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ORIGINAL CONTRIBUTION

Pramuan Tangboriboonrat
Chutamast Lerthititrakul

Morphology of natural rubber latex particles prevulcanised by sulphur and peroxide systems

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P. Tangboriboonrat (✉) · C. Lerthititrakul
Department of Chemistry,
Faculty of Science,
Mahidol University,
Rama 6 Road, Phyathai,
Bangkok 10400, Thailand
E-mail: scptb@mucc.mahidol.ac.th
Tel.: +66-2-2015170
Fax: +66-2-2477050

Abstract Transmission electron microscopy provided direct evidence of the morphology of sulphur- and peroxide-prevulcanised natural rubber latex particles. A mesh structure of all cross-linked rubber particles containing polystyrene, prepared using the phase-transfer/bulk polymerisation process, was found. Each peroxide-prevulcanised particle had a nonuniform network structure, whereas the rubber network in sulphur-prevulcanised particles was homogeneous, irrespective of size. The effects of maturation and sodium dodecyl sulphate on the swelling ratio of the sulphur-prevulcanised latex film were investigated.

Keywords Prevulcanised natural rubber latex particle · Morphology

Introduction

Prevulcanised natural rubber (NR) latex is a very convenient raw material mainly for the manufacture of thin-film products. Owing to the fact that the initial cross-linking takes place in latex particles during prevulcanisation, control of the physical properties of the final product can be effectively examined before articles are manufactured. It is known that the rate of the prevulcanisation reaction depends on the vulcanisation systems, and the extent of prevulcanisation has a profound effect on the formation of the latex film [1, 2]. A coherent film would not be achieved if the particles were highly cross-linked near their surface owing to the restricted mobility of the rubber chains at the particle surface. On the other hand, homogeneously cross-linked particles fuse well and form a film with optimum physical properties.

Vulcanisation of a NR latex is normally performed by sulphur, peroxide and γ-ray irradiation. We found that γ-ray irradiation of a NR latex leads to the formation of homogeneous cross-links inside the rubber particle, using transmission electron microscopy (TEM) [3, 4, 5]. However, from the economic point of view, the γ-ray irradiation vulcanisation (RV) method has not been widely used in industry, whereas the sulphur-prevulcanised process is more preferred although, up until the present, the chemical mechanism of the vulcanisation is not well understood and is still controversial [6, 7, 8, 9, 10]. It was postulated that the predissolved sulphur and accelerator in the aqueous phase completely diffuse into rubber particles prior to vulcanisation, resulting in homogeneously cross-linked particles [9, 10]. On the other hand, slow diffusion would provide the rubber particle with an unvulcanised core surrounded by a highly cross-linked shell [8]. Previous work also reported that a uniform cross-link structure in peroxide-cured NR latex is observed only in small particles [9, 10].

It is noted that the description of the structure of sulphur- and peroxide-prevulcanised NR particles in the aforementioned works was deduced from the study of latex films. However, owing to interparticle links resulting from chain entanglements and/or postvulcanisation in the film, it is not straightforward to interpret the actual cross-linking in latex particles [10]. Therefore, the phase-transfer/bulk polymerisation/TEM technique, successfully used in previous work to elucidate the cross-linking inside RVNR latex particles, was further extended to provide direct evidence of the morphology of sulphur- and peroxide-prevulcanised NR latex particles in the present work. This technique involves titration of the negatively charged latex particles with a cationic surfactant in the presence of styrene, which is a good solvent of rubber. At the end point, the neutralised particles transfer from the aqueous phase into the styrene phase. The styrene-containing swollen rubber particles are then polymerised in the bulk and the cross-linked rubber embedded in rigid polystyrene (PS) can be sectioned for the TEM study. After osmium tetroxide staining, stained black areas of cross-linked rubber and unstained white areas of PS are observed in the micrographs [3, 4, 5, 9, 10]. Owing to the omission of air in the freeze-drying stage of the rubber latex, the change in the particle structure would be minimised.

