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Rheological properties of glycolipid based creams for pharmaceutical and cosmetic applications

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ABSTRACT

Emulsifying property of five emulsifiers was explored and compared using their rheology. These emulsifier's possess same number of carbon in their alkyl tail but differ in their head group structure. The rheology of such emulsions strongly depended on average size distribution of the dispersed droplet (Misni, 2002). Flow behaviors of these glycolipid based creams were explored in this work with two types of rheology experiments, namely: steady shear and oscillatory shear experiments. These rheology properties A strain and stress controlled rheometer was used for this purpose. Shear sweep was carried out to observe the viscosity, η ($\dot{\gamma}$) behavior, where the oscillatory sweep was carried out to observe the $G'(\omega)$ and $G''(\omega)$ behaviors. Irrespective of surfactant type, examination of shear dependent viscosity profiles suggested that, depending upon the shear rates, all emulsions examined here showed mixed flow behaviors. A shear thinning behavior (non-Newtonian flow) at low shear rates characterized by an exponential decay of shear viscosity, whereas close to shear rate independent flow behavior (close to Newtonian flow) at higher shear rates. Degree of shear thinning increased with surfactant concentration. λ -Carrageenan stabilized emulsions also exhibited higher shear viscosity and showed zero shear viscosity compared to DDM, PEG 10,000, SDS and Brij35P stabilized emulsions at any given shear rate. As far as yield stress is concerned it depended highly on surfactant type and concentration. Compared to DDM, PEG 10,000, SDS and Brij35P stabilized emulsions λ -carrageenan stabilized emulsion exhibited higher magnitude of Yield Stress. As expected, yield stress increased with surfactant concentration. The combination of higher degree of shear thinning at low shear rates and higher yield stress exhibited by λ -carrageenan stabilized emulsions suggested that λ -carrageenan stabilized emulsions are more easily spread compared to DDM, PEG 10,000, SDS and Brij35P stabilized emulsions. Oscillation measurements within the linear viscosity region suggested that λ -carrageenan stabilized emulsions exhibited higher values of both the G' and G'' compared to emulsions stabilized by others over all frequencies ranges. Values of G'' was dominant over G' over all frequency ranges, suggesting ease of spreading but low stability and shelf life. Both the moduli were frequency dependent and both followed exponentially increasing power law. The good news is that, at low frequencies, values of G' could be increased gradually by increasing surfactant concentration. This in turn suggests that emulsions stability can be improved with surfactant concentration, without compromising its spreading property. As far as flow model is concerned much like Brij 35p and SDS stabilized emulsions polysaccharide chain stabilized emulsions showed close to Maxwellian like fluid behavior, further, though these emulsions seemed relatively stable and that no imminent phase separation was observed. © 2008 Trade Science Inc. - INDIA

KEYWORDS

Glycolipids; Emulsion; Rheology; Viscosity; Storage; Modulus; Loss; Modulus.

INTRODUCTION

Sugar-based surfactants are gaining interest owing to their excellent surface-active property, non-toxic and biodegradable in nature (Misni, 2002) due derived from renewable resources (Baker et al, 2000) and show good surface activity (Giffin, 1949). Another important advantage of sugar based emulsifier is that they are much less sensitive to temperature variation than other non-ionic emulsifiers (Stunbenrauch et al, 1996).

These sugar-based surfactants also soluble in both polar and non-polar solvents (Barnes, 2000). Due to these properties, sugar-based surfactants find increasing attention from cosmetic and pharmaceutical industries.

Considering their potential application this work explores emulsifying behaviors of λ -Carrageenan, Dodecyl- β -D-Maltoside (DDM), polyethylene glycol 10,000 (PEG 10,000), sodium dodecyl sulphate (SDS) and polyethylene glycol dodecyl ether (usually referred to as Brij 35P) with addition of UV- protect and moisturizing active ingredient that stabilized oil in water (O/W) emulsion using rheology profiles.

