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Effect of Sodium Dodecyl Sulphate and Polyoxyethylene Dodecyl Ether on the Rheological Behaviour and Stability of Natural Rubber Latex

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Surfactants are important class of material used in latexes to impart stability at the solid/liquid interface. Ionic surfactants and nonionic surfactants are known to provide electrostatic and steric stabilisation. In this study, two surfactants having chain length of twelve hydrocarbons were added to the natural rubber latex (NRL) respectively to determine its zeta potential values, adsorption isotherm and rheological properties. Previous study has shown that optimum stability was observed when the alkyl chain of surfactant contains twelve carbon atoms. The zeta potential magnitude of NRL in the presence of sodium dodecyl sulphate increased as the surfactant concentration increases, while polyoxyethylene dodecyl ether did not show a significant change in zeta potential. The isotherms were of Langmuir Type 1, the amount of surfactant adsorbed per unit area at the plateau region was 6.0×10^{-6} mol m^{-2} for sodium dodecyl sulphate and 2.1×10^{-6} mol m^{-2} for polyoxyethylene dodecyl ether. The elastic modulus and relative viscosity of the NRL suspensions increased significantly in the presence of sodium dodecyl sulphate and also with polyoxyethylene dodecyl ether as compared to the NRL system due to stronger colloidal forces. The maximum packing volume fractions of the NRL stabilised with sodium dodecyl sulphate and polyoxyethylene dodecyl ether were found to be lower than NRL itself.

Keywords: latex, sodium dodecyl sulphate, polyoxyethylene dodecyl ether, surfactants

I. INTRODUCTION

Natural rubber latex (NRL) particles are naturally stabilised by an adsorbed layer of hydrophilic proteins and phospholipids. This outer layer influences its surface charge, electrokinetic behaviour and the coagulation behaviour of the NRL, thereby important properties determining latex suspension properties. However, the proteins and lipids are partially removed during the centrifugation process. Surfactant, ammonia and diammonium hydrogen phosphate typically are added to impart colloidal stability to the latex.

NRL particles in a colloidal dispersion con-

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*corresponding author: evelyn@lgm.gov.my tain negatively charge surfaces and positively charged associated counter ions that have a high affinity for the particle's surface. The surface charge of the latex particles is balanced by unequal distribution of counter ions and co-ions which extend to some distance away from the surface. This constitutes the electrical double layer of the NRL particles in the dispersing medium which stabilises the NRL.

It is well known that the stability of NRL is greatly enhanced by addition of small amounts of water soluble fatty acid soaps (Walpalage, 2008). The stability of the NRL is enhanced by addition of small amounts of straight chain fatty acid soaps in practical usage. Blackley *et al.* (1979) has observed the optimum enhancement of mechanical stability is achieved when the alkyl chain of the surfactant contains approximately nine to eleven carbon atoms. The substantial enhancement is due to the strong adsorption of the added surfactant anions from the aqueous phase into the interface between the rubber particle and the aqueous phase.

Adsorption of laurate soaps on NRL particles was found to enhance mechanical stability time of NRL (Silva, 2009). Potassium laurate is the most commonly used surfactant in latex compounding and enhances the MST of the latex. With increasing laurate soap concentration, the extent of adsorption increases rapidly and begins to plateau off when the equilibrium concentration reaches which approximates the critical micelle concentration of potassium laurate in water. The plateau or saturation limit in the isotherms suggests monolayer coverage of laurate soap on the surface of the latex particles.

Nonionic surfactants are often added to the NRL in order to confer a degree of chemical stability not attainable by the use of anionic surfactants such as fatty acid soaps (Castelvetro, 2006). However, their effect on mechanical stability is dependent on the molecular structure of the nonionic surfactants (Miguel, 2008). The four main structural variations includes the length of the ethylene oxide chain, incorporation of aromatic groups into the aliphatic hydrophobe, nature of the linkage which connects the hydrophobe to the ethylene oxide chain and functionality of the molecule from which the hydrophobe is derived. Both electrostatic and steric forces confer colloidal stability to the latex system. However, thorough comparative study on rheological and colloidal properties of natural rubber latex stabilises with anionic and nonionic surfactant having the same alkyl chain length has been lacking. Thus in this work, adsorption of sodium dodecyl sulphate and polyoxyethylene dodecyl ether onto the NRL particles and its rheological properties were studied. Zeta potential measurements were also carried out.

