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EFFECT OF AMPHIPHILIC ALKYL CHAIN LENGTH UPON PURIFIED LATEX STABILITY

(Kesan Pemanjangan Rantai Alkil Ampifilik ke atas Kestabilan Lateks Tulen)

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Rubber particles in purified latex (PL) are stabilized by a film of protein and fatty acid soap (surfactant). Saturated straight-chain fatty acid soaps can assist an enhancement of latex stability. However, whether the alkyl chain length plays an important role in increasing the stability is still an issue. The aim of this study is to investigate the effect of alkyl chain length of anionic surfactant on the stability of purified latex. The fatty acid soap of decanoate (9), laurate (11), sodium dodecyl sulphate (SDS) (12) and palmitate (15) were used. The numbers in parentheses indicating the number of carbon present in alkyl chain of the soap. The results showed that the impact of alkyl chain length on the stability of latex is in the order of laurate > decanoate > SDS > palmitate > purified latex accordingly. The alkyl chain length does giving a significant effect on latex stability after longer stirring time. The particle size of latex with the presence of surfactant is greater compare to a single particle itself due to extension of particles diameter. Thus suitable interaction of the nonpolar tail of surfactant with the hydrophobic regions of latex surface played a major role in maintaining a stable latex system.

Keywords: anionic surfactant, conductometric titration, stability

Abstrak

Zarah-zarah lateks tulen distabilkan oleh protein dan asid lemak tepu (surfaktan). Panjang asid lemak tepu dapat meningkatkan kestabilan lateks tulen. Walaubagaimanapun, kesan terhadap panjang rantaian asid lemak tepu dalam kestabilan lateks tulen masih menjadi isu. Tujuan kajian ini adalah untuk menyiasat kesan panjang rantaian surfaktan anionik keatas lateks tulen. Asid lemak tepu iaitu dekanoat (9), laurat (11), natrium dodecil sulfat (SDS) (12) dan palmitat (15) telah digunakan. Nombor mewakili bilangan karbon pada rantaian alkil surfaktan. Hasil kajian menunjukkan pemanjangan rantai alkil memberi kesan terhadap kestabilan lateks tulen mengikut susunan laurat > dekanoat > SDS > palmitat > lateks tulen. Panjang rantai alkil dalam sistem lateks memberi kesan keatas kestabilan lateks selepas masa pengacauan yang lama. Saiz zarah juga menunjukkan peningkatan dengan kehadiran surfaktan di dalam sistem. Oleh itu, interaksi yang sesuai oleh ekor surfaktan tidak berkutub dengan permukaan hidrofobik lateks boleh berlaku dan seterusnya memelihara kestabilan sistem lateks.

Kata kunci: surfaktan anionik, pentitratan, kestabilan

Introduction

There is an increasing attention on dispersion latex stability because of its role in nature and has important consequences for different field including industry, biology and medicine [1]. Purified latex was prepared via incubation of commercial high ammoniated natural rubber. Rubber latex is a polydisperse emulsion of rubber in aqueous phase. In order to preserve and maintain stability of the latex for a considerable time before processing, ammonia which acts as a bactericide and causes hydrolysis of phospholipids and proteins is added [2]. The ability of rubber to maintain as latex depends on the colloidal stability due to non rubber materials layering on the rubber to form stable particles in aqueous phase [3]. Many industrial process arises difficulties because unable to retain their colloidal dispersion stability [4]. This difficulty can be overcome by means of suitable stabilizer such as surfactant, polymers, nanoparticle or combination of them to alter their stability so that they perform in the process properly [5,6].

Surfactants are normally added to the natural rubber latex system in order to maintain colloidal stability. In the past, carboxylate soap is said to be effective surfactant for natural rubber latex [7]. The magnitude of the effect depends upon the nature of the hydrophobic chain of the soap. The mechanical stability of natural rubber soap could enhance by the dissociation of the adsorbed soap anion that encourage from higher carbon-carbon double bonds, double bonds containing hydroxyl groups of the chain [8].

