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ORIGINAL CONTRIBUTION

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Prevulcanisation of skim latex: morphology and its use in natural rubber based composite material

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Abstract The prevulcanisation of skim latex, a by-product of field natural rubber (NR) latex concentrated by centrifugation, using sulphur and peroxide systems was investigated. Compared to the peroxide prevulcanisation, the lower swelling ratio of film casted from sulphur-prevulcanised skim (SPVS) latex was observed. The latter was then employed for preparation of NR/SPVS core–shell particles by using heterocoagulation technique whose driving force was an interpolymer complex between poly(ethylene oxide) (PEO) moieties of a non-ionic surfactant (Nonidet) adsorbed on small SPVS particles and the indigenous surfactant (protein–lipid) on a large NR particle. The value of zeta potential of heterocoagulated particle and the better oil resistance of films casted from the composite latex when compared to that of the NR film revealed the NR/SPVS core–shell structure.

Keywords Heterocoagulation · Vulcanisation · Natural rubber latex · Composites

Introduction

It is well known that the commercial high-ammonia (HA) natural rubber (NR) latex concentrate can be produced by centrifugation of field NR latex tapped from the rubber tree, *Hevea Brasiliensis*. By applying this process, most of the non-rubbers solids, about two-thirds of the water-soluble non-rubbers and small NR particles or skim rubber are removed [1, 2]. While the surface-active species or indigenous surfactants (derived from protein–lipid) remain in the serum and/or on the rubber particles in the concentrate fraction. However, the skim rubber has always been discarded and has not received much attention due to the high ratio of aqueous phase in the latex. Previous study reported that the skim latex contained about 7% total solid content (TSC) and 5% dry rubber content (DRC) [3]. From photon correlation spectroscopy measurement, a broad peak with a shoulder was observed. Investigation of the peak having high intensity showed that it contained small particle size with an average diameter of 124 nm. Although skim rubber was studied for its use as an urea encapsulant in the controlled release application, a better understanding of the properties of skim particle is still needed in order to facilitate its recovery and to explore other potential use. Recently, atomic force microscopy (AFM) and scanning electric potential microscopy (SEPM) have been applied to elucidate the ‘‘self-cleaned’’; skim rubber [2]. From particle volume obtained in the AFM images, its bimodal particle size distribution was observed and the calculated particle diameter of a primary population was found to be about 200 nm.

Owing to its small particle size, skim rubber would be a good choice for use as an agglomerating latex in the heterocoagulation process which involves agglomeration of small particles onto a large core particle [4–6]. This technique generally offers the possibility of a better control for certain composite latex particle morphology, especially the core–shell type. One of the advantages of this approach is that many different monomer pairs can be prepared, even in the case of hydrophilic core and hydrophobic shell latex particle. In addition, the driving force for the interaction between core and shell particles could be a controlled electrostatically driven heterocoagulation or hydrophobic interaction principle [7, 8]. An interpolymer complex principle was also successfully applied to prepare the heterocoagulated NR/polychloroprene (CR) with core–shell structure [9, 10]. In the latter case, a non-ionic surfactant (Tween 80) whose molecule bares poly(ethylene oxide) (PEO) moieties was adsorbed on CR latex particles and allowed to form complex between PEO and indigenous surfactant (protein–lipid) on the NR particle surface. Due to the low glass transition temperature (T_g), the NR/CR core–shell particle was obtained without annealing the aggregate at high temperature. The presence of Tween 80 in the outermost layer of composite particles proved by the decrease of the absolute value of the zeta potential when compared to that of the core NR particle indicated that CR acted as the agglomerating particles. Better oil resistance of film casted from heterocoagulated latex than that of NR film also confirmed the role of high polar CR, the agglomerating latex or shell layer. The study of replacing CR by skim NR latex, naturally abundant and low cost products, in the heterocoagulation technique was, therefore, of great interest. To improve oil resistant property, prevulcanisation was the minimum requirement for skim rubber modification. Since prevulcanisation involves initial crosslinking within the rubber particle and drying of the prevulcanised latex produces a crosslinked film without any need of further vulcanisation, physical properties of the final product can be controlled by the design of crosslink in latex particle [11, 12]. Similar to the case of HA–NR latex, the γ-radiation, sulphur or peroxide system would be suitable for use to prepare prevulcanised skim latex. To interprete the actual crosslinking in prevulcanised latex particles, the phase transfer/bulk polymerisation/transmission electron microscopy (TEM) technique has been successfully applied to provide a direct evidence of the morphology of the prevulcanised NR [10–13] and also skim particles vulcanised by irradiation with γ-ray [3]. The micrograph of γ-radiation vulcanised skim particles embedded in polystyrene (PS) matrix revealed a mesh-like structure of fine rubber-PS particle surrounded by membrane layer. However, from the economic point of view, the γ-radiation method has not been widely used in industry. In this present study, prevulcanisation of skim latex was, therefore, performed by using sulphur or peroxide system. The prevulcanised skim latex having high degree of crosslinking and homogeneous crosslink structure was then selected for further use in the preparation of composite latex particle of NR/prevulcanised skim rubber by heterocoagulation technique. The existence of non-ionic surfactant on prevulcanised skim rubber particles, the shell layer of heterocoagulated particles produced by various compositions, was characterised by zeta potential measurement [9]. Swelling ratios of the films, casted from the composite, unmodified NR and the prevulcanised skim latices, in a hydrophobic liquid were also investigated.

