

Impact of Lipophilic Surfactant on the Rheology and Stability of Water-in-Soybean Oil Emulsion

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Summary: In order to get long time stability in Water-in- Soybean oil emulsion the impact of self-structuring lipid, polyglycerol polyricinoleate (PGPR) has been investigated. The rheological and microstructural techniques were employed to characterize the stability and flow behavior of the material. Emulsions were prepared from 10- 40 wt. % water having 2-8 wt. % Polyglycerol polyricinoleate in phosphate buffer (pH 7, NaCl 100mM). It has been observed that an increase in water contents led to decrease in stability of emulsion while the impact of Polyglycerol polyricinoleate was other way round. The shear viscosity of the system was increased with the increase in water as well as polyglycerol polyricinoleate (PGPR) contents. The stated observations were also in accord with the optical micrographs and were helpful to explain the stability as well as the rheological results.

Key Words: Water-in-Oil Emulsion, rheology, food stability, self- structuring lipid, optical microscopy, Storage time

Introduction

Water-in-Oil emulsion is a multiphase fluid in which water is dispersed in oil phase. Such fluids have many applications in food (butter and margarine), cosmetics and pharmaceutical industries [1, 2]. However, these emulsions are thermodynamically unstable due to number of physicochemical factors. These factors affect the rheology, appearance, consistency, taste and shelf-life of emulsion [3-6]. Among these the most common factors are density difference of the phases, droplet size, electrostatic, Brownian and gravitational forces, which may result creaming/sedimentation, flocculation, coalescence and Ostwald ripening. The flocculation is the first step in which two or more droplets merge together keeping the size of the droplets same. Flocculation can be lead to sedimentation process that further causes the coalescence process [7, 8].

Generally coalescence process takes place in five basic steps [9, 10] which are: (i) The two droplets get the adhesive contact due to collision between the droplets; (ii) The draining of thin film occurs when two droplets approach in contact. This drainage process shows the thickness of the film at which rupturing takes place; (iii) Surface tension increased and plays a key role to decrease the surface area during drainage in emulsions. Along with surface tension, surface viscosity and surface

elasticity also affect the film drainage and increase the coalescence process; (iv) The drainage in the film gradually increases with the time and also reduces the thickness of film while it's rupturing increases with time; (v) Finally the droplets collide and the film disruption occurs and lead to coalescence process in food emulsion. This process is also affected by the composition of the emulsion, microstructures and environmental conditions such as variation in temperature, mechanical agitation, storage conditions etc [11-13].

As emulsion's stability is reflected in terms of variation in droplet's size with storage period and that can be delayed or enhanced by varying the surface charge of droplets surface tension of the continuous and / or dispersed phase. Therefore, several strategies have been developed to control the coalescence stability, rheology and its effects over the stability of food emulsion [10, 13, 14]. Among these, the lipophilic nonionic surfactant is considered to be more effective for lipid phases and can improve the stability of W/O emulsion.

Previously, we reported the impact of various parameters over the stability and investigated the physicochemical properties of Water-in-Vegetable oil emulsion [15, 16]. In the current study, the group selected the Polyglycerol polyricinoleate

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(PGPR) to stabilize the Water-in-Soybean Oil emulsion as it has excellent emulsifying agent properties, stabilizes the interface, introduces the rheological stability in the emulsion, turbidity agent, and can replace the fat in the food while keeping the texture of the food [17]. The specific objective of this work is to examine the effect of Polyglycerol polyricinoleate (PGPR- 4175) on the stability and rheology of Water-in-Oil emulsions having various aqueous phase contents.

Experimental

Materials

Oil soluble surfactant (PGPR 4175) obtained from Palsgaard A/S, Juelsminde, Denmark and was used to stabilize the emulsion [18, 19]. Soybean oil was purchased from the supermarket and was used as a continuous phase of W/O emulsions. Sodium phosphate (monobasic and dibasic anhydrous) and sodium chloride were obtained from Sigma-Aldrich, St. Louis MO and were used to control the pH and ionic strength of the aqueous phase. Double distilled water was used to prepare the aqueous solutions.