Experimental

Preparation of sulphur-prevulcanised NR latex

Vulcanising ingredients, i.e., sulphur (EMCO Intertrade Co., commercial), zinc diethyldithiocarbamate (ZDEC; EMCO Intertrade Co., commercial) and zinc oxide (Global Chemical Co., commercial), in the form of powders were prepared as a 50% aqueous dispersion by ball-milling. These ingredients were thoroughly ground for 72 h and their sizes were measured using a laser scattering technique (Mastersizer S, Malvern) at 25 °C. The formulations used for the preparation of the sulphur-prevulcanised NR latex are shown in Table 1 [11].

Commercial high-ammonia NR latex (N.Y. Rubber Co., Thailand) (60% dry rubber content) was filtered through a 250-mesh aluminium screen and charged in a reaction vessel equipped with a condenser and a thermometer. The latex was stabilised with potassium hydroxide (Merck, general reagent) or KOH/sodium dodecyl sulphate (SDS; Fluka, gel permeation chromatography) in formulations A and B, while the stabilisers were not used in formulation C. Aqueous dispersion agents of vulcanising ingredients, i.e., S, ZDEC and ZnO, were added to the latex at room temperature with stirring at 200 ± 20 rpm for 30 min. The mixture was left for 2 h in a dark cabinet for maturation and was subsequently heated in a water bath at 60 °C. During prevulcanisation, a portion (about 5 g) of the compounded latex was taken at intervals, cast on a Petri dish and dried at room temperature for 1 week. The dried rubber was cut into a square piece of known weight (about 0.2 g) and its cross-link density was then determined by immersing it in toluene (Fluka, commercial) (40 ml) to equilibrium-swell. The swelling ratio of the rubber was calculated as previously described [3, 4]. At the end of the reaction, the prevulcanised latex was cooled rapidly to room temperature to prevent further vulcanisation. The prevulcanisation of the NR latex without addition of any ingredients (or unmodified latex) was also carried out according to this procedure. In addition, residual vulcanising ingredients were eliminated from the prevulcanised latex using a Supraspeed centrifuge (Sorvall RC 5C Plus, DuPont) at 4,000 rpm, for 15 min (three times) at room temperature.

Table 1 Formulations used for sulphur-prevulcanisation of natural rubber (*NR*) latex [11]

Ingredients	Parts by wet weight (g)		
	A	B	C
Concentrated NR latex	167.0	167.0	167.0
Stabilisers			
KOH solution (10% w/v)	4.0	4.0	–
Sodium dodecyl sulphate solution (25% w/v)	0.8	–	–
Vulcanising ingredients (50% dispersion)			
S	2.5	2.5	2.5
Zinc diethyldithiocarbamate	2.0	2.0	2.0
ZnO	0.5	0.5	0.5

Preparation of peroxide-prevulcanised NR latex

The formulations used for peroxide-prevulcanisation of the NR latex are given in Table 2 [12]. *tert*-Butyl hydroperoxide (*t*-BuHP; Fluka, purum) (1.25 g) mixed with distilled water (11.2 g) (and 1.25 g SDS solution in formulation A) was poured, while stirring, into the NR latex in a glass reaction vessel at room temperature. D(-)-Fructose solution (25%) (Fluka, bacteriology) (8.5 g) and water (11.2 g) were then added into the mixture prior to heating at 60 °C. The remaining steps were conducted in the same manner as those employed in the case of sulphur prevulcanisation.

Preparation of the sample for morphological study

The phase-transfer technique, described in our previous works, was applied to transfer prevulcanised latex particles (6% total solid content) (15 g) from the aqueous phase into the styrene monomer (Fluka, purum) (30 g) by titration with an aqueous solution of 0.0121 M benzyldimethylhexadecylammonium chloride (Fluka, purum) [3, 4, 5]. The remaining trace of water in the styrene monomer, containing swollen transferred rubber particles for 24 h, was eliminated by centrifuging as previously mentioned. The upper styrene phase isolated and mixed with 1.0 wt% of benzoyl peroxide (BPO; Sigma, microscope) was then poured into a Teflon coated steel mould (10.4×10.4×2.6 cm^3) and polymerised at 70 °C in an oven (400UM, Memmert) for 16 h.