II. MATERIALS AND METHODS

A. Surfactants

Sodium dodecyl sulphate (SDS, $\geq$ 98%) consists of twelve carbon chain with sulphate group, polyoxyethylene dodecyl ether (Brij 35) having twelve carbon chain and 23 ethylene oxide groups, methylene blue (95%) and cobalt nitrate hexahydrate (98%) used were of analytical grade and from Sigma-Aldrich. Ammonium thiocyanate (98%) was purchased from Ajax Chemicals.

B. Zeta potential measurements

The zeta potential of the samples was measured using Brookhaven Zeta Plus, US. The zeta potential analyser utilises electrophoretic laser light scattering (solid state laser of red light (660nm), 35mW) to determine the electrophoretic mobility of charged colloidal dispersions. The latex was mixed with SDS and Brij 35 from 0.001 − 0.008 (% w/w) concentration and placed on a roller for 16 hours. It was then diluted to 0.01 (% w/w) and transferred into the plastic cuvette of 1cm^2, the palladium electrodes mounted on acrylic support were then inserted into the cuvette before being placed into the holder. A voltage of 100V, yielding a field of 278 V cm^{-1} was applied across the electrode (10mm × 5mm) with a gap of 3.6mm. Zeta potential measurements were conducted at 15^o detection angle.

C. Determination of adsorption isotherm of SDS, Brij 35 onto the NRL particles

The latex dispersions in the presence of surfactant solutions with known concentration, C_O were equilibrated. The dispersions were rotated in a Stuart roller for 16 hours at room temperature, 30 ± 1^oC for adsorption to take place. The dispersions were then centrifuged at 10,000g using the Beckman Coulter microcentrifuge machine for 60 minutes to remove the latex particles. The equilibrium concentration of the supernatant, C_{eq} was analysed for SDS and Brij 35 concentration using the calorimetric technique according to the MBAS (methylene blue active substances) and CTAS (cobalt thiocynate active substance) test respectively.

1. *MBAS test*

SDS (1mL) of different concentration was placed in small optical test tubes. The 0.5% methylene blue stock solution was diluted hundred fold with 0.7mM of sodium phosphate buffer, pH 7.2. The methylene blue (0.5mL) and 3mL of chloroform were added to each tube, followed by vigorous mixing using a vortex mixer (Hayashi, 1975). The aqueous and chloroform phases were then separated by centrifugation at 2,000rpm for 3 minutes. Absorbance of the chloroform phase at 652nm was measured in an ultraviolet visible (UV−Vis) spectrophotometer. The SDS reference standard solutions were prepared and the calibration curve was drawn by plotting the absorbance versus the SDS concentration.

2. CTAS test

The Brij 35 solution (1mL) of different concentration was placed in small optical test tubes. The ammonium cobalt thiocyanate reagent of 0.3mL was added to each tube. The ammonium cobalt thiocyanate reagent was prepared by dissolving 62g of ammonium thiocyanate, NH_4SCN and 28g of cobalt nitrate hexahydrate, $Co(NO_3)_26H_2O$ in distilled water and diluted to 100mL. The solution was left to stand for approximately 15 minutes before addition of 3mL of chloroform into the tubes followed by vigorous mixing using a vortex mixer. The aqueous and chloroform phases were then separated by centrifugation at 2,000rpm for 3 minutes. Absorbance of the chloroform phase at 620nm was measured in UV−Vis spectrophotometer. The Brij 35 reference standard solutions were prepared and the calibration curve was drawn by plotting the absorbance versus the Brij 35 concentration (Benito *et al.*, 2013).

The amount of surfactant adsorbed by the rubber particle in solution, Γ is as in Eq. 1, where a is the surface area of the particle and m is the total mass of the particles (Rosen, 2004).

$$\Gamma = \frac{C_o - C_{eq}}{ma} \tag{1}$$

D. Rheology

Oscillatory and steady state measurements were carried out on the NRL dispersions using a Bohlin CVO−R Rheometer, England. A coaxial cylinder with a moving bob (radius = 14mm) and a fixed cup (radius = 15.4mm) was used. The Bohlin Rheometer performs rheological measurements by turning the bob back and forth in a sinusoidal manner. SDS and Brij 35 were added to the latex dispersion at concentration corresponding to the plateau region of the adsorption isotherm. Measurements were carried out as a function of volume fraction of the latex from 0.40 to 0.60 for the two different surfactants. Time sweep test, dynamic oscillation and steady state measurement were performed. All measurements were made at 25 ± 0.1^oC.

