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SHORT COMMUNICATION

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Morphology of peroxide-prevulcanised natural rubber latex: effect of reaction time and deproteinisation

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Abstract A non-uniform mesh structure, i.e. a dense network near the surface of peroxide-prevulcanised natural rubber latex particles, was observed under transmission electron microscopy. In the initial period of prevulcanisation, the swelling ratio of the latex sheet decreased with longer reaction time while an increase in crosslink density of rubber particles containing polystyrene, prepared using the phase transfer/bulk polymerisation process, was noticed. The modulus of the rubber sheet increased up to maximum crosslinking and thereafter decreased. After removal of proteins from the latex membrane layer, derived from protein-lipid originally existing at the rubber particle surface, could not be detected. The absence of proteins, which act as free radical scavengers, resulted in a rapid diffusion of alkoxy radicals into the rubber phase of deproteinised latex and, therefore, a uniform crosslink distribution inside each particle was obtained.

Keywords Peroxide prevulcanisation · Natural rubber latex · Morphology

Introduction

Prevulcanisation involves heating raw natural rubber (NR) latex with vulcanising ingredients for initial crosslinking within rubber particles. Drying of the prevulcanised latex produces a crosslinked film without any need of further vulcanisation and, thus, the physical properties of the final product can be controlled by the design of crosslinks in the latex particles during prevulcanisation. Results from several studies revealed that the rate and extent of prevulcanisation within each latex particle, depending on the vulcanisation system, greatly affect the film's physical properties [1, 2, 3, 4, 5]. The prevulcanised latex film obtained from fusion of homogeneous crosslinked particles is superior in properties, whereas a coherent film is not achieved if the particles are highly crosslinked near their surface.

Normally, NR latex is prevulcanised by systems based on sulphur, γ-radiation or peroxide. The former is commonly used in industry, although the morphology of sulphur-prevulcanised particles deduced from the examination of films is still controversial [6, 7, 8, 9, 10]. The investigations of γ-radiation and peroxide prevulcanisations of NR latex are developed to avoid the presence of carcinogenic nitrosamines, and the –C–C– resulting from both systems gives rise to better compression set and heat stability values than the –S–S– from the sulphur system [11, 12]. Previous work on prevulcanised NR film indicated the non-uniform crosslink distribution in fructose-activated hydroperoxide-prevulcanised particles, which was significantly different from that in the sulphur and γ-radiation systems [9, 10]. Since the morphology of crosslinked NR particles might not relate to the data interpreted from film studies due to postvulcanisation, the phase transfer/bulk polymerisation/transmission electron microscopy (TEM) technique has been applied to investigate the actual crosslink distribution in particles [13]. In this technique, the negatively charged crosslinked particle is titrated with a cationic surfactant in the presence of styrene. After polymerising the styrene-containing swollen rubber particles, the crosslinked rubber embedded in rigid polystyrene (PS) can be sectioned for the TEM study. The micrographs obtained by this method showed a dense network near the particle surface of peroxide-prevulcanised latex particles which was different from the homogeneous distribution observed in the case of sulphur and γ-radiation. A mechanism based on dissolution of vulcanising ingredients (*tert*-butyl hydroperoxide; *t*-BuHP/fructose) in the aqueous serum of latex and the migration of generated radicals into the particles was mentioned [9, 10, 13]. However, this hypothesis is in need of additional evidence. The effects of prevulcanisation time and removal of proteins on the morphology of peroxide-prevulcanised rubber particles were, therefore, investigated in this present work. This was due to the assumption that the time needed for diffusion of alkoxy radicals generated from *t*-BuHP/fructose into the rubber phase and the proteins which act as free radical scavengers could affect the level of network structure in each particle and, hence, the film properties [14, 15]. The modulus and swelling ratio of rubber sheet cast from the peroxide latex prevulcanised at various times were also determined.