Sample Preparation

Preparation of Aqueous and oil phases

The aqueous phase of 10 to 40 wt % was prepared in buffer solution containing 10 mM phosphate (100 mM NaCl, pH 7.0) and was obtained from Sigma- Aldrich, St. Louis, MO. The soybean oil was prepared by dissolving the PGPR to soybean oil and was heated to 50 °C until the PGPR completely dissolved in oil phase. The oil phase was then cooled to ambient temperature prior to utilization.

Preparation of Water-in-Soybean oil Emulsion

The oil and aqueous phase was placed in a container and then blended for 2 minutes using a high shear mixer (M133/1281-0, Biospec Products Inc., ESGC, Switzerland). The resulting coarse emulsion was then recirculated through a high pressure homogenizer (Microfluidizer, Model 110 L, Microfluidics, Newton, MA) for 3 passes at 6,000 psi. [20, 21]. Six air tight conical flasks were used to keep the stored emulsions in a cold cabinet at 25°C.

Samples Characterization

The prepared Water-in-Oil emulsion was characterized using a variety of analytical techniques.

Microstructural Analysis

Emulsion was gently stirred to form a homogenous mixture without forming air bubbles. A small portion of these materials was then transferred to a microscope slide and covered with a glass cover slip. A small amount of immersion oil which was a Type A, Nikon, Melville, NY was placed on top of the cover slip and the microstructures of emulsion was characterized by optical microscopy, C1 Digital Eclipse, Nikon, Tokyo, Japan having a 60× objective lens.

Rheological measurements

Dynamic Shear Rheometer (Kinexus, Malvern, Worcestershire, UK) was used to measure the flow behavior of W/O emulsion. All measurements were performed with cup and bob cell –geometry at 30 °C. The apparent shear viscosity was determined from the measurements of shear stress versus shear rate at 30°C at constant frequency (1 Hz); the shear rate was varied from 0.1 to 100 s⁻¹.

Stability of Emulsion

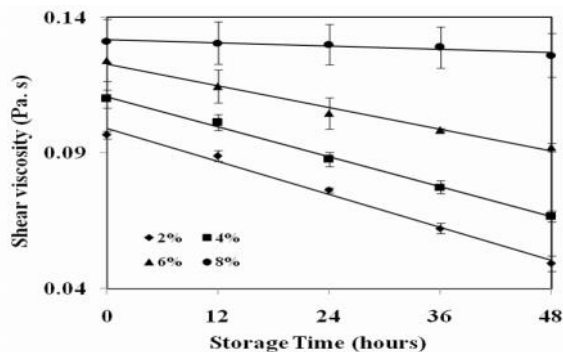
In order to investigate the stability, the prepared emulsion was stored in a clean air tight six conical flasks. Then these emulsions were kept in cold cabinet at ambient temperature. During characterization, one of the flasks containing the stored samples was opened and all the measurements were performed. The rest of the emulsion was discarded. The sample for each analysis like microscopy, rheology was taken from the same flask, using a very clean and dried pipette and sucking the emulsion very slowly. These considerations were made not to disturb rest of the stored emulsion during the characterization [15].

Results and Discussion

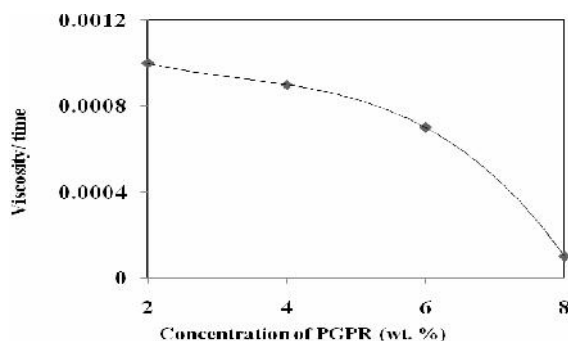
Effect of Polyglycerol polyricinoleate on the Stability of Emulsion

The stability process was made as a function Polyglycerol polyricinoleate (PGPR) concentration, water contents and storage time. The results indicated that the viscosity was decreased with the increase in storage time, irrespective of PGPR concentration (Fig. 1a). The data showed that during the storage time of 48 hours the viscosity of 8 wt. % remained almost constant (0.13 Pa. s) and was decreased (0.1 Pa. s to 0.05 Pa. s) for 2 wt. % PGPR concentration. This can be attributed due to existence of three different processes in emulsion i.e.

flocculation, sedimentation and coalescence, which, may take place separately or simultaneously and depend upon the viscosity of continuous media, droplet size, number and charge of droplets, as expected by the following Equations [18, 22, 23].