III. RESULTS AND DISCUSSIONS

A. Zeta potential of NRL in the presence of SDS, Brij 35

The influence of the amount of adsorbed surfactant ions on the zeta potential of NRL in the presence of SDS, Brij 35 as a function of concentration is shown in Figure 1. The zeta potential of the NRL at the time of experiment was −46mV. The zeta potential magnitude of NRL in the presence of SDS increases as the SDS concentration increases. Electrostatic repulsions were clearly reflected by the zeta potential values. The anions may dissolve preferentially in the oil phase and imparted a negative charge to the NRL particles. The negative charge of the surfactant ions in the interface causes them to repel each other thus stabilising the system. Ionic surfactants are known to produce a high potential at the surface of the dispersed phase (Petryshyn, 2010).

However, the increase in Brij 35 concentration did not cause a drastic change in zeta potential as it is known that the active portion of non-ionic surfactants bears no apparent ionic charge and do not ionise in aqueous solutions, thus non-contributory to the zeta potential values.

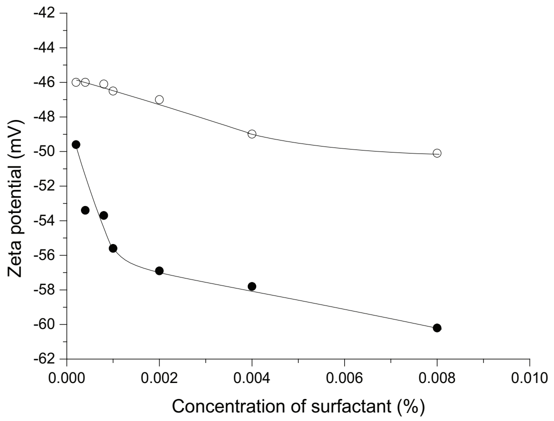

Figure 1. Zeta potential of NRL in the presence of SDS (●), Brij 35 (○) as a function of concentration

B. Adsorption isotherms of SDS, Brij 35 onto NRL particles

The adsorption of SDS and Brij 35 at the solid surface of the NRL was studied using adsorption isotherm. The amount of surfactant adsorbed was obtained by creaming the NRL and the serum obtained was analysed chemically. From the adsorption isotherm, the maximum total amount of surfactant that can be adsorbed on the surface and the affinity of the surfactant towards the surface can be known.

The amount of SDS and Brij 35 adsorbed on to the NRL particles surface at equilibrium concentration of the surfactants in the aqueous phase in mol fraction is shown in Figure 2 and 3. These isotherms were of a Langmuir Type 1 (Foo, 2010).

The results shows that the amount adsorbed per unit area, Γ at the plateau region was approximately 6.0×10^{-6} mol m^{-2} and 2.1×10^{-6} mol m^{-2} for SDS and Brij 35 respectively, which corresponded to a surface area of 28 $\mathring{A}^2$ per SDS molecule and 79 $\mathring{A}^2$ per Brij 35 molecule. The constant, k, related to the free energy of adsorption on the NRL particles for SDS were found to be 1.01×10^4 and 1.27×10^4 for Brij 35. The theoretical prediction fitted the experimental data fairly well. The adsorption area of the surfactant is known to depend on the nature of the adsorbing surface and solution (Malik, 2011).

The results shows that the adsorption amount were large due to the available sites of adsorption at the surface; however, it cannot be certain whether the adsorption took place at the "vacant sites" on the particle surface or by displacement of naturally occurring protein. The displacement of proteins by surfactants has been shown to take place in NRL (Baker, 1940; Martin, 1948).