The specimen of NR particles incorporating in PS matrix was finely trimmed and sectioned under an ultramicrotome (MT-7, RMC). The micrograph of the rubber particles embedded in PS after being stained with osmium tetroxide vapor (Electron Microscopy Sciences) was obtained using a transmission electron microscope (H-300, Hitachi).

Results and discussion

Sulphur-prevulcanised NR latex particles

Size of milled vulcanising ingredients

Although milling of vulcanising agents in water seems to be unnecessary because their sizes have no effect on the

Table 2 Formulations used for peroxide-prevulcanisation of NR latex [12]

Ingredients	Parts by wet weight (g)	
	A	B
Concentrated NR latex	166.7	166.7
tert-Butyl hydroperoxide solution (68% w/v)	1.25	1.25
Sodium dodecyl sulphate solution (20% w/v)	1.25	–
D(-)-Fructose solution (25% w/v)	8.5	8.5
Distilled water	22.4	22.4

rate or extent of cross-linking, the method is ubiquitous practice [13, 14, 15]. The size distributions of unmilled and ball-milled S, ZDEC and ZnO, measured using the Mastersizer S, are displayed in Fig. 1. These curves show that the size of the vulcanising ingredients decreased after ball-milling; however, their average size was still very large compared to that of a NR latex particle (0.7 μm).

Effect of maturation

The effect of maturation [9, 16, 17] is indicated by the swelling ratio of a rubber sheet cast from the sulphur-prevulcanised latex (formulation A) with and without maturation shown in Fig. 2. The swelling ratios in both curves decreased as the reaction time increased. After about 5 h, a relatively small change in the swelling ratio (about 450%) was found when vulcanisation of the rubber was complete [18]. It was noticed that in the initial period of prevulcanisation, maturation of the latex for 2 h before heating provided a higher cross-link density of the rubber sheet. This indicates that maturation allowed the maximum dissolution of sulphur accelerator species to migrate into the rubber particles. Consequently, cross-linking of rubber in the prevulcanised latex with maturation readily took place when the sample was heated. The prevulcanisation with maturation was selected for further experiments.