In this study different anionic chain length surfactant were used. Blackley et al. had reported that optimum enhancement of mechanical stability is achieved when the alkyl chain of the soap contains approximately eleven carbon atoms [9]. A substantial enhancement of mechanical stability of natural rubber latex is due to strong adsorption of the soap anions in aqueous phase at the interface of rubber particle. With increasing alkyl chain length, the fatty acid soap anions tend to be adsorbed at the rubber-water interface. Longer alkyl chains may tend to cohere in cluster and reduce the efficiency in conferring mechanical stability on rubber particles. Therefore, in this present investigation, the following anionic surfactants were used where number in parenthess indicating different alkyl chain length: palmitate(15), sodium dodecyl sulphate(SDS) (12), laurate(11) and decanoate(9) were added into purified latex individually to assess and compare their effect on stability.

Materials and Methods

Preparation of Purified Latex

Purified latex was prepared via urea incubation of commercial high ammoniated natural rubber latex in the presence of surfactants. The presence of non-rubber substance in natural rubber latex was then removed by double centrifugation. Purified latex is treated with four different soaps namely potassium palmitate, sodium decanoate, potassium laurate and SDS while purified latex used as control. An accurately weighted sample of latex containing 10 g and 5 g of soap was diluted to 125 ml with deionized water in 400 ml beaker. The samples were stirred for 10 minutes prior to titration with acid solution of H_2SO_4.

Conductivity Test

Both sets of electrodes of the pH meter and the Thomas-Serfass conductance assembly were placed in the diluted latex dispersion. The pH of the latex sample was adjusted to a pH of 11.5 with a dilute KOH solution. The conductivity values of samples at every 1.0 ml titration of 0.5 N H_2SO_4 and one minute intervals time were then recorded.

Particle Size and Zeta Potential Analysis

Particle size and zeta potential of all samples were measured by Brookhaven 90Plus Particle Sizer and BrookThaven BI-ZTU at room temperature 25C.

Results and Discussion

Conductivity at Different Stirring Time

The tittration curve of a purified latex with different soaps at different stirring time is shown in Fig 1-4. There are consists of three stages. The first stage represent the neutralization of surface bounce acid by H_2SO_4 where a conductivity slowly increased before the volume of H_2SO_4 reach 6 ml. The second stage involves a drastic increased in the range of 6 – 10 ml for certain mixture before plateau. The slope arises due to the immobility of the carboxyl group on the latex particle. Plateau stage is reach when the coagulation took place by excess of $H_2SO_{4.}$ However, plateau stage did not exist for certain mixture assuming they are easily saturated. At the first titration, for graph 1 and 2, the conductivity values of PL with laurate soap show higher conductivity value -184.6 mV followed by PL, decanoate, palmitate and SDS soap. It was believed that the surface bound acid by H_2SO_4 to the latex particle is rich in PL with laurate as compared to the others. Those have a lower value of conductivity were mainly due to the bounded carboxylic acid group at latex particle which therefore would be weaker in acid strength than their corresponding monomeric form [10]. The conductivity values begin to increase rapidly until the latex particle coagulated. From the graph, the rate of coagulation can be determined based on the volume of acid is titrated. Based on graph 1 and 2, palmitate soap shows the best effect as to maintain PL stability. This happen when the coagulation rate is slower than the other soaps since more volume of acid needed to trigger the coagulation. The titration was stopped once the coagulation occur. Graph 3 and 4 show different trend of optimum conductivity value as PL showed the highest point followed by the others soap. The decanoate soap contribute maximum stability to PL in graph 3 and 4. To conclude, at 5 and 30 minutes of stirring time, it was found that palmitate has large effect upon stability of PL. However, after 1 and 2 hour of stirring time, decanoate soap is contribute maximum stability to PL. This could possibly due to the longer chain length of palmitate which entangle and induce bridging flocculation after 1 and 2 hour stirring time while decanoate perform its effectiveness in stability after 1 and 2 hour stirring time since it could nicely rearrange itself with 9 alkyl chain [2, 11].

