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Measurement of Dry Rubber Content of Fresh Natural Rubber Latex by a Titration Method

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A quick method for measuring the dry rubber content (DRC) of fresh natural rubber (NR) latex is presented. Addition of potassium oleate soap was found to sensitise latex for quick coagulation. The volume of 0.05 N sulphuric acid required for coagulation of potassium oleate-treated fresh NR latex showed a linear relation with its DRC. From a calibration curve of volume of 0.05 N sulphuric acid required for coagulation and the corresponding DRC of latices of known DRC it is possible to determine the unknown DRC by noting the volume of the acid required for quick coagulation. The accuracy of the DRC values obtained was found to be much better than that obtained by the hydrometric method. The presence of metal ions and volatile fatty acids at normal concentrations in field latex was not found to affect the DRC values determined by using the new method.

Key words: dry rubber content; determination; natural rubber latex; estimation; metrolac; titration; field latex; potassium oleate soap

Natural rubber latex that has a dry rubber content (DRC) varying from roughly 20%–40% is a colloidal dispersion of rubber particles, in an aqueous serum. In addition it contains about 2%–4% non-rubber substances. The DRC of latex is an important quality parameter as it is required to be determined accurately and rapidly for chemical additions during processing, quick payment to latex producers and quick evaluation of yield for academic purposes. The most accurate method for determination of DRC is by standard laboratory method that has been subjected to several modifications to reduce the time of estimation, the most prominent of which is the Chee method[1,2]. Here a known volume of latex is withdrawn by a calibrated dipper, coagulated with a mixture of ten parts 10% formic acid and ninety parts methylated spirit (v/v) to accelerate the rate of drying and the coagulum is then weighed. Methods based on specific gravity[3–5], specific heat[6], microwave attenuation[7] and proton low resolution NMR[8] have been reported for quick estimations of DRC. But these methods are either inaccurate, costly, time consuming or difficult. The hydrometric method that has gained wide acceptability due to its simplicity and low investment has limited accuracy (variation up to 8%) especially in the presence of adulterants and there is wide variation in readings among metrolacs. The specific heat method that involves measure-

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ment of the specific heat of a mixture of latex and cold or hot water requires the use of a vacuum flask, very accurate measurement of temperature, arrangement for refrigeration *etc.* The principle of the microwave method is that the permittivity of microwaves in water is much higher than in latex and so, as DRC decreases the transmission co-efficient of microwaves increases. This technique requires a microwave oscillator, sensor, microwave detector, amplifier and power supply. The low-resolution pulsed NMR technique is based on the principle that pulsed NMR can distinguish between proton signals from the solid and liquid phases of the sample. This method requires the use of a NMR spectrometer. So it will be highly useful if a method for DRC estimation can be developed which is easier, more accurate and cheaper. In this work an attempt is made to standardise a rapid method for determination of DRC of fresh field latex by a fatty acid soap sensitised titration method.

The Basic Principles Involved

In NR latex the rubber particles have on their surface an adsorbed layer of proteins and other ions that are negatively charged. The quantity of adsorbed anions in turn depends on the size and number of particles present in unit volume of latex and hence on the DRC of the latex. Since coagulation is a process in which adsorbed anions formed from different sources in latex are neutralised by a coagulant, there can be a relation between adsorbed anions and amount of coagulant utilised for coagulation. If latex can be coagulated immediately, then a correlation can be made of the dry rubber content and the amount of coagulant required for coagulation. Normally fresh latex coagulation is a slow process and hence it has to be sensitised for quick coagulation. It has been reported that latex containing fatty acid soaps and other surfactants gets coagulated immediately by addition of acids[9–10].

When fatty acid soaps are added to latex, the fatty acid anions cause displacement of protein molecules and get strongly adsorbed on rubber particles. In this way the protein-stabilised latex gets transformed into a soap-stabilised system[11]. When acid is added to soap treated latex the adsorbed soap anions react with acid to form undissociated fatty acid, thus depriving the latex particles of stabilisers. As a consequence, latex coagulates immediately[12]. Assuming uniform size and spherical shape for rubber particles in latex, the number of particles present in unit volume of latex (N) and volume fraction of the dispersed polymer (φ) are related by the equation[13]:

$$N = 6\varphi/\pi x^3 \qquad \ldots 1$$

where x is the diameter of the particles. φ is related to DRC and N is proportional to the quantity of soap adsorbed. The above two assumptions are not fully true for NR latex particles. Even though there is variation in particle size, it is reported[14] that latices of different clones and different age group have maximum number of particles in the range 1 µm size. Similarly the shape of rubber particles may vary but the majority is of spherical shape. Considering these factors, *Equation 1* can become valid for fresh NR latex. As DRC of latex increases, the total adsorbed soap increases and the acid required to coagulate latex also increases. Thus, from the volume of acid required for coagulation of latex it is possible to calculate the DRC of latex. For this, a calibration curve is to be drawn with the volume of acid on X-axis and the actual DRC values on Y-axis, using latices of known DRCs. The DRC of the unknown latex can be directly read from the calibration curve knowing the volume of acid required for coagulating it.

Alternatively, an equation may be derived from the slope and Y intercept of the standard graph. The DRC may be calculated by substituting the volume of acid required for coagulation, in the equation derived above. An equation may also be derived by regression analysis. The volume of acid for coagulation may be substituted in this equation to get the DRC.

It is known that volatile fatty acids (VFA) formed in the latex, concentration of added stabiliser and metal ions such as Ca^{++} and Mg^{++} also affect the quantity of acid required for coagulation. Hence in the present method the effects of these parameters were also studied, at concentration levels normally present in field latex. However, the effect of adulterants deliberately added was not studied in this experiment.

MATERIALS AND METHOD

Fresh NR latex of different clones obtained from the Rubber Research Institute of India estate was used for the study. Sulphuric acid and oleic acid used were of laboratory reagent grade. 15% potassium oleate soap solution was prepared by the following procedure:

Ingredients:	Parts by weight	
Oleic acid:	100	A
Water:	500	
Potassium hydroxide:	25	B
Water:	100	

Mixture of oleic acid and water and solution of potassium hydroxide were prepared separately. *Mixture A* was warmed to 75°C and *Solution B* was added to it in small quantities with efficient stirring. When the addition of *B* was completed, the whole mixture was warmed to 75°C on a water bath and maintained at that temperature till a clear solution was obtained. It was then removed from water bath and allowed to cool to room temperature.

Method of Evaluation of DRC by Coagulation of Soap Treated Latex

For finding out the volume of 0.05 N sulphuric acid required for coagulation of soap sensitised field latex, the following procedure was adopted.

About 1 g of the fresh field latex was accurately weighed into a wet 250 mL beaker. To this, 0.133 mL of 15% potassium oleate soap solution was added, followed by 30 mL distilled water. If it was observed that the DRC of latex was above 40% then 50 mL distilled water was added instead of 30 mL, to the soap treated latex. In cases where the weight of latex was other than 1.0 ± 0.01 g, the quantities of 15% potassium oleate soap solution and water for dilution were proportionately modified. The dosage rate was 0.02 g potassium oleate (0.133 mL of 15% potassium oleate solution) and 30 mL/50 mL water for 1.0 g latex. To the diluted latex, two drops of phenolphthalein were added and the contents titrated till the pink colour just disappeared. The burette reading was noted. The titration was continued at a rate of 1 drop of 0.05 N H_2SO_4 per second till the end point, which was a curdy appearance followed by separation of latex into rubber and serum. The volume of titre value required for coagulation of latex was noted. The experiment was repeated using fresh field latex samples of different DRC values.

The actual DRC values of the latex samples were determined as per *ISO 126 – 1982 (E)* test method. A graph was plotted with the volume of 0.05 N H_2SO_4 required for coagulation on the X-axis and the actual DRC values of the latex samples on the Y-axis, which yielded a straight line. From this graph the DRC value of the unknown latex sample was directly read out using the volume of 0.05 N H_2SO_4 required for coagulating it.

Method for Determination of Metal Ions in Latex

The concentrations of calcium and magnesium in the sample solution were determined using an atomic absorption spectrophotometer. A stock solution required for this was prepared first. Five gram of total solids (TS) of latex was mixed with 1 mL of concentrated HNO_3 and ashed at 550°C. The ashed sample was digested with 2 mL of 1:1 HNO_3 [one part of concentrated HNO_3 mixed with one part of distilled water (v/v)] on a water bath and made up to 100 mL. The solution was filtered when necessary.