(A)



(B)

Fig. 1: Shear Viscosity of 40 WT. % Water-in-Soybean Oil Emulsions (A) as a function of storage time having different Polyglycerol polyricinoleate (PGPR) concentration. (B) Instability rate (=Shear viscosity/ time) as a function of PGPR concentration.

$$u = \frac{2(\rho_w - \rho_o)ga^2}{9\eta_B} \quad (1)$$

$$J = 4\pi \frac{KT}{6\pi\eta_B a} \varphi (1 - k\psi) \quad (2)$$

$$J = 4\pi \frac{KT}{6\pi\eta_B a} \varphi (1 - k\psi) = \left(\frac{3\Lambda\zeta^2}{2(1+H)(Ka)^2} \right) \quad (3)$$

where u is the sedimentation velocity, w , ρ_o are the density of aqueous and oil phases, η_B is the viscosity of continuous phase, g is the acceleration due to gravity, a is the size of dispersed droplet, J is the collision rate of two spherical particles, K is the constant, T is the temperature of the system, φ is the dispersed phase contents and Λ is the parameter

depending upon surface charge and size of the droplets. The fig also indicated that the viscosity was increased with the increase in concentration of Polyglycerol polyricinoleate because of the fact that the addition of PGPR decreases the interfacial tension and quality of the emulsion improved for a particular volume fraction of dispersed phase [24]. The stability was increased with the increase in Polyglycerol polyricinoleate (PGPR) concentration (Fig. 1b). It was explained in the following way: the addition of PGPR to the food emulsion is not only increased the viscosity of the continuous media but also got adsorbed over the surface of the droplets resulting a decrease in sedimentation rate, collision frequency and an increase in electrostatic as well as steric stability as expected by Equations (1, 2) [25]. An increase in water (dispersed phase) contents increased the number of droplets per volume of the emulsion resulting an increase in collision frequency and hence the stability was decreased (Fig. 2ab). The microstructure of the emulsion having different concentration of Polyglycerol polyricinoleate is depicted in Fig. 3. It was noted from the images that the size of the droplets reduced while the degree of dispersity was increased with the increase in Polyglycerol polyricinoleate concentration as observed by others [12, 13, 25]. Therefore, it was concluded that the stability in emulsion with the addition of PGPR was due to an increase in viscosity and decrease in size of the droplets. The optical microstructure of emulsion was also investigated as a function of water contents. These images show that the increase in water contents decreased the droplets size and increased the number and hence the quality of emulsion was improved (Fig. 4). It can be explained from the microstructures that after two days of emulsification the collision between the droplets was increased in higher water contents and so, the coalescence process was dominated (stored emulsions).

Effect of Polyglycerol polyricinoleate concentration on the Rheology of Emulsion

Initially the flow profile (shear stress vs. shear rate) was measured and then the apparent shear viscosities of the materials were calculated from the flow profile data. The emulsions having 2- 8 wt % contents of Polyglycerol polyricinoleate (PGPR) indicated that an increase in shear rate increased the shear stress non-linearly and decreased the shear viscosity showing shear thinning behavior up to some extent (Figs. 5a and 5b). However, the extent of shear thinning behavior was dependent over the shear rate as well as the concentration of PGPR. The

