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Composite natural rubber based latex particles: a novel approach

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Abstract

The oil resistance of natural rubber (NR) film could be effectively improved by using the heterocoagulation of large NR particle with small polychloroprene (CR) particles. In the preparation of NR/CR composite particle with a core-shell structure, a nonionic surfactant whose molecule bears poly(ethylene oxide) (PEO) was adsorbed on CR particles and allowed to form complexes between PEO and indigenous surfactant (protein–lipid) on the NR particle surface. Composite latex particle obtained was characterised by particle size, zeta potential and glass transition temperature measurements and the data indicated the presence of CR on the outer layer of composite particle. Better oil resistance of film casted from heterocoagulated latex when compared to that of NR film confirmed the NR/CR core-shell structure. The epoxidised natural rubber (ENR), crosslinked ENR and/or skim latex particles were investigated in order to replace the use of CR in the heterocoagulation process.

Keywords: Natural rubber latex; Polymer composite; Heterocoagulation

1. Introduction

Natural rubber (NR) latex, a renewable polymeric material displaying excellent physical properties, is widely used in the manufacture of thin film products. However, the film casted from NR latex is soft and tacky and, therefore, the latex must be prevulcanised by sulphur, peroxide or γ-radiation system in order to provide better quality product. Drying of the prevulcanised latex produces a crosslinked film and, thus, physical properties of the final product can be controlled by the design of crosslink in particle during prevulcanisation. It was reported that the rate of prevulcanisation reaction depends on the vulcanisation systems, and the extent of prevulcanisation has a profound effect on the formation of the latex film [1–5].

The deficient property such as poor oil resistance of NR, even after prevulcanisation, is also needed to be improved. Among the chemical modifications, epoxidation is a simple and efficient method for introducing reactive groups and polarity onto polyisoprene backbone [6–8]. Epoxidised natural rubber (ENR) shows better oil resistance, higher damping and lower gas permeation than those of NR [9–11]. In addition, the epoxy or oxirane group in ENR can act as a reactive site for further modification [12–14]. The epoxidation reaction can be carried out in solution and in latex forms but the latter is economical and considered to be environmentally safe [7,15].

Blending of NR with an appropriate rubber is an important technological process for increasing the oil resistance of NR. However, a high proportion of synthetic rubber is normally required for the blending with NR in solid form for satisfactory improvement of oil resistance of NR [16], whereas the use of latex blending would consume less energy and time because there would be no need of mastication. We, therefore, studied the heterocoagulation involving agglomeration of small particles of polar rubber latex onto a large core NR particle. The high polar and monodisperse synthetic polychloroprene (CR) was preliminary investigated as the agglomerating latex or shell particles. Owing to the low glass transition temperature (T_g) of both rubbers, the NR/CR core-shell particle can be obtained without annealing the aggregate at high temperature. A nonionic surfactant (Tween 80) whose molecule bears poly(ethylene oxide) (PEO) moieties was adsorbed on the CR particles for steric stabilisation of the latex. An

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interpolymer complex was allowed to form between PEO and indigenous surfactant (protein–lipid) on the NR particle. Heterocoagulated particle of NR/CR produced from various compositions was characterised by particle size, zeta potential and glass transition temperature measurements. Oil resistance of films casted from composite NR/CR latex was investigated. The NR/CR composite latex particle was then used as a model in the further study of replacing CR by ENR, crosslinked ENR, and/or skim NR latices in the heterocoagulation technique.

2. Experimental

2.1. Latices and their characterisations [17–19]

Particle size distribution of concentrated high ammonia preserved NR latex (N.Y. Rubber Co., Ltd, Thailand) was measured by using a particle size analyser (Mastersizer S, Malvern) while photon correlation spectroscopy (Autosizer S4700, Malvern) was used in the case of the CR (Neoprene 671A, DuPont) and skim (Rayong Bangkok Rubber Co., Ltd, Thailand). Zeta potential of particles in the latices was determined 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).

