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Surface characterization of a γ-radiation-crosslinked natural rubber latex by a phase transfer technique with cationic surfactants

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A phase transfer technique was used to characterize the surface of a γ-radiation-vulcanized natural rubber latex (RVNRL). This technique involves titration of the negatively charged natural latex with cationic surfactants in the presence of an organic phase. The surface charge of the RVNRL was calculated from the amount of surfactant required to cause transfer of the rubber to the organic phase (critical transfer concentration). The optimum conditions of phase transfer were obtained when the organic solvent used was a 'good solvent' for natural rubber and its volume fraction was less than 0.5. The success of this technique was found to be dependent on the structures of the cationic surfactants that were used. These surfactants must contain either two long alkyl chains or one long alkyl chain and a benzyl group in their structures.

(Keywords: natural rubber latex; phase transfer; cationic surfactants)

INTRODUCTION

Natural rubber latex (NR latex) has been commercially available and exploited for use in a great variety of manufacturing products. Current demands in the market place to meet stringent performances for high quality products rely on the stability of the rubber latex. Despite their widespread use, there is still no complete understanding of the particle–serum interface which has a definite influence on the colloidal properties of a latex.

In retrospect, several reports[1–5] have shown that the NR latex particles are stabilized by a complex layer of proteins and lipids. Nevertheless, little direct knowledge exists concerning the materials adsorbed on the latex particles because any attempt to remove this adsorbed layer inevitably results in the immediate coagulation of the latex. Previous investigations, using electrophoresis, only showed that the latex particles are amphoteric in nature, with an isoelectric point at pH 3.8[2,6].

Blackley and coworkers[4,7–12] have reported the effects of various surfactants upon the mechanical and chemical stability of the NR latex. They showed that the addition of small amounts of carboxylate, sulfate or sulfonate surfactants can enhance the mechanical and chemical stability of the latex. This ability depends largely upon the chain length of their alkyl group. The optimum enhancement is observed when the alkyl chain of the surfactants contains approximately 11 carbon atoms. In addition, the effect of a range of n-alkyltriethylammonium bromides upon the mechanical stability of NR latex was also reported[9]. It was found that small additions of these surfactants, whose alkyl groups contain 8–12 carbon atoms, can bring about a small increase in the mechanical stability of the latex. These observations have been explained by a hypothesis that the added surfactants are adsorbed at the rubber surface and thereby make the indigenous soaps more effective as stabilizers. Consequently, the alkyl chain should be long enough to be strongly adsorbed at the rubber–water interface and also be sufficiently short to modify the nature of the indigenous soaps of the latex particles.

Connor and Ottewill[13] investigated the adsorption of n-alkyltrimethylammonium ions onto polystyrene latex particles stabilized by carboxyl groups. They indicated that the adsorption of surface active cations can be used to determine the number of carboxyl groups on the surface. It was also found that the critical coagulation concentration (*CCC*) of the latex depends on the alkyl chain of the surfactants. This implied that there existed considerable areas of hydrophobic character on the surface of the polystyrene latex.

The interaction of cationic surfactants with the anionic stabilized latex has been studied systematically by Heim[14] in order to determine the surface charge of the crosslinked synthetic latex. This method involves titration of the latex with the surfactant solution, in the presence of a

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*To whom correspondence should be addressed non-water-miscible organic phase, until the critical transfer concentration (*CTC*) is reached. At this concentration, a hydrophobic layer is formed and the latex would be transferred from the aqueous into the organic phase. The quantity of surface charge of the latex was calculated from the critical transfer concentration of the added surfactant. The swelling ratio of the synthetic latex particles was also easily determined.

In this present paper, we intend to show that the phase transfer technique can be applied as a way of characterizing the surface of radiation-vulcanized natural rubber latex (RVNRL). Although it is well known that the use of γ-radiation vulcanization of NR latex gives certain advantages when compared to conventional sulfur vulcanization, the structure and surface properties, however, have not previously been studied. Therefore, the phase transfer technique was adapted to the study of this type of latex. Due to its ingredient-free nature, RVNRL was chosen as a model for natural rubber latex in our study.

The surface characterization of RVNRL by phase transfer with cationic surfactants, including the effects of organic solvent, latex content and structure of cationic surfactants, are presented in this work.