dependence of viscosity over the shear rate can be categorized into three regions: (i) low shear rate; (ii) Intermediate shear rate; (iii) High shear rate. The viscosity dependent over the shear rate was lowest in first and highest for the third region. Further this dependence was increased with the increase in the contents of Polyglycerol polyricinoleate. The trend was explained in terms of mainly two forces, the shear forces and interfacial/ surface forces. The high concentration of Polyglycerol polyricinoleate lowers the interfacial tension and the droplets became weak and easily deformable, hence the flow behavior was more pronounced in high concentration of Polyglycerol polyricinoleate hence, the results are according to literature [26, 27]. To have a clear idea about the impact of Polyglycerol polyricinoleate concentration and shear rate over the viscosity of emulsions, the shear viscosity was calculated at four different shear rates and plotted against Polyglycerol polyricinoleate concentration (Fig. 6). At very low shear rate, neither the aggregates can disintegrate nor do the deformations in droplets take place. Therefore, the viscosity of emulsion showed linear behavior at low shear rate (0.1 s^{-1}). However, with the increase in shear rate, the aggregates were broken up and the emulsion became apparently less viscous. Further increase in shear rate (up to 10 s^{-1}) resulted breaking of aggregates and shear viscosity was decreased. Similarly, an increase of shear rate up to 60 to 100 s^{-1} caused deformation of the droplets and hence the viscosity was further decreased as displayed in Fig. 6. It was observed that though the viscosity of emulsion was increased with the increase in Polyglycerol polyricinoleate concentration but more non-Newtonian behavior at high shear rate. This phenomenon was attributed to the decrease in interfacial tension with the increase in Polyglycerol polyricinoleate and lower the interfacial tension less

the shear force required deforming the droplets. To explore the impact of water contents over the emulsion rheology, the concentration of Polyglycerol polyricinoleate was kept constant (8 wt. %) whereas, the water contents were varied from 10 to 40 wt. % and the rheology of the emulsion was measured. The results showed that the shear stress and shear viscosity were decreased with the increase in shear rate as observed earlier. However, both the parameters were increased with the increase in water contents and that was consistent to the volume percentage at which the droplets become more aggregated at higher aqueous contents i.e. 30 & 40 wt. % (Figs. 7 & 8). This phenomenon was explained in terms of increase in viscosity with the increase in contents of dispersed phase as per Kreiger Dougherty equation [28].

$$\eta = \eta_0 \left(1 + \frac{\varphi_{\text{eff}}}{\varphi_c}\right) \quad (4)$$

Here, η_0 is the viscosity of the dispersion medium, φ_{eff} is the effective volume contents of the dispersed phase and φ_c is a critical packing parameter. It can be further noted that the shear viscosity was increased slowly with the increase in contents of aqueous phase, but the increase was sharp when the droplets become aggregated as φ_{eff} approached to φ_c . Fig. 8 also indicated that the shear thinning behavior was increased with the increase in water contents which might be due to high number of droplets resulting aggregate formation and with the increase in shear rate the aggregates were deformed at low shear rate and then disintegrated. This is the reason that less shear thinning is observed at low shear rate as well as low water contents and vice versa [15, 28].

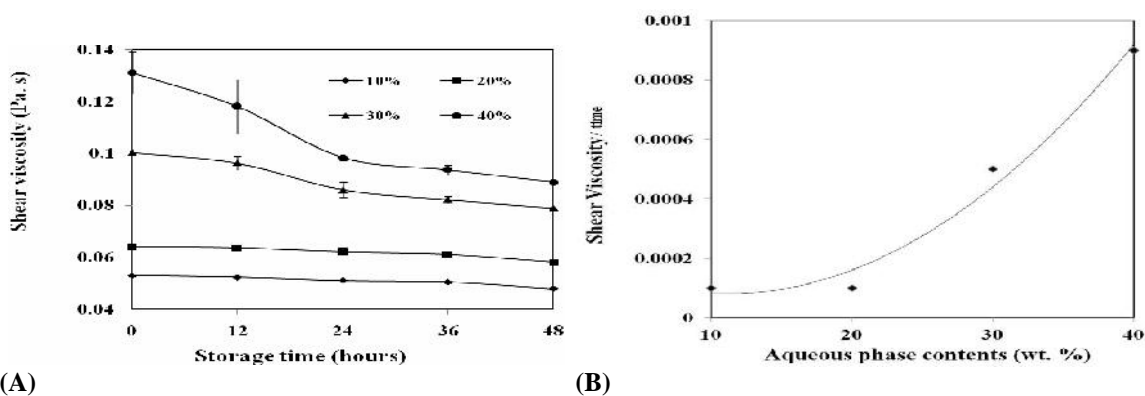


Fig. 2: Shear Viscosity of Water-in- Soybean Oil Emulsions measured at 60 s^{-1} (A) as a function of storage time (B) Instability rate (Shear viscosity/ time) vs. aqueous phase contents (pH 7, 100 mM NaCl, 25 °C). The oil phase contained 8% PGPR.