Experimental

Preparation of deproteinised natural rubber (DPNR) latex [16]

Commercial high ammonia (HA)-preserved NR latex concentrate (Rayong Bangkok Rubber Co. Ltd., Thailand) (60% dry rubber content (DRC)) was diluted with distilled water to 30% DRC. The latex was filtered through a 250-mesh aluminium screen and stabilised with aqueous sodium dodecyl sulphate (SDS; Fluka, GC) solution (1% by weight of DRC). The stabilised latex (pH~9, without any adjustment) was allowed to react with various concentrations (0.01, 0.02 or 0.04% w/v) of alcalase enzyme (Novo Industries) at 37 °C for 24 h before filtering. The mixture was centrifuged with a Supraspeed Centrifugation (J2-MC; Beckman Coulter) at 12,000 rpm for 15 min after which the lower serum layer was replaced by an equal volume of aqueous solution of SDS. The process was repeated twice and the DPNR-01, DPNR-02 and DPNR-04 latexes obtained were kept at room temperature for further use. The control NR or DPNR-00 latex was prepared employing the above procedure, except omitting the enzyme.

Nitrogen content (%N) of the dried film, cast from DPNR latex on a Petri dish at 60 °C for 24 h, was determined by using the Kjeldahl method as described in ASTM D 3533–90.

Preparation and characterisation of peroxide-prevulcanised rubber

NR or DPNR latex was filtered through a 250-mesh aluminium screen and charged in a reaction vessel equipped with a condenser and a thermometer. *t*-BuHP (Fluka, Purum) (0.75 pphr; parts per hundred of rubber) mixed with distilled water (11.2 g) and SDS solution (0.75 pphr) was poured, while stirring, into the latex at room temperature. d-(−)-Fructose solution (25%; Fluka, Bacteriology) (5.1 pphr) and water (11.2 g) were then added to the mixture prior to heating at 60 °C. During prevulcanisation, aliquots were taken at time intervals, rapidly cooled down to room temperature to prevent further vulcanisation and dried on a Petri dish or kept as latex in a dark cabinet at room temperature.

The dried rubber sheet was cut into a square piece of known weight (~0.2 g) and its crosslink density was then determined by immersing in toluene (Fluka, Commercial) (40 mL) to equilibrium swell. The swelling ratio of the rubber was calculated as previously described [13, 16].

FTIR-ATR spectra of the film–air interface were recorded on a single-beam spectrometer (EQUINOX 55, Bruker) and 64 scans at 4 cm^{-1} resolution were collected. Horizontal ATR spectra were obtained using a ZnSe crystal with an incident beam angle of 45°.

Preparation of sample for morphological study

The phase transfer technique 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 (BHAC; Fluka, Purum). The remaining steps for incorporating rubber particles in PS by bulk polymerisation were conducted as described in previous works [13, 17, 18]. A micrograph of crosslinked rubber particles embedded in PS after being stained with osmium tetroxide vapour ($\mathrm{OsO_4}$, Electron Microscopy Sciences) was obtained using transmission electron microscopy (TEM; H-300; Hitachi).

Tensile testing

Dried rubber sheet was prepared by casting the prevulcanised NR latex on a glass plate at room temperature. Tensile test pieces were punched out from the rubber sheet using a dumb-bell die (Wallace c-90023/27). The test was carried out according to ASTM D412 using a Testing Machine (Instron 4301). The 100, 300 and 500% moduli were determined and ten specimens were used for each measurement.

Results and discussion

Effect of prevulcanisation time on the morphology of NR latex particles

TEM micrographs of NR particles prevulcanised by using *t*-BuHP/fructose for a duration of 0.5, 1, 3 and 5 h are presented in Fig. 1a–d, respectively.

The micrographs reveal the two-phase morphology of the rubber particles (dark) dispersed in PS matrix (light). The natural polydispersity in the size of NR particles was clearly observed and their elliptical shape is considered to be an artefact of the sectioning process as mentioned in the earlier works [9, 10, 13]. The mesh structure showed dark threads of crosslinked rubber separated by unstained PS in all sizes of prevulcanised particles [9, 10]. It was also important to indicate the observable dark layer, possibly derived from protein–lipid complex, surrounding each NR particle [16, 18].