EXPERIMENTAL

γ-radiation-vulcanized natural rubber latex (RVNRL)

General characteristics. The characteristics of the concentrated NR latex which had been crosslinked by γ-rays, and the vulcanized conditions, are given in *Tables 1* and *2*, respectively.

Particle size determination. The particle size distribution of the RVNRL was measured by using a laser particle size analyser (COULTER, Model LS 130). This analyser calculates the average particle size and standard deviation from measurement of the sample diffusion and diffraction. The volume distribution curve of the latex particle sizes is shown in *Figure 1*.

The histogram in *Figure 1* indicates a wide range of particle diameters for the RVNRL. The results give the volume diameter as ranging from 0.2 to 2.3 μm and the volume average particle size obtained is 0.7 μm. It is well known that the rubber particles in NR latex are naturally polydispersed[1-3].

Table 1 Characteristics of the natural rubber latex used in this study

Property	Value
Total solids content (TSC) (%)	61.8
Dry rubber content (DRC) (%)	60.4
KOH number	0.59
Volatile fatty acid (VFA) number	0.01
Mechanical stability time (MST) (s)	1304

Table 2 Irradiation conditions used for vulcanization

NR latex	FELDA HA
Radiation source	^{60}Co, 7.38×10^{15} Bq
Irradiator	Rotating vessel system
Rotating speed (rev min^{-1})	10
Temperature (°C)	25
Dose rate (kGy h^{-1})	0.565
Total dose (kGy)	12
Sensitizer	(a) 2-ethylhexyl acrylate 5 phr (b) CCl_4 1 phr

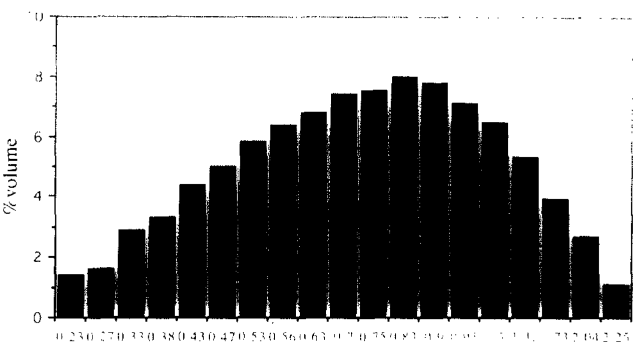

Figure 1 Histogram showing particle size distribution, by volume, of RVNRL

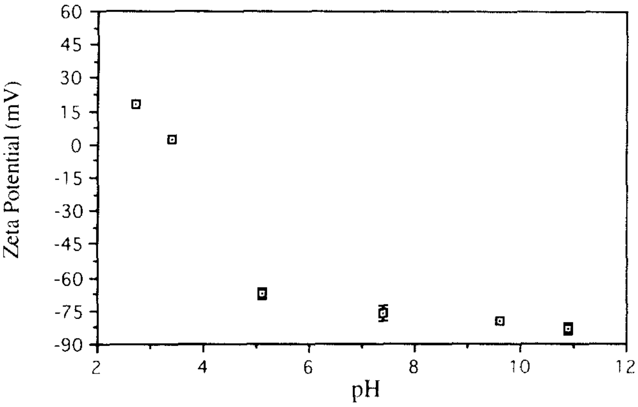

Figure 2 Zeta potential *versus* pH curve for RVNRL determined in the presence of NaCl (10^{-3} M)

Electrophoresis measurements. The RVNRL was diluted with sodium chloride solution (10^{-3} M), and the pH of the latex was then adjusted by adding an aqueous solution (1 M) of sodium hydroxide or hydrochloric acid. The zeta potential of the dispersion was determined by using a particle microelectrophoresis apparatus (Laser$_{ee}$^{tm}, Model 500, PENKEM), with measurements being carried out within 20 min after mixing and pH adjustment. The variation of the zeta potential of the RVNRL with pH at a concentration of sodium chloride of 10^{-3} M is shown in *Figure 2*.