For estimating the Mg^{++}, 1 mL stock solution was pipetted out into a 100 mL standard flask. 5 mL of strontium chloride solution was added to it and made up the volume to 100 mL. $SrCl_2$ solution was prepared by dissolving 91.16 g $SrCl_2 . 6H_2O$ in water and diluted it to 2 L. The absorbance of this solution was read out and the concentration in µg/mL was obtained from the standard curve of absorption *vs.* concentration plots. The percentage of magnesium on TS was calculated as: $\% \ Mg = R/W$; where R is the concentration of Mg^{++} in µg/mL of the diluted solution and W is the weight of TS content taken for ashing.

For estimating the Ca^{++} by atomic absorption spectrophotometry, 25 mL stock solution diluted to 50 mL after the addition of 2.5 mL $SrCl_2$ solution was used. The absorbance of this solution was read out and the concentration in µg/mL was obtained from the standard curve of absorption *vs.* concentration plots. The percentage of calcium on TS was calculated as: $\% \ Ca = R/10W$; where R is the concentration of Ca^{++} in µg/mL of the diluted solution and W is the weight of TS content taken for ashing.

RESULTS AND DISCUSSIONS

Effect of Concentration of Soap and VFA on Coagulation of Fresh NR Latex

Preliminary trials showed that addition of potassium oleate soap resulted in immediate coagulation of fresh field latex by a fixed volume of sulphuric acid. Without addition of potassium oleate soap there was no immediate coagulation of fresh field latex under the same condition. The effect of concentration of potassium oleate soap on coagulation of 1 g of fresh field latex was evaluated by taking field latex of three different dry rubber contents. The result obtained is shown in *Figure 1*. Soap at a concentration of 0.75% to 2.4% (w/w on latex) sensitised the latex for coagulation by sulphuric acid and above this optimum concentration, the volume of sulphuric acid required for coagulation increased with the amount of soap added to latex. From *Figure 1* it was obvious that the volume of acid required for immediate coagulation remained almost constant in the dosage range of 1.6% to 2.4% of soap. For the same DRC of latex, there was variation in the acid requirement outside this range. From the results of a large number of tests conducted by us, it was concluded that soap at a concentration of 2%, w/w on latex could be used to sensitise latex towards immediate coagulation, for the present purpose. Potassium oleate soap could exist in five different forms in latex[15,16]: (1) as individual molecules adsorbed at the particle surface; (2) as individual molecules adsorbed at the interphase between the aqueous phase

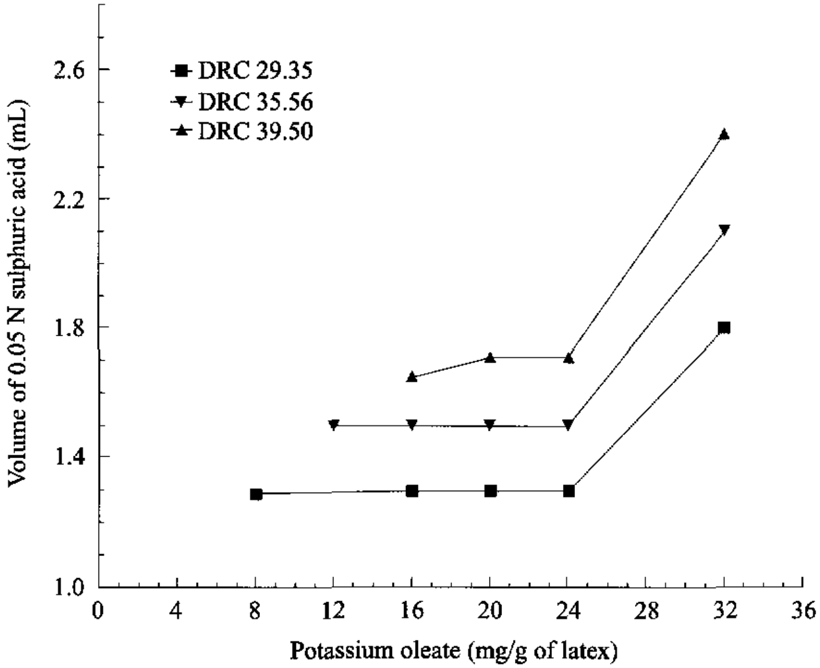

Figure 1. Effect of concentration of potassium oleate soap on coagulation of 1 g fresh field latex of varying DRC.

and the air above; (3) as individual molecules dissolved in aqueous phase; (4) as micellar aggregates which are just beginning to form and (5) as micellar aggregates above a critical micellar concentration.