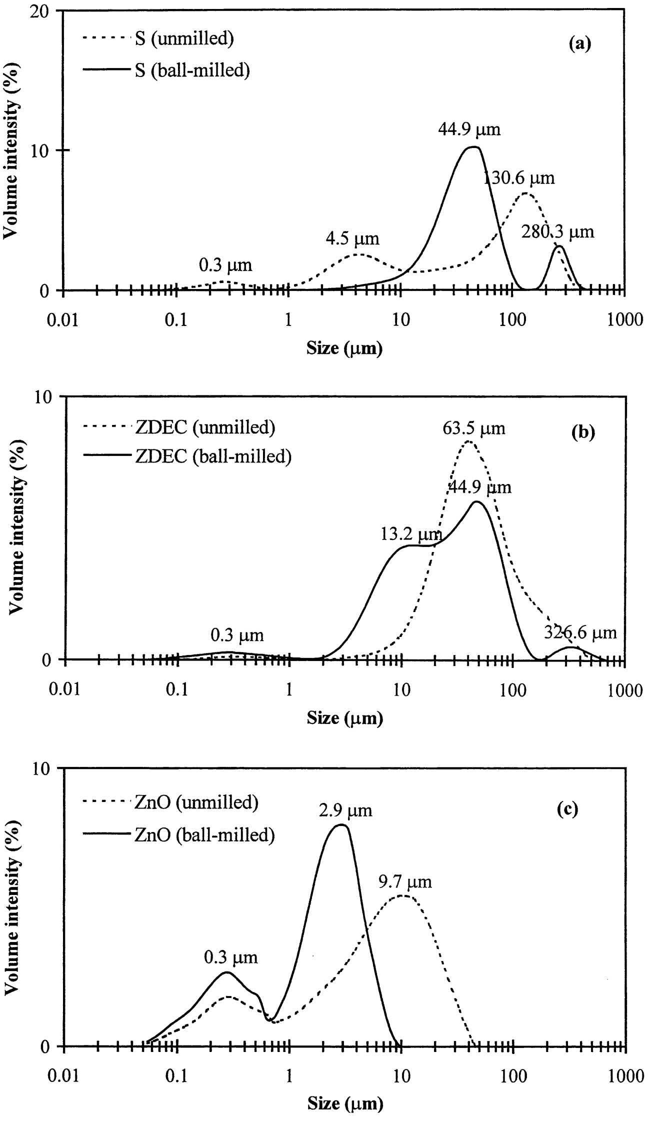

Fig. 1 Size distribution of **a** S, **b** zinc diethyldithiocarbamate (*ZDEC*) and **c** ZnO before and after ball-milling

Effect of addition of SDS

The effect of SDS on the efficiency of cross-linking for sulphur prevulcanisation of the NR latex was studied by measuring the swelling ratios of rubber latex sheets cast from latices with and without SDS. Their swelling ratios plotted against heating time are shown in Fig. 3.

From Fig. 3, it is observed that the swelling ratios of both types of sulphur-prevulcanised latex sheets slightly decreased with longer vulcanisation time. The constant value of less than 500% also indicated a fully cross-linked rubber. Although the resemblance of the two curves of the sulphur-prevulcanised latices was noticed, the presence of SDS caused an increase in the cross-link density of NR in the initial period. At present, there seems to be no direct evidence concerning the effect of SDS on the sulphur prevulcanisation. It was reported that addition of small amounts of carboxylate, sulphonate and sulphate surfactants enhanced the mechanical and chemical stabilities of NR latex by

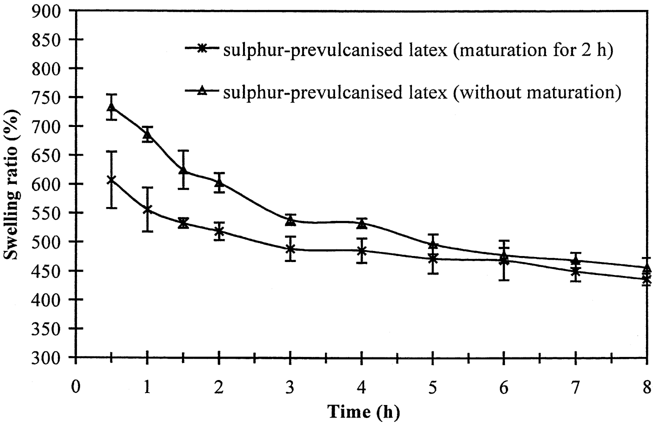

Fig. 2 Swelling ratio of rubber sheet cast from a sulphur-prevulcanised latex matured for 2 h compared to a system without maturation

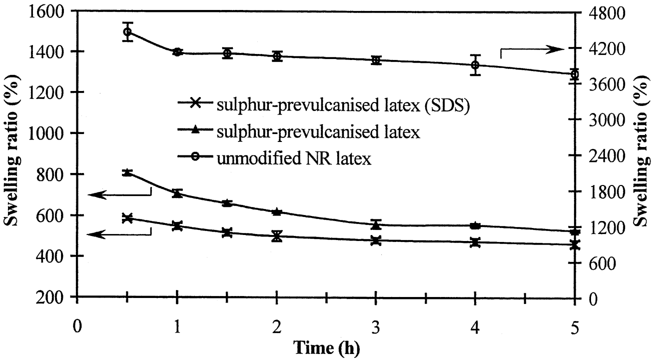

Fig. 3 Swelling ratio of a sulphur-prevulcanised latex with and without sodium dodecyl sulphate (*SDS*) compared to that of an unmodified latex heated at 60 °C