2.2. Heterocoagulation technique [17,18]

Tween 80, polyoxyethylene sorbitan monooleate, (Fluka, practical) (6% by weight of dry latex) was adsorbed onto the CR latex prior to mixing a known amount of the CR-Tween having 1% total solid content (TSC) with the NR latex (1%TSC, 10 g) at pH ~2 in an Erlenmeyer flask at room temperature. The blending ratio was determined from the theoretical number ($N_{\max}$) of shell particles required to form a close-packed particulate monolayer on a core particle, calculated by using the equation previously reported [20, 21].

T_g of the films casted from the heterocoagulated latex was analysed by using a differential scanning calorimeter (DSC7, Perkin Elmer) at a heating rate of 10 °C/min. The resistance to hydrophobic liquid of the films was determined by immersing a known weight of rubber sheet (about 0.05 g) in toluene (50 mL) at room temperature for 22 h. The swollen rubber was weighed after blotting with filter paper and percentage swelling ratio was consequently calculated [22].

2.3. Synthesis and characterisation of ENR latex

A nonionic surfactant, Nonidet P40, nonylphenylpoly(ethylene glycol), (Fluka, Biochemika) (5 g), and distilled water (133.3 g) were mixed with NR latex (Rayong Bangkok Rubber Co., Ltd, Thailand) (166.7 g) in a 1 L glass reactor. After stirring at room temperature for 1 h, the mixture was neutralised and then acidified by slowly adding 85% formic acid (Carlo Erba, RPE) (16.1 g). After increasing temperature to 40 °C, 30% aqueous solution of hydrogen peroxide (Carlo Erba, RPE) (121.3 mL) was added within 15–20 min. The epoxidation was then carried out at 50 °C. Aliquots were taken at various time intervals and immediately precipitated in distilled methanol, washed with distilled water and dried under vacuum at room temperature until a constant weight was obtained.

The epoxide contents of ENR were calculated from the spectra of proton-nuclear magnetic resonance spectroscopy (^{1}H-NMR, DPX300, Bruker) [23]:

$$\text{epoxide content (\%)} = I_{2.7}/(I_{2.7} + I_{5.1}) \times 100$$

when $I_{2.7}$ and $I_{5.1}$ are integrated area of peaks at chemical shifts 2.7 and 5.1 ppm, respectively.

The structure of ENR film was also characterised by using a fourier transform infrared spectroscopy (FTIR, Spectrum GX, Perkin Elmer) and DSC at heating rate of 10 °C/min was used to determine its T_g.

2.4. Prevulcanisation of ENR

Prevulcanisation of ENR latex (25 mol% of epoxide content) was carried out by using sulphur or peroxide system according to the methods previously reported [24, 25]. 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 from the swelling ratio of the rubber after immersing in toluene.

3. Results and discussion

3.1. Characterisation of NR, CR and skim latices [17–19]

The particle size distribution curves of the NR, CR and skim latices are shown in Fig. 1. A broad particle size distribution of NR (from 0.2 to 1.8 μm) with an average particle diameter 0.75 μm and a bimodal distribution of CR and of skim latices were observed. Most of CR particles ranged from 110 to 350 nm with an average large peak size of 180 nm while the size of the skim particles was also small having an average diameter of 123.5 nm.

Zeta potential values of NR and CR latices at various pHs are shown in Fig. 2. The data indicated that NR particles possessed positive character when the pH was below 4.7. Above this pH, the zeta potential was negative and changed rapidly with increasing pH. Results indicating amphoteric characteristic of the NR particles, with an isoelectric point at

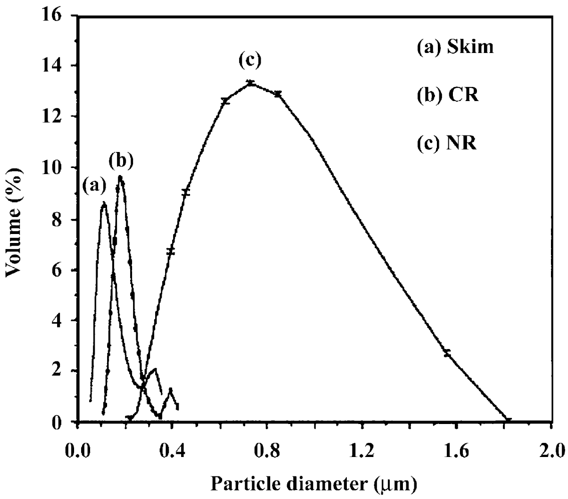

Fig. 1. Particle size distribution by volume of (a) skim, (b) polychloroprene (CR), and (c) natural rubber (NR) latices [17,18].

