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SHORT COMMUNICATION

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# Composite natural rubber–polychloroprene latex particles produced by the heterocoagulation technique

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**Abstract** Composite natural rubber (NR) based latex particles were prepared using the heterocoagulation technique. A nonionic surfactant (Tween 80) whose molecules bear poly(ethylene oxide) (PEO) was adsorbed on polychloroprene (CR) latex particles and allowed to form complexes between PEO and indigenous surfactant (protein–lipid) on the NR particle surface. The heterocoagulated NR/CR–Tween particles produced were characterised by particle size, zeta-potential and glass-transition temperature measurements and the data 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 films cast from heterocoagulated latex when compared with that of the NR film.

**Key words** Heterocoagulation · Natural rubber latex · Polychloroprene latex

## Introduction

Composite polymer particles with heterogeneous structures are generally prepared by using the seeded emulsion polymerisation technique [1, 2, 3, 4, 5]. It has been noted that factors such as the nature of the monomers, the compatibility among polymers and the addition sequence of monomers exert great influence on the final particle morphology [4, 5]. In the preparation of composite natural rubber (NR) based latex particles, the type of initiator used is also found to be an important parameter in controlling the site of polymerisation and, hence, the final structure of the particles [5, 6, 7].

Owing to the difficulty in the preparation of structured latex particles of absolute specification by using conventional methods, the heterocoagulation technique has recently been developed as an alternative method for producing composite latex particles, especially core–shell type [8, 9, 10, 11, 12, 13, 14]. This process involves agglomeration, based on neutralisation or complex formation principles, of small polymer particles onto a particle of another polymer. Core–shell particles can be obtained after annealing the aggregate at temperature higher than glass-transition temperature ($T_g$) of the shell polymer. By employing this process, many different types of monomer pairs can be prepared, even in the case of hydrophilic core and hydrophobic shell latex particles.

In the present work, the heterocoagulation of a rubber latex system using NR as the agglomerated latex and polychloroprene (CR) as the agglomerating latex was explored. A nonionic surfactant (Tween 80) whose molecules bear poly(ethylene oxide) (PEO) moieties was adsorbed on the CR particles for steric stabilisation of the latex and an interpolymer complex was allowed to form between PEO and the indigenous surfactant (protein–lipid) on the NR particle [15]. Heterocoagulated particles of NR/CR produced from various compositions were characterised by particle size and zeta-potential measurements. The oil resistance of films cast from composite NR/CR, unmodified NR and CR latices was also investigated.

## Experimental

### Materials and their characterisations

CR latex (Neoprene 671A, DuPont), was kindly supplied by the Chemical Innovation Co. (Bangkok, Thailand). Concentrated high-ammonia-preserved NR latex having about 60% dry rubber content was purchased from the N.Y. Rubber Co. (Chonburi, Thailand). The particle size distribution of the NR latex was measured using a particle size analyser on the basis of the laser diffraction principle (Mastersizer S, Malvern), while photon correlation spectroscopy (Autosizer S4700, Malvern) was used in the case of the CR latex. The zeta potential of the particles in both 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 or sodium hydroxide.

Tween 80 (Fluka, practical), $CaCl_2$ (Merck, GR), hydrochloric acid (Merck, GR) and sodium hydroxide (Merck, GR) were used without further purification.

### Adsorption of nonionic surfactant on CR latex particles

A CR latex having 60% total solid content (TSC) was diluted with deionised water to 1% TSC. An aqueous solution (10%) of nonionic surfactant, Tween 80 (1–8% by weight of dry CR latex), was then added in the diluted latex (50 g). After making the weight of each batch equal to 100 g by addition of water, the mixture was shaken (Burell) for 12 h at room temperature. The amount of Tween 80 adsorbed on the CR particles (CR–Tween) was deduced from the quantity of an aqueous solution of $CaCl_2$ (1 M) added to provoke visible coagula.

