เอกสารอ้างอิง

1) TANGBORIBOONRAT P., SUCHIVA K. and KUHAKARN S., "Phase Transfer Technique for the Characterisation of Non-Crosslinked Natural Rubber Latex", ***Polymer***, 1994, **35**, 5144

2) TANGBORIBOONRAT P., SUCHIVA K. and RIESS G., "Surface Characterisation of γ-Radiation Crosslinked Natural Rubber Latex by Phase Transfer Technique with Cationic Surfactants", ***Polymer***, 1995, **36**, 781

3) TANGBORIBOONRAT P., SUCHIVA K., KUHAKARN S. and TUCHINDA P., "Phase Transfer Technique for the Study of Deproteinised Natural Rubber Latex", ***J. nat. Rubb. Res.***, 1996, **1**, 26

4) HEPBURN C. and ARIZAL R., "A Controlled Release Urea Fertilizer. Part I : The encapsulation of urea fertilizer by rubber : processing and vulcanisation procedures", ***Plast. & Rubber Process. Appl.***, 1989, **12**, 129

5) HEPBURN C. and ARIZAL R., "A Controlled Release Urea Fertilizer. Part II : Preparation of the rubber-urea matrix and the split-feeding mixing technique", ***Plast. & Rubber Process. Appl.***, 1989, **12**, 135

6) HEPBURN C., YOUNG S. and ARIZAL R., "A Controlled Release Urea Fertilizer. Part III : Soil leaching and growth trials", ***Plast. & Rubber Process. Appl.***, 1989, **12**, 141

7) ABO-ELELA SI., HELALY FM. and ABDEL-BARY EM., "Solid and Cellular Styrene-Butadiene Urea Filled Matrices in Agriculture as a Means of Minimising Water Pollution", ***Plast. & Rubber Process. Appl.***, 1990, **14**, 43

8) ABDEL-BARY EM., EL-SHEKEIL AG., HELALY FM., SARHAN AA. and ABDEL-RAZIK HH., "Sustained Release Natural Rubber Formulations for Urea", ***Plast. Rubber Compos. Process. Appl.***, 1992, **17**, 99

9) POTTS TJ., "Colorimetric Determination of Urea in Feeds", ***J. Assoc. Off. Agric. Chem.***, 1963, **46**, 303

10) SIRICHAIWAT C., "A Study of Preparation of Controlled Release Urea Fertiliser by Using Natural Rubber Latex", ***M.Sc. Thesis***, Faculty of Graduate Studies, Mahidol University, 1996

11) GORTON ADT., "The Production and Properties of Prevulcanized Natural Rubber Latex", ***NR Technology***, 1979, **10**, 9

12) SAID MM., PENDLE TD. and BLACKLEY DC., "Peroxide Prevulcanisation of Natural Rubber Latex", ***J. nat. Rubb. Res.***, 1990, **5**, 27

13) TANUNCHAI T., "A Study of Preparation of Controlled Release Urea Fertiliser by Using Skim Latex", ***M.Sc. Thesis***, Faculty of Graduate Studies, Mahidol University, *In preparation*

14) TEERASUT P., "Development of the Encapsulation of Urea Fertiliser by Using Natural Rubber Latex", ***M.Sc. Thesis***, Faculty of Graduate Studies, Mahidol University, 1998

15) GAZELEY KF., GORTON ADT. and PENDLE TD., "Latex Concentrates: Properties and Composition" In ***Natural Rubber Science and Technology*** (ed. ROBERTS AD), Oxford Science Publications, Oxford, 1988, ch. 3

16) ประมวล ตั้งบริบูรณ์รัตน์, "Development of Property Studies of Natural Rubber Latex by Phase Transfer Technique", **รายงานการวิจัยพัฒนาและวิศวกรรม** ฉบับสมบูรณ์ เสนอ ศูนย์เทคโนโลยีโลหะและวัสดุแห่งชาติ, 2539

17) TANGBORIBOONRAT P. and SIRICHAIWAT C., "Urea Fertiliser Encapsulation Using Natural Rubber Latex", ***Plast. Rubber Compos. Process. Appl.***, 1996, **25**, 340

18) TIYAPIBOONCHAIYA C., "Development of Toughened Polystyrene from Natural Rubber Latex Using Phase Transfer Technique" ***M.Sc. Thesis,*** Faculty of Graduate Studies, Mahidol University, 1998

19) TANGBORIBOONRAT P. and TIYAPIBOONCHAIYA C., "Novel Method for Toughening of Polystyrene Based on Natural Rubber Latex", accepted for publication in ***J. Appl. Polym. Sci.***, 1998

20) SILER DJ., TANRIKULU MG., CORNISH K., STAFFORD AE. and MCKEON TA., "Composition of Rubber Particles of *Hevea brasiliensis, Parthenium argentatum, Ficus elastica* and *Euphorbia lactiflua* Indicates Unconventional Surface Structure", ***Plant Physiol. Biochem.***, 1997, 35, 881

21) VELIKY IA. and WILLIAMS RE., "The Production of Ethanol by Saccharomyces Cerevisae Immobilized in Polycation-Stabilized Calcium Alginate Gels", ***Biotechnol. Lett.*** , 1981, **3**, 275

22) SCHACHT E., VANDICHEL JC., LEMAHIEU A., DE ROOZE N. and VANSTEENKISTE S., "The Use of Gelatin and Alginate for the Immobilization of Bioactive Agents" in ***Encapsulation and Controlled Release*** (eds KARSA DR and STEPHENSON RA), Cambridge, Royal Society of Chemistry, 1993, pp 18-34

23) HUGUET ML., GROBOILLOT A., NEUFELD RJ., PONCELET D. and DELLACHERIE E., "Hemoglobin Encapsulation in Chitosan/ Calcium alginate Beads", ***J. Appl. Polym. Sci.***, 1994, **51**, 1427

24) LEE KY., PARK WH. and HA WS., "Polyelectrolyte Complexes of Sodium alginate with Chitosan or Its Derivatives for Microcapsules", ***J. Appl. Polym. Sci.***, 1997, **63**, 25

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เฉพาะที่ได้จากโครงการนี้

1) **TANGBORIBOONRAT P.** and SIRICHAIWAT C.
"Urea Fertiliser Encapsulation Using Natural Rubber Latex",
Plast. Rubber Compos. Process. Appl., 1996, **25**, 340

2) **TANGBORIBOONRAT P.**, CHINDAPRASERT S. and TIYAPIBOONCHAIYA C.
"Phase Transfer Technique for Surface Characterisation of Fresh Field Natural Rubber Latex"
submitted for publication in ***Eur. Polym. J.***, June 10, 1998

3) **P. TANGBORIBOONRAT P.**, TEERASUT P. and TANUNCHAI T.
(*in preparation*)

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1) **TANGBORIBOONRAT P.** and TIYAPIBOONCHAIYA C.
"Novel Method for Toughening of Polystyrene Based on Natural Rubber Latex"
accepted for publication in ***J. Appl. Polym. Sci.***, July 18, 1998

2) **TANGBORIBOONRAT P.**, TIYAPIBOONCHAIYA C. and LERTHITITRAKUL C.
"New Evidence of the Surface Morphology of Deproteinized Natural Rubber Particles"
accepted for publication in ***Polym. Bull.***, August 24, 1998