rearranging the indigenous soaps, derived from protein-lipid, and making them more effective as stabilisers [19, 20, 21]. This ability depended largely upon the chain length of their alkyl group and the optimum enhancement was observed when the alkyl chain of the surfactants consisted of approximately 11 carbon atoms [19, 20]. Several works indicated that small amounts of proteinaceous substances in the latex, being surface active, resulted in an increase in curative concentrations in rubber particles [7, 16, 22]. Thus, it could be assumed that the redistribution of soap-anion clusters throughout the particle was provoked by SDS and, hence, the sulphur prevulcanisation in rubber particles was enhanced.

The presence of SDS on the surface of the prevulcanised NR latex was investigated by determination of the critical transfer concentration (CTC; moles of surfactant used per gram of dry latex), which has been used to indicate the quantity of charge on surface particles [3, 4, 5]. The CTC values, determined by using the phase-transfer technique, of sulphur-prevulcanised and unmodified NR latices are shown in Table 3.

The data revealed that the CTC of the prevulcanised latex adsorbed with SDS was slightly higher than that of the others owing to the fact that SDS caused an increase in the amount of negative charge on the surface particles [23]. However, the CTC value of a prevulcanised latex having only KOH significantly decreased compared to that of the unmodified latex. This might be due to the neutralisation between KOH and adsorbed long-chain fatty acid soaps, the hydrolysis products of lipid, at the latex particle surface. Another possible explanation was the neutralisation of the native surfactants by the species formed from vulcanising agents notably containing a Zn^{2+} ion.

Table 3 Critical transfer concentration (*CTC*) values of sulphur-prevulcanised and unmodified latices

Sample	CTC ($\times 10^{-5}$)
Unmodified latex	4.66 ± 0.15
Sulphur-prevulcanised latex	
KOH/sodium dodecyl sulphate	4.73 ± 0.02
KOH	3.60 ± 0.05

Determination of residual vulcanising ingredients

Since excess vulcanisation reagents used in the sulphur prevulcanisation of the NR latex were believed to remain in the aqueous phase, the vulcanised latex was, therefore, centrifuged three times to eliminate the residue of these reagents. The experiment showed that the amount of residual chemicals in the latices with and without SDS was 0.52 and 0.63% w/w, respectively. Since these figures are very small compared to the concentration of the ingredients initially added to the latex, it was assumed that almost all the vulcanising ingredients probably diffused into the rubber particles. The lower amount of residue in the presence of SDS correlated well with the extent of cross-linking (Fig. 3).

When the phase-transfer technique was applied for the study of the centrifuged latex, it was found that trend and the values of the CTC of the latex with and without SDS were similar to those of the prevulcanised latex before centrifugation. The result indicates that residual agents had no effect on the surface charge of cross-linked particles.

Peroxide-prevulcanised NR latex particles

The swelling ratios of rubber sheets cast from the peroxide-prevulcanised NR latices with and without SDS at

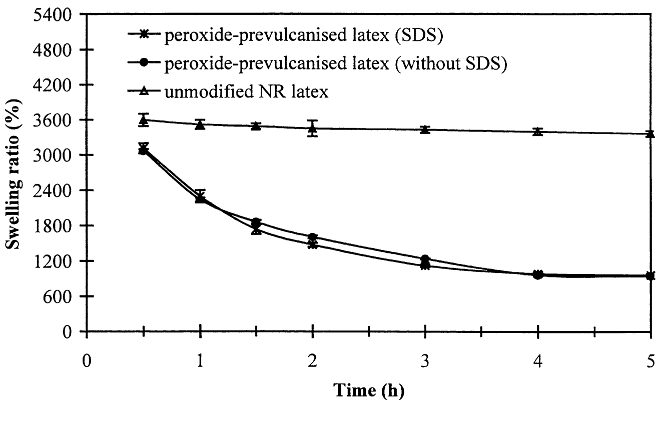

Fig. 4 Swelling ratio of sheets cast from a peroxide-prevulcanised latex (with and without SDS) at various vulcanisation times at 60 °C compared to that of an unmodified latex

various reaction times were determined and compared to that of the unmodified latex as shown in Fig. 4.