about pH 4.7 confirmed the presence of amino acid moieties on the surface of NR latex particle [26]. In the case of CR latex, the zeta potential showed a negative value over a range of pH, which indicated the presence of a negative charge possibly derived from the anionic surfactant on the CR particle surface.

3.2. Heterocoagulated NR/CR-Tween latex [17,18]

The adsorption of Tween 80 (6% by weight) on CR particle surface was indicated by the decrease in the absolute value of zeta potential at pH ~7 of CR-Tween latex (−35 mV) when compared to that of the original one (~52 mV) as indicated in Fig. 3. The adsorbed polymer caused the alteration of electrical double layer of charged particle due to the ion redistribution and, consequently, reduction of surface charge.

Owing to the amphoteric characteristic of the NR particles, carboxylic groups of the protein molecules on the NR surface at pH ~2 could form hydrogen bonds with the PEO chains of Tween 80 adsorbed on the CR particles.

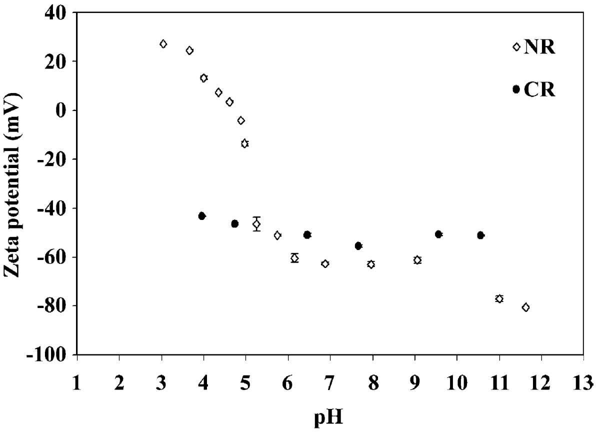

Fig. 2. Zeta potential of NR and CR latices versus pH [17,18].

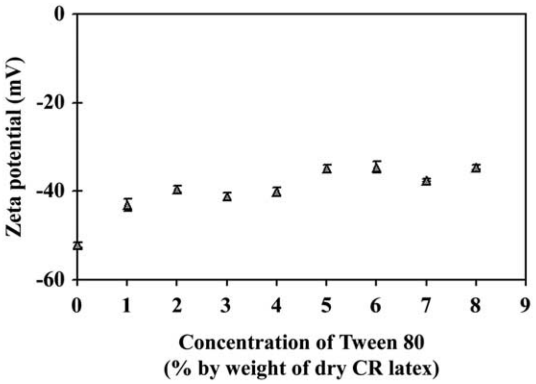

Fig. 3. Zeta potential of CR-Tween latex containing various concentrations of Tween 80 at pH ~7 [17,18].

The heterocoagulation of NR and CR-Tween was prepared with various blending ratios and the particle size distribution curves of all the latex blends, measured using a Mastersizer S are shown in Fig. 4.

A single peak with a broad size distribution of heterocoagulated NR/CR-Tween particles of both rubbers for all ratios. Their average diameter increased from $N_{\max}/8$ to $2N_{\max}$, indicating that heterocoagulation between the NR and CR-Tween latex particles was generated and more than one layer of CR particles surrounding a NR particle was formed. The negative value of zeta potential of all the NR/CR-Tween latex blends also confirmed that the outer shell of composite particles consisted of CR because the zeta potential of the NR latex showed a positive value at pH ~2 (in Fig. 2).