– *Oral Presentations*

1) **ประมวล ตั้งบริบูรณ์รัตน์ ***
"วิจัยและพัฒนาน้ำยางธรรมชาติในรูปแบบใหม่" เสนอในการประชุมวิชาการวิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทยครั้งที่ 22 กรุงเทพมหานคร 2539

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จากมูลนิธิส่งเสริมวิทยาศาสตร์และเทคโนโลยีในพระบรมราชูปถัมภ์)

2) **TANGBORIBOONRAT P.** and SIRICHAIWAT C.
"Encapsulation of Urea Fertiliser Using Natural Rubber Latex"
International Conference on Materials Technology : Recent Developments and Future Potential, Chiang Mai THAILAND 1997

3) **TANGBORIBOONRAT P.,**** SIRICHAIWAT C., TEERASUT P. and TANUNCHAI T.
"Urea Fertiliser Encapsulation Using Natural Rubber Latex"
International Rubber Conference, Paris FRANCE 1998

(** ได้รับ **ทุนเผยแพร่ผลงานในต่างประเทศสำหรับนักวิจัยผู้มีผลงานดีเยี่ยม**
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- กิจกรรมอื่น ๆที่เกี่ยวข้อง

วิทยานิพนธ์นักศึกษาปริญญาโท

1) SIRICHAIWAT C., "A Study of Preparation of Controlled Release Urea Fertiliser by Using Natural Rubber Latex", ***M.Sc. Thesis***, Faculty of Graduate Studies, Mahidol University, 1996

2) CHINDAPRASERT S., "Further Study to Apply Phase Transfer Technique for Surface Characterisation of Non-crosslinked Natural Rubber Latex", ***M.Sc. Thesis***, Faculty of Graduate Studies, Mahidol University, 1997

3) TEERASUT P., "Development of the Encapsulation of Urea Fertiliser by Using Natural Rubber Latex", ***M.Sc. Thesis***, Faculty of Graduate Studies, Mahidol University, 1998

4) TANUNCHAI T., "A Study of Preparation of Controlled Release Urea Fertiliser by Using Skim Latex", ***M.Sc. Thesis***, Faculty of Graduate Studies, Mahidol University, *In preparation*

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Urea fertiliser encapsulation using natural rubber latex

P. Tangboriboonrat and C. Sirichaiwat

Urea fertiliser encapsulated using natural rubber latex for the controlled release of urea has been prepared. Factors affecting the release rate of urea, for example, the type of rubber matrix, the concentration of sodium alginate used as the capsule coating agent, and the initial concentration of urea, were investigated. The lowest rate of urea released from the capsules was achieved using coated urea–unvulcanised rubber, from which the release was prolonged for ~50 days. The maximum urea concentration incorporated in the coated capsules was ~80% and the morphology of the prepared capsules was studied microscopically. PRCPA/1268

 The authors are in the Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Phyathai, Bangkok 10400, Thailand. Manuscript received 17 April 1996; in final form 4 June 1996.

INTRODUCTION

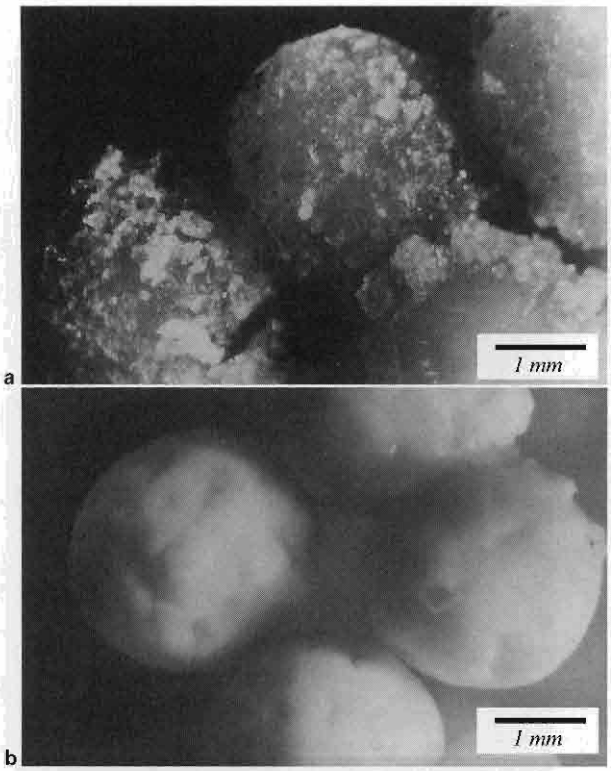
Agriculture is an important area of study for health, environmental pollution control, nutrition, and developmental issues. It is thought that current agricultural systems may be unable to support the exploding world population in the future. The popular method of increasing crop yield is to use fertilisers, particularly nitrogen.[1] Urea is usually used owing to its high nitrogen content and low cost. However, because it is highly soluble in water, less than half of the fertiliser applied is recovered in crops and the remainder is lost as atmospheric and water pollutants.[1–7] There has therefore been considerable interest in improving the efficiency of fertilisers using controlled release techniques.

It has been found that incorporation of urea in a rubber matrix may prevent both the high leaching losses and seedling damage associated with high concentrations of free urea.[2–7] Natural rubber (NR) has been found to be a suitable material for use as an encapsulant of the fertiliser because of its availability, biodegradability, and low processing cost.[2–6] In addition, many microorganisms are reported to attack untreated NR in both unvulcanised and vulcanised forms.[4] Using conventional rubber mixing equipment, NR has been used as a controlled release device to produce a slow release urea via a matrix system, which is relatively simple to prepare and free from any catastrophic failure when subjected to rough handing. However using a conventional method of mixing, the rubber did not contact well with urea particles, but a specifically devised split feeding technique, in which additional masticated NR was added to the previously mixed NR–curatives–urea masterbatch to provide an *in situ* enveloping uncured encapsulant in the vulcanisate, was found to give a superior product having considerably reduced urea extraction rates. The rubber–urea matrix under high watering regimes gave better yields and more efficient utilisation of nitrogen compared with control and commercial urea treatments. Many factors such as the method of preparation, crosslink density, moulding temperature, and pressure were found to influence the rate of urea released from the rubber matrix.[2–6]

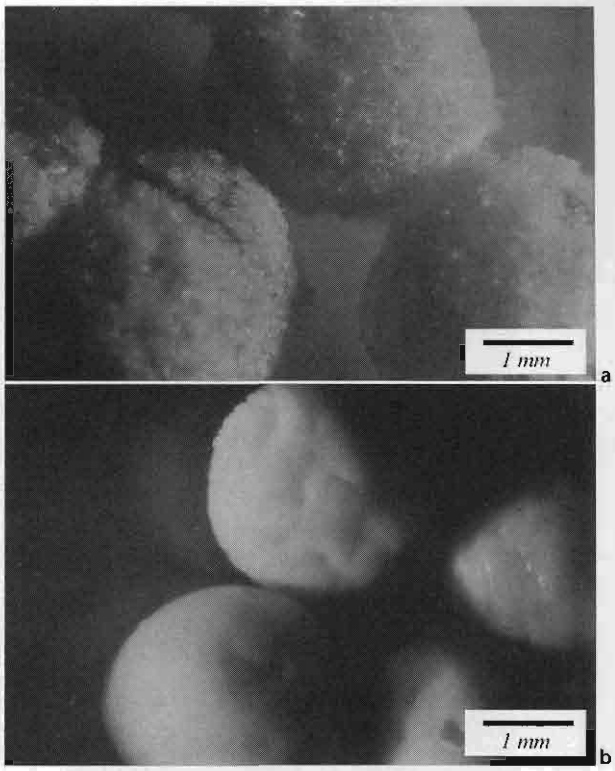
Since NR occurs in nature in a latex form, it is of interest to study the preparation of urea fertiliser directly encapsulated by a NR latex. If successful, the process would be very practical both in terms of improvement of crop yields and of utilisation of NR latex, of which Thailand is a major exporter. In the present work, the effects of crosslinked rubber (used as a matrix) and urea–NR capsules coated with sodium alginate have been investigated and the influence of the concentration of coating agent and urea on the amount of urea released from the prepared capsules has been measured. Micrographs of the capsules obtained are presented.