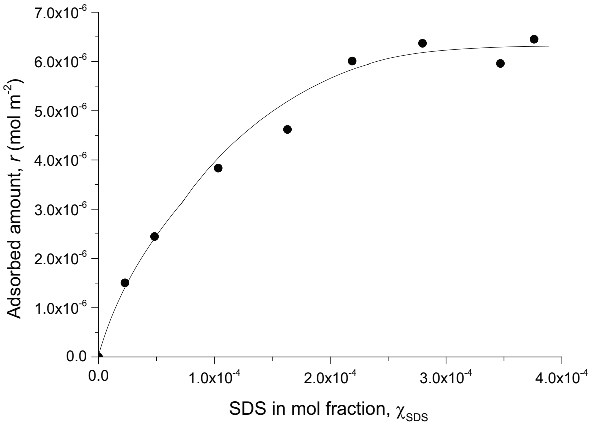

Figure 2. Adsorption isotherm of SDS on NRL particles at pH 8 and 30^{o}C

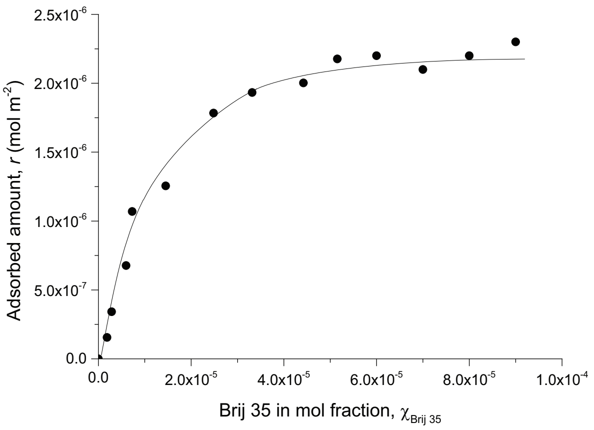

Figure 3. Adsorption isotherm of Brij 35 on NRL particles at pH 8 and 30^{o}C

C. Rheological properties of NRL in the presence of SDS, Brij 35

The rheological properties of NRL in the presence of SDS, Brij 35 at concentration corresponding to the plateau region of the adsorption isotherm were studied. Both surfactants contributed to the rheology of NRL by adsorbing onto the particles. One part of the surfactant molecule is preferentially attached to the NRL particle surface when the surfactant adsorbed on it. SDS adsorbed onto the charged surface of the NRL as electrostatic attraction took place between the sulphates head groups and the charged sites on the surface. When the double layers of the adsorbed layers begin to overlap repulsion took place. The rheology of the NRL stabilised with Brij 35 is determined by the steric repulsion of the adsorbed chain. The "anchor" chain is strongly adsorbed to the surface and the ethoxylate group is highly soluble in the water medium.

The elastic modulus of the NRL in the presence of SDS, Brij 35 at different volume fraction, ϕ from 0.50 to 0.60 as a function of strain, γ is shown in Figure 4 and 5. The elastic behaviour of the NRL in the presence of surfactant measured by elastic modulus, G' increases as the volume fraction increases, the observation was found to be the same in NRL. When SDS, Brij 35 was added into the NRL respectively, the G' value increased as compared to the NRL as shown in the previous study (Lim & Misni, 2016). The G' of dispersion is a good indicator of the dispersion's solid-like character. The increased G' value indicated that the stability of the NRL was enhanced against settling or separation by addition of SDS, Brij 35. The amount of SDS adsorbed per area of latex particle was found to be higher than Brij 35 as indicated in the adsorption isotherm study. The molecular weight of SDS is known to be lower than Brij 35. However, the G' value of NRL in the presence of SDS was lower than Brij 35 at the same volume fractions and strain. This might be due to the entanglement of ethylene group at the polymer chain of Brij 35 between two adjacent NRL particles. In the case of NRL in the presence of SDS, entanglement did not occur as it only contains straight alkyl chain with sulphate as the end group.

The elastic modulus, G' and viscous modulus, G'' of NRL in the presence of SDS, Brij 35 at different volume fractions as a function of strain is shown in Figure 6 and 7. The length of the linear viscoelasticity region (LVR) is a measure of stability. NRL in the presence of SDS, Brij 35 has a longer LVR than NRL by itself as found in the previous study (Lim & Misni, 2016). This indicates the addition of surfactants stabilised the NRL and the structure was not deformed easily.