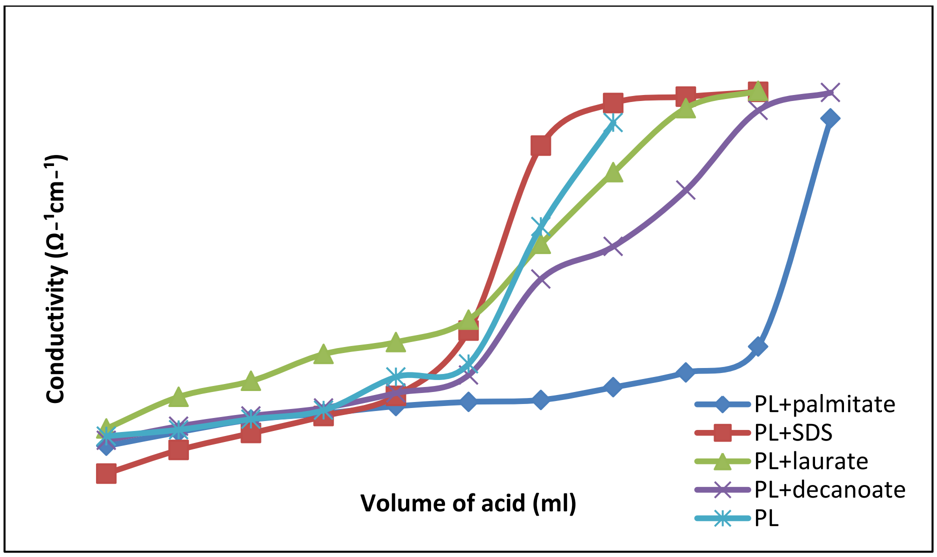

Figure 1. Conductivity studies of latex samples as a function of H_2SO_4 volume at 5 minutes stirring time

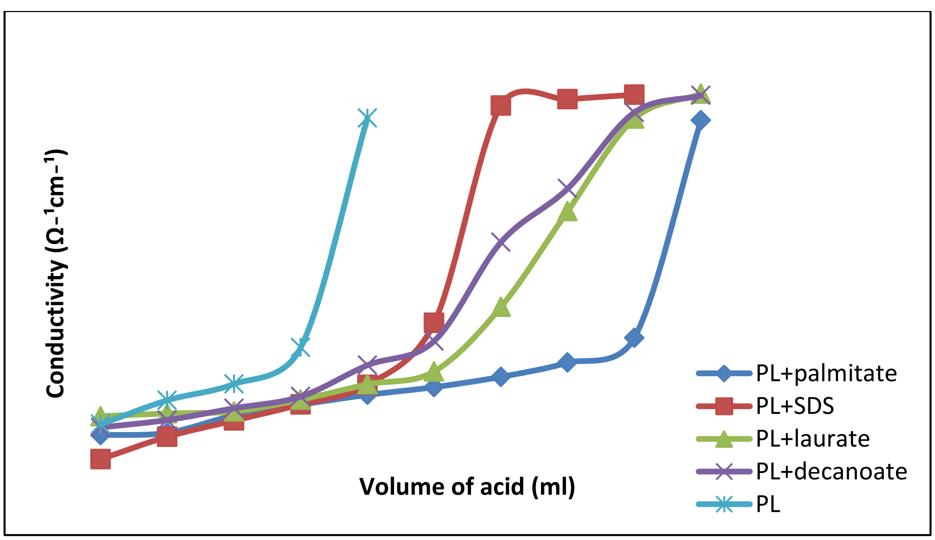

Figure 2. Conductivity studies of latex samples as a function of H_2SO_4 volume at 30 minutes stirring time