There are two rheological properties of particular importance to emulsion that are their gel and flow properties. These flow profiles are often intermediate between solid-like and liquid-like prototype fluids. A liquid-like behavior in a steady shear flow is characterized by the absence of shear thinning property at low shear rate domain. In this case the shear viscosity (η) is independent of shear rate ($\dot{\gamma}$). This means that the stress increases linearly with $\dot{\gamma}$.

On the other hand, while solid-like complex fluid is identified by $\dot{\gamma}$ independent σ responses, thermodynamically stable emulsions in steady shear regime show non-Newtonian shear thinning behavior, where the shear viscosity (η) in $\eta(\dot{\gamma})$ profiles decays exponentially as a function of shear rate ($\dot{\gamma}$) as $\eta \propto \dot{\gamma}^{-n}$, where the power law index (n) is used for the estimation of the degree of shear thinning^[10]. The lower the value of n the higher the degree of shear thinning and vice versa, whereas the higher the degree of shear thinning the better stabilized are emulsions.

Materials showing shear thinning property always show resistance to flow. Flow can only be induced to these materials with the application of a certain mini-

mum external stress (σ) referred to as yield stress (σ_y). The higher the σ_y the better stabilized are the emulsions, and the better they are structured materially^[11].

On the other hand, in an oscillatory shear regime, where the dynamic moduli are plotted against oscillatory frequency (ω), the domination of loss modulus (G'') response by storage modulus (G') response at a high ω domain indicates greater degree of emulsion stability with longer storage life, whereas domination of G' response over G'' response ($G' > G''$) at a low frequency domains indicates that emulsion are easily spread when applied to human skin^[12].

In addition, in a prototype Maxwell model representation of ω dependence of dynamic moduli, a liquid-like emulsion is characterized by G' response which is much lower than the G'' response, and that it scales with ω as $G' \propto \omega^2$, while the G'' is a linear function of ω , as $G'' \propto \omega$. Frequency dependence of dynamic moduli usually obey these laws at low frequency domain and the ω domain associated with it is called the terminal region^[13]. On the other hand, solid-like emulsion is characterized by G' response, which is much higher than G'' response, $G' \gg G''$, and that G' is nearly independent of ω .

Similarly, emulsion showing semi-circled shaped Cole-Cole plot in combination with small phase angle (δ) over a wide range of ω indicates that sample under investigation are viscoelastic in nature. The consequence is that their flow behavior can be characterized by Maxwell model type fluid flow behavior^[3]. The δ which is the ratio of loss and storage modulus $\tan[G''/G']$ range from 0° for ideal elastic solid to 90° for ideal viscous liquid over a wide range of ω . Higher value of δ indicates that emulsions are more liquid-like in nature, whereas lower values of δ indicates that emulsions are more solid-like in nature.

This work reports structure and viscoelastic property of dispersing agents stabilized o/w emulsions, whose dispersed phase contains molecular aggregates of surfactant in addition to emulsified droplets in it.

EXPERIMENTAL

Chemicals

All emulsions and surfactant solutions used in this work were prepared in deionized water with an ionic

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conductivity of 2.8 μ S/cm. All chemicals, including oil and surfactants used in this work were of at least TLC grade with a purity of 98%, at least. Paraffin oil used in this work was of 0.84-0.86 mg/ml density, sodium dodecyl Sulfate (SDS), Polyethylene Glycol (PEG), n-Dodecyl β -D-Maltoside (DDM), λ -Carragenan and Brij-35P was purchased from Fluka. These were used as they were received, without any purification similar with paraffin oil. The titania powder used was of cosmetic grade with a purity of \geq 98%. It was purchased from Erocham. To make it moisture free, before its use titania was placed in vacuum oven at an ambient temperature of 25 $^{\circ}$ C and for the period of 24 hours. A 15 mmHg vacuum was employed for this purpose

Sample preparation

Various ratio of emulsions in 1.0 wt% concentration of dispersing agent and 0.01% of titanium oxide were prepared to stabilized aqueous and oil phases ratio of 8:2. To give the emulsions with smallest droplet sizes, these samples were homogenized for a period of at least 5 minutes immediately after the mixing of these two phases. A homogenizer, with a rotational speed of 13,000 rpm, was employed for this purpose.