EXPERIMENTAL

The preparation of urea–NR capsules involved mixing 100 g urea powder (Merck, Darmstadt, Germany; pure) with 167 g commercial high ammonia preserved NR latex concentrate having ~ 60% dry rubber content (DRC) (Thai Rubber and Latex Co. Ltd, Thailand). The mixture was then dropped via a 2 mm diameter capillary tube into 100 mL 90% aqueous solution of acetic acid. The capsules obtained from the acid precipitation were rapidly immersed in distilled water for 30 s to leach out the acid before drying at 60°C. The capsules (1 g) were then immersed in 50 mL of distilled water at 25°C. Samples of water (5 mL) were taken at intervals to determine the urea concentration released by the *p*-dimethylaminobenzaldehyde (DMAB) method developed by Potts[8] using DMAB from Fluka, Switzerland (Puriss) as the indicator for spectrophotometric measurement, using a Jasco UVIDEC-650 spectrophotometer. The capsule sample was then resuspended in 50 mL water and the amount of urea released in the aqueous medium was determined. This procedure was repeated until the value of urea released into water was constant. Urea release was expressed as the amount of urea (mg) per weight of dry capsule sample (g) averaged over at least three determinations.



1 Optical micrographs of urea–unvulcanised natural rubber (NR) capsules (initial urea concentration 100 parts per hundred rubber, (pphr)) *a* before and *b* after release of urea



2 Optical micrographs of urea–sulphur prevulcanised NR capsules (initial urea concentration 100 pphr) *a* before and *b* after release of urea

Crosslinked NR latex was prepared by mixing 167 g NR latex with a 50% dispersion of vulcanising ingredients (commercial grade), i.e. sulphur, 2 parts per hundred of rubber (pphr), zinc diethyldithiocarbamate (4 pphr) and zinc oxide (0·4 pphr). Sulphur prevulcanised latex was prepared at 60°C for 6 h and was used to encapsulate urea by the process described above.

The wet capsules of urea–unvulcanised NR were dipped into an aqueous solution (1, 2, 3, or 4%) of sodium alginate (Fluka, AR grade) and then gelled by immersing in a 2% calcium chloride solution. The coated urea–NR capsules were dried at 60°C before determining urea release as previously described.

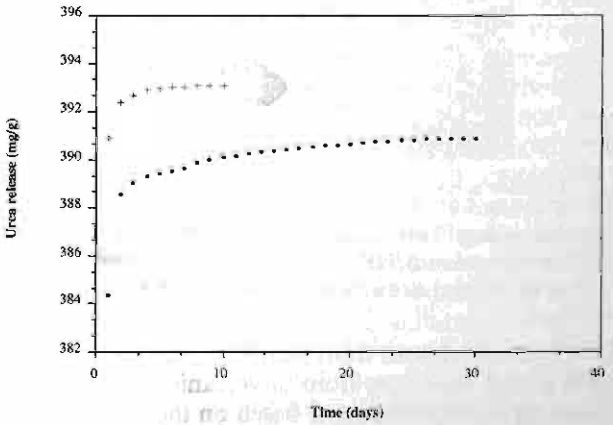
The morphology of samples was studied using optical microscopy (Olympus SZ-ST) and scanning electron microscopy (Hitachi S-5600).

RESULTS AND DISCUSSION

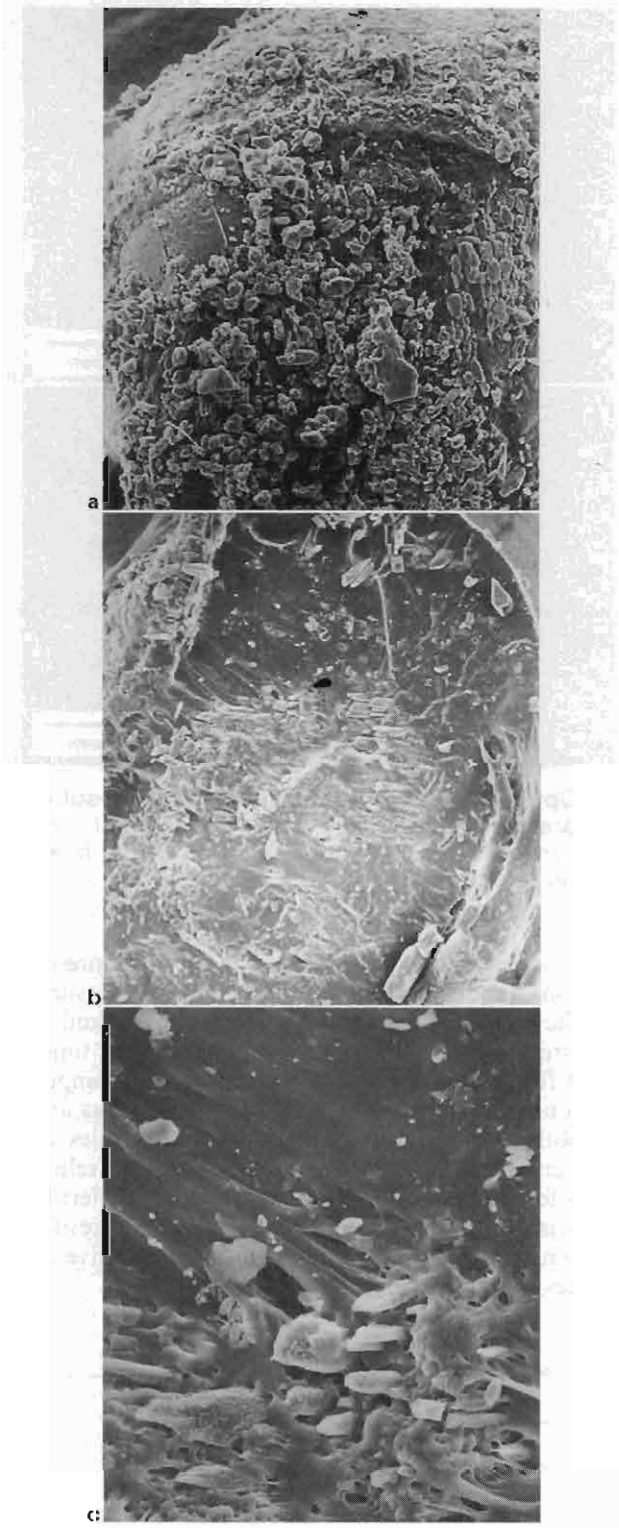
Since solid NR was capable of enveloping urea fertiliser and thus acting as a controlled release device for a slow release urea, it was of interest to extend the study by preparing urea encapsulated directly by using NR in latex form. To obtain a suitable preparation technique, the following important factors were investigated.

