law				Ellis				Cross			
	$K (Pa.s)^n$	n	R^2	S_{xy}	C (s)	m	R^2	S_{xy}	σc (Pa)	m	R^2	S_{xy}
1*	0.27	0.46	0.96	0.95	0.22	1.16	0.87	2.62	1.20	0.72	0.91	1.04
2	0.07	0.73	0.95	1.12	0.17	0.83	0.86	2.78	1.03	0.80	0.90	1.15
3	0.23	0.48	0.98	0.68	0.10	1.22	0.84	2.84	1.44	0.49	0.89	1.31
4	0.11	0.61	0.95	1.08	0.15	0.91	0.85	2.81	1.19	0.77	0.90	1.19
5	0.29	0.45	0.97	0.74	0.09	1.07	0.82	3.11	0.95	0.83	0.89	1.37
6	0.14	0.58	0.95	0.99	0.18	0.79	0.88	2.05	1.37	0.79	0.90	1.13

Determination Coefficient (R^2), Standard Error (S_{xy}). Bold numbers indicate the Highest and lowest R^2 and S_{xy} values.
* Numbers refer to formulations in table 1

apparent viscosity [37]. Shear-thinning behavior of emulsions was related not only to droplet deflocculation on the disperse phase, but also to the non-Newtonian behavior of the continuous phase. *Lorenzo et al.* (2008) reported that the pronounced transition between the second and third regions may be attributed to two different processes: one reversible and the other irreversible. In the first, high shear stresses disrupt the flocs, decreasing their effective volume fraction and therefore lowering the apparent viscosity [37]. Moreover, high shear stresses also induce coalescence [38]. Increasing droplet size produces weaker interparticle interactions, thus lowering the suspension apparent viscosity [39]. Figure 2 and Table 1 show that WPI concentration had no significant effect on the flow curves, which suggested that dispersion apparent viscosity was insensitive to the amount of unabsorbed WPI in the aqueous phase.

The presence of TG induced depletion flocculation in the emulsions. Entrapment of a certain amount of continuous phase in the flocculated structure resulted in an increase in the effective volume fraction of hydrodynamically interacting entities, which in turn increased the viscosity of aggregated emulsion systems [1,40]. On the other hand, the flocculated structure broke up under high shear rate, and a quantity of trapped continuous phase was released, as a result lowering the viscosity [40, 41]; a region of lower Newtonian viscosity was expected at very high shear rate indicative of complete disruption of flocculated structure. Increase in TG concentration raised the zero shear viscosity. Higher TG concentration increased the junction zones between

polymer chains, which were reflected in the higher true yield stresses and the sharp decay observed [42]. However, when the oil volume fraction was raised, the apparent viscosity increased but there were no noticeable changes in the shape of the flow curves; this suggests that the oil effect was not as pronounced as the effect of TG content in the range of studied composition. Similar results have been reported by [37].

Power-law, Ellis and Cross models were applied to find the best fit shear stress-shear rate plots to describe the flow curve of dispersions. Table 2 the parameters obtained with power law, Ellis and Cross models for emulsions. Results showed that in our work power law model was the better than cross model for its highest determination coefficients and least standard error (Fig. 9 and Table 2).

According to Table 2 the flow behavior index (n) decreased when TG concentration increased indicating a marked shear thinning effect at higher concentration of TG, which suggested that shear thinning behavior was mainly due to the presence of TG. This phenomenon has been explained to be related to droplet flocculation through domination of the attractive forces over repulsive forces which in turn become greater than the thermal energy of the system [1,20]. The WPI concentration had no significant effect on flow behavior index (n). A small hydrodynamic force at low shear rate are notable to disrupt the flocs and has an effect of increasing the shear rate the hydrodynamic forces will dominate and disrupt the flocs causing a reduction in viscosity [20,43]. The K value in power law model increased with increase
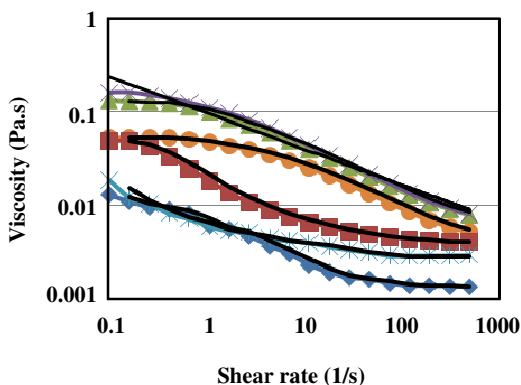
Fig. 9: Flow curves of samples and power law fitting (——)(Numbers refer to formulations in Table 1).

Fig. 10: Amplitude sweep test of 0.5% Gum, 4% WPI and 5% Oleic acid.

in TG concentration, which indicated that increasing TG concentration enhanced particle interactions and the suspensions were more structured. The WPI concentration had no significant effect on consistency Indies of samples.