Fresh Emulsion

Stored Emulsion

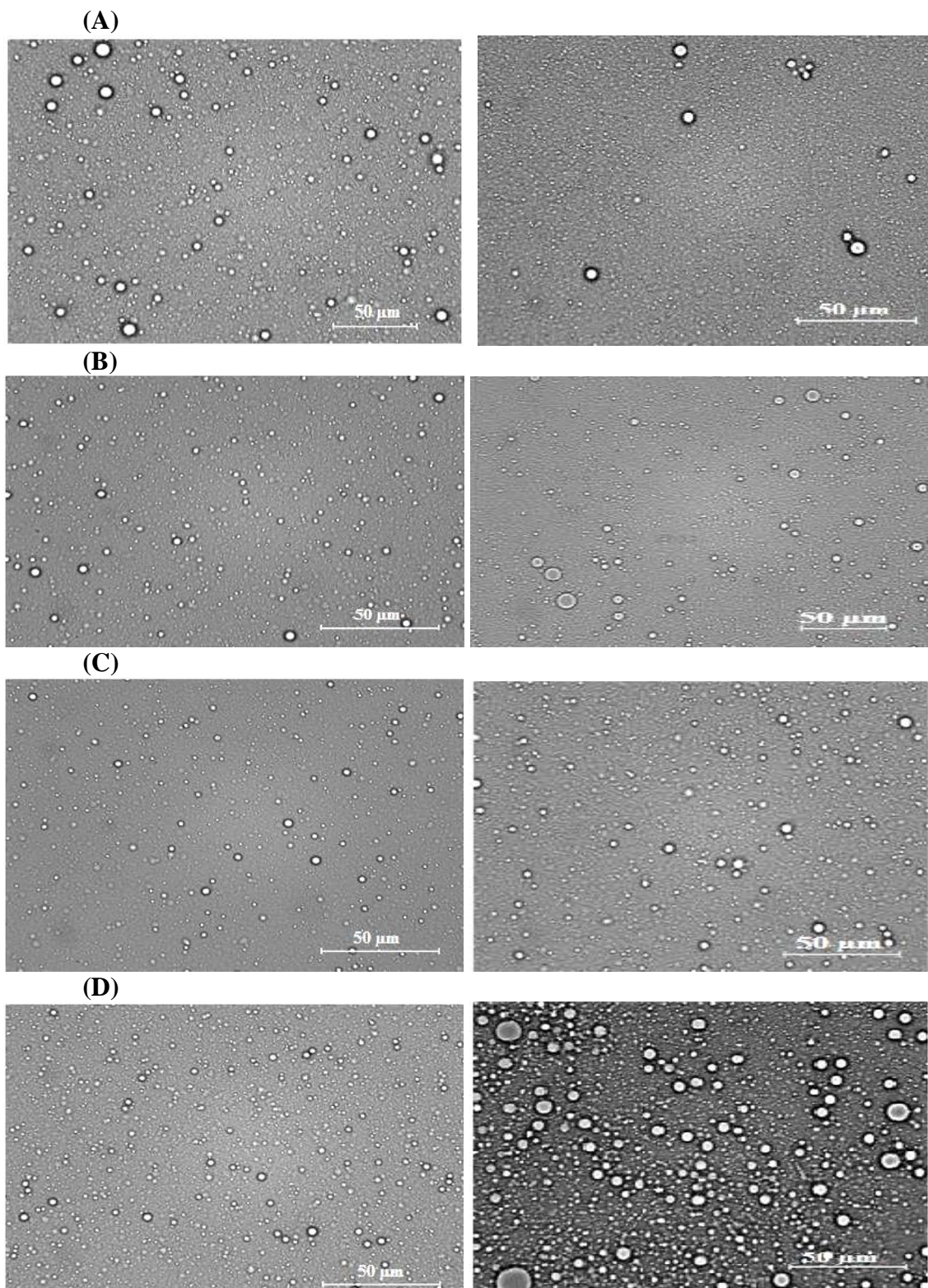
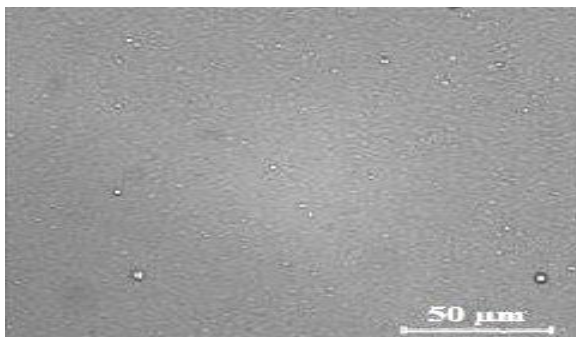