### Heterocoagulation

Tween 80 (6% by weight of dry latex) was adsorbed onto the CR latex prior to mixing a known amount of the CR–Tween (1% TSC) with the NR latex (1% TSC, 10 g) at pH $\sim 2$ 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, as calculated from the following equation [8, 9, 14].

$$N_{\max} = \frac{2\Pi}{\sqrt{3}}\left(\frac{R_C + R_S}{R_S}\right)^2 , \tag{1}$$

where $R_C$ and $R_S$ are the radii of the core (NR) and shell (CR) particles, respectively. The ratio of NR to CR particles in the latex blend was varied for $N_{\max}/8$, $N_{\max}/4$, $N_{\max}/2$, $N_{\max}$ and $2N_{\max}$.

### Differential scanning calorimetry

The base latices (NR and CR) and the heterocoagulated latex were cast on a Petri dish and dried at 70 °C in a vacuum oven. The $T_g$ of the films was analysed by using a differential scanning calorimeter (DSC7, Perkin Elmer) at a heating rate of 10 °C/min.

### Determination of oil resistance

The resistance to hydrophobic liquid of films cast from NR, CR and composite NR/CR–Tween latices using the procedure described earlier was determined [16]. A known weight of rubber sheet (about 0.05 g) was immersed in toluene (50 ml) at room temperature and then allowed to swell for 22 h. The swollen rubber was weighed after blotting with filter paper and the percentage swelling ratio was calculated from

$$\%\ \text{swelling ratio} = \frac{W_1 - W_0}{W_0} \times 100 , \tag{2}$$

where $W_0$ and $W_1$ are the weights of the rubber sheet before and after swelling, respectively.

## Results and discussion

### Characterisation of NR and CR latices

The particle size distribution curves of the NR and CR latices are shown in Fig. 1. The broad size distribution of the NR latex is indicated in Fig. 1a. The particle diameter of the latex varies from 0.2 to 1.8 μm and the average particle diameter is 0.8 μm. The data obtained agree well with the value reported in the literature [17]. The curve in Fig. 1b shows a bimodal distribution with

