

Heterocoagulation of Polychloroprene on Natural Rubber Latex Particles for Use in the Preparation of Toughened Polystyrene

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ABSTRACT: The toughness of high-impact polystyrene based on γ -radiation-vulcanized natural rubber (NR) was effectively enhanced by the addition of a block copolymer at the NR/polystyrene interface. An NR/polychloroprene (CR) composite latex particle was produced by the heterocoagulation technique for its use as a model in a compatibilization study. A nonionic surfactant (Tween 80), whose molecule bore poly(ethylene oxide) (PEO), was adsorbed onto the CR particle and allowed to form a complex between PEO and an indigenous surfactant (protein-lipid) on the NR

particle surface. The presence of CR-Tween on the outer layer of the obtained composite polymer particle was characterized by the particle size, ζ potential, and glass-transition temperature. That the film cast from the heterocoagulated latex showed better oil resistance than the NR film confirmed the NR/CR core-shell structure. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 9–13, 2003

Key words: core-shell polymers; rubber; polystyrene

INTRODUCTION

In addition to its high molecular weight and botanical and, therefore, renewable origin, natural rubber (NR) latex containing particles with a wide range of diameters effectively acts as an impact modifier for several polymers.^{1–4} An attractive method for the incorporation of NR particles into polystyrene (PS) producing high-impact polystyrene (HIPS) involves the use of a γ -radiation-vulcanized natural rubber (RVNR)/phase-transfer/bulk polymerization technique.^{1,2} The unnotched Izod impact energy of HIPS is higher than that of unmodified PS.

Because it had been postulated that an NR particle coated or grafted with PS could improve the impact resistance of HIPS, we decided to study the use of a block copolymer, which contained PS and polyisoprene (PI), as a compatibilizer in HIPS based on RVNR. In addition, a heterocoagulation technique involving the agglomeration of small polymer particles onto a particle of another polymer was applied, with NR as the agglomerated latex.^{5–7} Instead of PS as the agglomerating latex, polychloroprene (CR) was preliminary investigated because of its low glass-transition temperature (T_g); that is, a core-shell particle

could be obtained without the annealing of the aggregate at a high temperature. A nonionic surfactant (Tween 80), whose molecule bore a poly(ethylene oxide) (PEO) moiety, was adsorbed onto the CR particles for steric stabilization of the latex, and an interpolymer complex was allowed to form between PEO and the indigenous surfactant (protein-lipid) on the NR particle. Heterocoagulated particles of NR/CR produced from various compositions were characterized by the particle size, ζ potential, and T_g . The oil resistance of films cast from composite NR/CR, unmodified NR, and CR latices was also investigated.

EXPERIMENTAL^{8,9}

Materials and characterization

Concentrated and high ammonia preserved NR latex (N.Y. Rubber Co., Thailand), CR latex (Neoprene 671A, DuPont, Bangkok), and the block copolymer (PS-*b*-PI-*b*-PS; KRATON 1107, Shell, Bangkok) were used as received. The particle size distribution of NR was measured with a particle size analyzer (MasterSizer S, Malvern, London), whereas photon correlation spectroscopy (Autosizer S4700, Malvern) was used for the CR latex. The ζ potential of the latex particles was determined with a microelectrophoresis apparatus (ζ Sizer 4, Malvern) at 30°C after the adjustment of the pH by the addition of an aqueous solution (0.1M) of hydrochloric acid (Merck, GR, Germany) or sodium hydroxide (Merck, GR).

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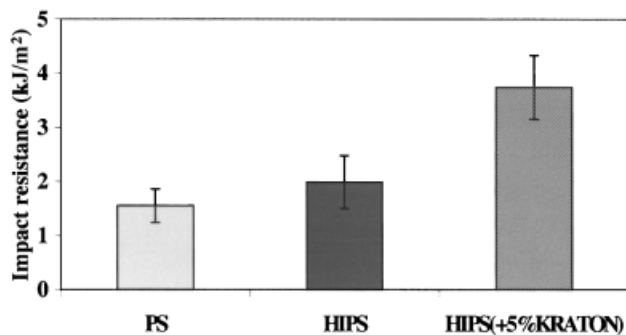


Figure 1 Unnotched Izod impact resistance of PS and HIPS containing 5% RVNR with and without 5% KRATON and polymerized with 1% BPO at 70°C in bulk form.