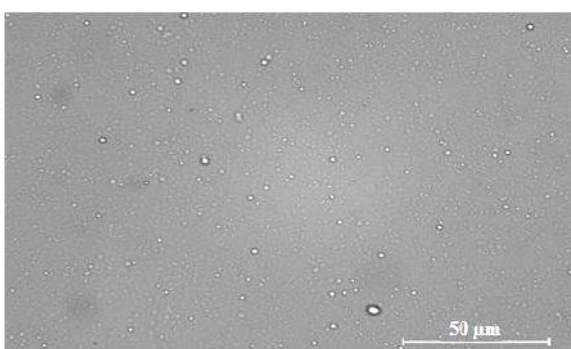
Fig.3: Optical Microstructures of 40 wt. % Water-in- Soybean Oil Emulsion for Fresh and Stored for two days; the concentration of PGPR was (A) 2% (B) 4% (C) 6% and (D) 8%.

Fresh Emulsion

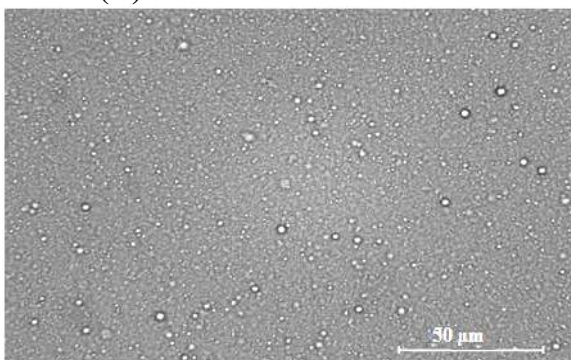
(A)



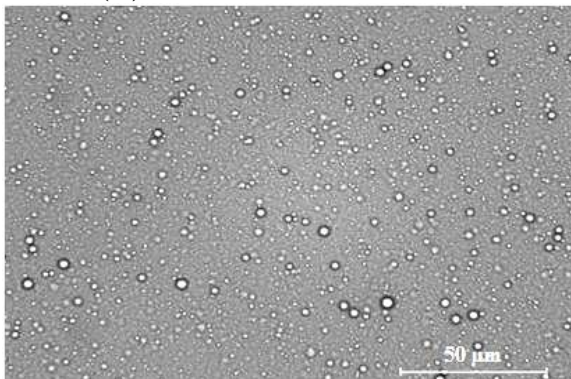
(B)



(C)



(D)