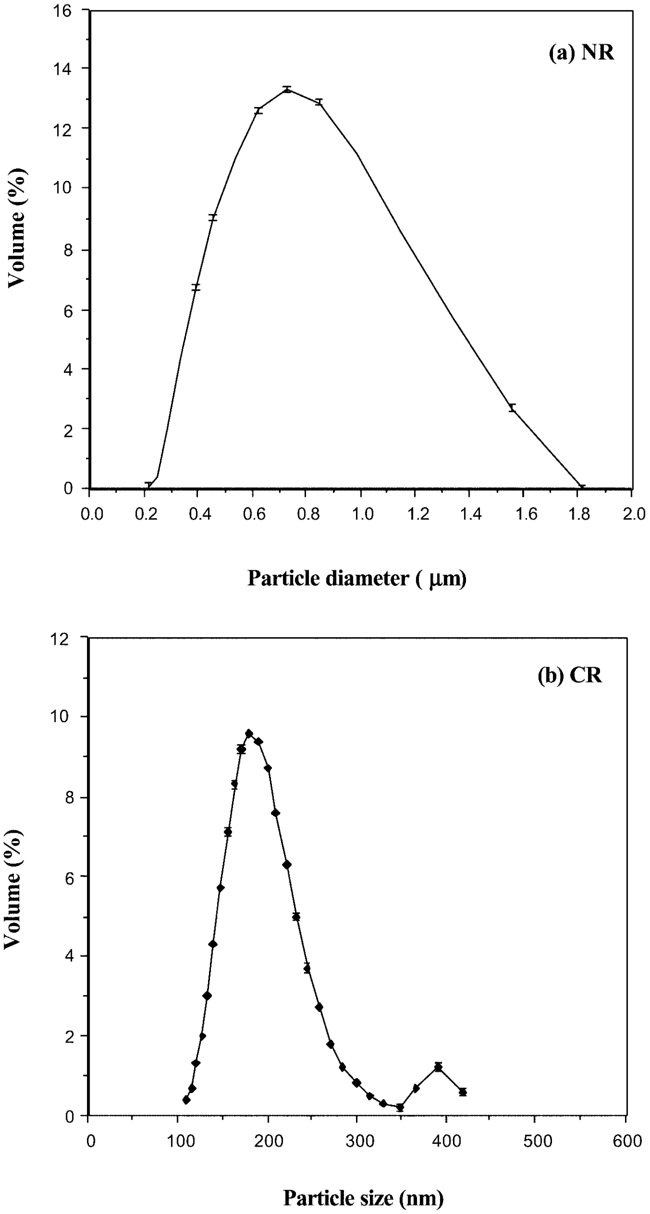

**Fig. 1** Particle size distribution by volume of **a** natural rubber (*NR*) and **b** polychloroprene (*CR*) latices

an average size of the large peak around 180 nm which was close to that reported by the supplier (210 nm). Small amounts of particles corresponding to the second peak at 390 nm are believed to be the result of the coalescence of polymer particles during storage [18]. Owing to the fact that for most of the CR particles the diameter ranged from 110 to 350 nm, it can be stated that the size was monodisperse.

Zeta-potential values of NR and CR latices at various pHs are shown in Fig. 2. The data indicated that the NR particles possessed positive character when the pH was below 4.7. Above pH 4.7, the zeta-potential was negative and changed rapidly with increasing pH. The curve in Fig. 2, therefore, indicated amphoteric characteristics of the NR particles, with an isoelectric point at about pH 4.7. The results confirmed the presence of amino acids on the surface of the NR latex particle [17, 19]. In the case of the 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.

## Effect of concentration of Tween 80

Theoretically, an electrolyte solution, especially that having multivalent ions, can effectively destabilise an ionic latex, whereas a latex particle carrying nonionic surfactant is not sensitive to the presence of electrolyte owing to its steric stabilisation [20, 21]. In this study, Tween 80 was selected as the nonionic surfactant to be adsorbed on the anionic CR latex. An aqueous solution of 1 M $CaCl_2$ was employed to detect the change from electrostatic to steric stabilisation of the CR–Tween latex using various amounts of Tween 80. The quantity of $CaCl_2$ solution used for provoking visible coagula of CR–Tween versus that of Tween 80 added is plotted in Fig. 3.

As shown in Fig. 3, it was found that the volume of $CaCl_2$ causing coagulation of the CR–Tween latex increased linearly with an increase in the concentration of Tween 80 from 1 to 5%. At these concentrations, the latex coagulated immediately after the addition of $CaCl_2$ aqueous solution. On using 6% or more of Tween 80, the volume of $CaCl_2$ added to coagulate the CR–Tween latex could not be determined precisely owing to the fact that all latices remained visually stable after adding the highest amount of $CaCl_2$. The insensitivity to $CaCl_2$ of the CR–Tween latex in the latter case indicated that 6% of Tween 80 was sufficient to modify the type of stabilisation of the latex from electrostatic to steric. The presence of Tween 80 on the CR particles was shown by the decrease in the absolute value of the zeta-potential at pH $\sim$ 7 of the CR–Tween latex when compared to that of the original one (–52 mV) in Fig. 4. As reported in the literature, adsorbed polymer causes the alteration of the electrical double layer of a charged particle because of ion redistribution and, consequently, the reduction of surface charge [20, 21, 22]. The larger particle size distribution of the CR–Tween latex (6%) also supported the previous observation (Fig. 5). The increase in the hydrodynamic volume of the CR–Tween latex particles was due to the presence of a hydrophilic layer of Tween 80 adsorbed onto the surface of the particle.