The amounts present as forms (3) and (4) which are more reactive than that present in form (5), increase as the amount of soap added to latex increases. As a consequence, the volume of acid required for coagulation increased as the amount of soap increased. Fresh field latex of VFA ranging from 0.005 to 0.01 was found not to affect the volume of 0.05 N sulphuric acid required for coagulation of latex. Hence it was expected that VFA present in normal fresh field latex would not interfere with the results of the test.

Effect of DRC on Volume of 0.05 N H_2SO_4 Required for Coagulation of Fresh Field Latex

The volume of 0.05 N H_2SO_4 required for coagulation of definite quantities of fresh latices (1 gram) of varying DRC under standard conditions of concentration of potassium oleate soap (0.02 g/g of latex), level of dilution (1 g in 30 mL water) and pH (pH 8 obtained by neutralisation of alkali against phenolphthalein as indicator), is shown in *Figure 2*. Volume of acid required to coagulate latex and the DRC showed a linear relationship represented by the general equation:

$$\text{DRC}\ \% = mV + C \qquad \dots 2$$

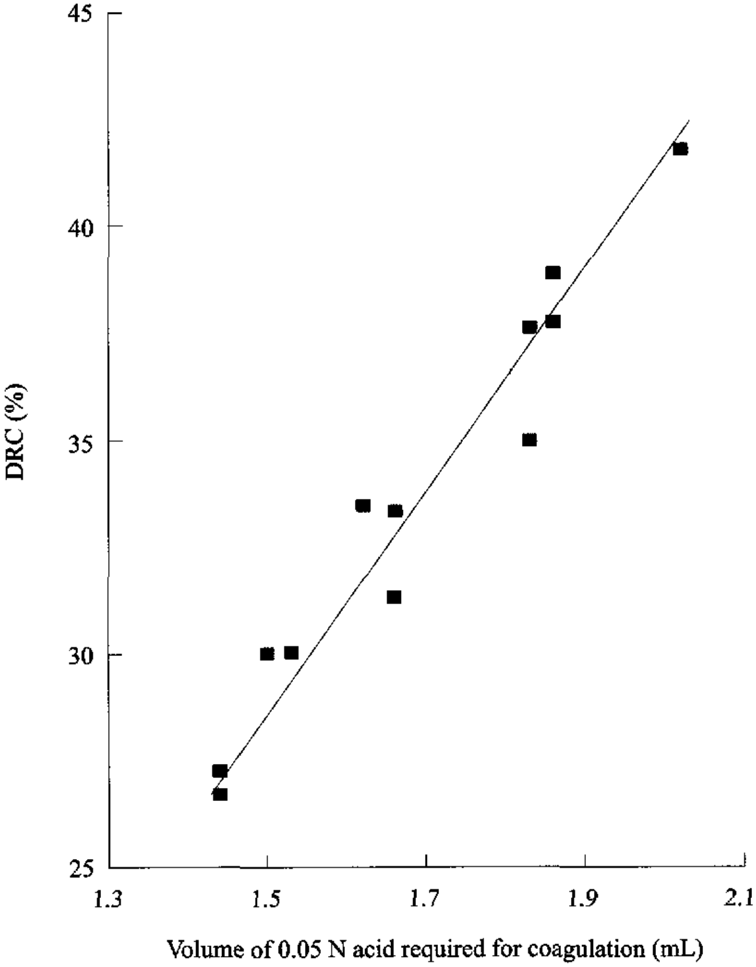

Figure 2. Volume of acid required for coagulation versus *DRC of fresh NR latex.*

where *m* is the parameter that characterises the change in volume of acid with the dry rubber present in latex. V is the volume of the 0.05 N sulphuric acid required for coagulation and C is a constant. The data given in *Figure 2* could be generalised by the equation:

$$\text{DRC \%} = 23.59\,V - 6.156 \quad \ldots 3$$

The value of correlation coefficient (r) obtained by regression analysis was 0.94, which showed that the variation of DRC with volume of acid was highly significant.