Preparation of HIPS

A phase-transfer technique was applied to transfer RVNR latex particles, prepared from γ -ray (14 kGy) irradiation of concentrated NR latex, into styrene monomer (puriss, Fluka, Switzerland) containing 5% KRATON 1107 according to a method previously described.^{1,2,8} An unnotched sample of HIPS based on 5% RVNR was produced when the styrene phase was polymerized in bulk form at 70°C with 1% benzoyl peroxide (BPO). The impact resistance of HIPS was measured with an Izod apparatus (Zwick 5102, Germany) according to ASTM Standard D 4812-93, whereas its morphological study was conducted with transmission electron microscopy (TEM; H300, Hitachi, Japan).

Heterocoagulation of CR particles on NR latex particles

Tween 80 (6 wt % dry latex) was adsorbed onto the CR latex surface. A known amount of the treated CR latex (1% total solid content (TSC)) was mixed with NR latex (1% TSC, 10 g) at approximately 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:^{5,6}

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

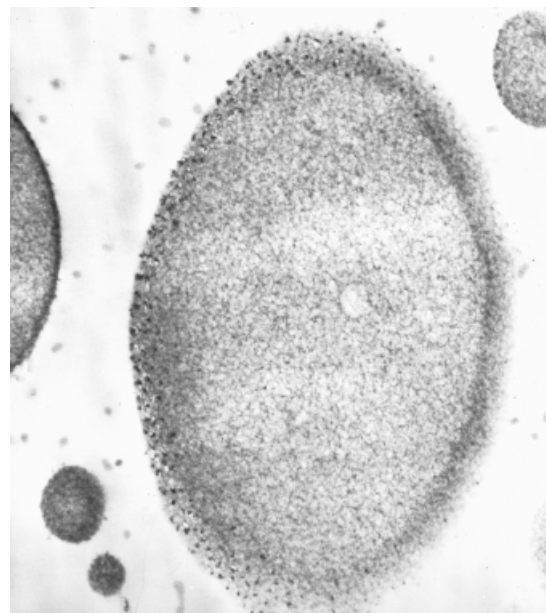
where R_c and R_s are the radii of core (NR) and shell (CR) particles, respectively. The ratios of NR to CR particles in the latex blend were varied from $N_{\max}/8$, $N_{\max}/4$, $N_{\max}/2$, N_{\max} to $2N_{\max}$.

Analysis of latex films

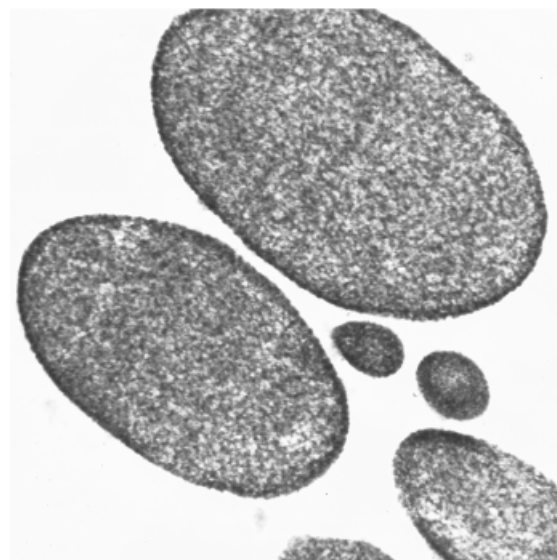
The T_g values of films cast from base latices (NR and CR) and heterocoagulated latex were analyzed with a

PerkinElmer DSC7 differential scanning calorimeter at a heating rate of 10°C/min.

The resistance of the films to hydrophobic liquids was determined by the immersion of a known weight



(a)



(b)

Figure 2 TEM micrographs (40,000 \times) of HIPS containing 5% RVNR (a) with and (b) without KRATON.

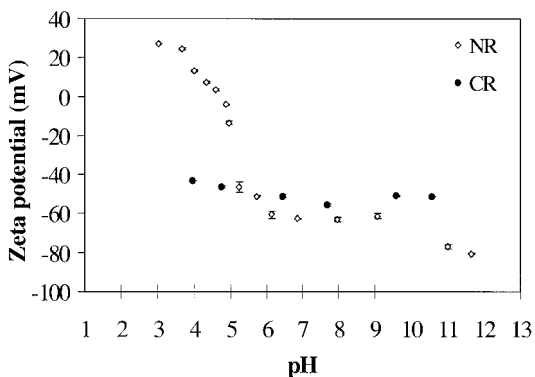


Figure 3 ζ potential of NR and CR latices versus pH.

of a rubber sheet (ca. 0.05 g) in toluene (50 mL) at room temperature for 22 h. The swollen rubber was weighed after blotting with filter paper, and the swelling ratio percentage was subsequently calculated.^{1,2}

RESULTS AND DISCUSSION^{8,9}

Impact resistance of HIPS

The unnotched Izod impact resistance of HIPS with and without 5% KRATON in comparison with that of the unmodified PS is presented in Figure 1. The HIPS impact resistance was greatly enhanced by the addition of KRATON, which acted as a good compatibilizer. The presence of KRATON (dark spots) at the RVNR (dark)/PS (light) interface is clearly shown in Figure 2(a) in comparison with the uncompatibilized HIPS in Figure 2(b).