Experimental

Latices and their characterisations

Total solid content (%TSC) of HA–NR and skim rubber latices (Rayong Bangkok Rubber Co., Thailand) were determined by using the method described in ASTM D1076:1988. To determine the amount of dry rubber content (%DRC), 5% acetic acid and distilled acetone were respectively used to coagulate HA–NR and skim rubber [3].

Particle size distribution of HA–NR latex was measured by using a particle size analyser (Mastersizer S, Malvern) while photon correlation spectroscopy (Coulter N4, Coutronics) was used in the case of skim latex. The zeta potential values of all latices were measured by using a microelectrophoresis apparatus (Zetasizer 4, Malvern) at 30°C after adjusting the pH by addition of an aqueous solution (0.1 M) of hydrochloric acid (Merck, GR) or sodium hydroxide (Merck, GR). Nitrogen content of the skim rubber, coagulated with distilled acetone and then dried at 50°C, was determined using a CHN elemental analyser (2400 CHN, Perkin Elmer).

Preparation of sulphur-prevulcanised skim (SPVS) latex

Fifty percent of aqueous dispersions of vulcanising ingredients, i.e. sulphur (S; EMCO Intertrade Co., commercial), zinc diethyldithiocarbamate (ZDEC; EMCO Intertrade Co., commercial) and zinc oxide (ZnO; Global Chemical Co., commercial) were prepared by thoroughly ground with ball-milling for 72 h.

Skim latex (5% DRC) was filtered though a 250-mesh aluminium screen before charging in a reaction vessel equipped with a condenser and a thermometer. Then, an antibacterial agent, 2,2′-dimethylenebis(4-chlorophenol, 0.11 g) (Aldrich, technical) and 50% aqueous dispersions of S (0.25 g), ZDEC (0.2 g) and ZnO (0.05 g) were respectively added into the latex stabilised with 10% of potassium hydroxide solution (Merck, general reagent, 0.4 g) and 25% of sodium dodecyl sulphate solution (Fluka, gel permeation chromatography, 0.08 g) at room temperature under continuous stirring at 200 ± 20 rpm for 30 min [12, 14]. The mixture was kept for 2 h in a dark cabinet for maturing before being heated at 60°C. During that period, portions (about 30 g) of prevulcanised latex were taken at time intervals and then dried on a petridish coated with Teflon. The swelling ratio of latex film in toluene was determined as described elsewhere [15]. At the end of the reaction, the prevulcanised latex was rapidly cooled to room temperature to prevent further vulcanisation.

Preparation of peroxide-prevulcanised skim (PPVS) latex

A peroxide emulsion was firstly prepared by mixing *tert*-butyl hydroperoxide (*t*-BuHP; Fluka, purum, 0.125 g) with distilled water (1.12 g). The emulsion was then added, while stirring, to the skim latex stabilised with 2,2′-dimethylenebis(4-chlorophenol) at room temperature. D(-)-fructose solution (25%; Fluka, bacteriology; 0.85 g) was then added, followed by water (1.12 g) before carrying out the reaction at 60°C [12, 16]. The remaining steps were conducted in the same manner as previously employed in the case of sulphur prevulcanisation.

