

Applications of Phase Transfer Technique to the Study and Development of Natural Rubber

P. TANGBORIBOONRAT, S. KUHAKARN, C. TIYAPIBOONCHAIYA

Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Phyathai, Bangkok 10400, Thailand

Received 10 March 2000; accepted 2 May 2000

ABSTRACT: The phase transfer technique was used for surface characterization of natural rubber latex and for preparation of toughened polystyrene based on γ -radiation vulcanized natural rubber. This process was extended to embed deproteinized natural rubber latex particles, crosslinked by γ -ray, in polystyrene for morphologically study. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1505–1509, 2000

Key words: phase transfer; natural rubber latex; toughened polystyrene

INTRODUCTION

It has been believed that natural rubber (NR) latex particles are stabilized by a complex layer of proteins and lipids.^{1,2} Several methods, e.g., electrophoresis and spectroscopy, are applied for the study of the layer; however, there has been no complete understanding up until the present.^{3,4}

A phase transfer technique is a method used for characterization of the surface of NR particles. This technique, developed to determine the surface charge of crosslinked synthetic latex such as polystyrene, poly(butyl acrylate), and poly(methyl methacrylate), involves titration of the negatively charged latex particles with cationic surfactants in the presence of a nonwater-miscible organic phase.⁵ At the titration end point, a hydrophobic layer is formed and the particles transfer from the aqueous phase into the organic phase. The quantity of surface charge was calculated from the amount of the surfactant required to cause transfer of the particles. Recently, the phase transfer

technique has been applied as a novel process for the study of rubber particle morphology and also for the preparation of toughened polystyrene.

EXPERIMENTAL^{6–10}

Natural Rubber Latex

γ -Radiation vulcanized natural rubber (RVNR) and deproteinized natural rubber (DPNR) latices were prepared from concentrated high ammonia preserved NR latex having ca. 60% dry rubber content (DRC).

Phase Transfer Procedure

A known amount of NR latex was diluted with distilled water to a required concentration. A given volume of organic solvent was added, the mixture was continuously stirred with an electromagnet, and then a cationic surfactant solution was slowly added via burette. The titration end point was determined when the mixture became translucent. By stopping the agitation at this point, the phase separation occurred immediately with the appearance of the clear aqueous phase.

Bulk Polymerization

RVNR or crosslinked DPNR latex particles were transferred into the styrene monomer, and al-

Correspondence to: P. Tangboriboonrat.

Contract grant sponsors: The Thailand Research Fund; Mahidol University; National Metal and Materials Technology Center, National Science and Technology Development Agency; ENO Science Foundation (Japan).

Journal of Applied Polymer Science, Vol. 78, 1505–1509 (2000)
© 2000 John Wiley & Sons, Inc.

lowed to swell for 24 h at room temperature. The styrene containing swollen transferred rubber particles was gently centrifuged by using a Supraspeed Centrifuge (Sorvall RC 28S, Du Pont) to eliminate trace of water before the addition of a benzoyl peroxide (BPO). The mixture was poured into a teflon coated steel mold ($10.4 \times 10.4 \times 2.6$ cm) and then heated in an oven at 70°C .

Determination of Properties and Morphology

Impact resistance of unnotched sample ($63.5 \times 12.7 \times 3.2$ mm, according to ASTM D4812-93) was measured by using an Izod apparatus (Zwick 5102). The average value of 10 specimens was reported for each measurement.

Morphology of rubber-modified polystyrene was studied by means of a transmission electron microscope model H 300 (Hitachi). The specimens were prepared according to osmium staining principle.

RESULTS AND DISCUSSION

Surface Characterization of Natural Rubber Particles

In our experiment, RVNR latex was first selected as a model for NR latex because the crosslinked structure provided easily transferable behavior, and also because of its ingredient-free nature compared to conventional sulfur vulcanization.⁶ Results showed that the optimum conditions of phase transfer, i.e., all of rubber particles were transferred instantly and their dispersion was visually homogeneous in organic phase after the phase transfer, were obtained when the solvent used was a "good solvent" for NR, e.g., cyclohexane, butyl acrylate, methyl methacrylate, toluene, and styrene. In this case, the critical transfer concentration (CTC; mole of used surfactant per gram of dry latex) did not depend on the type of organic solvent. However, coagulations of the RVNR latex were observed when the "poor solvents" such as heptane, *n*-octane, and acrylonitrile were used. The rubber particles were destabilized and suspended at the interface between organic solvent and water. This was explained by considering the solubility parameter of both materials because the latex particles were stabilized in organic phase after the phase transfer process due to polymer-solvent interaction.