## Heterocoagulated NR/CR–Tween latex

Owing to the amphoteric characteristics of the NR particles, carboxylic groups of the protein molecules on

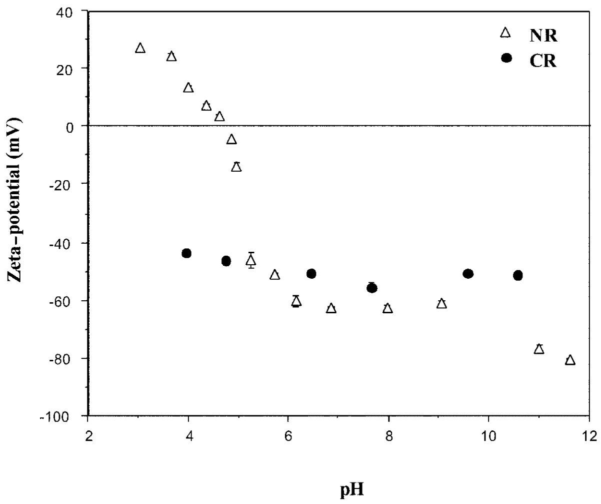

**Fig. 2** Zeta-potential of NR and CR latices at different pH

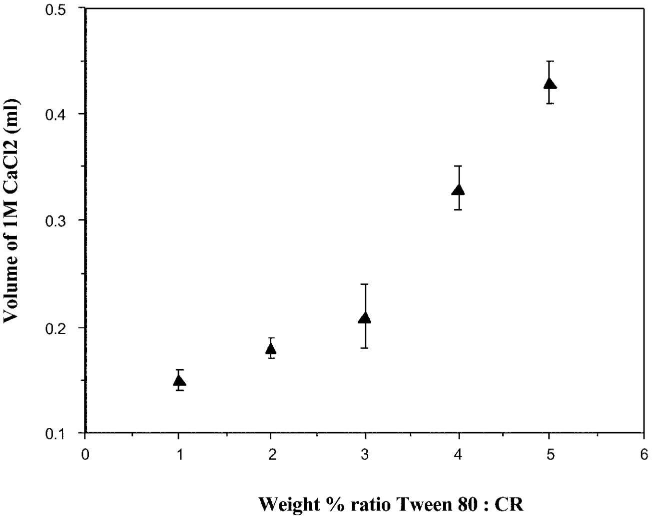

**Fig. 3** Volume of 1 M $CaCl_2$ added to coagulate CR–Tween particles containing various concentrations of Tween 80 at pH $\sim$ 7

the NR surface at pH ~ 2 could form hydrogen bonds with the PEO chains of Tween 80 adsorbed on the CR particle. The heterocoagulation of NR and CR–Tween was prepared with various blending ratios (i.e., $N_{\max}/8$, $N_{\max}/4$, $N_{\max}/2$, $N_{\max}$ and $2N_{\max}$). The particle size distribution curves of all the latex blends measured using a Mastersizer S are shown in Fig. 6a and the volume plotted as a function of the reduced particle diameter, defined as $R = r/r_0$, where $r$ and $r_0$ are, respectively, the particle diameter and the average diameter, is presented in Fig. 6b.