Preparation of the sample for morphological study

The phase transfer technique, described in our previous works [11–13, 15], was applied to transfer prevulcanised latex particles (1% TSC, 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). The remaining trace of water in the styrene monomer, containing swollen transferred rubber particles, was eliminated by centrifuging. The upper styrene phase was isolated and then mixed with 0.6 wt% of benzoyl peroxide (BPO; Sigma, microscope) before pouring into a Teflon coated steel mould (10.4×10.4×2.6 cm^3) and polymerised at 70°C in an oven (400 UM, Memmert) for 16 h.

Specimen of the skim particles incorporated in the PS matrix was finely trimmed and sectioned under a microtome. The micrograph of rubber particles embedded in PS after being stained with osmium tetroxide vapour (Electron Microscopy Sciences) was obtained using a transmission electron microscope (TEM-1230, JEOL).

Adsorption of non-ionic surfactant on SPVS latex particles

The SPVS latex having 9.9% TSC was diluted with deionised water to 1% TSC. Nonidet (Fluka, biochemika) (1–6% by weight of dry SPVS latex) was then added into the diluted latex (50 g) before shaking (Burell) for 12 h at room temperature. The amount of Nonidet adsorbed on the rubber particle was deduced from the quantity of an aqueous solution of calcium chloride (0.5 M; $CaCl_2$; Merck, GR) added to provoke visible coagula.

Preparation of heterocoagulated SPVS and NR particles

Nonidet (6% by weight of dry latex) was used for adsorption onto SPVS particle surface. A known amount of the SPVS-Nonidet latex (1% TSC) was mixed with NR latex (1% TSC, 10 g) at pH 2 in an Erlenmeyer flask at room temperature. The blending ratio was calculated from the theoretical number ($N_{\max}$) of shell particles required to form a closely packed particulate monolayer on a core particle from the following equation [4, 5, 9]:

$$N_{\max} = \frac{2\pi}{\sqrt{3}}\left[\frac{\mathrm{R_c} + \mathrm{R_s}}{\mathrm{R_s}}\right]^2,$$

where R_c and R_s are the radii of core (NR) and shell (SPVS) particles, respectively. The ratios of NR to SPVS particles in the latex blend were varied from $N_{\max}/8$, $N_{\max}/4$, $N_{\max}/2$, $N_{\max}$ to $2N_{\max}$.

Resistance of the latex film to a hydrophobic liquid was determined by immersion of a known weight of rubber sheet (ca. 0.05 g) in toluene (50 mL) at room temperature for 22 h.

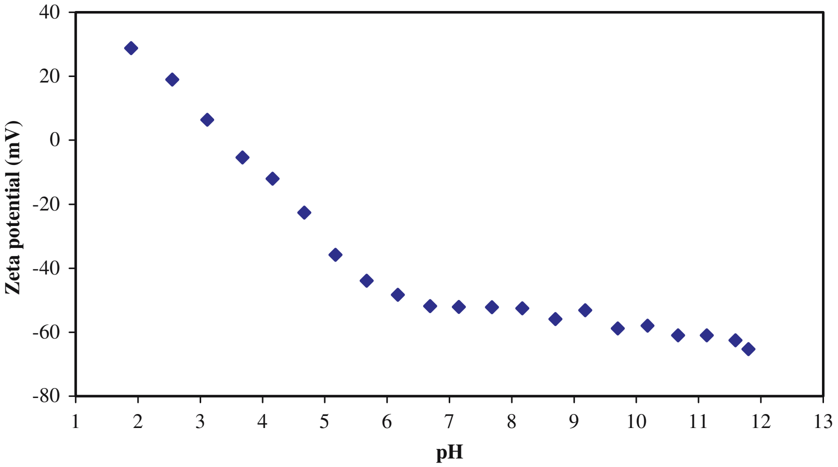
Results and discussion

General characteristics of latices

Some important characteristics of NR and skim latex particles were reported in our previous works [3, 9–13, 15, 17]. In this study, the broad particle size distribution of NR ranging from 0.2 μm to 1.8 μm with an average particle diameter 0.75 μm and its zeta potential values, respectively at pHs 7 and 10, of −75.5 and −86.4 mV were confirmed. For the skim rubber, its average diameter was 134 nm and their zeta potential values at various pHs are shown in Fig. 1.