Characterizations of NR, CR, and CR-Tween latices

ζ potential values of NR and CR latices at various pHs are displayed in Figure 3. NR particles showed a pos-

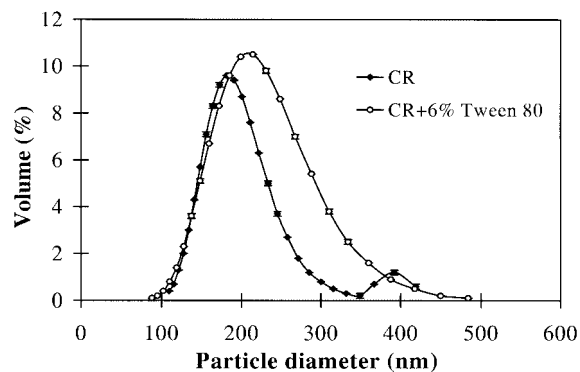


Figure 5 Effect of Tween 80 (6 wt %) on the particle size distribution of the CR latex.

itive character when the pH was less than 4.7. Above pH 4.7, the ζ potential was negative and changed rapidly with increasing pH. The data confirmed the amphoteric characteristic of NR particles, with an isoelectric point at pH 4.7, due to the presence of amino acids on the NR latex particle surface.^{1,2} For the CR latex, the ζ potential showed a negative value over a range of pHs correlating to the presence of a negative charge, which was possibly derived from the anionic surfactant on the CR particle surface.

The adsorption of Tween 80 (6 wt %) onto the CR particle surface was indicated by the decrease in the absolute value of the ζ potential at approximately pH 7 of the CR-Tween latex (-35 mV) with respect to the value of the original one (-52 mV), as indicated in Figure 4. The adsorbed polymer caused the alteration of an electrical double layer of charged particles because of ion redistribution and, consequently, a reduction in the surface charge. The larger particle size distribution of CR-Tween (6%), presented in Figure 5, also supported the previous observation.

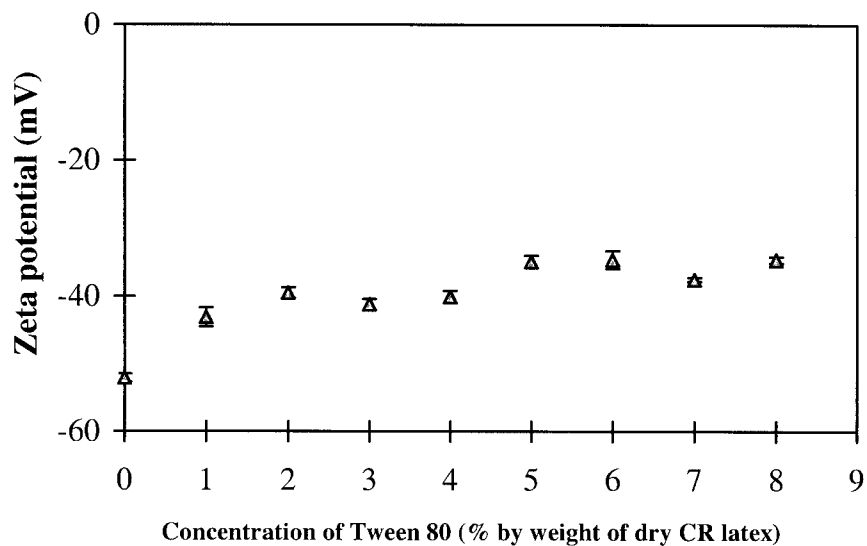


Figure 4 ζ potential of CR-Tween latices containing various concentrations of Tween 80 at approximately pH 7.

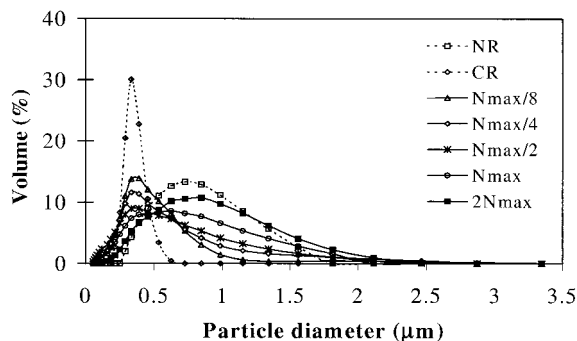


Figure 6 Particle size distribution of heterocoagulated NR/CR-Tween latices prepared in various blending ratios.