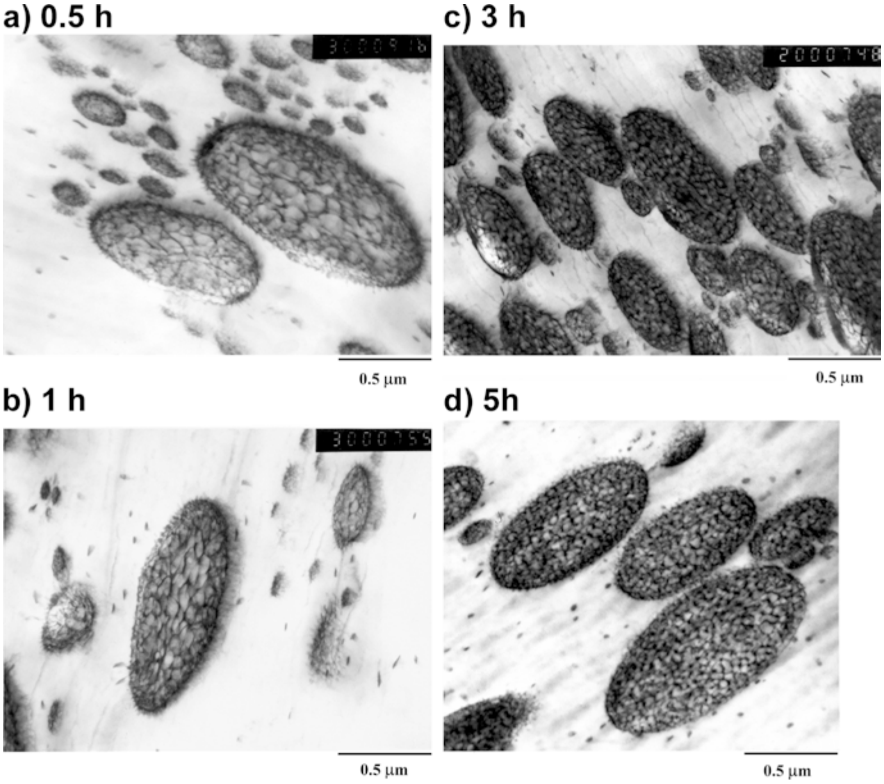

Fig. 1 TEM micrographs of NR particles embedded in PS matrix, using latex prevulcanised by peroxide for **a** 0.5 h, **b** 1 h **c** 3 h and **d** 5 h

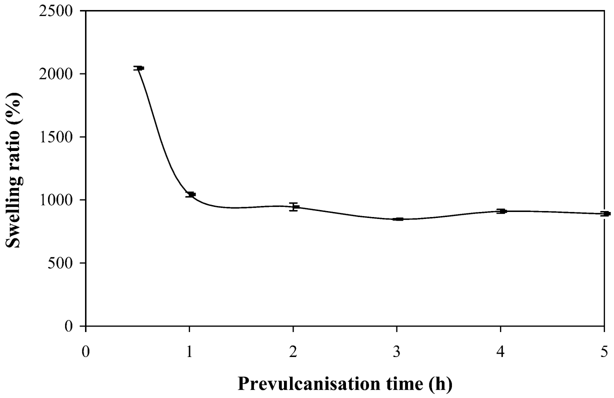

Fig. 2 Effect of prevulcanisation time on swelling ratio of rubber sheet prepared from peroxide-prevulcanised NR latex

As noticed in the previous study, the network structure in each NR particle was not homogeneous, i.e. a dense network near the particle surface as compared to that of the central region [13]. It has been described that the alkoxy radicals formed in the serum reacted first with the rubber molecules on the particle surface, followed by production of rubber radicals which readily combined to form crosslinks [9, 13]. This explanation is additionally supported by the direct evidence of rubber particles presented in Fig. 1, in which more crosslink density within each particle was obtained when the prevulcanisation time was increased. This morphology was due to the fact that crosslinking took place before the alkoxy radicals or rubber radicals could diffuse very far into the rubber particles. However, the change in density was not clearly observed after 3 h of prevulcanisation. The data agreed well with the percentage swelling ratio of peroxide-prevulcanised NR sheet, which rapidly decreased with increasing reaction time and then approached a constant value as presented in Fig. 2.