As in the case of sulphur prevulcanisation, the percentage swelling ratio of peroxide-prevulcanised NR decreased rapidly with increasing reaction time and then approached a constant value of about 950% within 4 h, i.e., lightly vulcanised rubber was obtained [18]. It was found that the presence of SDS did not affect the swelling ratio of the film cast from the peroxide-prevulcanised NR latex.

Owing to the contribution of SDS to the increase in the number of negative charges on the surface particles as already mentioned, the presence of SDS in the peroxide-prevulcanised latex also resulted in a higher CTC value ($4.70 \pm 0.04 \times 10^{-5}$) compared to that of the latex without SDS ($4.10 \pm 0.03 \times 10^{-5}$) and of the uncured latex.

Bulk polymerisation of styrene containing sulphur-prevulcanised rubber particles

Prior to the morphological study of sulphur-prevulcanised rubber particles embedded in a PS matrix, the percentage conversion of styrene containing swollen, transferred vulcanised rubber (3% NR, with SDS), when using various initiator concentrations (0.4, 0.6 or 1.0% w/w of BPO), at 70 °C was determined and the data are shown in Fig. 5.

From Fig. 5, it is observed that the conversion of styrene monomer promptly increased in the initial period of polymerisation and then approached about 100%. With the increase in the amount of BPO, the rate of polymerisation increased and the time required for complete conversion was reduced, i.e., within about 20 and 16 h from 0.4 to 1.0% of BPO.

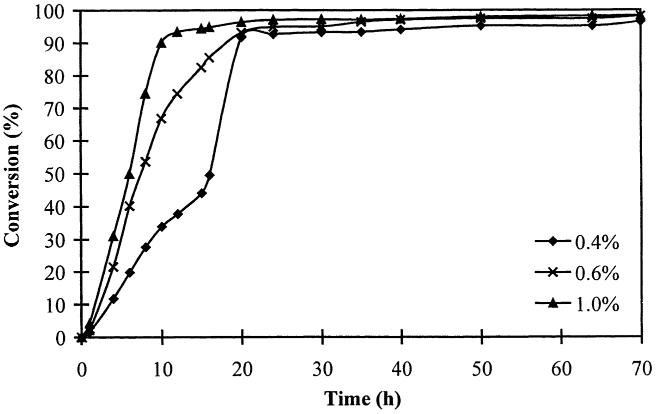

Fig. 5 Conversion of styrene containing transferred sulphur-prevulcanised rubber (3% natural rubber, *NR*, with SDS, 70 °C) at various initiator (benzoyl peroxide) concentrations

TEM of prevulcanised latex particles embedded in a PS matrix

A specimen for morphological study of sulphur-prevulcanised NR particles was obtained after polymerising the styrene containing 3% w/w of transferred NR at 70 °C for 16 h with 1% of BPO. Direct evidence of the actual sulphur-cross-linked particle structure obtained in the TEM micrographs with two magnifications (20,000 and 40,000) is presented in Fig. 6a and b, while that of peroxide-prevulcanised latex particles is shown in Fig. 6c and d.

All the micrographs show two-phase morphology of the rubber particles (dark) dispersed in the PS matrix (light). The broad size distribution of the cross-linked particles is clearly evident. Their elliptical shape is probably considered to be an artefact of the sectioning