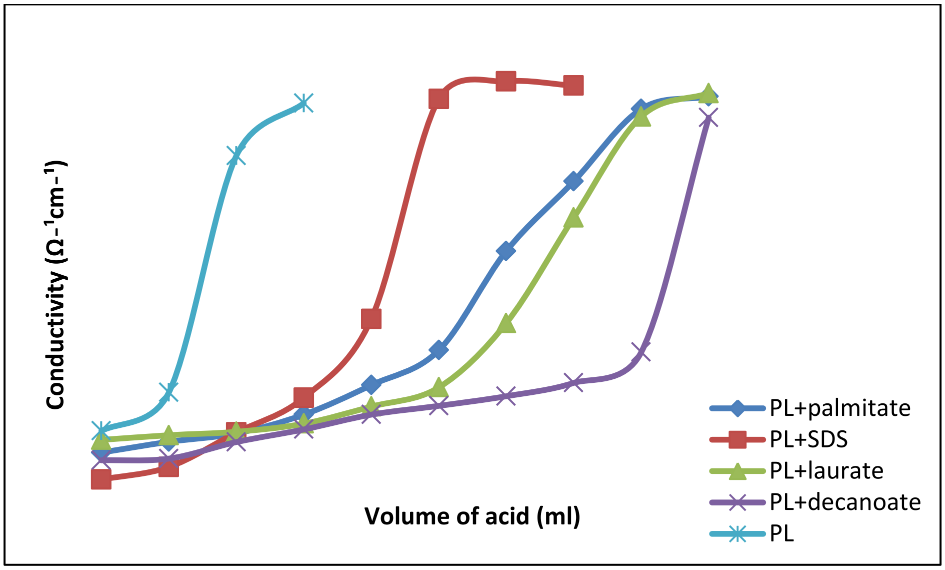

Figure 3. Conductivity studies of latex samples as a function of H_2SO_4 volume at 1 hour stirring time

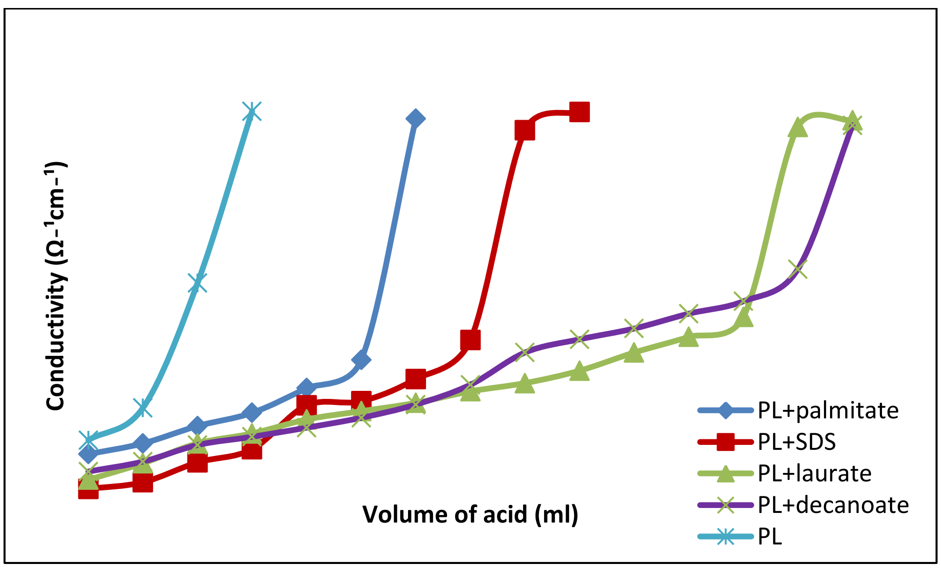

Figure 4. Conductivity studies of latex samples as a function of H_2SO_4 volume at 2 hour stirring time

In order to confirm the conductivity test, the amount of acid present in the latex system was further calculated (Table 1). The amount of acid present in PL is decreasing as the stirring time increase. This happen when less amount of acid is needed since the coagulation occurred at the early stage. At the first 30 minutes of PL with decanoate, the amount of acid present is same in the system. However, it is increased after 30 minutes of stirring time indicates that the latex particle is not easy to destabilize thus need more amount of acid. The similar situation happens for PL with laurate soap. For SDS, the amount of acid present drop after 30 minutes and began to increase after one hour stirring time. This results support the conductivity results whereby PL with decanoate and laurate soap show more stable system compare to others.