The emulsified samples were then stored for a period of 3 days before exploring their Rheology. This would allow equilibration and stabilization of dispersed phase in continuous phase. Please note that oil-water mixing ratio other than 8:2 gave unstable emulsions at all dispersing agents concentrations and ratios, with a evident phase separation within a couple of hours after homogenization.

Instrumentation

1. Homogenizer

A vortex mixer model KMC-1300V was used to mix the solution prior the homogenization process. An IKA Labortechnik model T25 was used to homogenize the emulsions.

2. Rheometer

A Bohlin C-VOR strain and stress controlled Rheometer with a cone plate measuring geometry CP4/40 was used in this work. This geometry with a cone of 40 mm diameter, cone angle 4.0 $^{\circ}$, and with a measurement gap of 150 μ m. The temperature control unit help run Rheology experiments at any given temperature with

the accuracy of 0.1 $^{\circ}$ C. This work, all Rheology measurements were carried out at 25.0 $^{\circ}$ C.

The advantage of using this instrument is that it can be configured to measure a variety of Rheology characteristics within a wide range of shear rate and oscillation frequencies. It covers 5 orders of magnitude in shear rate from 10 $^{-3}$ to 0.5 \times 10 3 , which allows measuring a wide range of shear stress ranging from 10 to 10 4 Pa. The accessible range of viscosities is being 10 $^{-2}$ to 10 4 Pas. Oscillation experiments can be run from 10 $^{-3}$ to 20 Hz, covering shear strain values from 0.01 to 20 s $^{-1}$.

While the steady state shear sweep experiments were run to monitor $\eta(\gamma)$ and $\sigma(\gamma)$ profiles, the oscillatory shear sweep experiments were run to monitor ω dependence of dynamic moduli profiles. As the $\eta(\gamma)$ profile did not show an apparent Newtonian plateau at low γ domain, the estimation of zero shear viscosity (η_0) was not possible. For this same reason, instead of η_0 , $\eta(\gamma)$ was monitored at a γ of 0.01 s $^{-1}$ and it is referred to as low shear viscosity (η_{low}). While the σ_y was obtained from $\sigma(\gamma)$ profiles through the extrapolation of the stress towards zero-shear rate.

It should be noted that, before running any oscillatory shear tests, a strain sweep test was carried out for the estimation of optimum strain amplitude so that each samples is examined below its linear viscoelastic region. In these cases, the lower limit is usually automatically set by built-in transducer, whilst the upper limit was set within the limit of the linear viscoelastic regime of samples under investigation. Because these emulsions did not show an apparent plateau modulus within the measured frequency range, the liquid-like entanglement storage modulus (G_N^0), could not be estimated. In such situations G_N^0 is usually estimated from the onset of plateau region at high frequency $G'(\omega=100\text{Hz})$.

It is also worth noting here that all results shown in this work are within the sensitivity range of the Rheometer, whereas data collected below Rheometer sensitivity of 20 mPa were discarded.

3. Polarizing microscope

The optical microscopy consists of a high voltage beam source, a polarizing unit and a detector unit. Images were focused between cross polarizers both at the dark field and bright field modes. Objectives with long working distance and magnifications of 20x, 50x

(oil immersion) and 100x were used for these purposes. The detector unit was interfaced with a personal computer equipped with image analysis Leica QWin Standard version 2.6 software. This software is designed to help capture and import optical images of the samples from the microscope detector filed into the personal computer, whereby they can be processed further electronically.

RESULTS AND DISCUSSIONS

Morphological studies

The rheological properties of emulsion used in pharmaceutical and cosmetics industries can be directly related to emulsion stability and product quality. The emulsion stability and product quality largely depend on the property of dispersed phase, namely droplet sizes. Phase separation frequently occurs from inter-droplet interaction, which due to coalescence, deformation and followed by rupture of droplets (Isrealachvili, 1976). These may happen any time from the emulsion formulation to storage. Microscopy helps us to observe and evaluate emulsion structure.

