Characterization of non-crosslinked natural rubber latex by phase transfer technique

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Phase transfer technique, using benzyldimethylhexadecylammonium chloride as a titrant, was employed for the characterization of non-crosslinked natural rubber latex. The critical transfer concentration values were reproducible in each solvent studied and the increase was found to coincide with the decrease of the difference between the solubility parameter of organic solvent and that of natural rubber. Results indicated a complete phase transfer process in which 96% of rubber was transferred.

(Keywords: phase transfer technique; natural rubber latex; cationic surfactant)

Introduction

Phase transfer technique was first developed by Heim[1] to determine the surface charge of crosslinked synthetic latex such as polystyrene, poly(butyl acrylate) and poly(methyl methacrylate). This technique involves titration of the anionic stabilized latex with an aqueous solution of cationic surfactant in the presence of a non-water-miscible organic solvent. At a certain concentration of the added cationic surfactant, the critical transfer concentration (*CTC*), which is just sufficient to form a hydrophobic layer, the latex particles transfer from the aqueous phase into the organic phase. The surface charge of the particles is calculated from the amount of added surfactant at the *CTC*. Also, the swelling ratio of the crosslinked synthetic latex particles can easily be determined by measuring the sizes of swollen and unswollen particles.

Tangboriboonrat and co-workers[2,3] applied the phase transfer technique for the surface characterization of γ-radiation vulcanized natural rubber latex (RVNRL). It was found that at pH values greater than the isoelectric point ($pH = 3.6$), the negatively charged RVNRL, derived from an adsorbed layer of a protein–lipid complex, could be transferred into the organic phase by titration with cationic surfactants with molecules bearing either two long alkyl chains or one long alkyl chain and a benzyl group. The resulting *CTC* values depended on the alkyl chain length. As observed in the case of synthetic latex[1], the quantity of rubber transferred and the volume of organic phase had no effect on the *CTC* values. Furthermore, the optimum conditions of the phase transfer technique were obtained when the solubility parameter of solvent was close to that of natural rubber.

At present it is not completely understood whether the non-rubber substances adsorbed on the natural rubber (NR) particles exhibit a definite influence on the colloidal properties of latex[4]. Since the surface of raw NR latex might be different from that of RVNRL previously studied, it was the objective of this work to use phase transfer technique for the characterization of non-crosslinked NR latex. Results of the effect of organic solvents used on the *CTC* values of non-crosslinked NR latex transferred by titration with benzyldimethylhexadecylammonium chloride are presented here.

Experimental

Concentrated high ammonia preserved NR latex (15 g), having 0.6% solid content, was diluted with distilled water (45 g), and the pH of the mixture was found to be ~ 9 without any adjustment. Organic solvent (30 g) was added and the mixture was titrated, while stirring, with 0.0121 M aqueous solution of benzyldimethylhexadecylammonium chloride, using a burette. The titration end point was detected when the mixture became translucent. Stopping the agitation at this point immediately caused a phase separation, with the appearance of a clear rubber-free serum aqueous phase.

The surface charge, which directly corresponds to the *CTC*, is calculated from the following equation:

$$CTC = \frac{VC}{10\,TSC\,m}$$

where CTC = critical transfer concentration (mole of used cationic surfactant per gram of dry latex), V = quantity of used cationic surfactant at titration end point (ml), C = surfactant concentration ($\mathrm{mol\,l^{-1}}$), TSC = total solid content of latex (%) and m = weight of latex sample (g).