Oscillatory testing is the most common dynamic method to study the viscoelastic behavior of food. It describes material properties in terms of storage modulus G' (elastic behavior) and loss modulus G" (viscous behavior). Initially, stress sweeps at an angular frequency of 1 Hz were performed to establish a maximum oscillatory stress within the linear viscoelastic range of the emulsions. Well within the linear viscoelastic region, an oscillatory stress of 0.01 Pa was chosen and samples were subjected to an angular frequency sweep from 0.1 to 20 rad/s.

Dynamic strain sweep data of the all suspensions studied are shown in Fig. 10. The WPI concentration had no significant effect on the linear range of storage modulus, G'. As was expected, higher concentration of TG contributed to an increase in G'. The results indicated the extent of the linear region decreased with increasing TG concentration from 0.5% to 1% v/v. It could be described by this fact that dispersions may undergo a behavior transition from predominantly entropic behavior to predominantly enthalpic behavior with increasing TG concentration. Of interest in the frequency sweep (Fig.11) is the relationship between the two components of the shear modulus, G" and G' . The frequency dependence of the storage modulus (G') and loss modulus (G") at 20° C as a function of composition were characterized. As illustrated in Fig. 11 all samples showed liquid-like
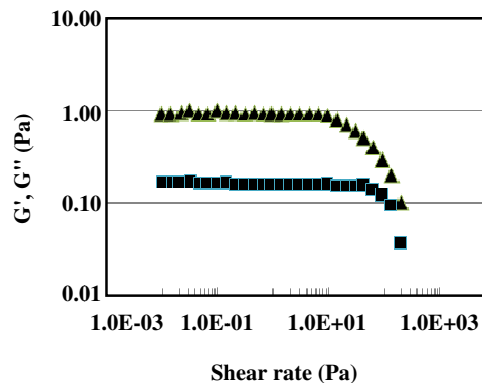
behavior (G"> G') over the whole frequency range. At higher frequency our data show a cross-over, G' again exceeding G". Similar cross-overs have been reported for polymeric systems where the high-frequency feature is at tribute to relaxation time and may be the onset of glassy behavior [44]. As the TG concentration increased to 1%, crossover frequencies reduced. The cross over frequency provides a good indication of the viscoelastic behavior of the material. Materials with a lower crossover value generally implied a higher elastic contribution to their viscoelastic properties [45, 46].In other words, under comparable concentrations, suspensions containing 1% wt behaved more solid-like than others. The G' and G" values generally increased with concentration of TG, which may be explained by the increase in both the number and the average size of junction points [47].

Power law parameters used to model the frequency dependence of G' and G" are shown in Table 3. Exponents x and y represent the slopes of the relationships between modulus and frequency and coefficients a and b represent the magnitude of G' and G" respectively at a given frequency. For instance, an exponent x near zero means that G' does not change with frequency, representing a characteristic behavior of a fully cured gel [48].

In this study, parameter b was higher than parameter a in all samples, indicating that G" predominates in the mayor part of the spectra and liquid-like behavior was observed. However, the solid-like mechanical spectra has been observed in some native globular protein aqueous systems and interpreted in terms of the formation of colloid crystals [49, 50-52].

Table 3: Power law parameters for the elastic ($G' = a\omega^x$) and viscous moduli($G'' = b\omega^y$) of emulsions

Samples	G'			G''		
	a (Pa.s)	x	R^2	b (Pa.s)	y	R^2
1*	0.033 ± 0.004[ab]	0.426 ± 0.012[f]	0.994	0.043 ± 0.005[ab]	0.941± 0.011[b]	0.992
2	0.017 ± 0.002[d]	0.899 ± 0.011[a]	0.995	0.020 ± 0.002[d]	1.116 ± 0.012[a]	0.996
3	0.029 ± 0.002[b]	0.461 ± 0.014[e]	0.995	0.038 ± 0.004[b]	0.951± 0.013[b]	0.994
4	0.023 ± 0.003[c]	0.663 ± 0.012[b]	0.996	0.026 ± 0.003[c]	0.798 ± 0.012[d]	0.995
5	0.034 ± 0.002[a]	0.527 ± 0.013[d]	0.998	0.047 ± 0.004[a]	0.809± 0.011[c]	0.997
6	0.020 ± 0.003[cd]	0.615 ± 0.012[c]	0.997	0.029 ± 0.003[c]	0.755 ± 0.014[e]	0.998

Mean values and standard deviations of three samples.
Values with different letters in each column are significantly different (P <0.05).
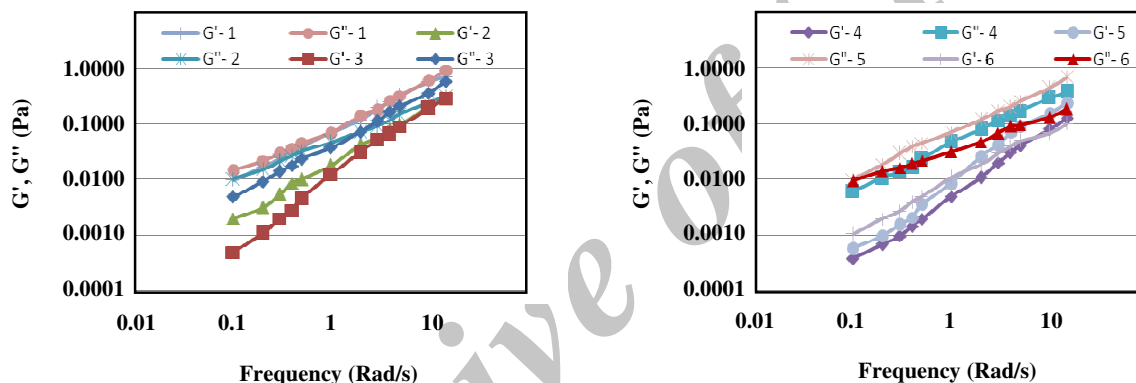** Numbers refer to formulations in Table 1*