Figure 1-5 showed typical micrograms of λ -Carrageenan, DDM, PEG 10,000, SDS and Brij 35P stabilized emulsions. These micrograph images were scanned after one-day preparation of the emulsion and stored at 45.0°C in an oven. These microscopic images suggest that emulsified droplets were poly-dispersed. The emulsion droplets (figure 1-5) are relatively small with mean sizes for λ -Carrageenan, DDM, PEG 10,000, SDS and Brij 35P emulsion droplets are 0.60 μ m, 0.67 μ m, 0.70 μ m, 0.80 μ m and 0.97 μ m respectively. Creams with smaller droplets, behaved more viscoelastic than creams with larger droplets. Viscoelasticity increased with decreased in droplets sizes.

It is known that the dispersed phase of surfactant stabilized emulsion plays a vital role in both the emulsion stability and its rheology properties. In particular, density of dispersed phase and its droplet sizes play an important role in emulsion stability. As evident from figure 6-7, droplet sizes highly depended on surfactant concentration respectively with or without O/W emulsion. It means that the emulsions prepared in the presence of higher surfactant concentration were better sta-



Figure 1: Light micrograph image of λ -Carrageenan based cream at 25°C at 20 micron



Figure 2: Light micrograph image of DDM based cream at 25°C at 20 micron



Figure 3 : Light micrograph image of SDS based cream at 25°C at 20 micron



Figure 4 : Light micrograph image of PEG 10,000 carrageenan based cream at 25°C at 20 micron



Figure 5: Light micrograph image of Brij 35 P based cream at 25 °C at 20 micron

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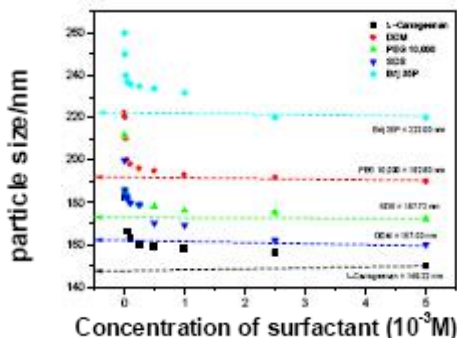


Figure 6: Mean size profiles versus different concentration of surfactant stabilized ti_2 solution without emulsion

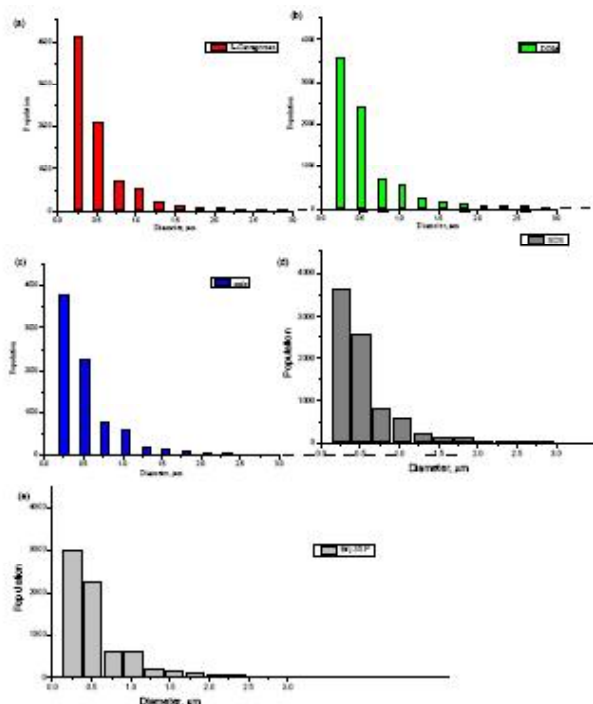


Figure 7: Droplets size distribution of different Surfactant to formulate based creams. (Total 8000 droplets). (a) λ -Carrageenan, (b) DDM, (c) PEG 10,000, (d) SDS and (e) Brij 35P

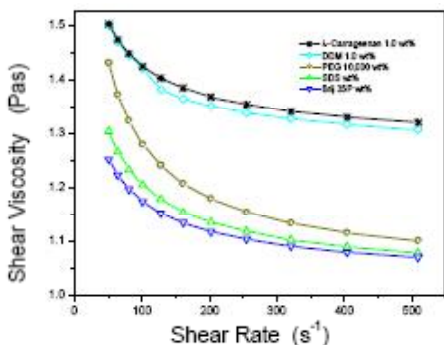


Figure 8: Shear viscosity profile of different type of based creams

bilized due to the smaller droplets tends to be more rigid., and with better rheology properties as evident from both the rheology and microscopy results.