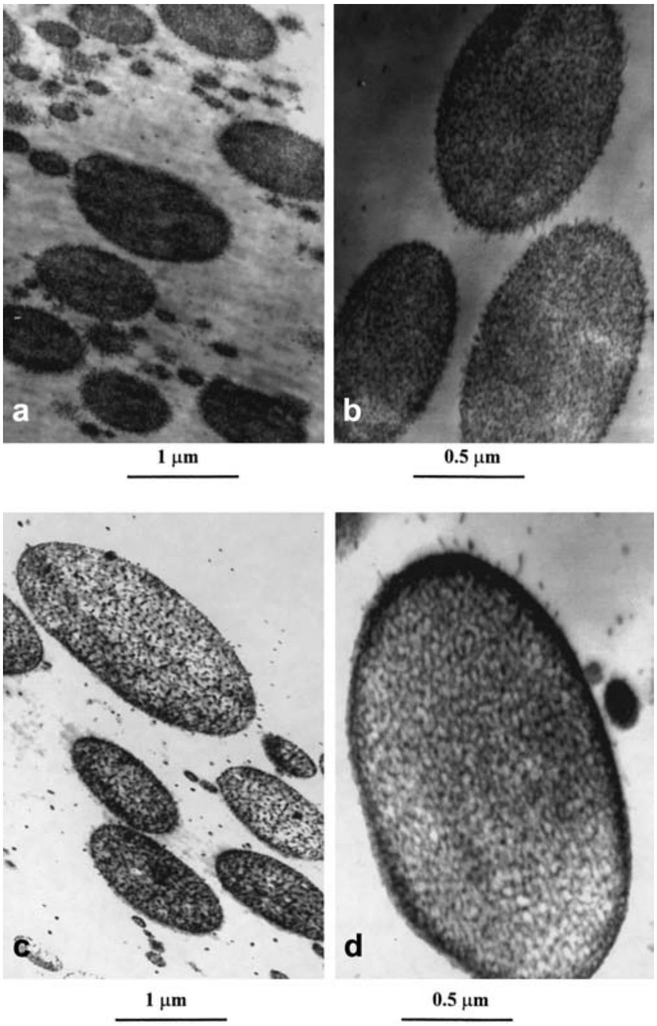

Fig. 6 Transmission electron microscope micrographs of cross-linked NR embedded in a polystyrene matrix: **a**, **b** sulphur-prevulcanised and **c**, **d** peroxide-prevulcanised latex particles

process as mentioned in earlier work [3, 4, 5, 9, 10]. The mesh structure, in which the dark threads of cross-linked rubber are separated by unstained PS, is apparent inside the NR particles as previously noticed in the case of the RVNR latex [3, 4, 5]. This structure may arise from the polymerisation of styrene absorbed in cross-linked NR [3]. During radical polymerisation, long-chain PS was produced and the PS concentration increased within 16 h. Phase separation between the two incompatible polymers took place and PS inside the rubber network forced the rubber chains to form threads. It is emphasised that the network structure was observed in all sizes of vulcanised particles [9, 10].

Since the rubber network in each sulphur-prevulcanised NR particle in Fig. 6a and b is uniform, the mechanism involving dissolution of the reactants in the aqueous phase before diffusing into the rubber particles was, therefore, favourable [9, 10]. The relative rate of diffusion of the vulcanising reagents in the rubber phase was faster than vulcanisation. The diffusion possibly took place during the maturation stage. This explanation is consistent with work previously reported [6].

The morphology of peroxide-cross-linked NR particles in Fig. 6c and d was generally similar to that of the sulphur-prevulcanised sample. However, the network of rubber chains in each particle was not homogeneous, i.e., a dense network was observed near the particle surface compared to that of the central region. A difference in the cross-link distribution in peroxide-prevulcanised rubber particles from sulphur- and radiation-prevulcanised rubber particles was also observed in the morphological study of latex films [9, 10]. It was explained that the inhomogeneous nature of the cross-linking in NR latex particles prevulcanised by using the *t*-BuHP/fructose system resulted from the dissolution of vulcanising ingredients in the aqueous serum of the latex [9, 10, 24]. Consequently, the alkoxy radicals generated in the aqueous phase reacted first with the rubber molecules on the surface of the latex particles followed by abstraction of hydrogen atoms to produce rubber radicals which readily combined to form cross-links. Also in the reported work, the more rubber-soluble cumene hydroproxide was used in place of *t*-BuHP for the prevulcanisation and the resulting film gave the same pattern as in the case of *t*-BuHP. Therefore, it was concluded that the solubility of the peroxide in the rubber did not play a significant role. Similar explanation was also reported when a bipolar redox initiation system of *t*-BuHP/tetraethylene pentamine in conjugation with a semicontinuous process was used in the preparation of NR-based core–shell particles [25].