Heterocoagulated NR/CR-Tween latex

Because it was possible that, at approximately pH 2, carboxylic groups of protein molecules on the NR surface could form hydrogen bonds with PEO chains on CR particles, the heterocoagulation of NR and CR-Tween was performed for various blending ratios. The particle size distribution curves of all the latex blends measured with a Mastersizer S are shown in Figure 6.

A single peak with a broad size distribution of heterocoagulated NR/CR-Tween particles of both rubbers was observed in all samples. The average particle diameters increased from $N_{max}/8$ to $2N_{max}$ indicating that heterocoagulation between the NR and CR-Tween latex particles was generated and that more than one layer of CR particles surrounding an NR particle was formed. The negative values of the ζ potentials of all the NR/CR-Tween latex blends also

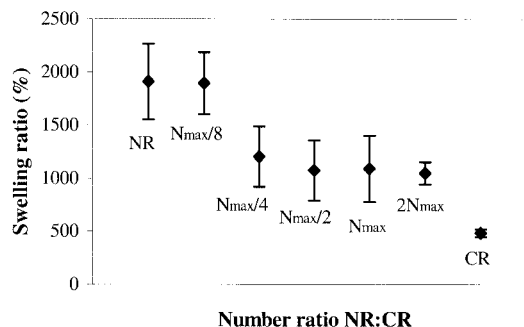


Figure 8 Swelling ratios of films cast from NR, CR, and heterocoagulated NR/CR-Tween latices.

confirmed that the outer shells of composite particles consisted of CR.

NR/CR latex films

Differential scanning calorimetry (DSC) thermograms of films cast from NR, CR, and heterocoagulated NR/CR-Tween latices are presented in Figure 7. Two separated T_g 's, corresponding to those of NR (-66°C) and CR (-43°C), were observed in each composite film, indicating the phase separation between the two rubbers.

The oil-resistant property, inversely proportional to the swelling ratio of the composite films, was also used as evidence indicating 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 Figure 8. As expected, there was a decrease in the swelling ratio of heteroco-

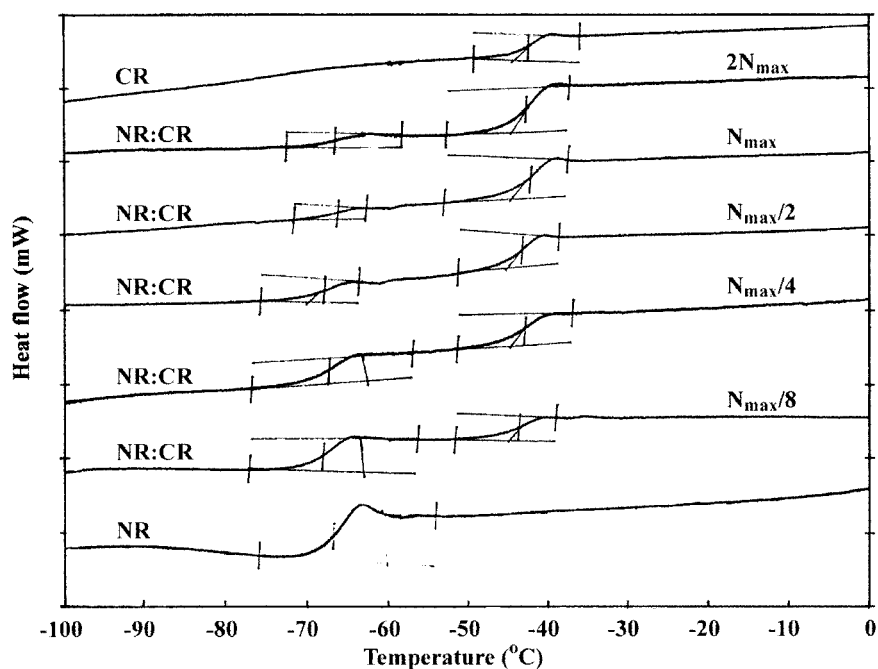


Figure 7 DSC thermograms of films cast from NR, CR, and heterocoagulated latices.

agulated NR/CR-Tween latex films with respect to that of NR (1900%). This could be explained by the fact that the outer shell, consisting of CR particles, which resisted oil, was responsible for preventing the penetration of toluene into the NR core in the composite films.

CONCLUSIONS

The HIPS impact resistance, based on RVNR, was enhanced by the addition of KRATON, which acted as a good compatibilizer at the NR/PS interface. An NR/CR-Tween 80 composite latex particle was successfully produced by the heterocoagulation technique and acted as a model for the study of the NR/PS core-shell structure, which theoretically could be suitable for the toughening of PS.

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