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Published Online 25 February 2015 **Research Article**

Scrutinizing the Characteristics of Deproteinised Natural Rubber Latex Containing Sodium Dodecyl Sufate

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ABSTRACT

An extension study on the role of sodium dodecyl sulphate (SDS) in deproteinised natural rubber latex (DPNRL) was performed. It was observed that SDS effectively facilitated the removal of proteins during the deproteinisation process of which about 20 – 80% of proteins was removed. Almost a complete reduction (97%) in extractable proteins (EP) was seen in cast films prepared from these SDS-DPNR mixtures. The presence of SDS had resulted in smaller particle size diameter however there was no distinct difference in their effective particle size diameter as the SDS concentration increases. Slight agglomeration was seen at high SDS concentration. The zeta potential was enhanced as the SDS concentration increased indicating higher colloidal stability. Depending on the SDS concentration the presence of SDS in DPNR latex also rendered stabilization effect as observed during the mechanical stability test. SDS resulted in low flow behaviour where the latex became viscous with increasing SDS concentration. Deproteinisation caused marked reduction in crosslinking density consequently leading to lower mechanical strength.

Keywords: Deproteinised natural rubber latex, sodium dodecyl sulphate, proteins reduction, latex characteristic

INTRODUCTION

Deproteinisation of natural rubber latex involves certain purification treatments either physically[1,2] or chemically [3,7] of which it permanently removes most of non-rubber constituents including proteins that are present in latex system. The presence of proteins is commonly associated with inferior effects observed in rubber for example poor creep, stress relaxation and storage hardening behaviour [8,9]. Moreover, the polemic allergenic issue which originated from the extractable proteins of latex products has initiated the development of low protein latices [10]. As such, deproteinisation of natural rubber latex is considered as a strategic method to address the above-mentioned issues.

Of the many methods, urea in combination with surfactants proposes a valuable approach for effective protein reduction in natural rubber latex. Urea causes the proteins to lose their conformation state and favours the unfolding shape [11,15]. Urea exerts its influence directly by binding to the proteins, or indirectly by altering the solvent environment. The protein unfolding mechanism can be attributed to both routes. In the direct mechanism, the most favourable interaction of urea is with the peptide backbone of proteins and this interaction results in the unfolding process. In the indirect mechanism, it is postulated that urea promotes ready solvation of the proteins hydrophobic groups by altering the water structure.

To facilitate the removal of proteins, addition of anionic surfactant is necessary. Anioinic surfactants for instance, sodium dodecy [l] sulphate (SDS), binds to most of proteins with high affinity [7,16,17]. SDS may bind to proteins via sulphate group and positively charged amino side chain, or between the alkyl chain and hydrophobic side chain. The unfolding process *via* SDS may proceed through two different modes closely concomitant to the

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changes of micelles structures. Spherical micelle leads to simpler ligand-binding-type while cylindrical micelles unfold proteins by wrapping themselves around the proteins and bind progressively. The latter mode usually occurs at higher SDS concentration.

SDS binds onto the surface of unfolded proteins and imparts negative charges. This phenomenon results in the proteins having higher net negative charges compared to their previous state consequently creating high electrostatic forces that cause the proteins to remain unfolded. The unfolded proteins are then easily removed during the centrifugation process. As such, the effective protein removal activities are attributed to the synergistic effect driven by the unfolding mechanism of proteins by urea and subsequent action of SDS.

Although the deproteinisation mechanism *via* urea-SDS route is well established, it yet distinct the exact function of SDS during the deproteinisation process in affecting the characteristics of deproteinised natural rubber (DPNR) latex. Thus the aim of this paper is to present more evidence, elucidating the functions of SDS in influencing the latex characteristics. The study included the effects of SDS on rubber particle size, surface charge behaviour of rubber particle, protein content, stability, and flow behaviour of NR latex. Further to that, the vulcanization efficiency after removal of proteins and the resulting latex film properties were also examined.

MATERIALS AND METHODS

Natural rubber latex concentrate grade, preserved with 0.7 wt. % ammonia (HA-NRL) and all chemicals were used as supplied without further purification.

2.1 Sample preparation and formulation:

HA-NRL was firstly diluted to approximately 30% total solid content (TSC) with 25% NH3 solution. Methods of preparing the SDS-containing-deproteinised natural rubber (DPNR) latex are as described in *Figure 1*. To study the effect of SDS on the characteristics of DPNR latex, the concentration of SDS was varied at (0, 0.6%, 1.8%, and 3% w/w) whilst the concentration of urea was fixed at 1.2% w/w. The resulted latex was collected at each centrifugation stage and characterized accordingly. The latex was centrifuged using alfa-laval type throughout this study as described elsewhere [18].