Effect of crosslinking

When urea powder was mixed with both unvulcanised and sulphur prevulcanised NR latex during capsule preparation, it was observed that the wet capsules obtained were white spherical particles having smooth and tacky surfaces. After drying at 60°C, the presence of considerable amounts of free urea on the surface of the dry capsules was evident (Figs. 1*a* and 2*a*). Figure 3 shows the cumulative release with time of urea from the capsules for vulcanised NR compared with unvulcanised rubber. The same trend was found in both types of capsule, i.e. when the capsules were immersed in water, almost all of the urea was released in a few days. It is suggested that the free fertiliser present on the surface of the capsules (as a result of blooming phenomena) quickly dissolved to give high values of initial leaching rate.

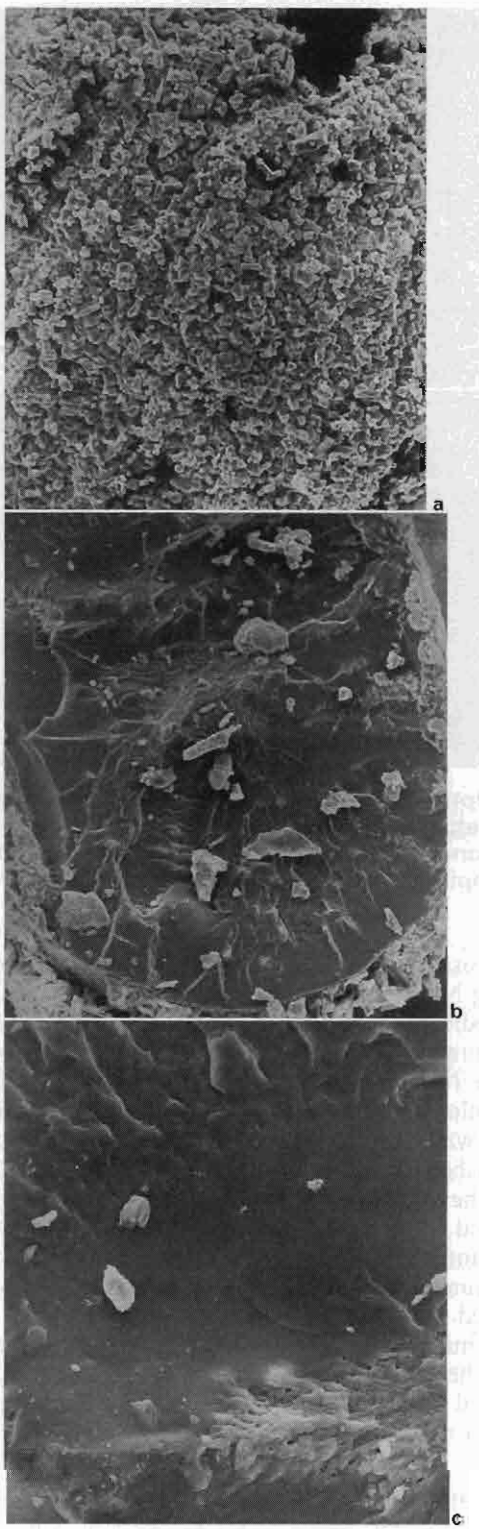


3 Cumulative release of urea from capsules prepared using (+) non-crosslinked and (●) crosslinked NR matrix *v.* time (initial urea concentration 100 pphr)



a capsule surface (×30); *b* capsule cross-section (×30); *c* capsule cross-section (×150)

4 Scanning electron micrographs of urea–unvulcanised NR capsules before release of urea (initial urea concentration 100 pphr)

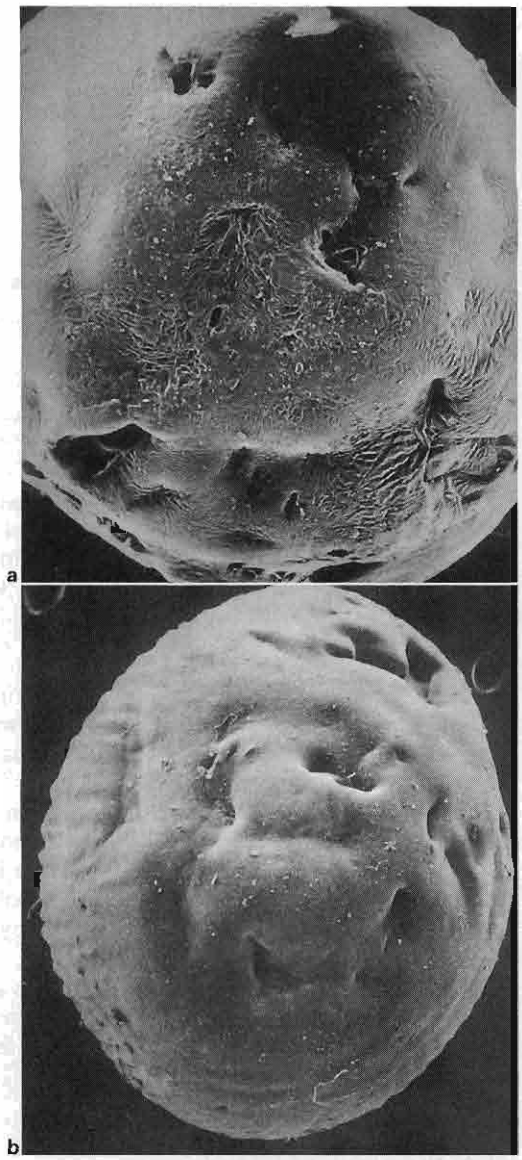


a capsule surface (×37·5); *b* capsule cross-section (×30); *c* capsule cross-section (×150)

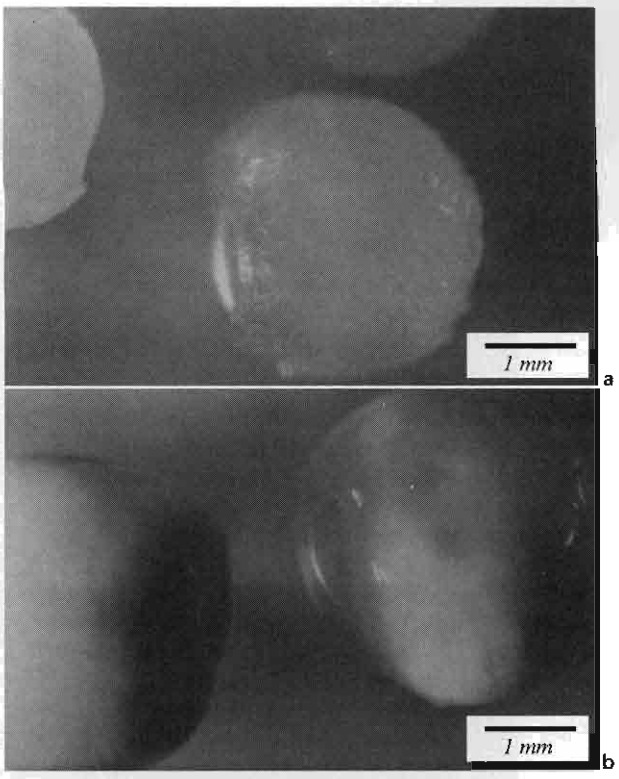
5 Scanning electron micrographs of urea–sulphur prevulcanised NR capsules before release of urea (initial urea concentration 100 pphr)

The urea released from the vulcanised NR capsules was higher than that from unvulcanised NR. As has been reported previously,[2] based on the experience of incorporating urea into solid NR on a two roll mill, 'pure' rubber absorbs urea faster than 'non-pure' rubber (i.e. rubber that had been previously mixed with vulcanising systems). This suggested that the pure rubber had a particular ability to wet the urea during milling and hence the urea particles may not mix well with vulcanised NR and be more easily ejected from the urea–vulcanised NR capsules.