Table I CTC (mole of Cationic Surfactant per Gram of Dry Latex) of RVNR Latex Using Toluene as Organic Solvent Determined by Phase Transfer Technique and CMC (mole/L) Values of the Cationic Surfactants Used as Titrant

Cationic Surfactant	CMC ($\times 10^{-3}M$)	CTC ($\times 10^{-5}$)
Benzyltrimethyloctadecylammonium chloride	0.12	5.7 ± 0.1
Benzyltrimethylhexadecylammonium chloride	0.15	5.8 ± 0.1
Benzyltrimethyltetradecylammonium chloride	1.8	6.5 ± 0.1
Benzyltrimethyldodecylammonium bromide	3.3	7.4 ± 0.1

Another important factor affecting phase transfer of RVNR latex was the structure of cationic surfactant used as the titrant. To obtain phase transfer of the latex, the surfactant must possess either two long alkyl chains, or one long alkyl chain and a benzyl group in the molecule. Two hydrophobic chains seemed to be necessary, one promoting the adsorption on the proteins at the rubber surface and the other contributing to the stabilization of the particles in the organic solvent after the neutralization of the surface charges. The CTC values depended on the alkyl chain length, and a direct correlation existed between CTC and critical micelle concentration (CMC) values of surfactant as presented in Table I.

Next, benzyltrimethylhexadecylammonium chloride (BHAC) was used as a titrant for phase transfer of the noncrosslinked NR latex.⁷ It was observed that the transfer of rubber took place immediately where three phases were noted, i.e., the upper organic phase containing the soluble rubber, the destabilized and suspended rubber at the interphase between organic solvent and water, and the lower rubber-free serum aqueous phase. Molecular weight of the soluble rubber in the upper toluene phase (in the case where toluene was used as solvent), measured by viscosimetric method, was about 10^6 . The combined solid content in the upper phase and the interphase was determined by evaporation method to reveal a 96% solid content, which indicated that the phase transfer process was completed.^{1,11} The partly coagulated and suspended rubber at the interphase between solvent and water in all sol-

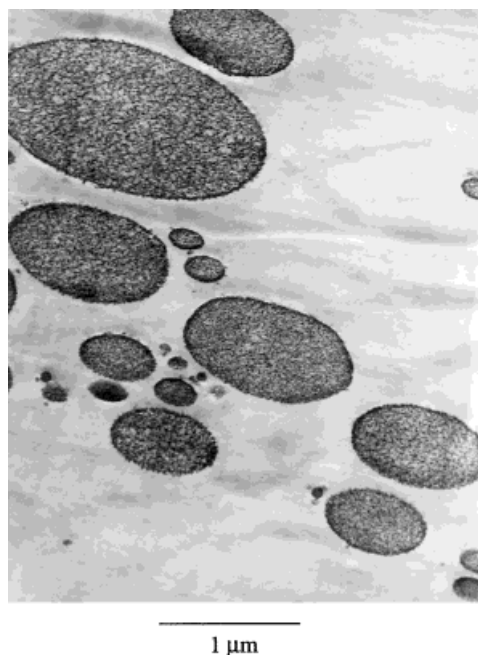


Figure 1 TEM of toughened PS based on 3% RVNR (14 kGy).

vents studied could be explained in terms of denaturation of proteins by cationic surfactant.¹² The neutralized polyisoprene chain chemically linked with denatured proteins might be unstable either in water or in organic medium.

For better understanding, this phase transfer technique was then extended to the study of DPNR latex (treatment of latex with alcalase enzyme).⁸ Similar observations to the case of non-crosslinked NR were noted, i.e., after phase transfer of the DPNR latex particles, three phases were also noticed where the destabilized and suspended rubber at the organic solvent–water interphase still existed. This might be attributed to the remaining proteins in the DPNR latex, bonded to rubber chain, which could not be removed by the enzyme and the proteins were consequently denatured by added cationic surfactant.

Bulk Polymerization of Styrene Containing Transferred NR

Besides surface characterization, the phase transfer technique has been used as a novel process for the preparation of toughened polystyrene.⁹ The negatively charged RVNR latex was titrated with BHAC in the presence of a styrene monomer. The crosslinked rubber particles transferred from the aqueous phase into the styrene phase in which

they swelled depending on the irradiation dose used. By bulk polymerization of the styrene phase containing transferred particles, the polymer blends exhibited two-phase morphology similar to that of commercial high impact polystyrene (HIPS), as shown in Figure 1. In the micrograph, the rubber particles (dark) dispersed in PS matrix (light) were revealed. The size distribution of crosslinked NR particles was rather broad and the shape elliptical. In the rubber particles, the presence of internal PS was found and the size was controlled by the crosslink rubber network as normally occurred in interpenetrating polymer networks.¹³