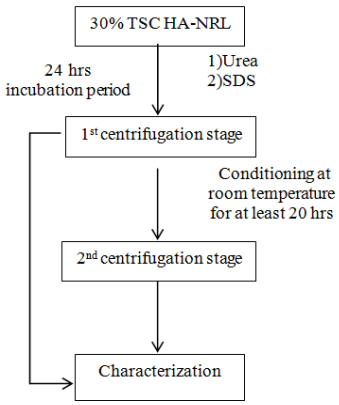

Fig. 1: DPNR latex preparation method.

2.2 Sample characterisation:

Surface tension measurement of SDS was performed using the pendent drop method. Calibration curve was then plotted for surface tension against log SDS concentration. The mathematical equation derived from the calibration curve was used to estimate the concentration of SDS that remained in the latex serum after it underwent certain treatments including centrifugation process.

The mechanical stability time of DPNR latex was determined using a Klaxon Mechanical Stability Testing Machine (14000 r.p.m. speed) according to the ISO 35 test method.

Total extractable protein (EP) content was determined according to the ASTM D5712-05e test method. The water soluble proteins were extracted out from latex film specimen (6 X 6 cm2) by leaching in phosphate-buffered saline (PBS) with extraction ratio of 1 g / 5 mL under temperature of 23°C±2°C for 2 hours. The eluted proteins were precipitated out with combination of acids and then dissolved and quantified colorimetrically. Total protein content of the samples was measured using the Kjeldahl procedure.

Particle size distribution and surface charge behavior for all resulting DPNR latices were measured using the 90Plus/BI-MAS and ZetaPlus from Brookhaven Instrument Corporation respectively. About 0.01wt% of sample was prepared by diluting the sample with distilled water and the pH of dispersion sample was adjusted with 0.1M H2SO4 and 0.1M KOH prior to the test.

The rheological behaviour of sample was measured via Discovery Hybrid Rheometer (DHR), TA Instruments. Experiments were performed at 25±3oC using a peltier concentric cylindrical geometry and all accessories were calibrated before use. Viscosity and shear stress test of samples were characterized using flow ramp at shear rate of 0.01-900s-1.

For studies on the vulcanization efficiency, latex was compound with curative ingredients as tabulated in *Table 1*.

Table 1: Compounding formulation for pre-vulcanization study.

Compounding Formulation	Weight (g)
LATEX	167
50% Sulphur	4
50% ZnO	2
50% ZDEC	1
10% KOH	2.5

Compounded latex was stirred continuously at room temperature. Crosslinking density at 48 hours of maturation period was estimated using the swelling equilibrium method.

The films were die-cut and weighed before being immersed in closed vessel containing chloroform at room temperature for about 48 hours. Excess chloroform solvent was blotted from the swollen sample using filter paper and the equilibrium-swollen weight was determined. Then the swollen films were dried in vacuum-oven at temperature of about 50±0.5ºC until no further change in the weight could be detected. A constant dry weight was obtained after 3 days (72hours). The crosslinking density was then calculated based from Flory-Rehner equation19-21 (1)

$$\ln(1-Vr)-Vr-\chi Vr2 = 2\rho Vo\eta physVr1/3 \quad (1)$$

Where; Vr is the volume fraction of rubber in swollen condition, Vo is molar volume of swelling agent, χ is the polymer-solvent interaction parameter, ρ is the mass per unit volume of network and ηphys is the concentration of physically effective crosslink density.

Tensile strength of unaged casted film (0.3±0.05mm thickness) was performed using an Instron Tensile Machine 5565 with a crosshead speed of 500 mm/min according to ISO 37 test method.

RESULTS AND DISCUSSION

Figure 2 shows the calibration curve of surface tension as a function of SDS concentration. The equation derived from the linear part of the curve was used to estimate the concentration of SDS that remained in the latex serum (*Table 2*).

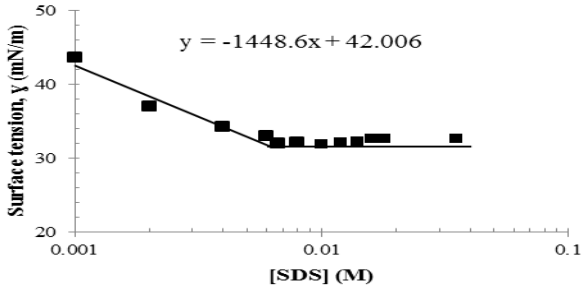

Fig. 2: SDS calibration curve determined from surface tension.

The influence of SDS concentration remaining in the latex system towards effective particle size diameter and zeta potential (ZP) is as tabulated in Table 2.