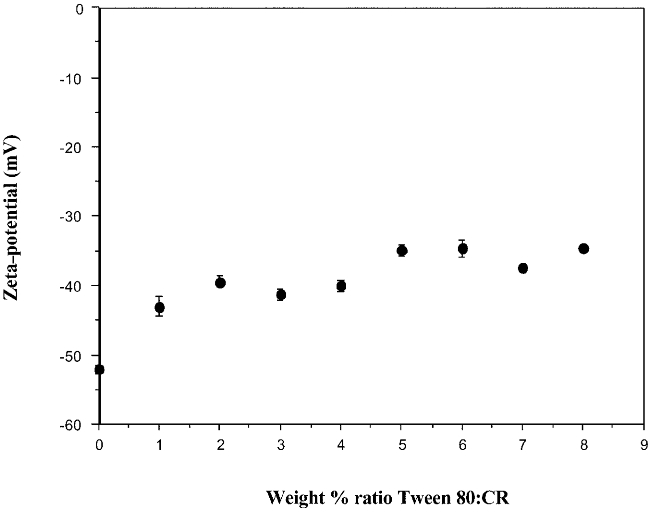

**Fig. 4** Zeta-potential of CR–Tween latex containing various concentrations of Tween 80 at pH ~ 7

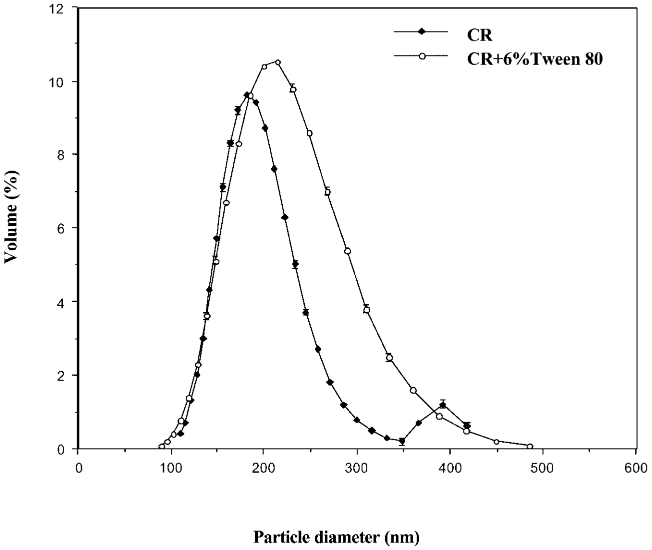

**Fig. 5** Effect of Tween 80 (6% by weight) on the particle size distribution of the CR latex

From Fig. 6a, a single peak with a broad size distribution of heterocoagulated NR/CR–Tween particles of both rubbers was observed at 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. In Fig. 6b, the plots are not well superimposed and the peak height of each plot is different, possibly owing to the polydispersity in size of the agglomerated NR particles. In addition, more than one layer of CR particles surrounding a NR one was formed. The negative value of the zeta-potential of all the NR/CR–Tween latex blends in Fig. 7 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 (Fig. 2).

## Differential scanning calorimetry of heterocoagulated NR/CR latex films

The $T_g$ of the film cast from NR, CR and heterocoagulated NR/CR–Tween latices was investigated using the

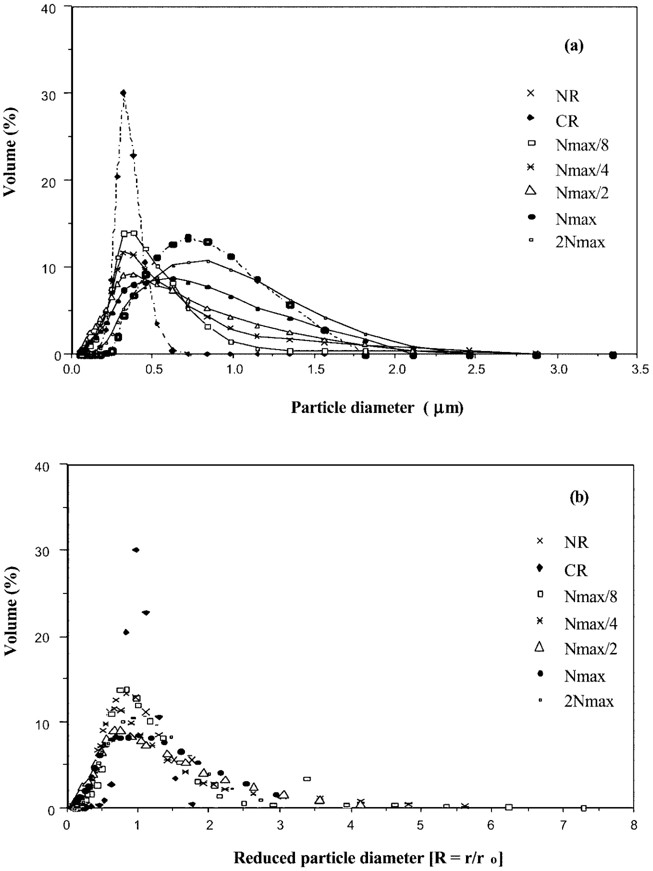

**Fig. 6** Volume (%) of heterocoagulated NR/CR–Tween latices prepared with various blending ratios versus **a** particle diameter and **b** reduced particle diameter