Modulus of prevulcanised NR latex sheet

Figure 3 shows the modulus at 100, 300 and 500% elongation of rubber sheets cast from latex prevulcanised at various reaction times. As the prevulcanisation time was increased (until about 2 h) the modulus significantly increased, then levelled off afterwards. Since the modulus values can be used as an estimation for the extent of the apparent crosslinking in the latex films, its increase to a maximum could be due to the increase in crosslink density of rubber [2, 3, 4, 5]. By increasing prevulcanisation time the rubber particles became more crosslinked, as shown in Figs. 1 and 2, and hence, became harder. The denser and shorter network chains in the crosslinked particles with longer prevulcanisation could be used to explain cases of poor film forming, resulting in a decrease of modulus value after 2 h duration. The lower modulus the films may be attributed to low interparticle fusion of peroxide-prevulcanised

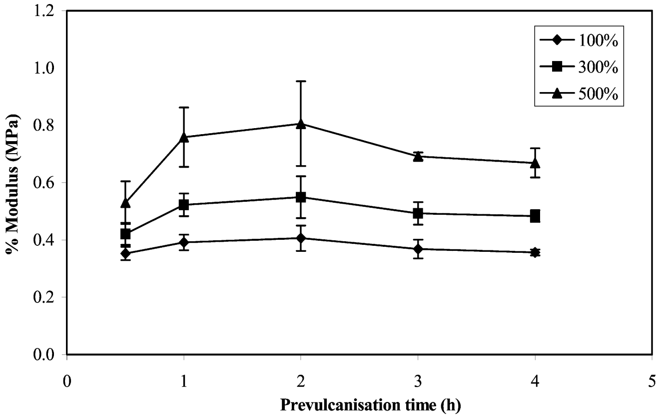

Fig. 3 Effect of prevulcanisation time on modulus of rubber sheet prepared from peroxide-prevulcanised NR latex

latex particles which have highly crosslinked near the surface, i.e. the particles did not fuse well to provide a coherent film due to the restricted mobility of the rubber chains at their surface. The increase in surface hardness of the latex particles with prevulcanisation time would also reduce the ability of particles to coalesce among themselves [2, 3, 4, 5].

Morphology of prevulcanised DPNR latex particles

TEM micrographs of DPNR-00, DPNR-01, DPNR-02 and DPNR-04 latex particles, prevulcanised for 8 h, embedded in PS matrix are presented in Fig. 4a–d, respectively.

The morphology of peroxide-crosslinked DPNR particles in Fig. 4 was generally similar to that of the prevulcanised NR sample in Fig. 1. However, the crosslink distribution of rubber chains in each DPNR particle was more homogeneous than that in NR. It could be explained that the rate of diffusion of alkoxy radicals into the rubber phase was greater than the vulcanisation. The absence of membrane consisting of protein–lipid might be responsible for the rapid diffusion of radicals into the DPNR particle and uniform network distribution in each particle. It is known that non-rubber substances in NR can act as an inhibitor in a free radical polymerisation reaction [14]. The role played by the protein–lipid surrounding rubber particles on relatively low conversion in NR was reported when the in situ polymerisation of styrene in NR and DPNR latex particles was investigated. A similar observation was also reported in the graft copolymerisation of both latexes with methyl methacrylate (MMA) using *t*-BuHP/tetraethylene pentamine (TEPA) as a redox initiating system [15]. It was believed that the indigenous proteins in NR reacted with free radicals or acted as free radical scavengers, resulting in retardation of polymerisation and termination during the grafting reaction. However, the effect of nitrogen content remaining in DPNR, shown in Table 1, on the crosslink distribution in the particles was insignificant. An explanation could be put forward, that the removal of a large proportion of the proteins caused a broken membrane at the DPNR particle surface [16]. The alkoxy radicals could, therefore, diffuse from the aqueous phase into the rubber phase within the DPNR particle through the small voids left on the membrane,