Table 2: Effect of SDS concentration on effective particle size diameter and zeta potential of DPNR latex.

Treatment	[SDS], mM1	Effective Particle Size Diameter (µm)	Zeta Potential (mV)2
With 0% SDS+Urea	0	0.36±0.03	-54.76±4.57
With 0.6% SDS+Urea(2)	2.64	0.32±0.01	-43.86±3.01
With 1.8% SDS+Urea(2)	3.79	0.28±0.02	-35.95±2.73
With 0.6% SDS+Urea(1)	5.34	0.21±0.02	-36.20±2.86
With 3% SDS+Urea(2)	5.63	0.28±0.01	-37.71±1.44
With 1.8% SDS+Urea(1)	6.20	0.29±0.02	-49.54±6.29
With 3% SDS+Urea(1)	6.98	0.31±0.02	-55.98±2.31

1Concentration determined using pendent drop method
2Zeta potential measured at pH10

Number in parentheses referring to stage of centrifugation:

The presence of SDS resulted in a smaller particle size diameter as compared to latex without SDS treatment. The reason could be due to adsorption or encapsulation of SDS on the particle surface resulting in enhanced steric stabilization22 which prevented the individual particle from closing in together. Unlike the absence of SDS where particle could come closer with possible pseudo-agglomeration, this steric stabilization would push particles further apart, resulting in them being detected as highly separated particles of smaller size range. Another possible reason for the smaller particle size could be due to the loss of protein macromolecules having been stripped off from the surface of latex particles during deproteinisation process.

However, varying the different SDS concentrations in the latex system did not bring about marked changes in the effective particle diameter. Nonetheless, it is worth mentioning that the latex particle began to agglomerate when higher concentration of SDS was employed. One possible reason is that when added SDS concentration has reached its saturation point23, the amount of adsorbed or encapsulated SDS could be high enough to create overcrowding of the extended chains in the medium and triggered entanglement between the particles, leading to agglomeration.

The ZP values did not change much although different SDS concentrations were detected in the treated latex. Initially, a reduction trend in ZP was observed when the SDS concentration increased up to 3.79mM, following a continuous increase after that. A slight drop in the ZP value at lower SDS concentration might be due to adsorption of SDS molecules that brought about shifting effect to the plane of shear, hence compressing the electrical double layer24. The ZP value subsequently increased at higher SDS concentration (6.98mM). This is possibly due to increase in potential of Helmholtz inner layer with increasing of surface coverage, hence leading to increase in ZP value when SDS concentration increases.

The mechanical stability of latex as a function of SDS concentration remaining in the latex system is shown as in *Figure 3*.

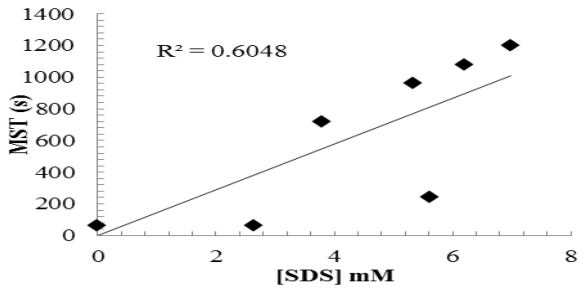

Fig. 3: Mechanical stability time of DPNR latex as a function of SDS concentration.

Results showed an almost linear relationship (correlation factor of about 0.6048) between MST and SDS concentration at higher SDS concentrations, suggesting the stabilization effect in the presence of SDS in DPNR latex. Evidently, latex without SDS showed very low MST value suggesting deteriorated stability of the latex during the deproteinisation process by urea alone. Stability of DPNR latex was conferred by the presence of SDS; stability of latex improved as the SDS concentration which remaining in the latex system increased.

Figure 4 shows that about 20-80% of proteins were removed during the deproteinisation treatment. This could be attributed to the synergistic effect of urea in combination of SDS. The most effective removal of proteins was observed when the system contained about 5.34mM SDS concentration equivalent to lowest protein content among all samples (0.74%).

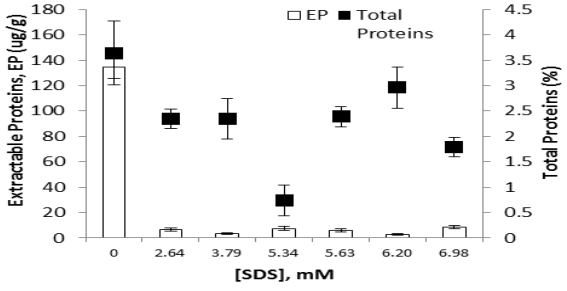

Fig. 4: Extractable proteins (EP) content (lowry method) and total proteins (Kjeldahl method).