In each composite film casted from the heterocoagulated NR/CR-Tween latex, two separated T_gs, corresponding to those of NR (−66 °C) and of CR (−43 °C), were observed in the DSC thermograms as shown in Fig. 5. The existence of phase separation between the two rubbers in the film implied that the heterocoagulated NR/CR-Tween latex particles were formed. In addition, it was noticed that the peak at −66 °C in the heterocoagulated latex system was wider than that of NR film, i.e. the interaction between the surface of the NR and CR particles possibly took place.

The oil-resistant property, inversely proportional to the

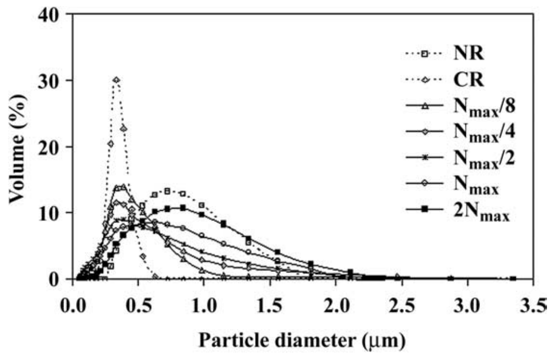

Fig. 4. Particle size distribution of heterocoagulated NR/CR-Tween latices prepared with various blending ratios [17,18].

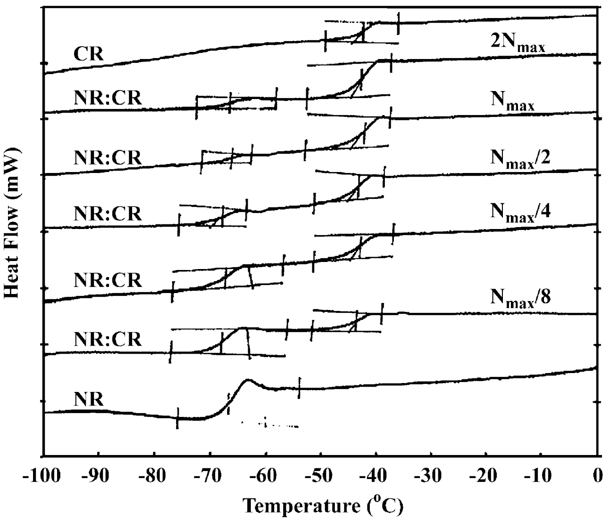

Fig. 5. DSC thermograms of films casted from NR, CR and heterocoagulated latices [17,18].

swelling ratio of the composite films, was also used as an evidence to indicate that CR particles coagulated around the NR core. The swelling ratios of NR, CR and composite films in toluene plotted against the blending ratios are shown in Fig. 6. As expected, the decrease of swelling ratio of heterocoagulated NR/CR-Tween latex films when compared to that of NR (1900%) was noticed. It could be explained that the outer shell, consisting of CR particles, which resisted to oil was responsible for preventing the penetration of toluene into NR core in the composite films.

3.3. Analysis of ENR latex

ENR latex was characterised by ^{1}H-NMR and FTIR. The NMR spectrum in Fig. 7 shows olefinic proton peak at 5.1 ppm and a methine proton peak at 2.7 ppm, assigned to the proton attached to the oxirane ring [7,27]. These two peaks were also observed in the epoxidised skim latex.

ENR latex having various epoxide contents was synthesised by varying the reaction times. The epoxide content, determined by the ratio of the integrated areas of olefinic and epoxy methine protons NMR absorptions, plotted versus the reaction time is shown in Fig. 8.

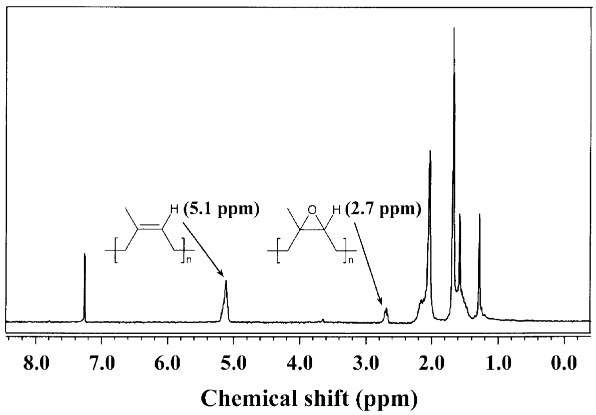

Fig. 7. ^{1}H-NMR spectrum of ENR.