Stored Emulsion

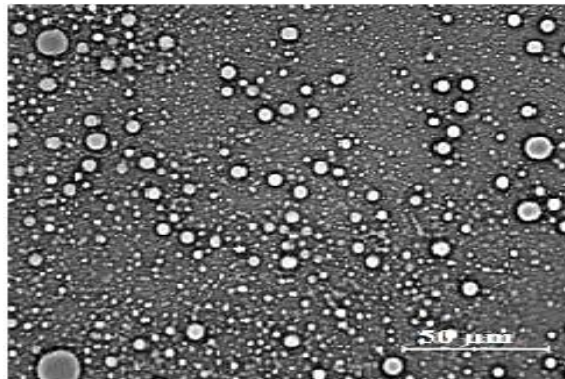
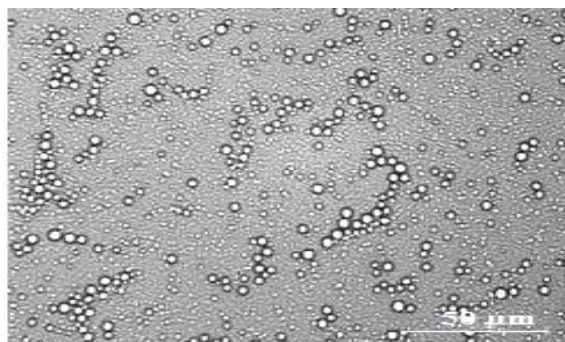
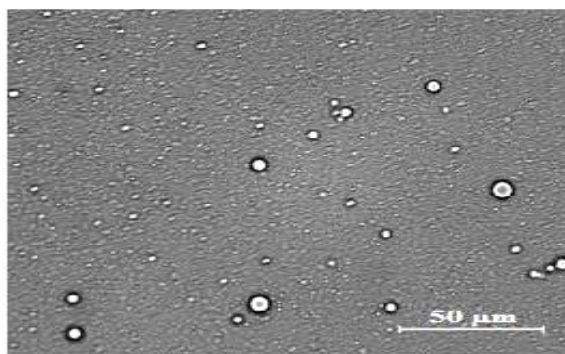
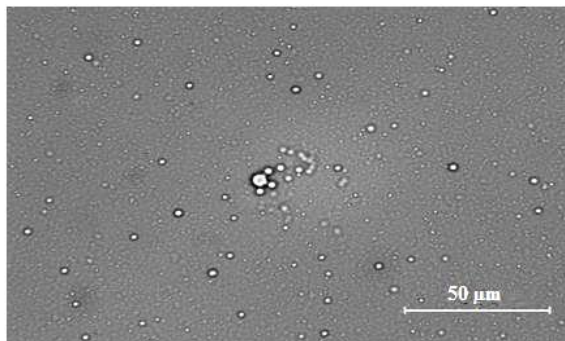


Fig.4: Optical Microstructures of Water-in- Soybean Oil Emulsions of Fresh and Stored for two days; the concentration of aqueous phase was (A) 10% (B) 20% (C) 30% and (D) 40% while the PGPR concentration was 8 wt. %.

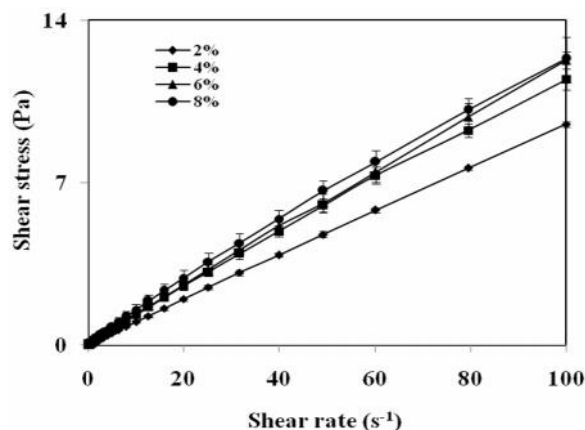


Fig.5a: Flow Profile (Shear Stress versus Shear Rate) of Water-in- Soybean Oil Emulsions having 2 to 8% PGPR concentration. The aqueous phase was prepared with 40% water (pH 7, 100 mM NaCl, 25 °C).

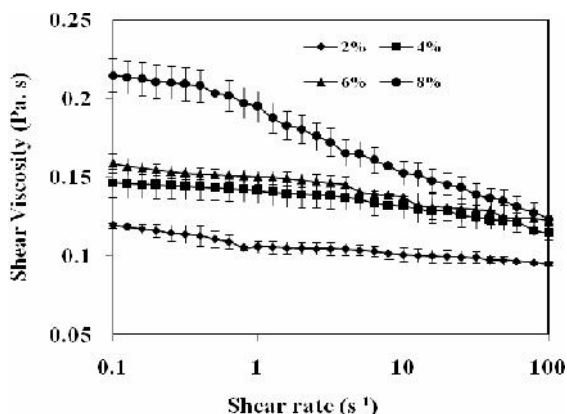


Fig.5b: Shear Viscosity versus Shear rate of Water-in- Soybean Oil Emulsions, containing 2 to 8% PGPR. The aqueous phase was prepared with 40% Water (pH 7, 100 mM NaCl, 25 °C).