The modulus of the NRL in the presence of SDS, Brij 35 showed a gradual change from more viscous to elastic with increasing volume fraction. NRL in the presence of SDS, exhibited more elastic response at $\phi > 0.53$, where G' was larger than G''. At $\phi < 0.53$, G'' was larger than G', where the dispersion shows more viscous response than elastic response. At $\phi > 0.44$, NRL in the presence of Brij 35 was more elastic. At $\phi < 0.44$, more viscous response was observed. The dispersion behaves as a viscous fluid at a relatively low volume fraction due to the weak interaction between the adsorbed layers of latex particles. Greater interparticle interaction is obtained when G' became relatively large. Strong

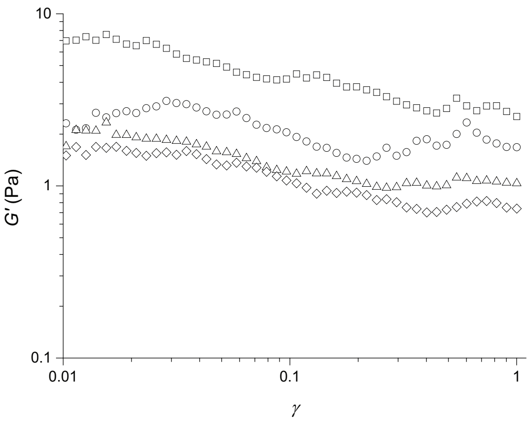

Figure 4. Elastic modulus of NRL in the presence of Brij 35 at different volume fractions □ = 0.60, ○ = 0.56, Δ = 0.53 and ◇= 0.51 as a function of strain at 25^{o}C

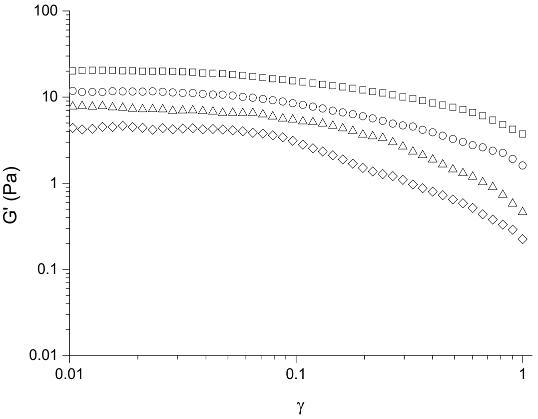

Figure 5. Elastic modulus of NRL in the presence of Brij 35 at different volume fractions □ = 0.60, ○ = 0.56, Δ = 0.53 and ◇ = 0.51 as a function of strain at 25^{o}C

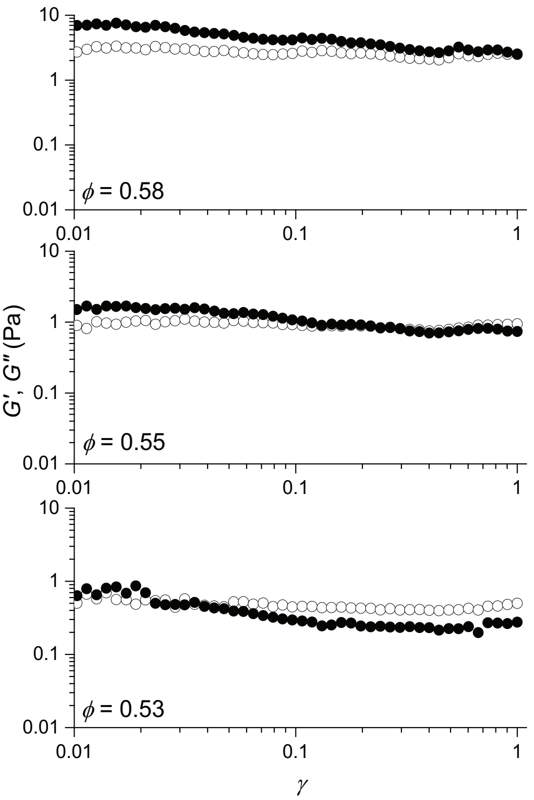

Figure 6. Elastic modulus (●) and viscous modulus (○) of NRL in the presence of SDS at different volume fractions as a function of strain at 25°C