Conclusions

The phase-transfer/bulk polymerisation/TEM technique was successfully applied to the study of the cross-link distribution in sulphur- and peroxide-prevulcanised NR latex particles. The network of NR chains in each sulphur-cross-linked rubber particle, irrespective of size, was uniform, indicating that the relative rate of diffusion of vulcanising agents dissolved in the rubber phase was faster than vulcanisation. In the peroxide-cured latex, a nonuniform network structure inside each rubber particle, i.e., a dense network near the particle surface compared to that in the central region of particle, was noticed.

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References

1. Varkey JT, Rao SS, Thomas S (1996) J Appl Polym Sci 62:2169
2. Claramma NM, Mathew NM (1997) J Appl Polym Sci 65:1913
3. Tangboriboonrat P, Tiyapiboonchaiya C (1999) J Appl Polym Sci 71:1333
4. Tangboriboonrat P, Tiyapiboonchaiya C, Lerthititrakul C (1998) Polym Bull 41:601
5. Tangboriboonrat P, Tanunchai T, Tiyapiboonchaiya C (1999) Plast Rubber Compos 25:357
6. Porter M, Rawi R, Rahim SA (1992) J Nat Rubber Res 7:85
7. Blackley DC (1997) Polymer latices; science and technology, 2nd edn. Chapman & Hall, London, pp 441–507
8. Ho CC, Khew MC (1999) Langmuir 15:6208
9. Cudby PEF, Davies RT (1997) J Nat Rubber Res 12:67
10. Cook S, Cudby PEF, Davies RT, Morris MD (1997) Rubber Chem Technol 70:549
11. Baharin BA, Pun MY, Ahmad M, Mohd Y, Mohd NZA (1993) In: Aziz A, Kadir SA (eds) Natural rubber current developments in product manufacture and applications. Cetaktama Sdn Bhd, Malaysia, pp 440–447
12. Pendle TD (1997) Plast Rubber Compos Proc Appl 26:147
13. Gazeley KF, Gorton ADT, Pendle TD (1988) In: Roberts AD (ed) Natural rubber science and technology. Oxford University Press, Oxford, pp 63–98
14. Blackley DC (1987) In: Mark HF, Bikaks NM, Overberger CG (eds) Encyclopedia of polymer science and engineering, vol 8, 2nd edn. Wiley, Canada, pp 647–677
15. Gorton ADT, Pendle TD (1981) Nat Rubber Technol 12:1
16. Won g NP, Loo CT (1985) Proceeding of the international rubber conference Kuala Lumpur, Malaysia, pp 487–501

17. Gorton ADT (1978) International polymer latex conference, London, p 11/1
18. Gorton ADT, Pendle TD (1976) Nat Rubber Technol 7:77
19. Blackley DC (1981) In: Bassett DR, Hamielec AE (eds) Emulsion polymers and emulsion polymerization. ACS symposium series 165. American Chemical Society, Washington, DC, pp 171–188
20. Blackley DC, Haynes AC (1981) Plast Rubber Proc Appl 1:73
21. Blackley DC, Aisah AAN, Twaits R (1979) Plast Rubber Mater Appl May:77
22. Othman AB, Hepburn C, Hasma H (1993) Plast Rubber Proc Appl 19:185
23. Tangboriboonrat P, Suchiva K, Kuhakarn S, Tuchida P (1996) J Nat Rubber Res 11: 26
24. Said MM, Pendle TD, Blackley DC (1990) J Nat Rubber Res 5:27
25. Schneider M, Pith T, Lambla M (1996) J Appl Polym Sci 62:273