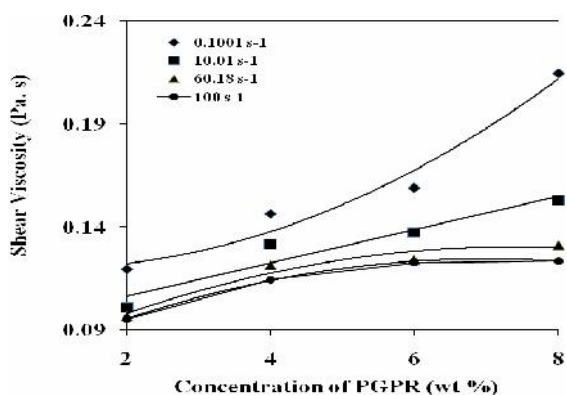


Fig. 6: Shear Viscosity versus PGPR concentration of 40 wt. % Water-in- Soybean oil Emulsion at four different shear rates.

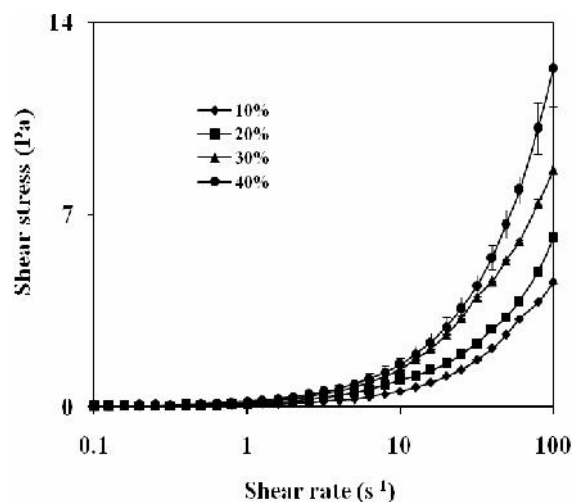


Fig. 7: Flow profiles (Shear stress versus Shear rate) of Water-in- Soybean oil Emulsions having 10 to 40% wt. % aqueous phase contents (pH 7, 100 mM NaCl, 25 °C). The oil phase contained 8% PGPR.

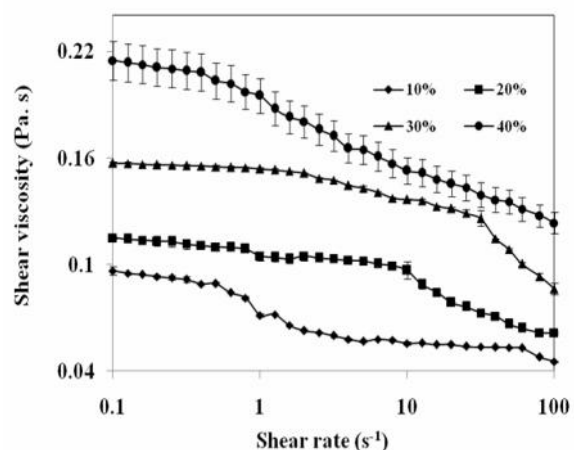


Fig. 8: Shear Viscosity of Water-in- Soybean oil Emulsions containing 10 to 40 wt. % aqueous phase contents (pH 7, 100 mM NaCl, 25 °C). The oil phase contained 8% PGPR.

Conclusion / Acknowledgments

We have explored the impact of lipophilic surfactant, Polyglycerol polyricinoleate (PGPR) on the stability and rheology of Water-in-Soybean oil Emulsion. This material was characterized by using microstructural and rheological techniques. Both techniques were helpful to observe the stability of Water-in-Oil emulsions. It was observed that the apparent viscosity of emulsion was increased with the increase in Polyglycerol polyricinoleate

concentration and water contents. However, the stability was decreased with the increase in aqueous phase contents but increased with the increase in PGPR concentration. This work could be helpful to investigate the physicochemical and stability purposes of fatty food products such as margarine and low fat spreads.

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