Table 1. Amount of acid present in latex system with different stirring time

Stirring time	PL	PL + Decanoate(9)	PL + Laurate(11)	PL + SDS(12)	PL + Palmitate(15)
5minute	0.80	0.80	0.80	0.80	0.80
30minutes	0.53	0.80	0.93	0.80	1.20
1 hour	0.27	1.20	0.93	0.67	0.80
2 hour	0.27	1.73	1.73	1.06	0.80

PL: Pure Latex

The amount of acid present is express as equation 1below;

$$x = \frac{V \times N}{W \times S} \qquad (1)$$

where V is volume of H2SO4 titrant, N is normality of the H2SO4, W is sample weight of the latex and S is the fraction of the polymer solid in the latex

Zeta Potential and Particle Size Analysis

Zeta potential gives an indication of the charge present on the particle surface. Positive value indicates that the particles are positively charged and negative value for negatively charged. In colloid stability, the magnitude and sign of zeta potential are used as a guideline to measure of how saturated the surface is with adsorbed species (surfactant, wetting agent etc). Basically zeta potential greater than 30MV or more negative than -30MV the repulsion is sufficient and the dispersion is said to be stable. From the table 2, PL with laurate gives more negative value as compared to other soap indicating a good stability condition.

Table 2. Average Zeta potential of latex system

Latex system	Average Zeta Potential (mV)
PL	- 35.18
PL + Palmitate(15)	- 28.67
PL + SDS(12)	- 34.43
PL + Laurate(11)	- 44.91
PL + Decanoate(9)	- 35.40

Figure 5 shows the graph of intensity as a function of diameter where the addition of surfactant was found to increase the particle size of the purified latex. The alkyl chain fatty acid soap that bound onto the latex particle surface could form an adsorbed layer that contributes to colloidal stability of the latex [11]. Amongst the surfactant used, PL with palmitate soap has found to give biggest particle size diameter of PL. These results suggest that the adsorption between the PL hydrophobic regions with nonpolar attraction of the soap was effectively performed in longer alkyl chain. However, the particle size is getting smaller from laurate, SDS, decanoate and PL itself. Purified latex without surfactant shows smallest in particle size since no absorbed chain on latex particle that results in an immediate coagulation of the latex. Therefore, the system is easily destabilized. It is found that the length of alkyl chain play a role to increase the particle size as a result of bounded and absorbed soap onto the latex particle. This further supported the idea that the main adsorption mechanism was the attraction tail-hydrophobic surface region which was similar for all soaps [12].