Highest EP was detected in DPNR latex without SDS, while further action of SDS resulted in about 90% reduction of EP for all SDS concentrations. It is worth to note that the SDS-containing-DPNR latex produced resulting latex film with EP below the detection limit (5ug/g).

The flow behaviour of SDS containing DPNR latex is as shown in *Figure 5*.

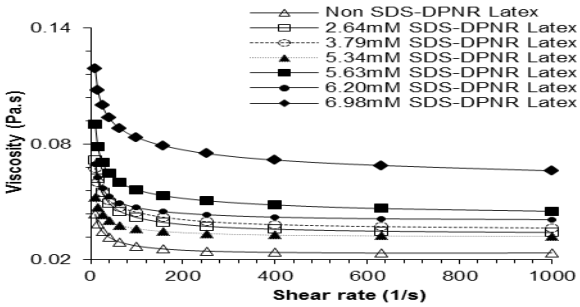

Fig. 5: Viscosity against shear rate plot for all DPNR latex samples.

It is apparent that the viscosity of all DPNR latex samples was found to obey a non-newtonian with shear thinning behaviour as shear rate increased. The absence of SDS in DPNR latex casued latex with low viscosity while SDS present in DPNR latex serum (after underwent centrifugation process) contributed to higher latex viscosity. Generally, latex viscosity was observed to increase as concentration of SDS in DPNR latex became higher. It is well known that the presence of adsorbed materials such as SDS will cause an increasing in latex viscosity25. It is postulated that the adsorbed materials may have fill up the total volume fraction of materials or their carbon chain may entangle with each other hence, restricting further movement of particle, resulting in higher viscosity.

The crosslinking density measurements were carried out to further analyse the effect of NRL deproteinisation on vulcanization efficiency. *Figure 6* represents the vulcanization efficiency of selected concentrations of SDS containing DPNR latex.

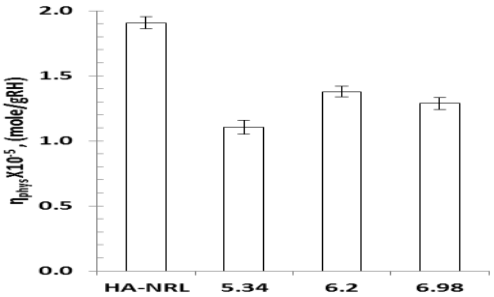

Fig. 6: Comparative studies on crosslinking density of HA_NRL and SDS (mM) treated deproteinised NRL.

The selection for DPNR latex was made according to their MST values (*Figure 3*) > 700s which is the quality accepted criteria for latex concentrates. It is obvious that deproteinisation process of NRL lead to lower crosslinking density. Proteins have been reported to serve as an active spots18,26 which promote and accelerate the vulcanization efficiency. It is also possible, the presence of surfactants hindered further diffusion of curing agents27-28 hence acquiring a longer maturation period to achieve the density of crosslinking in DPNR latex.

*Figure 7*depicts film mechanical properties of DPNR latex in comparison with HA-NRL. As expected, the mechanical properties of SDS containing DPNR latex revealed a lower tensile strength than normal HA-NRL. This is due to the lower crosslinking density during the vulcanization process. It was observed that different concentrations of SDS remaining in the serum did not affecting much the tensile strength of dipped film. This lower mechanical strength could be due to the inefficiency of rubber particles to crosslink via inter-particle29.

Conclusion:

This study shows that SDS facilitated removal of proteins in NRL rather than urea alone. SDS was found to improve the colloidal stability of latex during and after the deproteinisation process. The flow behaviour of latex was reduced in the presence of SDS, and became more viscous as the SDS concentration increased. The lower vulcanization

efficiency could be attributed not only to the deproteinisation process, but possibly to the encapsulation of surfactant on rubber particle which restricts further diffusion of curing agents into the rubber phase.

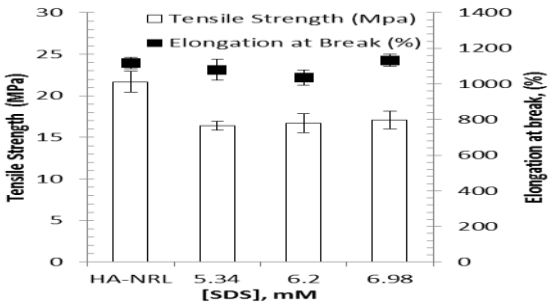

Fig. 7: Mechanical strength of SDS (mM) containing deproteinised NRL in comparison with HA-NRL.

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