Linearity between volume of acid required for coagulation and the DRC was observed when the DRC of original undiluted latex was in the range of 20%–40%. For latex containing greater than 40% DRC, 1 gram of latex must be diluted to 50 mL to get a linear relationship between DRC and the acid required for coagulation. The data generated for lattices of DRC varying from 38%–44% is shown in *Table 1*. The equation generated by regression analysis is:

$$\text{DRC\%} = 10.34\,V + 19.98 \qquad \ldots 4$$

In this case, the correlation coefficient obtained was 0.92. The calculated and the actual values of DRC were very close. These data clearly showed that the volume of acid required for coagulation was related to percentage DRC of latex. This observation could be explained by considering the fact that as the amount of rubber in latex increased, a greater amount of soap was utilised in displacement of adsorbed proteins. Consequently, a greater amount of soap had to be removed in order to destabilise latex resulting in higher volume of acid needed for coagulation. It is expected that when latex is destabilised the main reaction involving the stabiliser takes place on the particle surface itself.

Deviation observed in the DRC value obtained by using the equations was in the range of 0–2.5 which is better than that normally observed for quick methods such as metrolac and microwave techniques for DRC determination. The metrolac method has an error[3] varying up to 8% or even more especially in the presence of adulterants[5]. Another advantage of the present method is that the quantity of latex required for the test is very low as compared to the metrolac method. A comparison of the DRC values obtained by the metrolac method (*Table 2*) indicated that the present method yielded DRC values much closer to the actual DRC, than that obtained using the metrolac.

Effect of Metal Ions on the Soap Sensitised Coagulation of Fresh Field Latex

It has been reported that soap stabilised latex is not stable in the presence of calcium and magnesium ions since the soap is likely to react with these ions to form the insoluble soap[11]. We have determined the concentration of Ca^{-+} and Mg^{++} ions present in latex collected from four different clones. The concentration of Ca^{-+} ions varied from 0.001% to 0.02% and that of Mg^{+-} ions from 0.048% to 0.18% on TS (*Table 3*). The DRC values of the latex from these clones as determined by the present method and the standard method are in good agreement. These data indicated that the presence of Ca^{++} and Mg^{++} ions in these concentration levels did not interfere with the sulphuric acid coagulation of NR latex.

It is expected that higher concentrations of Ca^{++} and Mg^{++} ions can interfere with the estimation of DRC proposed in this method, since these metal ions could consume a portion of the soap added for sensitising the latex towards coagulation. Similarly the observation that a higher concentration of soap increased the acid requirement for coagulation indicated that deliberate addition of excess soap in the latex could affect the estimated DRC values. Thus deviations in the estimated values of DRC can occur due to deliberately added materials of these types.

CONCLUSION

This study revealed that potassium oleate soap at a concentration of 1.6 to 2.4 parts in 100 parts of latex was useful to achieve quick coagulation of fresh latex when acid was added. The volume of acid required for quick coagulation increased with quantity of soap added and also with the DRC of latex. Under

TABLE 1. DRC CALCULATED BY TITRATION METHOD FOR FRESH NR LATEX OVER A PERIOD OF SIX MONTHS

Latex sample	Actual DRC (%)	Calculated DRC (%)	TS (%)	DRC Error
1	40.28	41.07	43.04	+0.79
2	40.47	41.38	43.44	+0.91
3	40.00	39.93	43.34	–0.07
4	40.02	40.65	42.79	+0.63
5	40.41	40.04	44.28	–0.37
6	43.90	43.86	47.00	–0.04
7	39.86	40.00	41.80	+0.14
8	42.90	41.04	45.05	–1.84
9	42.50	42.00	44.87	–0.50
10	42.10	44.10	46.39	+2.00
11	44.20	43.80	45.41	–0.40

TABLE 2. COMPARISON OF DRC OBTAINED BY METROLAC AND TITRATION METHOD

Latex sample	Metrolac (%)		Titration method (%)	Standard laboratory method (%)
	1	2		
1	45.0	39.0	37.40	38.39
2	36.0	30.0	30.15	30.18
3	33.0	39.0	35.74	36.69
4	30.0	27.0	29.65	29.49
5	27.0	27.0	24.98	22.84
6	45.0	34.5	38.19	37.84
7	42.0	36.0	34.42	34.11

TABLE 3. EFFECT OF METAL IONS ON COAGULATION OF FRESH FIELD LATEX

Clone	Actual DRC (%)	Calculated DRC (%)	Mg on latex (%)	Mg on TS (%)	Ca on TS (%)	Ca +Mg on TS (%)
RRII 105	41.45	42. 00	0.075	0.170	0.010	0.180
KRS 28	39.77	40. 30	0.058	0.140	0.006	0.146
PB 280	35.95	36. 31	0.080	0.210	0.038	0.248
PB 260	29.60	27. 15	0.030	0.095	0.018	0.113

standard conditions of pH, concentration of potassium oleate soap added to latex and a definite level of dilution, the volume of 0.05 N sulphuric acid required for coagulation of fresh field latex was found to be related to the DRC of latex and it followed the general equation: DRC % = $mV + C$; where, m is the parameter that characterizes the change in volume of acid with the dry rubber present in latex, V is the volume of standard acid required for coagulation and C is a constant.