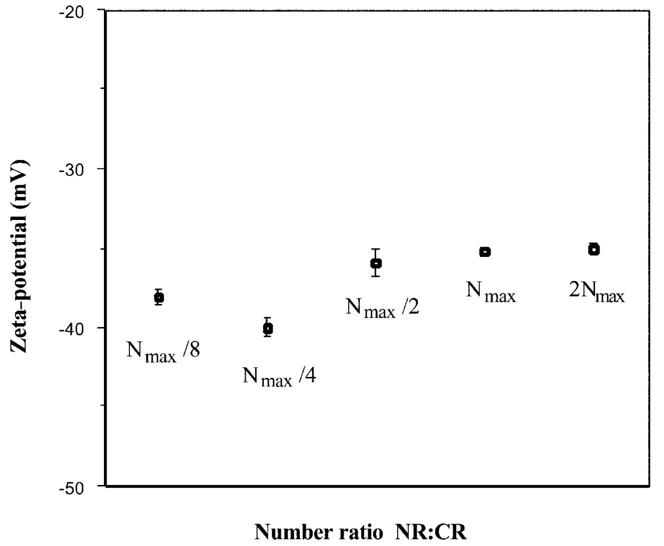

**Fig. 7** Zeta-potential of heterocoagulated NR/CR–Tween latices prepared with various blending ratios at pH ~ 2

differential scanning calorimetry technique and the thermograms are presented in Fig. 8. In each composite film, two separated $T_g$s, corresponding to those of NR (−66 °C) and CR (−43 °C), were observed. The existence of phase separation between the two rubbers in the film implied that 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 the NR film, i.e., interaction between the surface of the NR and CR particles possibly took place.

## Oil resistance of heterocoagulated latex film

The difference in the swelling ratio of NR and CR latex films in toluene was used as a tool to investigate the structure of film cast from the heterocoagulated NR/CR–Tween latex. The swelling ratio of the composite films plotted versus the blending ratios is shown in Fig. 9. It was noted that the swelling ratio of all the heterocoagulated films was lower than that of NR (1900%) but higher than that of CR (480%). This is