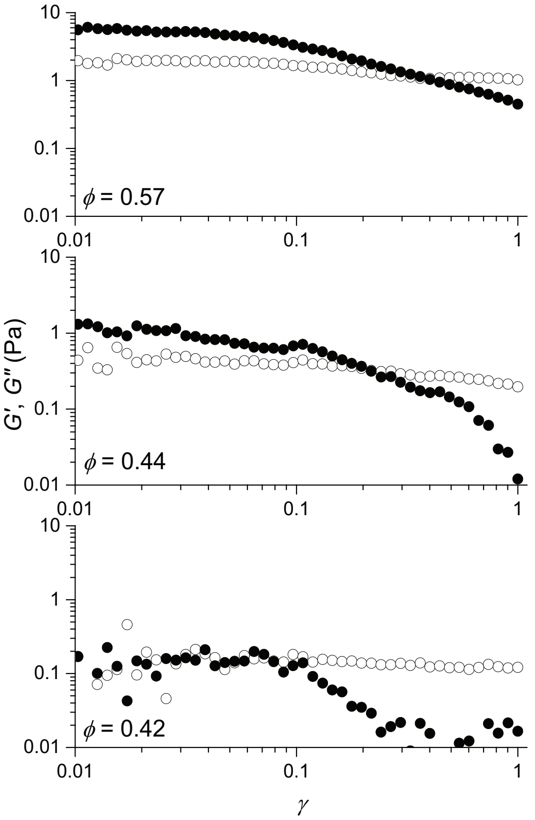

Figure 7. Elastic modulus (●) and viscous modulus (○) of NRL in the presence of Brij 35 at different volume fractions as a function of strain at 25°C

double layer interaction is indicated when G' is greater than G'' (Tadros, 1990).

Figure 8 shows that tan $\delta > 1$ occurred at $\phi = 0.53$ for SDS and $\phi = 0.42$ for Brij 35. The ratio of the viscous modulus to the elastic modulus is defined as the tan δ. The transition from elastic to viscous response of NRL in the presence of SDS occurred at a much higher volume fraction compared to NRL and NRL in the presence of Brij 35. The reason might be the effective adsorbed layer of SDS was thicker than Brij 35 due to the higher adsorbed amount of surfactant at CMC (Liang et al, 1995).

The relative viscosity of NRL in the presence of SDS, Brij 35 over a function of volume fraction is shown in Figure 9 and 10. The relative viscosity data was analysed using the Krieger-Dougherty equation (Norbert, 2013). The Krieger-Dougherty equation (equation 2) relates viscosity to the particle concentration, where $[\eta]$ is the intrinsic viscosity having a value of 2.5 for spherical particles and ϕ_p

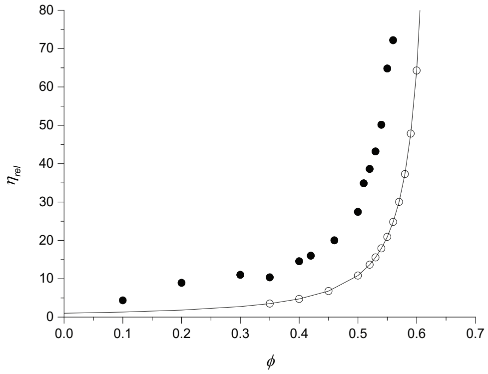

Figure 8. tan δ of NRL in the presence of SDS (○) and Brij 35 (●) at various volume fractions at 4% strain and 25^{o}C

is the maximum packing volume fraction. ϕ_p can be obtained using the empirical procedure (equation 3), where ϕ_p was obtained from a plot of ϕ versus $1/(\eta_{rel})^{\frac{1}{2}}$ and extrapolation to $1/(\eta_{rel})^{\frac{1}{2}} = 0$.

$$\eta_{rel} = \left(1 - \frac{\phi}{\phi_p}\right)^{-[\eta]\phi_p} \tag{2}$$

$$\phi = \phi_p + \frac{K}{(\eta_{rel})^{\frac{1}{2}}} \tag{3}$$

The relative viscosity curve of the NRL in the presence of SDS, Brij 35 gave a curve that was significantly higher compared with the theoretical prediction of the hard sphere model. This might be due to the adsorbed layer. The relative viscosity was found to change exponentially with volume fraction. When the effective volume fraction becomes sufficiently large, relative viscosity increased to infinity. Incorporation of SDS, Brij 35 increased the relative viscosity of the NRL significantly. The stabiliser layer is known to result in viscosity rise (Mewis, 2000). The stabilising layer contributes significantly to the effective volume and thus gives rise to strong viscosity increase. The thickness of the stabilising layer depends on the ionic strength and steric repulsion that gives rise to viscosity due to the surfactants.