Similar to NR, the results indicated amphoteric characteristic of the skim particle with an isoelectric point (pI) at about pH 3.4. The skim rubber particle possessed a positive charge when the pH was below 3.4. Above this pH, the value of the zeta potential was negative and changes rapidly with increasing pH. At pH greater than 7, the zeta potential values slightly changed indicating a complete ionisation of the ionogenic groupings [18, 19]. This amphoteric character confirmed the presence of amino acid moieties on the surface of skim latex particle [15]. The protein content, calculated from the nitrogen content (3.53 ± 0.01%), of the skim rubber was 22.1 ± 0.1%. However, the values obtained for the pI did not fall within the normal range of protein (4.0–6.0) [19] indicating that there was a preponderance of negative groups over positive groups on the particle surface. It was not unreasonable to assume that in

Fig. 1 Zeta potential of skim latex versus pH



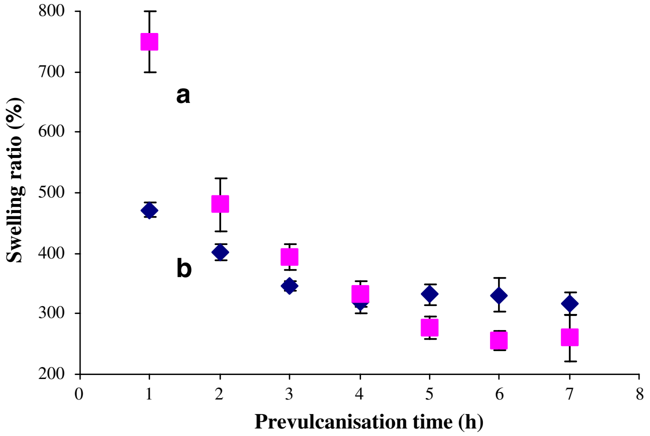


Fig. 2 Swelling ratios of **a** sulphur- and **b** peroxide-prevulcanised skim latex sheets

addition to proteins, fatty acids were also present on the skim particle surface [18–20].

Swelling ratio of SPVS and PPVS latex sheets

The values of swelling ratio, inversely proportional to the degree of crosslinking, of dried rubber sheets casted from the sulphur- and peroxide-prevulcanised skim latices are shown in Fig. 2.

It was observed that the swelling ratios of both types of prevulcanised skim latex sheets rapidly decreased with increasing prevulcanisation time in the initial period. After 5 h, a relatively small change in the swelling ratio was found, indicating a complete vulcanisation of the rubber. Although the resemblance of two curves was noticed, the higher initial slope having lower minimum swelling ratio of SPVS film (250%), when compared to those of PPVS (330%), was significantly observed. It might be explained that the presence of amino acids, the hydrolysis product of skim latex protein, could facilitate the rate of diffusion of vulcanising reagents into the rubber phase and act as sulphur-cured activator [21, 22]. Previous works reported that small amounts of proteinaceous substances in NR latex, being surface active, resulted in an increase in curative concentrations in rubber particles [23–25]. Since the rate of diffusion of alkoxy radicals derived from *t*-BuHP/fructose system into the rubber phase was lower than that of the vulcanisation, the radicals generated in the aqueous phase reacted first with the rubber molecules on the surface of PPVS latex particles followed by abstraction of hydrogen atoms to produce rubber radicals which readily combined to form crosslinks. The high dissolution of alkoxy radicals in the initial stage resulted, therefore, in the high crosslink density and, hence, low swelling ratio of the PPVS latex film. However, with longer prevulcanisation time, the constant swelling ratio of PPVS rubber was obtained and its value was higher than that of SVPS. This might result from the effect of non-rubber substances which acted as an inhibitor in the free radical polymerisation reaction [26]. The role of protein–lipid surrounding rubber particles on relatively low conversion in NR was reported when the in situ polymerisation of styrene in NR and deproteinised (DP) NR latex particles was studied. It was believed that the indigeneous proteins in NR acted as free radical scavengers which retard polymerisation and termine the grafting reaction altogether. In the case of SPVS latex with maturation for 2 h in this present study, the effect was not clearly noticed possibly due to the fact that the vulcanising agents had enough time for thoroughly diffusing into rubber phase. After the maturation period, the crosslinking inside skim particle could take place, when heating, without retardation induced by the non-rubbers. However, the low value of less than 500% swelling ratio indicated fully crosslinked rubber in both prevulcanised skim latices [27]. The small size of skim particle or large particle surface area should also be responsible for the high degree of crosslinking.