As previously mentioned, the variation of irradiation doses also caused the difference in ability of styrene monomer to swell the crosslinked rubber particles, and consequently, provided the difference in rubber volume phase and the amount of PS occlusions in the final toughened PS. However, the insignificant effect of irradiation doses used on impact property of the product was observed. This might be due to the rubber particles being fully crosslinked. The rubber volume phase and the amount of PS occlusions in the toughened PS prepared by using RVNR latex in the dose range (10–26 kGy) appeared to be similar. It was noted that the use of 14 kGy produced the highest impact of materials. Furthermore, there existed an optimum rubber content at 5% for maximum unnotched Izod impact resistance attainable as presented in Figure 2. A possible reason for this behavior was that, at lower rubber contents, the energy dissipated by the crack during propagation was not sufficient to prevent fracture of the specimen,¹⁴ whereas the higher rubber loading

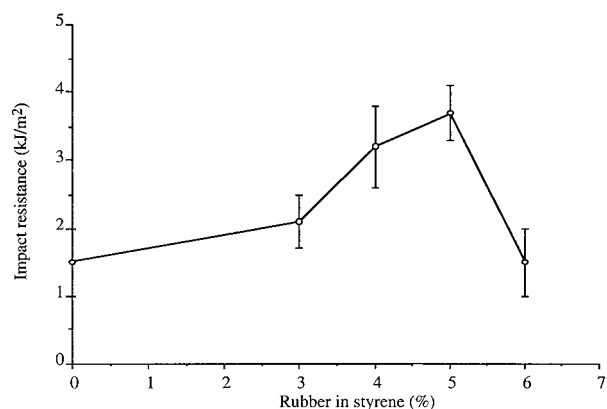


Figure 2 Unnotched Izod impact resistance of toughened PS based on RVNR latex (14 kGy) as a function of the rubber content.

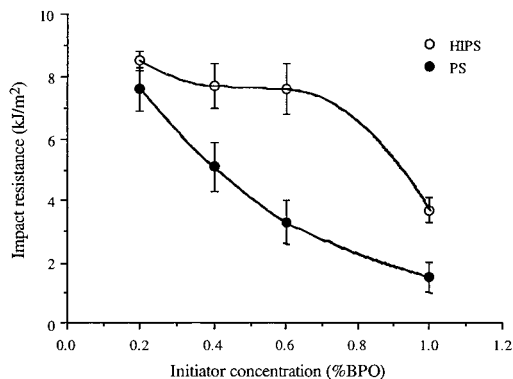


Figure 3 Unnotched Izod impact resistance of unmodified PS and toughened PS (5% of RVNR, 14 kGy) polymerized by using various concentrations of BPO at 70°C.

might affect the interparticle spacing in the matrix.

An increase in the unnotched Izod impact energy of the toughened PS, prepared by using 5% of RVNR (14 kGy) polymerized at 70°C, over the unmodified polystyrene at all concentrations of initiator, i.e., BPO, is shown in Figure 3.

Considering the CTC values, they were found to be dependent on the irradiation dose used. Figure 4 reveals that the CTC values decreased with increasing the irradiation dose, which corresponded to an increase in crosslink density of rubber. It could be explained that the highly crosslinked rubber particles would slightly swell in the styrene monomer, and consequently, exposed less surface charges than those in the case of the lightly crosslinked. However, these values are reproducible and do not depend on the quantity of rubber transferred (3–6% w/w).

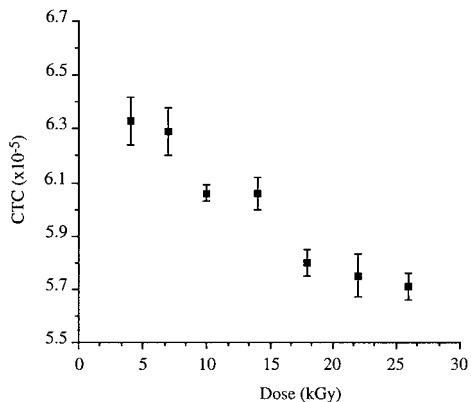


Figure 4 CTC values of RVNR latex irradiated with various doses.

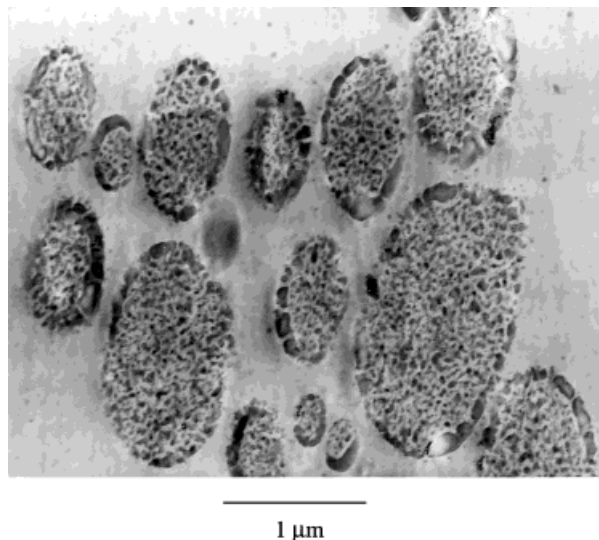


Figure 5 TEM of DPNR crosslinked by γ -ray (14 kGy) in PS matrix.