Steady shear sweep rheometry

Figure 8 showed $\eta(\dot{\gamma})-\dot{\gamma}$ profiles of different types of 1.0 wt% surfactant stabilized creams and titania concentration as a function of shear rate.. According to the changes in the slope of the line and the trend of these flow curves, these flow profiles can be divided into two regions, which non-Newtonian in low shear strain rate region and Newtonian in high shear rate region. Shear thinning properties was observed in shear strain rate region where as shear strain rate was increased, shear viscosity decreased. This figure suggests that in addition of shear strain rate, the shear viscosity of cream depend on type of surfactant .These suggested that cream resemble to shear thinning non- ideal plastic like semisolid material, with yield stress response (S.R Derkach et al, 2000). This also implies that, creams behave like pseudoplastic. This is turn suggested that creams under investigated underwent and structuring changes with applied shear or deformation.

In addition to degrees shear thinning, Figure 8 also suggests that, λ -Carrageenan and DDM showed greater degree of shear thinning compared to cream stabilized lower emulsifying agents such as PEG 10,000, SDS and Brij 35 P. It is evident that better structured and more stable creams are produced based on the presence of type of emulsifying agents. This can be probably be ascribed to the fact that, emulsifying property of a homologue series of emulsion with same alkyl tail but differing head group structure/polarity varies strongly with HLB values that influence a good stabilizer. Note that the lower water solubility of the surfactant the lower its HLB, and the better it acts as emulsifying agent for an oil-water system (Misni, 2004), it is obvious that it λ -Carrageenan and DDM displayed greater emulsifying affect compared to, PEG 10,000, SDS and Brij 35P

Nevertheless, this figure clearly suggest that droplet size distribution plays a strong influence on η of these emulsion and its behavior is in good agreement with that reported previously, the shear viscosity is inversely related to droplet size, and that it increased with decreasing droplet size.

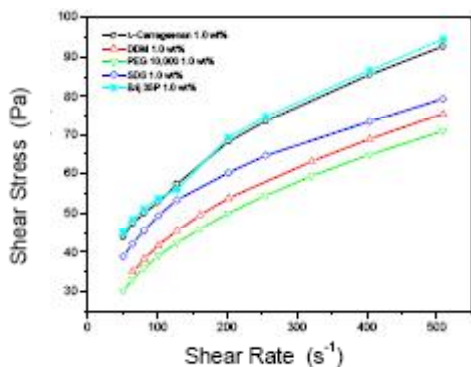


Figure 9: Shear stress versus shear rate profiles of different type of based creams