TEM of prevulcanised skim latex particles

Specimens for morphological study of SVPS and PPVS particles were obtained after polymerising the styrene containing transferred rubber at 70°C for 16 h with 0.6 wt% BPO. Micrographs of SPVS particles in latices, crosslinked for 1, 2 and 5 h, are presented in Fig. 3a–c and that of latex prevulcanised by peroxide for 5 h is shown in Fig. 3d.

All micrographs show two-phase morphology of the skim rubber (dark) dispersed in PS matrix (light). The dark layer, possibly derived from protein–lipid complex, surrounding each individual small SPVS particles was also observed. The presence of large particle in Fig. 3b was not expected due to the fact that under the centrifugation conditions, used for preparing concentrate NR latex, particles of this size range should be in the upper cream phase [2]. Their elliptical shape in Fig. 3a, b was considered to be an artefact of the sectioning process as already mentioned in the earlier works [10–12]. In Fig. 3c, mostly spherical particle shape was observed possibly due to the hard rubber which correlated well with the complete vulcanisation within 5 h of prevulcanisation in Fig. 2. The appearance of mesh-like structure, in which the dark threads of crosslinked rubber were separated by unstained PS, inside SPVS particles was similar to that previously noticed in the γ-radiation vulcanised (RV) skim samples [3]. It was described that during bulk polymerisation, long-chain PS was produced in the crosslinked rubber and the increase in PS concentration enhanced a phase separation between the two incompatible polymers. Consequently, PS inside the rubber network forced the rubber chains to form the threads in all particles, irrespective of size. This might be