Figures 4 and 5 show scanning electron micrographs of capsules prepared from unvulcanised and sulphur prevulcanised NR latex, respectively.



6 Scanning electron micrographs of urea–NR capsules after 30 days release of urea (initial urea concentration 100 pphr): *a* unvulcanised NR and *b* sulphur prevulcanised NR ×25·5



7 Optical micrographs of urea–unvulcanised NR capsules coated by dipping in 4% aqueous sodium alginate solution (initial urea concentration 100 pphr) *a* before and *b* after release of urea

A substantial amount of urea on the surface of the capsules before release can be seen in Figs. 4*a* and 5*a* and the distribution of urea particles in the rubber matrix can be seen from the cross-sectional surface of the capsules in Figs. 4*b* and *c*, and 5*b* and *c*. It was evident that the capsules obtained were monolithic systems from which the release pattern of urea depended on many factors, e.g. the geometry of the system, the matrix material, and the loading agent.[9] The urea particles appeared to be expelled from the NR matrix and the vulcanised rubber tended to form a smooth surface of the inner part of the capsule (*see* Fig. 5*c*). This matrix was free from porosity compared with the unvulcanised rubber (Fig. 4*c*), in which the urea particles were captured. It is probable that the crosslinking reduced chain mobility, increased the rigidity of rubber particles, and consequently the vulcanised rubber moved less freely to encapsulate urea. In addition, the phase separation between the matrix and the urea could occur when the rubber was crosslinked, which would promote high urea release within a short period. The micrographs agreed well with the curves of urea release shown in Fig. 3. When the morphology of the capsules after 30 days release was examined (Figs. 1*b*, 2*b*, and 6), those using unvulcanised and vulcanised NR showed a highly wrinkled and porous capsule surface (*see* Figs. 6*a* and *b*).

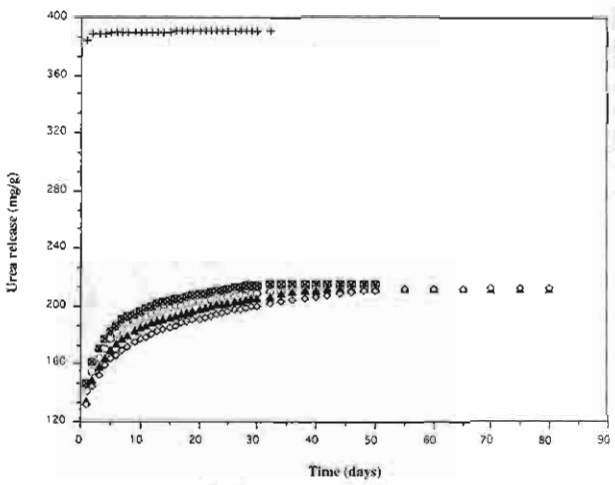
Effect of coating

Since the split feeding mixing procedure was better than conventional procedures in slowing the release rate of urea from the matrix, presumably because the raw rubber added at the last stage of mixing enveloped the urea particles as an internal sealant, the present work was extended by coating 100 g urea encapsulated with 167 pphr unvulcanised NR. It was thought that this would improve the barrier wall. Since the basic criteria for selection of the coating material are that it must be non-reactive, essentially immiscible with the material being encapsulated, and capable of being rapidly hardened to form a film,[10] sodium alginate was found to be suitable. After acid leaching the wet urea–rubber capsules were dipped into 1, 2, 3, and 4% aqueous solutions of sodium alginate to form a coating, which was hardened by aqueous calcium chloride as described above. After drying, the alginate coated urea–NR capsules obtained were generally spherical, having a smooth surface without the presence of urea as a result of blooming (*see* Figs. 7*a* and 8*a*). In addition, the surface became less tacky and the capsules did not adhere to one another. It

a capsule surface (×37·5); *b* capsule cross-section (×30); *c* capsule cross-section (×150)

8 Scanning electron micrographs of urea–unvulcanised NR capsules coated by dipping in 4% aqueous sodium alginate solution before release of urea (initial urea concentration 100 pphr)

was remarkable to note the increase of homogeneous distribution of urea in the rubber matrix (Fig. 8*b* and *c*) compared with the uncoated capsules (Fig. 4*b* and *c*).



(+) 0%, (⊠) 1%, (○) 2%, (▲) 3%, and (◇) 4% sodium alginate

9 Effect of sodium alginate concentration on cumulative release of urea from non-crosslinked NR matrix capsules *v.* time (initial urea concentration 100 pphr)

The effect of the sodium alginate concentration on the urea release at various time intervals is shown in Fig. 9. It is apparent that the presence of the coating agent reduced the amount of urea release from ~90% to ~30% of the incorporated urea in the initial period, i.e. the higher the concentration of sodium alginate, the slower the urea release. It was observed that the coating technique could be used to prolong the duration of urea release from capsules by up to 50 days.

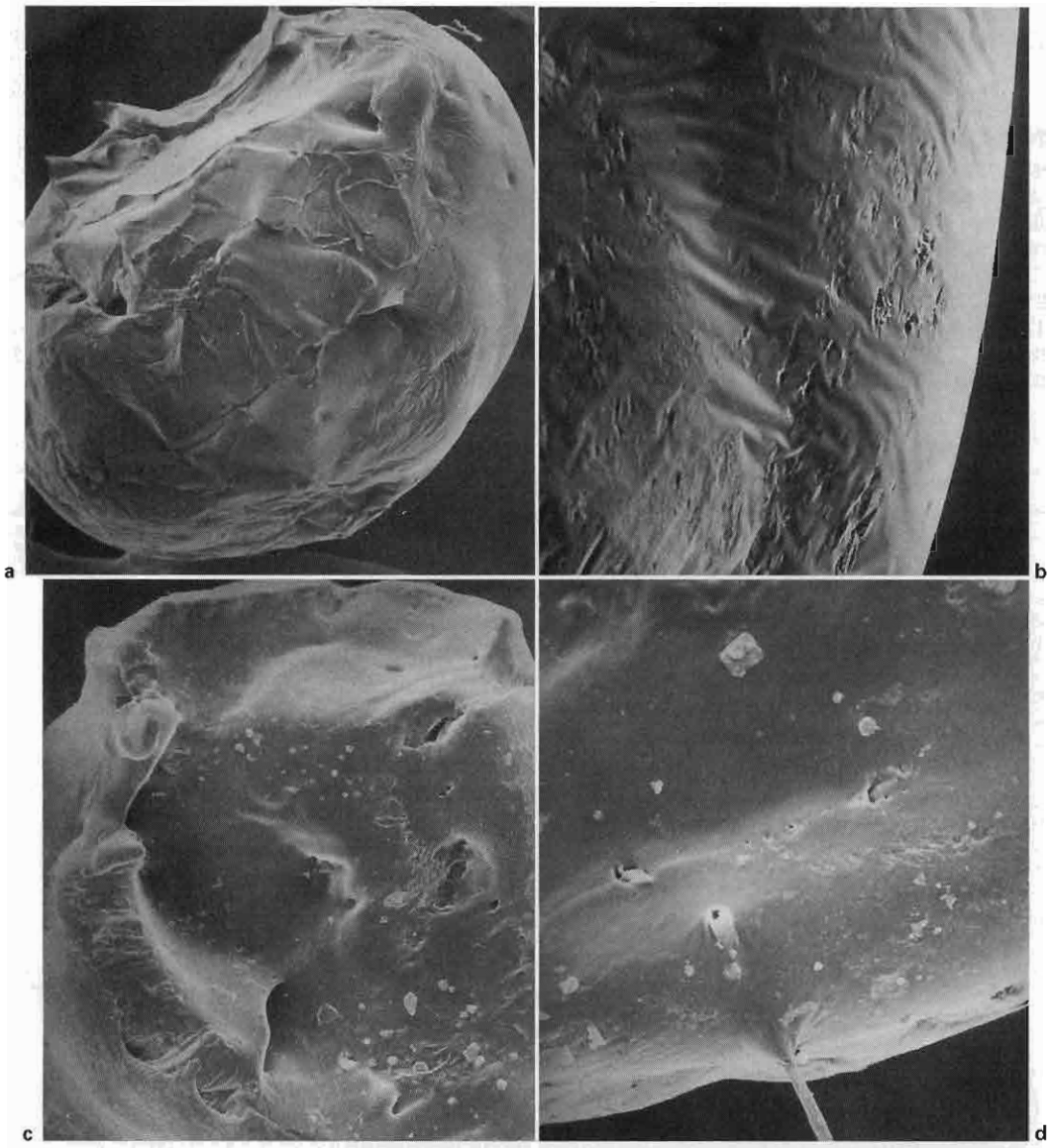
Figure 10 shows SEMs of the coated capsules after release. The capsule surface was wrinkled as for the uncoated capsules, but there were considerably fewer pores on the surface of the capsules.