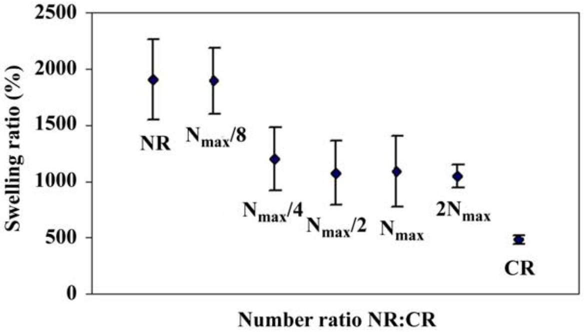

Fig. 6. Swelling ratio of films casted from NR, CR and heterocoagulated NR/CR-Tween latices [17,18].

It was clearly observed that the epoxide content of ENR was directly proportional to the reaction time. The maximum epoxide content obtained within 13 h was 40 mol%. When the reaction was prolonged for more than 13 h, the latex immediately coagulated. This could be explained in term of an increase in polarity in molecular structure of ENR and also on their particle surface affected the adsorption of nonionic surfactant on ENR particles. The decrease of efficiency of steric stabilisation of nonionic surfactant of latex would provoke the spontaneous coagulation. It was observed that only 9 mole% epoxide content was obtained in the case of skim latex even the reaction time was longer than 24 h.

The IR spectrum of the ENR having 40 mol% of epoxide content in Fig. 9 showed absorption peaks at 870 and 1250 cm^{-1} corresponding to half ring and whole ring stretching of the epoxide ring [6,13]. The peaks at 1740 and 3500 cm^{-1} relating to C=O and O–H stretching might be derived from side reactions of epoxide ring opening.

The T_g of all ENR films analysed by DSC was greater than that of NR. It could be explained that the insertion of oxygen atoms in polyisoprene decreased rotational freedom of the polymer backbone. Increase of the level of epoxidation in ENR certainly increased its polarity and T_g

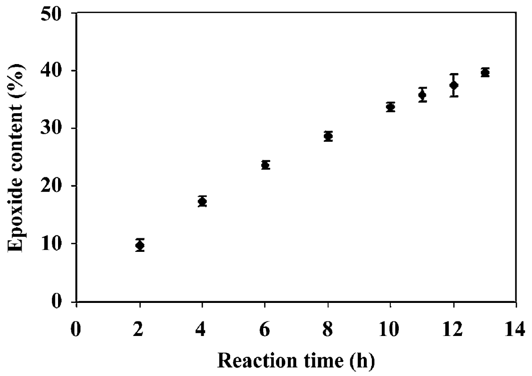

Fig. 8. Epoxide contents of ENR synthesised from various reaction times.

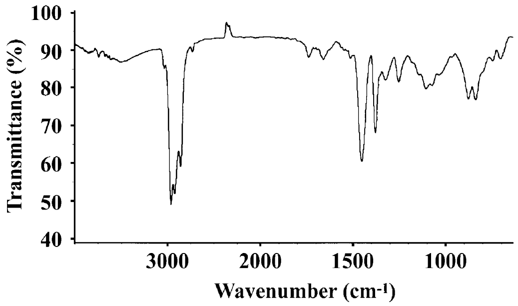

Fig. 9. FTIR spectrum of ENR having 40 mol% epoxide content.

due to the intermolecular interaction between polar groups in ENR chains [10] as displayed in Fig. 10.

3.4. Swelling ratio of prevulcanised ENR

The swelling ratios of rubber sheets casted from the sulphur- and peroxide-prevulcanised ENR latices synthesised from various prevulcanisation times are presented in Fig. 11.