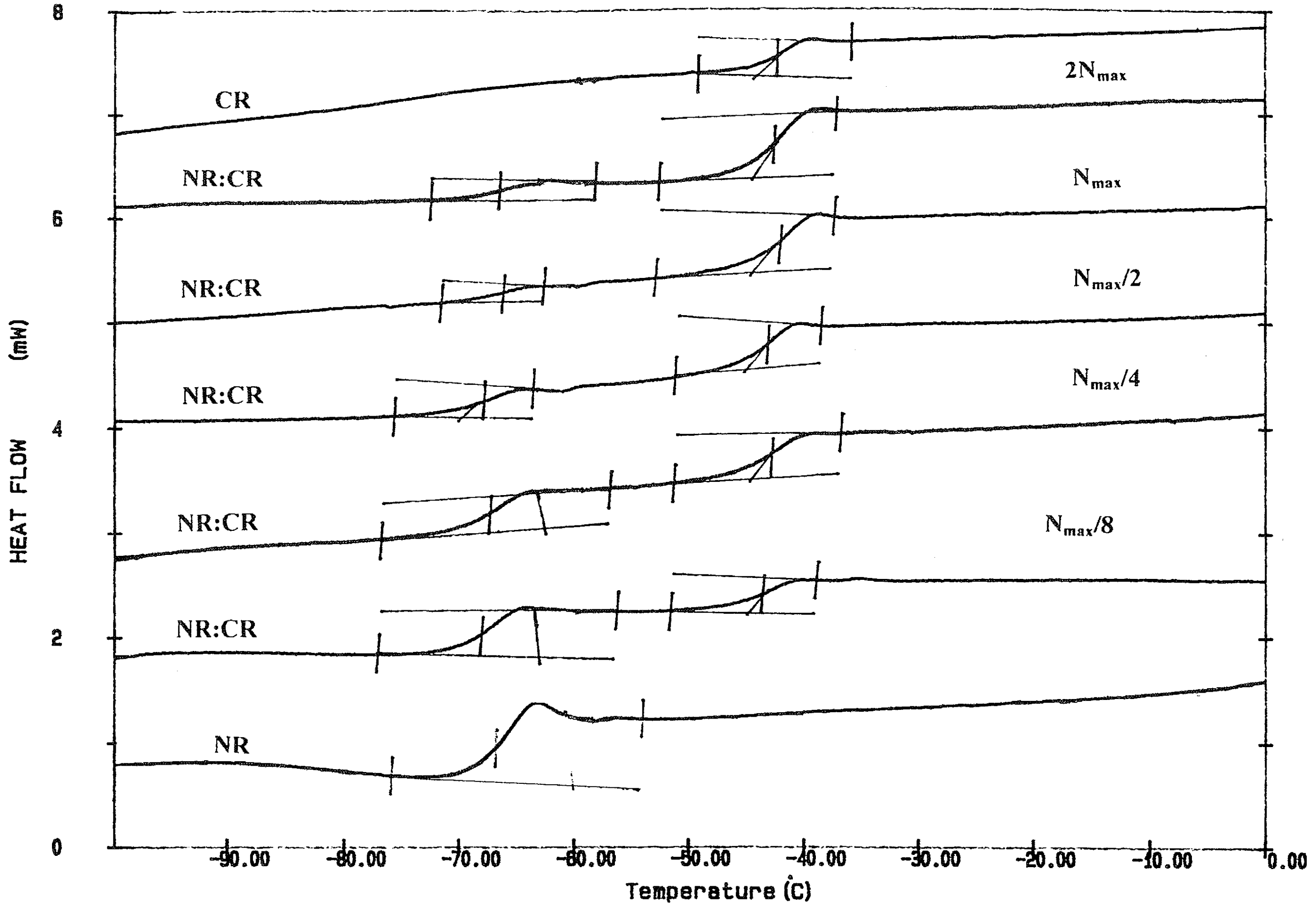

**Fig. 8** Differential scanning calorimetry thermograms of films cast from NR, CR and heterocoagulated NR/CR–Tween latices

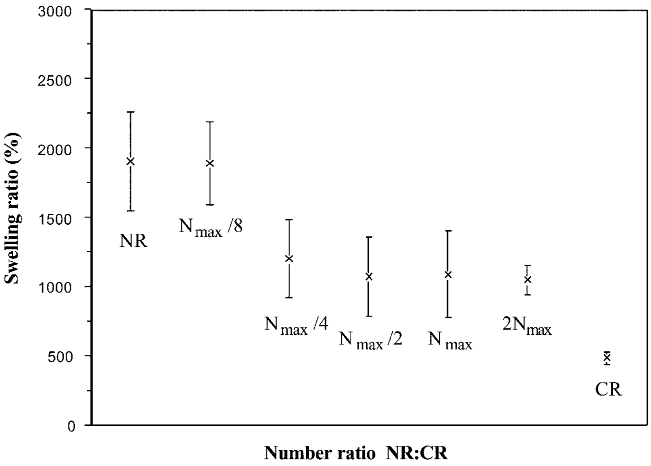

**Fig. 9** Swelling ratio of films cast from NR, CR and heterocoagulated NR/CR–Tween latices

evidence to indicate that CR particles coagulated around the NR core and reduced the penetration of toluene into the film and, hence, improved the oil-resistance properties of the composite films.

## Conclusions

Tween 80 adsorbed on CR latex particles provoked the heterocoagulation of CR latex particles on NR particles. Evidence from 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-resistant film cast from the heterocoagulated latex when compared with that of the NR film.

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