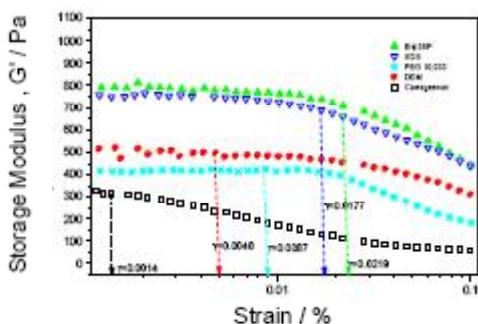


Figure 10: Shear rate sweep of different types of based creams

Shear stress versus shear rate profiles

Figure 9 exhibits effect of droplet size distribution on σ - $\dot{\gamma}$ profiles of different based creams are shown in figure 9. These profiles suggested that shear stress responses are not proportional to shear rate at all shear rate domain. The rate of change of shear stress depends largely on the rate of change of shear rate. From σ - $\dot{\gamma}$ profile, while the σ responses does not change linearly with $\dot{\gamma}$ at low $\dot{\gamma}$ domain, it changes linearly at high $\dot{\gamma}$ domain. This mean these emulsions showed solid-like viscoelastic property at low $\dot{\gamma}$ domain and show liquid-like flow behavior at high $\dot{\gamma}$ domain. this is turn suggests that emulsions under investigation underwent structural changes past a certain shear rate, called critical shear rate (R.Almero et al, 2008). This critical shear rate corresponds to the critical shear stress referred to as yield stress. It means that these emulsions do not flow under the influence of gravity below the critical stress, whereas they deform and flow past that critical yield stress (D.Bais et al, 2005). These flow curves also suggest that λ -Carrageenan stabilized emulsions showed higher yield stress (>68 Pa), DDM (65 Pa)

compared to PEG 10,000 (55 Pa), SDS (50 Pa) and Brij 35p (45 Pa) and stabilized emulsions, indicating that yield stress largely depends on surfactant type, and in particular, probably on the HLB values of surfactant (Weiss et al., 1997).

Also, as shown in figure 8, at zero shear rate, the σ responses are not zero. This means that these emulsions showing shear thinning behaviors. In other words, they behave like pseudoplastic material, which implies that flow can only be induced on these emulsions with the application of a certain minimum amount of stress.

Fitting of these steady shears Rheology data into model flow equations proved that these flow profiles data can be best described by Herschel-Bulkley model flow equation. The Herschel-Bulkley is defined $\sigma = \sigma_y + \eta \dot{\gamma}^n$, where σ_y is yield stress, above the σ_y these samples assume a linear shear stress-shear rate relationship, suggesting the validity of this equation. This suggested that these emulsions do not follow ideal Newtonian flow behavior even at high shear rate domain. By contrast, the shear stress-shear rate relationship increase exponentially at low shear rate domain, suggesting that the flow behaviors of these emulsions switch to pseudoplastic like material at these low shear rate domain.

Oscillatory shear rheometry

Emulsion showing high value of yield stress and high shear viscosity at low shear domain usually show viscoelastic properties. The viscoelastic property of a material is usually accessed with the help of frequency dependence of dynamic moduli, which in its turn can be used to describe property of emulsions such as storage stability and ease of spreading (Yasuski et al, 2008). Despite of that, the strain amplitude sweep test, which was performed at a fixed oscillatory shear of 10.0 Hz, suggested that the storage moduli of based creams are independent of applied strain at a wide range of strain amplitude (Figure 10). The based creams, exhibited wide Linear Viscoelastic Region (LVR) showing the ability of emulsion droplets resistance towards external stresses. Deviation form LVR gives a critical strain value at which indicates a minimum energy required to disrupt the structure as well as an indication of dispersion quality (Misni, 2004). The greater the critical strain, the more viscoelastic the cream will exhibit.

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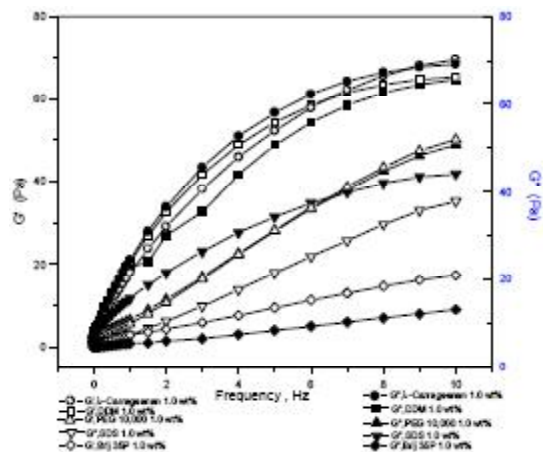