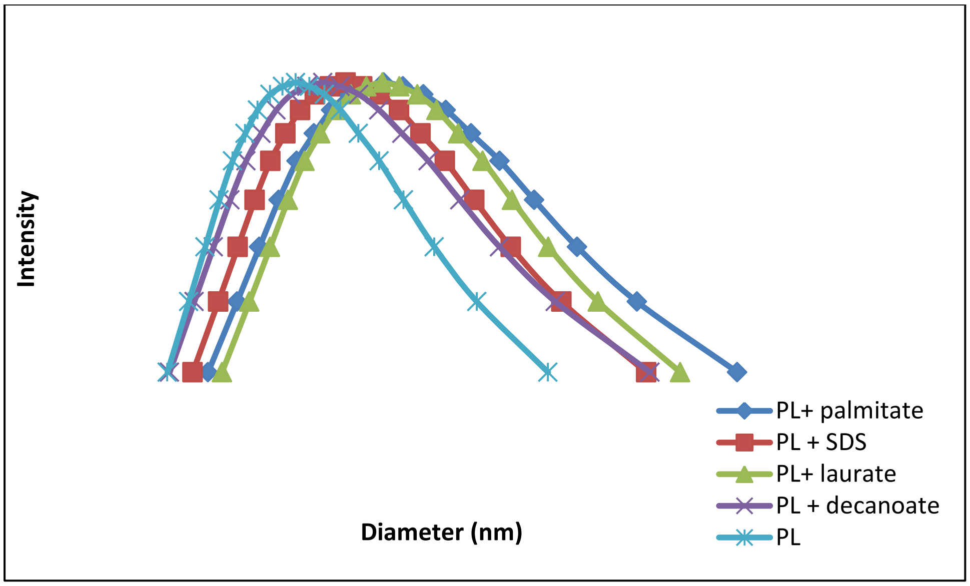

Figure 5. Particle size of purified latex with and without surfactants

Conclusion

The work reported in this paper has confirmed that addition of different alkyl chain of anionic surfactant in purified latex system can contribute to different stability effects. Based on the results achieved, it suggesting that among all the soap used, decanoate and laurate has the optimum performance to maintain a good colloidal stability of purified latex. This is due to the alkyl chain length (range 9 to 11) who was effectively adsorb onto the PL particle surface to maintain the stability of the latex system.

References

1. Dobias, B., Qiu, X., von Rybinski, W.(1999). Solid-Liquid Dispersion, in: Science Series, Vol. 81, Dekker, New York.
2. Lim, H.M. and Misran M. (1979).Effect of Sodium Dodecyl Sulphate, Brij 35 on Natural Rubber Latex Properties. *J. Rubber Res*, 16(3): 162-168.
3. Ho, C.C and Ng, L.W. (1979). Surface Study on The Rubber Particle in Pretreated Hevea Latex System. *Journal of Colloid and Polymer Sci*. 257:406-412.
4. Southorn, W.A. and Esah Yip. (1968). Latex Flow Studies III. Electrostatic Considerations in the Colloidal Stability of Fresh Hevea Latex. *Journal of the Rubber Research Institute of Malaya*. 20(4): 201-215.
5. Nambam, J.S. and John Philip. (2012). Competitive adsorption of polymer and surfactant at a liquid droplet interface and its effect on flocculation of emulsion. *Journal of Colloid and Interface Science*. 366: 88-95.
6. Catherine, P.W., Daniel, F. & John Ralston.(2009). Effect of adding anionic surfactant on the stability of Pickering emulsion. *Journal of Colloid and Interface Science*. 329: 173-181.
7. Blackley, D.C and M. Azas. (1980). Effect of potassium C_{18} carboxylate soaps upon mechanical stability and heat sensitivity of natural rubber latex. *Journal of plastic and rubber: Materials and applications*. 57-64.
8. Manroshan, S. & Lim, H. M. (2013). Surfactants and their Use in Latex Technology. *Malaysia Rubber Technology Development*. 13(2): 33-36.

9. Blackley, D.C., Nor Asiah, A.A. & Twaits, R. (1979). Effects of Potassium Fatty Acid Soaps upon Mechanical and Chemical Stability of Natural Rubber Latex. Plastics and Rubber: *Materials and Applications*: 77-86.
10. John Hen. (1974). Determination of Surface Carboxyl Groups in Styrene/Itaconic Acid Copolymer Latexes. *Journal of Colloid and Interface Science*. 49(3): 425-432.
11. Ho, C.C. (1989). Changes in electrokinetic properties of natural rubber latex after surface chemical modifications. *Journal of Colloid Polymer Science.*267:643-647.
12. Jodar-Reyes, A.B., Ortega-Vinuesa, J.L. and Martin-Rodrigues, A. (2004). Adsorption of different amphiphilic molecules onto polystyrene lattices. *Journal of Colloid and Interface Science*. 282: 439-447.