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REFERENCES

1. RUBBER RESEARCH INSTITUTE OF MALAYSIA (1973) Methods for Measuring the Dry Rubber Content of Field Latex. *Plrs' Bull. Rubb. Res. Inst. Malaysia*, **124**, 4–13.
2. CHIN HONG CHEAW (1981) Metrication and Changes to the 'Chee' Method of Determining the Dry Rubber Content of Field Latex. *Plrs' Bull. Rubb. Res. Inst. Malaysia*, **169**, 136–149.
3. NADARAJAH, M. AND MUTHUKUDA, S. (1963) The Determination of the Dry Rubber Content of Natural Rubber Latex by the Use of the Metrolac. *Quart. J. Rubb. Res. Inst. Ceylon*, **39**, 85–93.
4. NAIR, K.K. AND SIVARAMAKRISHNAN, N.H. (1970) Correlation of Metrolac DRC with Actual DRC of Field Latex. *Rubber Board Bulletin*, **11(1)**, 17–23 .
5. RUBBER RESEARCH INSTITUTE OF MALAYSIA (1974) Effect of Some Adulterants on the Metrolac DRC of Field Latex. *Plrs' Bull. Rubb. Res. Inst. Malaysia*, **130**, 21–29.
6. HARRIS, E.M., NOR AISHAH, A. A. AND MORNI AMIRUDDIN (1985) Measurement of Dry Rubber Content of Natural Rubber Latex and Wet Crepe Using Specific Heat. *Proc. Int. Rubb. Conf. Kuala Lumpur*, 271–285.
7. KAIDA BIN KHALID, YAHYA MAT HASSAN AND ABD RAHMAN RAMLI (1989) Measurement of Dry Rubber Content and Total Solids Content of *Hevea* Latex by Microwave Techniques. *Proc. RRIM Growers' Conference, Malacca*, 493–504.
8. GAMBHIR, P.N., JOSHI, D.K., TIWARI, P. N. AND MANI, J. (1993) Quick Determination of Dry Rubber Content of Natural Rubber Latex by Low-Resolution Pulsed NMR Technique. *J. nat. Rubb. Res.* **8(3)**, 208–212.
9. JOHN, C.K. AND NEWSAM, A. (1969) Continuous Coagulation of *Hevea* Latex. *Plrs. Bull. Rubb. Res. Inst. Malaya*, **105**, 289–293.
10. JOHN, C.K. (1971) Coagulation of *Hevea* Latex with Surfactant and Salt: I. Development of the Process and its Effect on Raw Rubber Properties. *J. Rubb. Res. Inst. Malaya*, **23(2)**, 147–156.
11. VAN GILS, G.E. (1947) Spontaneous Coagulation of *Hevea* Latex. *Trans. Inst. Rubber Ind.*, **23**,74–76.
12. KHOO, T.C., ONG, C.O. AND ABDUL RAHMAN RAIS (1991) A New Process for Skim Rubber Production. *Proc. RRIM Rubb. Growers' Conf. Malaysia*, 495–510.
13. BLACKLEY D.C. (1997) *Polymer Latices: Science and Technology Vol. 1, Fundamental Principles*, Some Fundamental Characteristics of Latices, Chap. 2, pp. 35–38, London: Chapman and Hall Publishers.
14. SAOVANEE KOVUTTIKULRANGSIE AND YASUYUKI TANAKA (1999) NR Latex Particle Size and its Molecular Weight from

Young and Mature *Hevea* Trees. *J. Rubb. Res.*, **2(3)**, 150–159.

15. COCKBAIN, E.G. (1952) Determination of Particle Size of Natural Latex. *Trans. Inst. Rubber Ind.*, **28**, 297–302.

16. BLACKLEY, D.C. (1997) *Polymer Latices: Science and Technology Vol. 1,* Fundamental Principles, Investigation of Some Latex Properties, Chap. 8, pp. 492–495. London: Chapman and Hall Publishers.