Figure 11: Dynamic moduli of different type of based creams

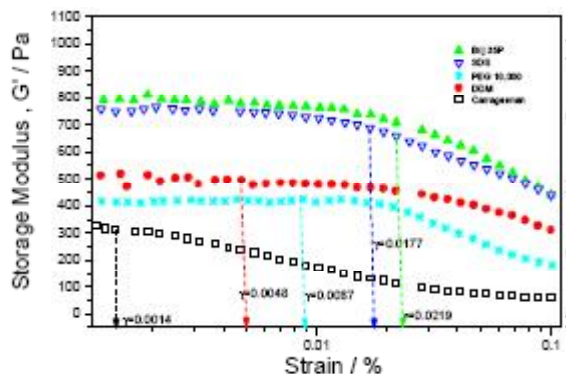


Figure 12: Plot of δ against ω as a function of different type of surfactant

Although they have the same concentration at 1% wt, λ -Carrageenan has lower critical strain and less viscous, therefore it has better leathering ability. The λ -Carrageenan based creams also exhibits a good viscoelasticity property indicating that the droplets are more stable and resist the deformation or rupture as shown by its higher storage and loss moduli.

Profiles describing frequency dependence of G' and G'' is given in Figure 11. These profiles, suggest that, both G' and G'' responses increased with frequency. G' responses of these emulsions are dominant over their G'' responses at all measured frequency domain, it is evident that the storage stability and shelf-life stability of these emulsion is high. And what more, irrespective of surfactant type, all emulsions examined here showed higher values of G'' over G' , suggesting that these emulsions spread easily. As expected, λ -Carrageenan and DDM stabilized emulsions exhibited higher values of both the loss and storage modulus compared to PEG

10,000, Brij35p and SDS stabilized emulsions, suggesting that it performs better as an emulsifying agent and it is evident that λ -Carrageenan stabilized emulsion is more elastic in nature compared to others. It could be due existences of anionic sulfate groups, carrageenan can interact strongly with oppositely charged by ionic interaction (Aguzzi et al., 2002; Bonferoni et al., 2004) and this λ -carrageenan are non digestible polysaccharides, extensively used in cosmetic formulations where they function as thickeners, emulsifiers, stabilizers, etc. (Dickinson & Stainsby, 1988; Camacho et al, 1999). Meanwhile, DDM that have maltose ester, shows low HLB value, high biocompatibility and non-toxic nature (causes no or minimum adverse effect on human health and skin). Low HLB value means excellent emulsifying properties, which in turn suggests that glycolipids can be used to produce highly stable creams and lotions with long storage life (Misni, 2000). Interestingly, it not shows a good stabilizer as well as λ -Carrageenan.

δ dependent ω profile- However, frequency dependence of dynamic moduli is not enough to judge whether or not the solid like elastic behavior dominate over liquid like viscous behavior in any emulsion samples. A better picture can be obtained by examining ω dependence of phase angle profile. Plot of $\delta(\omega)$ is given in figure 12, which suggests that, while δ of these emulsion is independent of ω , it depends both on type and concentration of surfactant (D. Bais, 2005), and that it decreases with increasing both the surfactant concentration. This implies solid like elastic property become enhanced and dominant with the increase in concentration and a good surfactant or stabilizer. Irrespective of type and concentration surfactant and the value of δ of these emulsions was lower than 45° , it is evident solid like elastic property dominate over liquid like viscous property. This probably explains why σ_y and η_{low} of these samples were high at all surfactant concentration.

CONCLUSION

We have successfully formulated glycolipid based creams emulsions with a simple formulation, where only using a simple single surfactant but posses excellent ability.

As far as emulsion structure and storage stability is concerned, both properties enhanced and improved with

the decrease of droplets size. There were evident from both visual observation and rheological properties of these emulsions. Shear viscosity increased with the decreased in droplet size.

On the other hand, the degree of viscoelasticity as evaluated from frequency dependance of dynamic moduli suggested that the viscoelasticity of these emulsions showed good results. This evidence from the G' responses for all these emulsions are dominant toward the G'' responses.

These in turn suggest that in addition to emulsion droplets and droplet size distribution, surfactant molecular aggregates and their size play a great role in imparting both the emulsion structuring and its stability, let along their strong influence on Rheology properties.

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