Recently, the NR latex/phase transfer/bulk polymerization process was developed to embed the crosslinked NR and DPNR particles in polystyrene to be further ultramicrotome-sectioned for morphological study under transmission electron microscopy (TEM).^{9,10} By using this method, the air, freezing, or chemical drying step of rubber latex, normally required prior to the embedding step for specimen preparation,¹⁵ is omitted, and hence, the disturbance of actual DPNR particle structure was minimized. It was important to observe, in Figure 1, that the RVNR latex particles were surrounded by a membrane layer, possibly derived from the protein–lipid complex.^{1–4} This membrane was clearly broken out in the case of the crosslinked DPNR particles (Fig. 5). It was explained that the deproteinization of the latex before irradiation removed a large proportion of the proteins and therefore the membrane might be partly destroyed during deproteinization. These micrographs can be regarded as the direct evidence to confirm the presence of proteins in the membrane layer around the NR particles, and moreover, the elimination of major proteins in DPNR latex.

CONCLUSIONS

The work described above contributed the following:

1. The phase transfer technique could be successfully used as a method for isolation of

- rubber from the aqueous phase. For the optimum phase transfer, the organic solvent used must be a "good solvent" for natural rubber, and the cationic surfactant must possess either two long alkyl chains or one long alkyl chain and a benzyl group.
- The quantity of surface charge of NR, corresponding to the CTC values, was determined from the amount of surfactant required in the titration.
 - The phase transfer/bulk polymerization process was a new method for preparation of toughened PS, based on RVNR latex, which exhibited the HIPS-like morphology. The irradiation dose was responsible for the control of the crosslink density of the rubber particles and consequently the size of occluded PS in the particles. The unnotched Izod impact resistance of the toughened PS prepared was generally higher than that of the unmodified PS.
 - By using the phase transfer/bulk polymerization process, the deproteinized γ -radiation vulcanized NR particles could be embedded in PS for further ultramicrotome-sectioning. The TEM micrograph revealed the destruction of the membrane layer surrounding the DPNR particles.

The authors gratefully acknowledge The Thailand Research Fund; Mahidol University; National Metal and Materials Technology Center, National Science and Technology Development Agency; and ENO Science Foundation (Japan) for financial support.

REFERENCES

- Gazeley, K. F.; Gorton, A. D. T.; Pendle, T. D. In *Natural Rubber Science and Technology*; Roberts, A. D., Ed.; Oxford Science Publications: Oxford, 1988; Chap 3, pp 63–97.
- Ho, C. C.; Ng, W. L. *Colloid Polym Sci* 1977, 257, 406.
- Ho, C. C. *Colloid Polym Sci* 1989, 267, 643.
- Eng, A.-H.; Tanaka, Y.; Gan, S.-N. *J Nat Rubber Res* 1992, 7, 152.
- Heim, Ph. Ph.D thesis, Université de Haute Alsace, Mulhouse, France, 1987.
- Tangboriboonrat, P.; Suchiva, K.; Riess, G., *Polymer*, 1995, 36, 781.
- Tangboriboonrat, P.; Suchiva, K.; Kuhakarn, S., *Polymer*, 1994, 35, 5144.
- Tangboriboonrat, P.; Suchiva, K.; Kuhakarn, S.; Tuchinda, P. *J Nat Rubber Res* 1996, 11, 26.
- Tangboriboonrat, P.; Tiyaipiboonchaiya, C. *J Appl Polym Sci* 1999, 71, 1333.
- Tangboriboonrat, P.; Tiyaipiboonchaiya, C.; Lerthittrakul, C. *Polym Bull* 1998, 41, 601.
- Nair, S. *Rubber World*, 1988, 198, 4.
- Hiramatsu, K.; Ueda, C.; Iwata, K.; Aoki, K. *Bull Chem Soc Jpn* 1977, 50, 368.
- Sperling, L. H. *Polymer Blends and Mixtures*; Walsh, D. J., Higgins, J. S., Macconnachie, A., Eds.; Martinus Nijhoff Publishers: Dordrecht, 1985; pp 267–287.
- Bucknall, C. B., *Toughened Plastics*; Applied Science Publishers: London, 1977; Chaps 8–10.
- Sawyer, L. C.; Grubb, D. T. *Polymer Microscopy*, 2nd ed.; Chapman & Hall: London, 1996; Chap 4.