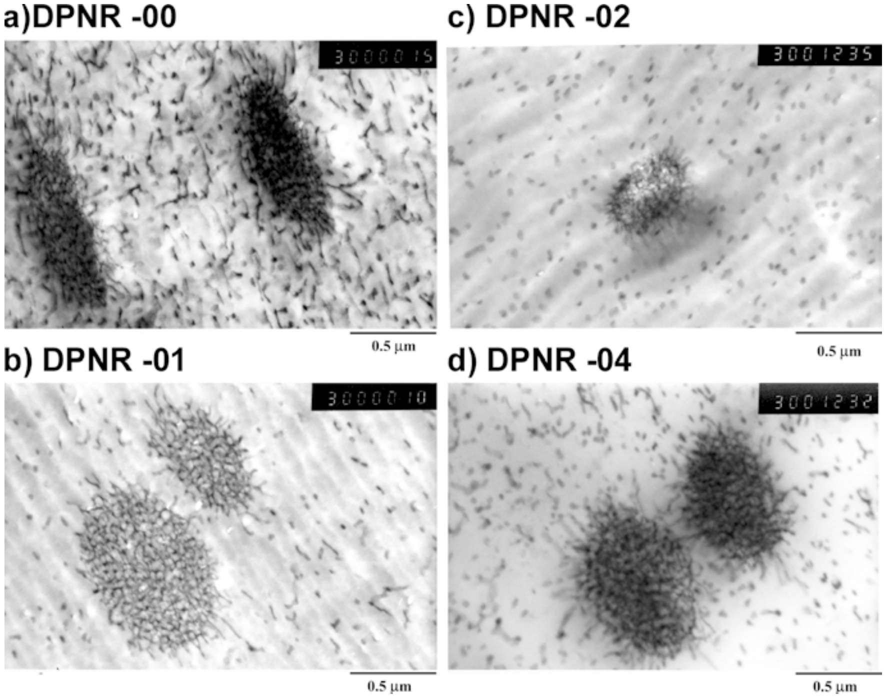

Fig. 4 TEM micrographs of prevulcanised DPNR latex particles embedded in PS matrix **a** DPNR-00 (multicentrifugation without adding enzyme), **b** DPNR-01 (0.01% enzyme), **c** DPNR-02 (0.02% enzyme) and **d** DPNR-04 (0.04% enzyme)

Table 1 Nitrogen content of dried rubber samples prepared from NR or DPNR latex (DPNR-00, multicentrifuged latex without adding enzyme; DPNR-01 using 0.01% enzyme; DPNR-02 using 0.02% enzyme; and DPNR-04 using 0.04% enzyme)

Sample prepared from latex	Nitrogen content (%)
NR	0.470 ± 0.012
DPNR-00	0.086 ± 0.009
DPNR-01	0.044 ± 0.002
DPNR-02	0.041 ± 0.003
DPNR-04	0.036 ± 0.001

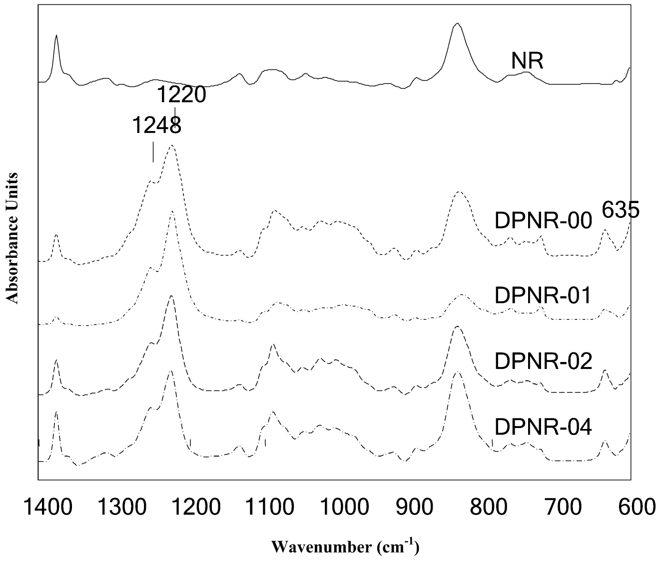

Fig. 5 IR spectra of peroxide-prevulcanised NR and DPNR latex films

despite of the existence of SDS. It was of interest to emphasise that the SDS added in peroxide-prevulcanised NR latex did not affect the crosslink density or swelling ratio of prevulcanised latex sheet [13]. However, the presence of SDS might be responsible for the brittle, cracked and undetachable sheet formed from the DPNR latex [19]. IR spectra of the DPNR film surface in Fig. 5 show absorption peaks at 1248 and 1220 cm^{-1} corresponding to asymmetric stretching of S–O (SO_4) and at 635 cm^{-1} corresponding to the deformation of sulfate (SO_4) groups [20].

Conclusions

Evidence of a non-uniform network structure inside each peroxide-prevulcanised NR latex particle, i.e. a dense network near the surface when compared to that at the central region of the particle, irrespective of size, was clearly demonstrated. The crosslink density in each particle varied with reaction time, indicating that the rate of diffusion of vulcanising agents dissolving in the aqueous phase affected vulcanisation within the particle and, consequently, the film's modulus. Removal of proteins accelerated the diffusion rate of radicals and produced a uniform crosslink density in each rubber particle.

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