Fig. 11: Frequency sweep of samples (Numbers refer to formulations in Table 1).

Slope x was almost close to y, indicating that G' increases as fast as G'' as frequency increased in all studied suspensions (Table 3).

Increasing WPI concentration enhanced the parameter b and slope x and decreased the slope y. This could be explained by fact that WPI acted as bridges among the oil droplets and led to droplets flocculation and network formation.

As the TG content increases, the parameter a and b increased and slope x and y decreased. Also, increase in oleic acid content increases the parameter a, b and slope y and decreases the slope x.

Fig.11 demonstrates the effect of TG, WPI and oleic acid concentrations on frequency dependence of delta degree (δ) of suspensions. Fig.12 indicates that the δ is not only frequency dependent, but also dependent on TG and WPI contents; it decreases as a function of the frequency and increases as TG and WPI contents increased. The ratio of G'' to G' (tan δ) was greater than 0.1, meaning that samples were not true gels [53]. Gel structure existence arises from droplet network association, due to depletion flocculation. Therefore, according to *Mandala et al.* (2004) and *Krstonosic et al.* (2009) these systems could be characterized as weak gels [54, 55].

As shown, the δ of suspensions in all formulations and elevated levels of frequency increased with frequency, suggesting that liquid like viscous behavior dominates these samples over solid like elastic behavior.
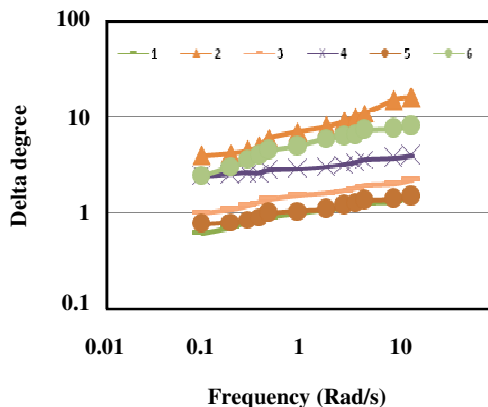
79

Fig. 12: Frequency development of the delta degree of samples (Numbers refer to formulations in Table 1)).

At these concentrations of TG and WPI, liquid like behaviors were identical; indicating increase in TG and WPI concentrations alone cannot be considered as factors for dispersion stability. The increase in the loss tangent may be related to the increase in droplet size that leads to a reduction of interactions among particles. However, the increase in both moduli does not match with what should be expected from the evolution of droplet size.

Increase in the TG concentration result in decrease in the specific gravity and apparent viscosity differences between disperse and continuous phases. As a result, the loss modulus (G'') dominated the elastic modulus (G') and the delta degree (δ) increased. The δ of the suspensions slightly decreased with increasing the TG concentration over the whole frequency range and accompanied the domination of the viscose over the elastic behavior (G''> G'>45°).

CONCLUSIONS

The results have shown that relative scaling and Reynolds scaling do not reduce the data in fact in most cases it is spread more by these methods, but in all cases, Peclet scaling works better. For all the systems examined the scaling works were better when used for relative viscosity and shear stress, especially with lower shear rates and higher concentrations. Increases in WPI at these concentrations had no significant effect on rheological properties but did affect the droplet size of dispersions. This suggests that WPI may be useful to modify physical properties without significantly changing a product's rheological properties. In this work the best fitted rheological model for flow behavior in all samples was power law model.

Nomenclature

WPI	Whey protein isolate
Pa	Pascal (unit of pressure), N/m^2
Hz	Hertz (unit of frequency), 1/s
N	Flow behavior index
k	Consistency index, Pa.sn
Re-	Reynolds number
Pe	Péclet number
k_B	Boltzmancinstant, $m^2\,kg/s^2\,K$
T	Temperature, K
k_BT	Thermal energy, $m^2\,kg/s^2$
d_{43}	Volume weighed mean
d_{32}	Surface weighed mean
rpm	Revolution per minutes
G''	Loss modulus, Pa
G'	Storage modulus, Pa
δ	Delta degree
γ	Shear rate, 1/s
η_o	Zero-shear viscosity, Pa.s
η_∞	Infinit-shear viscosity, Pa.s
η_r	Relative shear viscosity, Pa.s
α	Droplet diameter, m^2
ρ_o	Medium density, kg/m^3

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