Effect of urea concentration

To study the effect of urea concentration on the amount of released urea, urea–unvulcanised NR capsules coated with 4% sodium alginate were prepared by varying the initial urea concentrations, i.e. 25, 50, 75, and 100 pphr. Since the urea could be partly lost during acid precipitation, the concentration of initial urea was higher than the urea incorporated in the prepared capsules, i.e. they contained 24, 48, 66, and 80 pphr urea. Figure 11 shows the effect of initial urea concentration on the cumulative amount of urea released from the coated capsules with time. It was found that the released urea increased with the increase of initial urea concentration in the capsules. It is suggested that the amount of urea released is dependent on its hydrophilicity in addition to its solubility in water. Thus, the desired amount of urea release can be controlled by manipulation of its concentration in the matrix.[6]

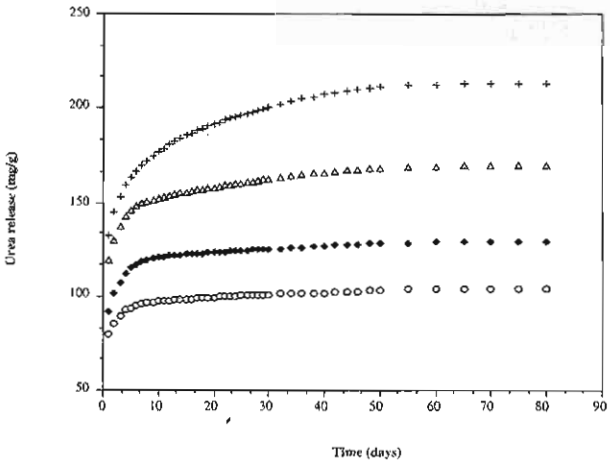
CONCLUSIONS

Natural rubber (NR) latex was used to prepare urea–rubber capsules by an acid precipitation technique. The simple binding of fertiliser into a NR matrix, which resulted in a high release rate of urea from the



a capsule surface (×27); *b* capsule surface (×180); *c* capsule cross-section (×36); *d* capsule cross-section (×180)

10 Scanning electron micrographs of urea–unvulcanised NR capsules coated by dipping in 4% aqueous sodium alginate solution after 30 days release of urea (initial urea concentration 100 pphr)



(○) 25; (◆) 50; (△) 75; (+) 100 pphr

11 Effect of initial urea concentration on cumulative release of urea from non-crosslinked NR matrix 4% sodium alginate coated capsules *v.* time

capsules when immersed in water, was not suitable for use. Coating the urea–NR capsules with sodium alginate had a pronounced effect on slow release urea fertiliser. Microscopy showed that sodium alginate could be used successfully as a barrier, to give a better distribution of urea in the rubber matrix and consequently a more efficient release of urea compared with the uncoated samples. In addition, the release rate of urea was proportional and inversely proportional to the concentration of urea and sodium alginate, respectively.

Further investigations concerning the effect of fillers and the diffusion through NR film will be published in the future.

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REFERENCES

1. A. AKELAH and A. MOET: 'Functionalized polymers and their applications', Ch. 7, 217–248; 1990, London, Chapman and Hall.
2. C. HEPBURN and R. ARIZAL: *Plast. Rubber Process. Appl.*, 1989, **12**, 129–134.
3. C. HEPBURN and R. ARIZAL: *Plast. Rubber Process. Appl.*, 1989, **12**, 135–140.
4. C. HEPBURN, S. YOUNG, and R. ARIZAL: *Plast. Rubber Process. Appl.*, 1989, **12**, 141–145.
5. S. I. ABO-ELELA, F. M. HELALY, and E. M. ABDEL-BARY: *Plast. Rubber Process. Appl.*, 1990, **14**, 43–47.
6. E. M. ABDEL-BARY, A. G. EL-SHEKEIL, F. M. HELALY, A. A. SARHAN, and H. H. ABDEL-RAZIK: *Plast. Rubber Compos. Process. Appl.*, 1992, **17**, 99–107.
7. F. M. HELALY, E. M. ABDEL-BARY, A. A. SARHAN, and H. H. ABDEL-RAZIK: *Plast. Rubber Process. Appl.*, 1993, **19**, 111–115.
8. T. J. POTTS: *J. Association Official Agricultural Chemists*, 1963, **46**, 303–306.
9. R. W. BAKER and H. K. LONSDALE: *Chemtech*, 1975, **5**, 668–674.
10. G. SOMERVILLE and J. GOODWIN: in 'Controlled release technologies', (ed. A. Kydoniens), Ch. 8, 155–164; 1980, Boca Raton, FL, CRC Press.

Phase Transfer Technique for Surface Characterisation of Fresh Field Natural Rubber Latex

P. TANGBORIBOONRAT* S. CHINDAPRASERT and C. TIYAPIBOONCHAIYA

Department of Chemistry, Faculty of Science, Mahidol University,
Rama 6 Rd., Phyathai, Bangkok 10400 THAILAND

ABSTRACT

Phase transfer technique, using benzyldimethylhexadecylammonium chloride as a titrant and toluene as a solvent, was extended to characterise the surface of fresh field natural rubber latex. The critical transfer concentration (CTC) values of the fresh latices tapped from 6 different biological clones were directly proportional to the nitrogen contents derived from the indigeneous proteins. The values of CTC and nitrogen contents of the latex samples collected in rainy season were higher than those collected in winter. The effect of seasonal variations was supported by the zeta potential. However, neither clonal variations nor seasonal changes was detected by mechanical stability time (MST) measurements.