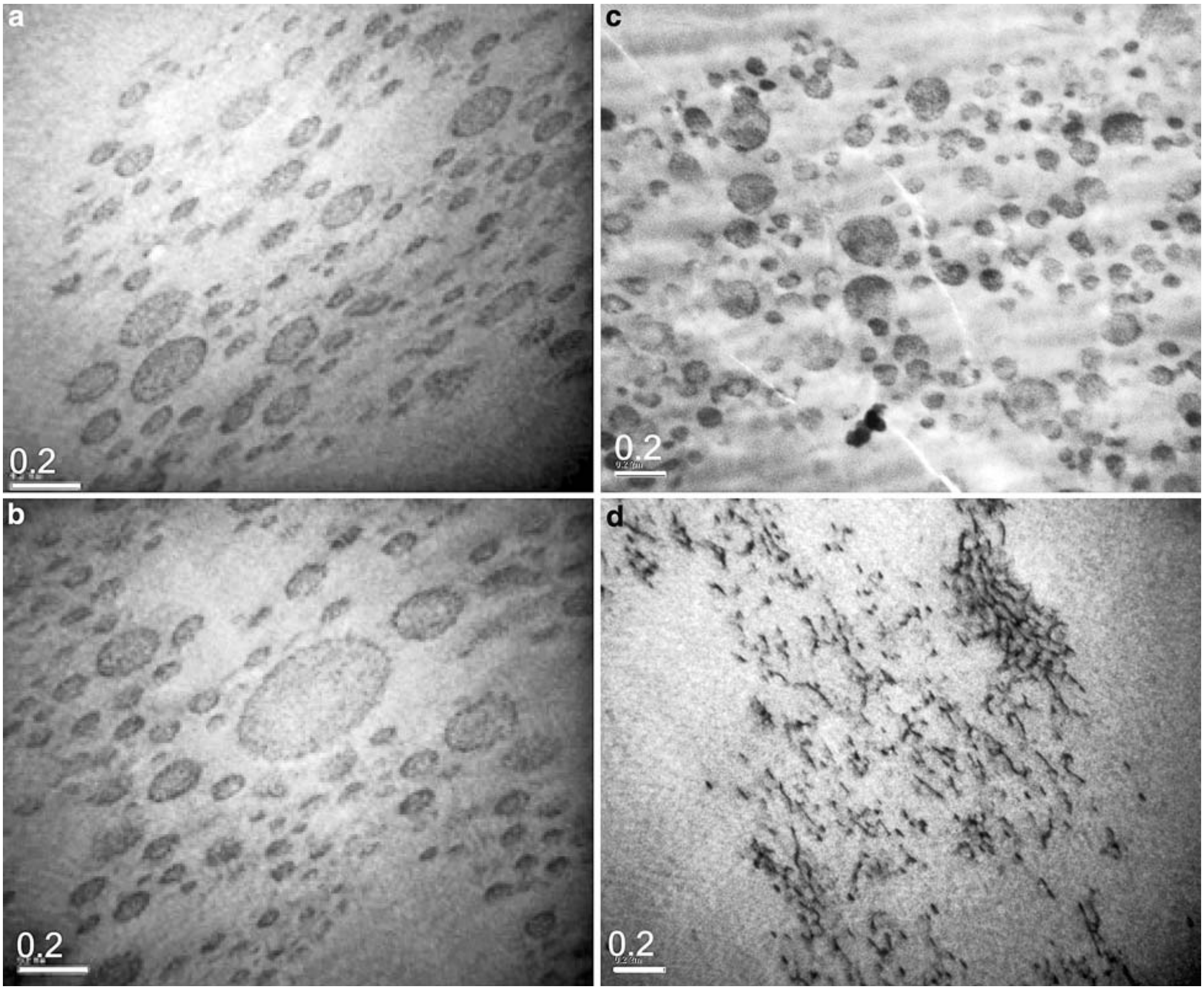


Fig. 3 TEM micrographs of skim latex particles, prevulcanised by sulphur for **a** 1 h **b** 2 h **c** 5 h and **d** that prevulcanised by peroxide for 5 h, embedded in PS matrix

also responsible for the unexpected results obtained in the case of PPVS particles, i.e. the mesh-like structure appeared mostly in the form of film as shown in Fig. 3d while the boundary of individual particle, even using prevulcanisation time of 5 h, was rarely detected. It might be explained, based on the data of morphologies of sulphur- and peroxide-prevulcanised NR in the previous works [11, 12], that the network of NR chains in each sulphur-crosslinked rubber particle was uniform whereas a dense network near the particle surface of peroxide-prevulcanised NR particle was found. Although the values of minimum swelling ratio of both prevulcanised skim latex films were not largely different, it is believed that the loosely network in the core of PPVS particles, whose size was small compared to that of NR, could be greatly swelled by styrene. Subsequently PS formed at the central region of PPVS might cause the particles' burst. Due to the uniform structure and high degree of crosslinking, skim particles prevulcanised for 5 h by the sulphur system was selected for its use in further experiments.

Heterocoagulation of NR/SPVS-Nonidet latex particles

Since at pH 2, the formation of hydrogen bonds between carboxylic groups of protein molecule on NR particle surface and PEO chains adsorbed on CR particle effectively provoked the heterocoagulation of NR and CR particles [9, 10], this method was adapted to heterocoagulate SPVS particles onto NR core particle. To check the adsorption of Nonidet whose molecule bears PEO on the skim particles, the change of stabilisation from electrostatic to steric of SPVS-Nonidet latex was detected by adding an electrolyte solution. The quantities of 0.5 M $CaCl_2$ added into the SPVS-Nonidet latex to provoke the visible coagula plotted versus concentration of Nonidet are presented in Fig. 4.

Similar to CR, the data showed that when using Nonidet less than 6%, the latex was immediately coagulated after adding $CaCl_2$ aqueous solution. On the other hand, the latex remained stable when Nonidet concentration was equal to or higher than 6%. The sensitivity to $CaCl_2$ of the latex, therefore, indicated that 6% of Nonidet was a sufficient concentration to alter the latex stabilisation from electrostatic to steric. At pH 2, PEO chains of Nonidet adsorbed on the SPVS latex particles could form the interpolymer complex via hydrogen bond with carboxylic groups of the protein molecules on the NR surface. The negative value of the zeta potential of all heterocoagulated latices (ca. −50 mV) which was not different from that of SPVS-Nonidet (−48 mV) in Fig. 5 confirmed the presence of SPVS latex particles as the outer layer of the composite particles.

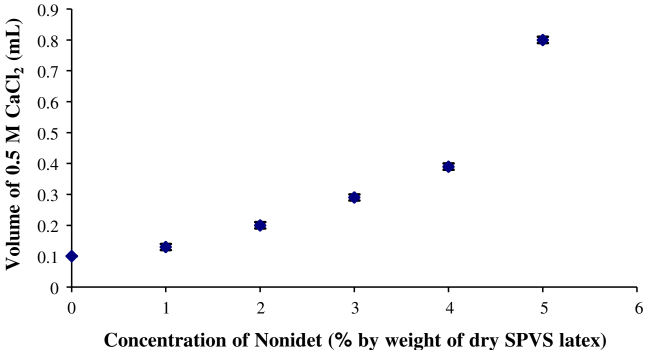


Fig. 4 Volume of 0.5 M $CaCl_2$ used for precipitating SPVS latex adsorbed by various concentrations of Nonidet