The swelling ratios in both curves decreased with increasing reaction times. After 3 h, a relatively small change in the swelling ratio was found, indicating a complete vulcanisation of the rubber. The value of swelling ratio of peroxide-prevulcanised latex film was higher than that obtained from the sulphur system as previously observed in the prevulcanisation of NR [24]. It was explained that the inhomogeneous nature of the crosslinking in NR latex particles prevulcanised by using *t*-BuHP/fructose system resulted from the dissolution of vulcanising ingredients in the aqueous serum of the latex. In the peroxide-cured latex, a non-uniform network structure inside each rubber particle, i.e. a dense network near the particle surface when compared to that at the central region of particle, was noticed. The network of NR chains in each sulphur-crosslinked 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. However, it could be assumed that the lightly crosslink was obtained in both cases. Unfortunately, the heterocoagulation of ENR or sulphur-prevulcanised latex particles on a NR-core might not be possible due to their great size as shown in Fig. 12. However, the results obtained from measuring swelling ratio of latex film indicated that the ENR latex could be vulcanised by using both systems. These conditions could be further applied for prevulcanisation of skim whose size was small compared to that of NR (Fig. 1) before being used as agglomerating latex in the heterocoagulation procedure.

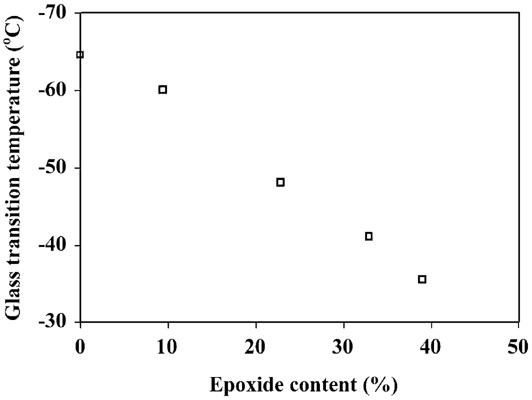

Fig. 10. T_g, determined by DSC, of ENR having various epoxide contents.

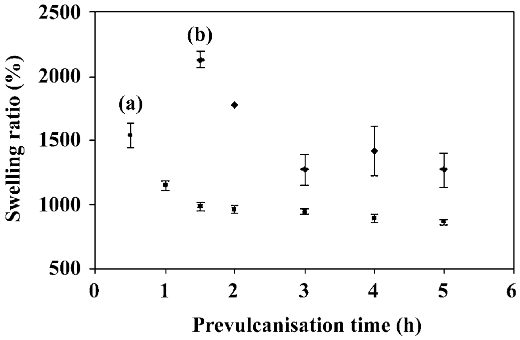

Fig. 11. Swelling ratio of (a) sulphur-prevulcanised ENR, and (b) peroxide-prevulcanised ENR.

4. Conclusions

Tween 80 adsorbed on CR latex particles provoked the heterocoagulation of CR latex particles on NR particle. Evidence from particle size, zeta potential and T_g determinations indicated the presence of CR-Tween on the outer layer of the composite polymer particles. The results agreed well with the better oil resistance of film cast from the heterocoagulated latex when compared with that of the NR film. The extension of the study was the use of ENR or prevulcanised ENR and/or skim as the agglomerating latex.

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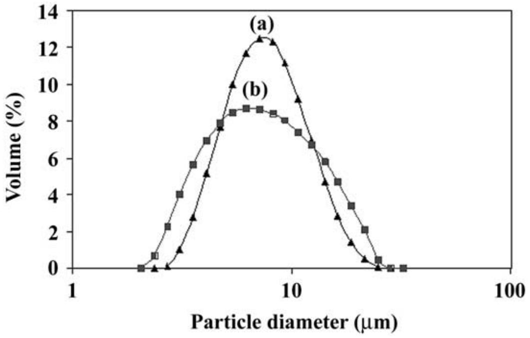

Fig. 12. Particle size distribution by volume of (a) ENR, and (b) sulphur-prevulcanised ENR latices.

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