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*To whom correspondence should be addressed.

INTRODUCTION

Natural rubber (NR) latex tapped from *Hevea brasiliensis* has been commercially available and exploited for a great variety of manufacturing products due to its attractive properties unmatched by most synthetic rubbers e.g., strength, elastic and dynamic properties (1). Being a natural product, it is not surprising that the composition of NR latex varies. It was reported that besides *cis*-1,4-polyisoprene in the rubber particles, the non-rubber substances such as carbohydrates, proteins, lipids and inorganic salts are constituents of the exuded latex (1, 2). These substances are reported to have significant influences to the variable properties of NR such as thermal oxidative stability, vulcanisation properties (1-3). The amount of non-rubber substances in *Hevea* latex is dependent on biological clones, soil conditions, climate and seasons. Practically, large variations of usual rubber grades can be compensated by blending of latex from various sources.

The non-rubber substances exist in various parts of NR latex e.g., in aqueous serum or at the surface of rubber particles. Many works have shown that the NR particles are stabilised by a complex layer of proteins and lipids (1-8). However, up until present, there is no complete understanding of the particle-serum interface. The previous study of proteins on the surface of rubber particles has not caught much attention as compared to that present in serum or in the other fractions. Electrophoresis only showed that the latex particles are amphoteric in nature with an isoelectric point (pI) at pH 3.8 (9). The study of enzyme deproteinised NR revealed the presence of residual proteins or amino acids bonded to the NR molecules (4). Recently, phase transfer technique has been employed for the surface characterisation of γ-radiation vulcanised natural rubber (RVNR), non-crosslinked NR and deproteinised NR (DPNR) latices at pH greater than pI (10-12). This technique, originally developed for determination of the surface charge of crosslinked synthetic latex, involves titration of the anionic stabilised latex with an aqueous solution of cationic surfactant in the presence of a water immiscible organic solvent (13). The surface charge of the particles is calculated from the amount of the added surfactant at the critical transfer concentration (CTC). For the RVNR latex, the negatively charged latex particles (pH~9) could be transferred into the organic phase by titration with cationic surfactants whose molecules bear either two long alkyl chains or one long alkyl chain and a benzyl group. In addition, the solubility parameter of the solvents must be close to that of the natural rubber. At CTC, the transfer of crosslinked NR took place immediately where two phases were noted, *i.e.*, the upper organic phase containing the swollen rubber particles and the lower rubber-free serum aqueous phase. When the technique was applied to the study of non-crosslinked NR latex by using benzyldimethylhexadecylammonium chloride as a titrant, it was found that the latex particles completely transferred and a direct correlation existed

between the CTC and the difference between the solubility parameter of organic solvent and that of natural rubber. Phase transfer of non-crosslinked NR latex resulted in three phases, the additional phase being the destabilised and suspended rubber at the interphase between organic and aqueous phases. The observed phenomenon was explained in terms of the denaturation of the proteins, linked with rubber chains, by the added cationic surfactant (10). Due to the remaining proteins, this feature was also found when the DPNR latex (treatment of NR latex with enzyme) was subsequently studied (12).

Since our previous results indicated the efficiency of phase transfer technique for characterisation of the NR latex particles surface, this technique has been extended to the study of freshly-tapped NR latices in order to understand the original nature of the surface structure of rubber particles. The effect of clonal and seasonal variations on the CTC values determined by using the phase transfer technique has also been explored. The data obtained were then compared with the zeta potential and mechanical stability time (MST).

EXPERIMENTAL

NR Latices

Fresh-field latices from 6 different clones, i.e., RRIM 600, GT 1, PB 5/51, RRIC 110, KRS 25 and SONGKLA 36, cultivated in the same area were obtained from Chachoengsao Rubber Research Center (Thailand). The latices were tapped at 4 a.m. and collected at about 8 a.m. and preserved by the immediate addition of ammonia solution (0.7% by weight). To study the effect of seasonal variations, the latices used were collected in winter (January) and rainy (June) seasons. Since the trees shed their leaves once a year during summer months, the tapping is normally suspended.

Total solid content (%TSC) and dry rubber content (%DRC) of the NR latices were determined according to the methods described in ASTM D 1076-88 (14).

Phase Transfer Procedure

Latex sample (15g, having 0.6% solid content) was diluted with distilled water (45g), and the pH of the mixture was found to be ~ 9 without any adjustment. Toluene (30g) was added and the mixture was titrated, while stirring, with 0.0121M aqueous solution of benzyldimethylhexadecylammonium chloride (BHAC), using a burette. The titration end point was observed when the mixture became translucent. Stopping the

agitation at this point immediately caused a phase separation with the appearance of a clear rubber-free serum aqueous phase.

The quantity of surface charge was calculated directly from the critical transfer concentration (CTC) by the following equation :

$$CTC = \frac{V \times C}{10 \times TSC \times m}$$

where

CTC = critical transfer concentration (mole of used cationic surfactant per gram of dry latex)
V = quantity of used cationic surfactant at titration end point (ml)
C = surfactant concentration (mole /l)
TSC = total solid content of latex (%)
m = weight of latex sample (g)

Electrophoresis Measurement

To determine zeta potential, the NR latex was diluted with 10^{-3} M sodium chloride solution, then the pH of latex was adjusted by adding 1 N aqueous solution of sodium hydroxide or hydrochloric acid. The zeta potential of the dispersion was determined by using particle microelectrophoresis apparatus, Zetasizer 4 (Malvern) within 20 min after mixing and pH adjustment.

Mechanical Stability Test

Mechanical Stability Time (MST) of NR latices was measured according to the method described in ASTM D 1076-88 (14) except that the %solid content of the fresh latices was less than that indicated in the ASTM (55%) as presented in Table 1.

Determination of Nitrogen Content

Nitrogen contents (%N) of the rubber sheets, cast from NR latices and dried at 50°C for 24 h, were determined by using Kjeldahl method as described in ASTM D 3533-90 (15).

RESULTS AND DISCUSSION

General Characteristics of NR Latices

The solid content of the fresh field NR latices from 6 clones, i.e., RRIM 600, GT 1, PB 5/51, RRIC 110, KRS 25 and SONGKLA 36, was determined. The data in Table 1 indicated that the total solid content (%TSC) and dry rubber content (%DRC) varied in the range of 27-40% and 23-35% respectively. The highest solid content was found in PB 5/51 whereas SONGKLA 36 indicated the lowest value. Results obtained were not surprising because it was reported that many factors including clonal origins, seasonal variations, tapping intensity and age of the rubber plants exert strong influences on the foliage and yields of rubber and non-rubbers of latices (16). It was also found that the average value of the difference between %TSC and %DRC for all latices was about 5% due to the presence of non-rubber substances (1, 2, 10).

Table 1 : Solid contents of fresh field NR latices from 6 clones

Clones	%TSC	%DRC
RRIM 600	35.9 ± 0.2	29.1 ± 0.5
GT 1	35.2 ± 0.1	30.1 ± 0.7
PB 5/51	40.2 ± 0.1	32.4 ± 0.4
RRIC 110	29.8 ± 0.1	25.8 ± 0.2
KRS 25	38.5 ± 0.1	34.7 ± 0.1
SONGKLA 36	27.1 ± 0.1	22.8 ± 0.1

The particle size of these latices was analysed by using a laser particle size analyser, Mastersizer X (Malvern), which calculates the average particle size from the measurement of the sample diffusion and diffraction. The size polydispersity of all latices was observed with the volume average particle size of about 0.8 μm and the average diameters of the particles from 6 clones were not significantly different.