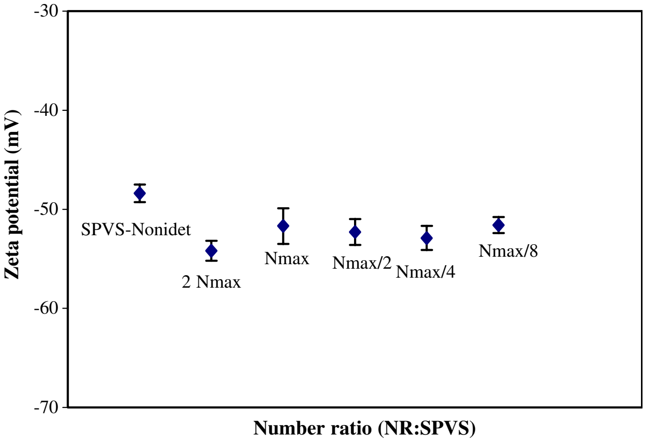


Fig. 5 Zeta potential of heterocoagulated NR/SPVS-Nonidet composite latices at various blending ratios

Moreover, the envelopment of highly crosslinked SPVS particles around NR core should cause the improvement of resistance to toluene of the film casted from the heterocoagulated NR/SPVS-Nonidet latex compared to that of NR film. The swelling ratios of the heterocoagulated NR/SPVS composite films at various blending ratios are presented in Fig. 6.

As expected, it was observed that swelling ratio of the composite latex film was greatly lower than that of NR (2370%) but significantly higher than that of SPVS-Nonidet film (425%). The improvement of oil resistant property of NR was reasonably due to the highly crosslinked SPVS shell particles surrounding the NR core. Owing to its low T_g, the SPVS latex particles could form film onto the core particle at room temperature.

Conclusions

Transmission electron microscopy provided a direct evidence of the morphology of SPVS and PPVS latex

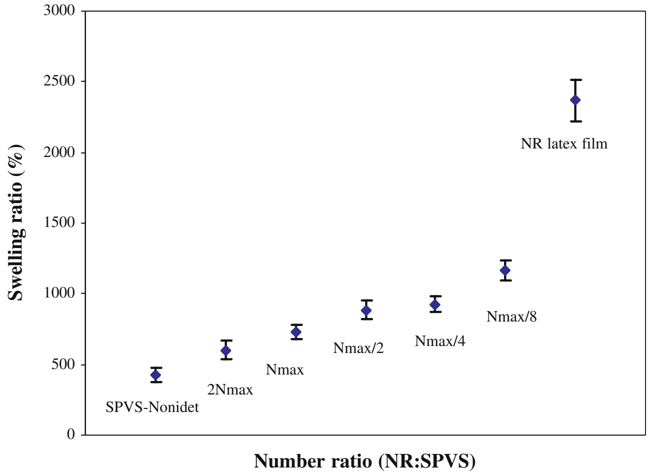


Fig. 6 Swelling ratios of films casted from NR, SPVS-Nonidet and heterocoagulated NR/SPVS-Nonidet latices for various blending ratios, N_{max} being the theoretical number of shell particles required to form a closely packed monolayer on a core particle

particles. A mesh structure of all sulphur-crosslinked skim particles containing PS, prepared by using the phase transfer/bulk polymerisation process, irrespective of size, was uniform. In the peroxide-cured latex, the network structure was noticed mostly in the form of film. Within 5 h of prevulcanisation, the minimum and constant swelling ratio of the latex sheet was obtained. The skim rubber crosslinked by sulphur for 5 h was then used as the agglomerating latex for preparation of core–shell composite particles containing NR and SPVS. Due to the interaction between PEO of Nonidet adsorbed on SPVS latex particles, heterocoagulation of SPVS latex particles onto NR particle took place. Data from zeta potential measurement and the better resistance to toluene of films casted from the heterocoagulated latices when compared with that of the NR film indicated the existence of SPVS on the outer layer of the composite particles. Due to the fact that the epoxidation is a simple and efficient method for introducing reactive groups and polarity onto rubber chains, the epoxidised NR (ENR), crosslinked ENR and/or skim latex particles will be further investigated in order to prepare composite particles for improvement of oil resistance of NR. The use of crosslinked skim as agglomerating latex in the encapsulation of disinfectant agent for the preparation of NR medical glove is also the ongoing research.

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