To obtain the maximum packing volume fraction, ϕ_p for NRL in the presence of SDS, Brij 35, it was determined from a plot of ϕ against $1/(\eta_{rel})^{\frac{1}{2}}$ (Figure 11) and extrapolation to $1/(\eta_{rel})^{\frac{1}{2}} = 0$. The ϕ_p for NRL in the presence of SDS, Brij 35 was found to be 0.65 and 0.67 respectively which corresponded to face-centred cubic packing (Pingret, 1992). The increase in particle diameter decreases the maximum particle volume fraction (Shay, 2000).

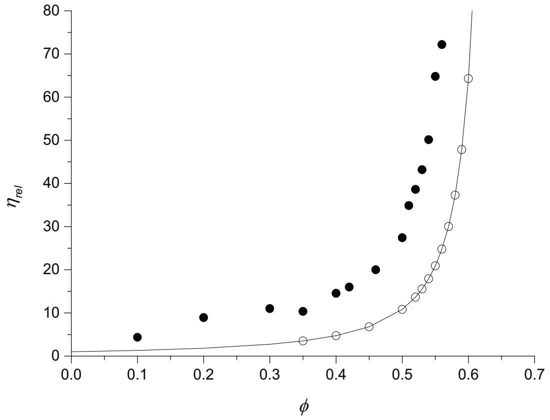

Figure 9. at 25^{o}C, ● experimental data, ○ Krieger-Daugherty fit

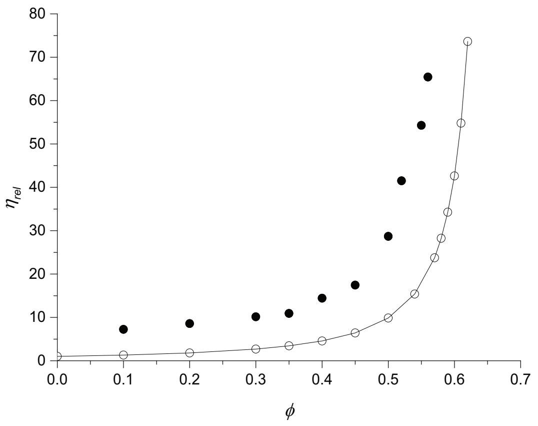

Figure 10. at 25^{o}C, ● experimental data, ○ Krieger-Daugherty fit

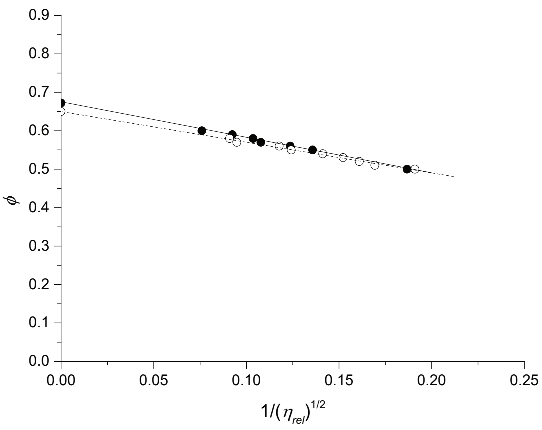

Figure 11. Volume fraction as a function of $1/(\eta_{rel})^{\frac{1}{2}}$ curve for NRL in the presence of SDS , Brij 35 at 25^{o}C, ○ SDS (slope = -0.7987, y-intercept = 0.6502, R^2 = 0.995), ● Brij 35 (slope = -0.9139, y-intercept = 0.6721, R^2 = 0.997)

IV. SUMMARY

Sodium dodecyl sulphate and polyoxyethylene dodecyl ether was added to the natural rubber latex respectively in this study. The zeta potential magnitude of NRL in the presence of SDS increased as the SDS concentration increases, while increase in Brij 35 concentration did not cause a drastic change. The amount of SDS and Brij 35 adsorbed per unit area of NRL particles at the plateau region was approximately 6.0 × 10^{-6} mol m^{-2} and 2.1 × 10^{-6} mol m^{-2} respectively, which corresponded to a surface area of 28 $\mathring{A}^2$ and 79 $\mathring{A}^2$. The G' value increased as compared to the NRL when SDS, Brij 35 was added indicated enhanced stability. Incorporation of SDS, Brij 35 was found to increase the relative viscosity of the NRL significantly. The maximum packing volume fraction for NRL in the presence of SDS, Brij 35 was found to be 0.65 and 0.67 respectively. SDS was found to be more effective in stabilising the NRL as compared to Brij 35.

V. ACKNOWLEDGMENT

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conflict of interest regarding the publication of this paper.

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