Surface Characterisation of Fresh Field NR Latices

Phase transfer technique was used to characterise the surface structure of fresh field NR latices from 6 clones by determination of their CTC values. The relations between the CTC and the nitrogen contents of the latices are presented in Figure 1.

Figure 1

Results showed that CTC values and nitrogen contents of almost all of NR latices (except RRIM 600) varied in related manner. It should be noted that the nitrogen contents generally indicated the quantity of proteinaceous materials, which mainly existed at the surface of NR particles, in NR latex . This part of proteins could generate electric charges which contribute to the stability of NR latex particles. Therefore, it is reasonable to basically assume that the CTC values could be used to indicate the quantity of charges on the surface of rubber particles derived from the proteins attached to the particles.

However, apart from the proteins the negative charges on the surface of NR particles were attributed to the adsorption of natural fatty acids resulted from hydrolysis of phospholipids present in the latex. The amount of fatty acids in NR latex has been found to increase during storage as measured by the MST values (16). It is of interest to study the contribution of fatty acids to the CTC values obtained in this work. The freshly-tapped NR latices were, therefore, concentrated by using commercial centrifugation method until %DRC was *ca.* 60. The CTC values of the concentrated high ammonia (HA) latex were determined over the period of storage (100 days). The data are plotted in Figure 2.

Figure 2

The results in Figure 2 clearly indicated the influence of storage time on the CTC values of the NR latices. The CTC values rapidly decreased over the first 40 days and then significantly unaltered thereafter. This trend was completely different from the increase of MST during storage of the latices, as presented in Figure 3, which was believed to be a consequence of phospholipid hydrolysis (16).

Figure 3

At this stage it is not unreasonable to presume that the CTC values of the latices were mainly affected by the charges derived from proteins while the fatty acids influenced on the MST. The addition of small amounts of fatty acids, carboxylate, sulphate or sulphonate surfactants was reported to be able to enhance the mechanical and chemical stability of latex by adsorption at the rubber surface and thereby making the indigenous soaps more effective as stabilisers (17-20). The mechanism of phase transfer technique stated that one of the optimum conditions for a complete transfer the NR particles was the adsorption of added cationic surfactants on proteins at the surface of rubber particles (11). The efficiency of adsorption, indicated by the CTC values, depended on the alkyl chain length of the surfactants. This mechanism could be used to explain the results obtained in this work. Initially the cationic surfactant might be adsorbed on the protein-lipid membrane without any effect from fatty acids. The latter hydrolysis products of lipids, would be adsorbed on the chains of remaining proteins and would impede the exposure of proteins to the surface of rubber latex particles. The concentration of cationic surfactant required for adsorption and neutralisation of the proteins causing phase transfer would be lowered and, hence, the decrease of CTC values during the initial storage period. The constant CTC values after 40 days of storage might be due to the complete hydrolysis of lipids providing the unchanged of surface structure of rubber particles, *i.e.*, the latex has reached maturity.

The appearance of the fresh field NR latices at the end point of phase transfer was the same as that found in the case of high ammonia concentrated NR latex (10), *i.e.*, the mixture of NR latex and toluene became translucent and after stopping agitation three phases were noted; the upper toluene phase containing the soluble rubber, the destabilised and suspended rubber at the interphase between toluene and water, and the lower rubber-free serum aqueous phase. However, it is of interest to remark that the end point in the study of

fresh latices was easily detected comparing with the concentrated latex. In this case, the lower aqueous phase has become instantly very clear and the quantity of rubber coagulated in flask was quite low. This might be due to the unchanged structure of protein-lipid membrane and the lack of gel effect caused by storage hardening. Therefore, the phase transfer technique can be conveniently employed for characterisation of the freshly-tapped NR latices.

The zeta potential of the latices from 6 clones at pH ~10 was measured and the data are presented in Table 2. It should be noticed that this technique relates directly to the movement of particles in aqueous medium under influence of an applied electric field and, therefore, it can be generally employed as a powerful method for measuring the surface charge on particle and as an index of colloidal stability.

Table 2 : Zeta potential measured at pH ~10 and MST of fresh NR latices from 6 clones

Clones	Zeta potential (mV)	MST (s)
RRIM 600	-60.2 ± 0.5	341 ± 16
GT 1	-63.3 ± 0.6	324 ± 8
PB 5/51	-67.1 ± 0.4	343 ± 6
RRIC 110	-62.2 ± 0.4	328 ± 9
KRS 25	-62.9 ± 0.7	312 ± 8
SONGKLA 36	-63.5 ± 0.5	319 ± 15

Results from Table 2 indicated that the zeta potential values between 6 latices were slightly different and the surface charges on the latex particles in each rubber clone could not be significantly distinguished by the measurement of zeta potential. This incapability was also found when measuring MST as shown in Table 2. It must be noted that solid content of the fresh latices used for MST measurement was only about 27-40% (Table 1) instead of 55% of concentrated latex as indicated in the ASTM.

Seasonal effect was then investigated while other variables such as hereditary, soil or climate were eliminated by collecting the fresh field NR latices from the *Hevea* trees planted in the same area. The solid contents of 6 clones of the latices collected in winter (January) and rainy (June) seasons were firstly determined and, as expected, both %TSC and %DRC collected in the rainy season were higher than those collected in winter. This could be due to higher dissolved nutrients in the soil in the wet season thus producing higher chemical constituents. The effect of seasonal variations on the CTC values and nitrogen contents of these 6 latices were explored and results are presented in Figures 4 and 5 respectively.

Figure 4

Figure 5

From the Figures, it can be seen that the CTC values and the nitrogen contents of almost all of latices showed the same trend and they were dependent on seasons, i.e., the latices collected in June (rainy season) gave higher values than those collected in January (winter). As already mentioned, this might be because of the high activity of plant metabolism in the former season. Consequently, high amounts of rubber and non-rubber substances, including proteins, as indicated by nitrogen contents, were produced. Thus, it was reasonable to state that the phase transfer technique could suitably be used for study on the effect of clonal and seasonal variations of fresh field latex particles.

Values of zeta potential of the latices collected in both seasons are displayed in Figure 6.

Figure 6

As evident in Figure 6, the absolute values of zeta potential of all NR samples from different clones collected in rainy season were higher than those collected in winter. In general, the higher the absolute value of zeta potential corresponded to the greater amount of negative charges on rubber particles. The evidence from the zeta potential measurement, therefeore, supported the CTC values in Figure 4 and the nitrogen contents in Figure 5 that the NR latices in wet season produced higher negative charges derived from proteins on the rubber particles. It should be noted that the MST of these latices were also measured in our experiments but the seasonal variations in MST, if they exist at all, are small in magnitude (16).

CONCLUSIONS

The phase transfer technique could suitably be applied for surface characterisation of freshly-tapped natural rubber (NR) latex. The end point was easily detected and the phase separation was complete. For different biological clones, the CTC values of latices were proportional to the nitrogen contents indicating the amount of negative charges derived from proteins. Both clonal and seasonal variations affected the CTC and nitrogen contents of all latices while only seasonal variation provided a significant difference between the zeta potential of the fresh latices. The variations in the MST of these latices were insignificant.

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