Results and discussion

It was previously shown that crosslinked synthetic latex could be transferred with any cationic surfactants[1]. In the case of RVNRL, however, cationic surfactants having either two long alkyl chains or one long alkyl chain and a benzyl group were required for similar phase transfer, i.e. all of the rubber particles were transferred instantly and their dispersions were visually homogeneous in the organic phase. The latter cationic surfactants were therefore used in this present study on the transfer of non-crosslinked NR latex. It was observed that the transfer of rubber particles took place immediately where

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Table 1 *CTC* values (mole of titrant per gram of dry latex) of non-crosslinked NR latex using different organic solvents, determined by titration with benzyldimethylhexadecylammonium chloride

Solvent	δ^a $(\mathrm{J\,cm^{-3}})^{1/2}$	*CTC* $(\times 10^{-5})$
Cyclohexane	16.8	11.1 ± 0.1
Xylene	18.0	8.1 ± 0.2
Toluene	18.2	5.4 ± 0.4
Styrene	19.0	4.3 ± 0.1
Cyclohexanone	20.3	3.5 ± 0.1

^{a} δ = solubility parameter[7]; δ of natural rubber = 16.2–17.09 $(\mathrm{J\,cm^{-3}})^{1/2}$

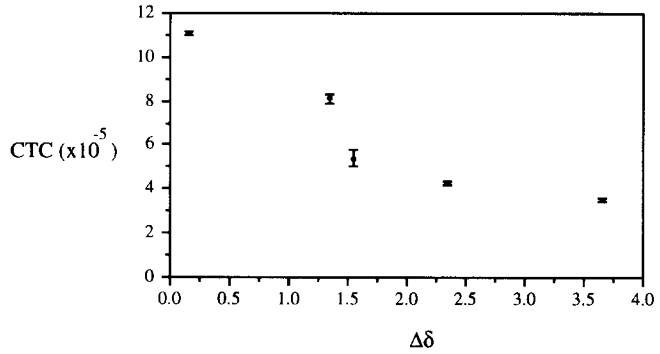

Figure 1 Relation between the *CTC* values of natural rubber latex (determined by titration with benzyldimethylhexadecylammonium chloride) and the difference between the solubility of organic solvent and that of natural rubber (using δ average of natural rubber = 16.65 $(\mathrm{J\,cm^{-3}})^{1/2}$)

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. The molecular weight of soluble rubber in the upper toluene phase (in the case where toluene was used as solvent), measured by viscosimetry, was about 10^6. The solid content in the upper phase and the interphase was determined by evaporation to reveal a 96% solid content, indicating that the phase transfer process was completed[4]. The partly coagulated and suspended rubber at the interphase between solvent and water in all solvents studied could be explained in terms of denaturation of proteins by cationic surfactant[5,6]. It is possible that the neutralized polyisoprene chains chemically linked with denatured proteins were unstable either in water or in organic medium. The chains having high molecular weight might be hydrophobic enough for dissolving in 'good' organic solvents.

The *CTC* values for the transfer of negatively charged non-crosslinked NR latex in various organic solvents, determined by titration with benzyldimethylhexadecylammonium chloride, are shown in *Table 1*.

Table 1 reveals that the observed *CTC* value depends on the type of organic solvent used. The *CTC* values are reproducible in each case and a direct correlation exists between the *CTC* value and the difference between the solubility of solvent and that of natural rubber (using δ average of NR), as shown in *Figure 1*.

It can be seen from *Figure 1* that the *CTC* value decreases with the increase in the difference between the solubility parameter of the rubber and that of the solvent. An explanation can be put forward that polymers in contact with solvents of 'like solubility parameter' show greatest solvation effect, i.e. expansion of the rubber chains. The greater the affinity of solvent for rubber, the larger the exposed surface charge would be and hence the increase of *CTC* values. On the contrary, as the solvent–polymer interactions decrease, intramolecular interactions become more important, which would lead to contraction of the rubber chains.

Conclusions

The phase transfer technique with benzyldimethylhexadecylammonium chloride could be used as a method for isolation of rubber from the aqueous phase. It was found that the organic solvent exhibited a direct influence on the *CTC* value, whereby this value increased with the extension of polymer chain in 'good' solvent. Details on the effects of biological origin of rubber tree and storage time of latex will be presented in a subsequent paper.

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