The results obtained indicated that the surface of the RVNRL is amphoteric in nature, with an isoelectric point at pH 3.6. *Figure 2* shows that the rubber particles possess a positive charge when the pH is below 3.6. Above this pH, the value of the zeta potential is negative and changes rapidly with increasing pH. On the other hand, a small change in the zeta potential was found at pH values greater than 7 i.e. complete ionization of the ionogenic groupings occurs. This amphoteric character confirms the presence of proteins on the latex particles. However, the values obtained for the isoelectric point did not fall within the normal range of proteins (4.0–6.0)[2] which indicated that there was a preponderance of negative groups over positive groups on the particle surface. This observation could be reasonably explained only if, in

Table 3 Characteristics of the cationic surfactants used in the phase transfer experiments

		Number of carbon atoms (%)							
Code	Name	C10	C12	C14	C16	C18	C20	Molecular weight	Supplier
a	Tetramethylammonium bromide	–	–	–	–		–	154.1	Fluka
b	Tetrabutylammonium bromide	–		–				322.4	Fluka
c	Benzyltrimethylammonium bromide	–	–	–	–		–	230.2	Fluka
d	Dodecyltrimethylammonium bromide	–	100	–				308.4	Fluka
e	Tetradecyltrimethylammonium bromide	–	–	100	–	–	–	336.4	Fluka
f	Hexadecyltrimethylammonium bromide	–	–	–	100	–	–	364.5	Fluka
g	Benzyldimethyldodecylammonium bromide	–	100	–			–	384.5	Fluka
h	Benzyldimethyltetradecylammonium chloride	–	–	100	–	–	–	404.2	Fluka
i	Benzyldimethylhexadecylammonium chloride	–	–	–	100	–	–	414.2	Fluka
j	Benzyldimethyloctadecylammonium chloride	–	–	–	10	90	–	442.2	Aldrich
k	Dialkyldimethylammonium chloride (Präpagen WK)	–	1	2	30	66	1	565[a]	Hoechst
l	Didodecyldimethylammonium chloride	–	100	–	–	–	–	462.7	Aldrich

[a] Calculated value

addition to proteins, fatty acids are also present on the rubber particles[1–5].

Cationic surfactants

A series of quaternary ammonium salts were investigated and the specifications of these surfactants are given in *Table 3*. They were used as received, without any further purification.

Organic solvents

All of the organic solvents used in this work were commercial grades, obtained from various suppliers.

Phase transfer procedure

A known amount of the RVNRL was diluted with distilled water to a required solid content in an Erlenmeyer flask; the pH of the mixture was found to be ~9 without any adjustment. A given volume of organic solvent was added and the mixture was continuously stirred with a magnetic stirrer, and a cationic surfactant solution was then slowly added via a burette. The titration end point was taken as the point when the mixture became translucent. By stopping the agitation at this point, phase separation occurred immediately with the appearance of a clear aqueous phase. The upper phase was the organic phase which contained the homogeneously dispersed rubber particles, while the lower phase was the rubber-free serum aqueous phase.

The quantity of surface charge was calculated directly from the critical transfer concentration (*CTC*, which is the number of moles of surfactant used per gram of dry latex) by the following equation:

$$CTC = \frac{VC}{10 TSC m} \qquad (1)$$

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

RESULTS AND DISCUSSION

The phase transfer technique was used to determine the surface charge of the RVNRL. In order to determine the optimum conditions for this process it is necessary to consider the effect of organic solvents, the solid content of the latex, the volume fraction of the organic phase and the nature of the cationic surfactants[15].

Effect of organic solvents

The experiments were carried out by mixing 5 g of RVNRL (6% solid content) with 15 g of distilled water and 10 ml of various organic solvents (see *Table 4*). The mixture was titrated at pH 9 with an aqueous solution of cationic surfactant ($5\,\mathrm{g\,l^{-1}}$, i and k in *Table 3*). The effects of the various organic solvents are shown in *Table 4*. From *Table 4*, it is apparent that reproducible values for the *CTC* were obtained by the use of both cationic surfactants. It should be noted that the *CTC* did not depend on the type of organic solvent used. In addition, the results gave the optimum conditions for phase transfer when using the organic solvents shown as nos. 3–7 in *Table 4*, i.e. all of the rubber particles transferred instantly and their dispersions were visually homogeneous in the organic phase after phase transfer. To confirm this observation, the organic phase was separated by using a Sigma 202 MK centrifuge, operating at a speed of 5000 rev $\mathrm{min^{-1}}$ for 10 min. The solid content in this phase was determined by an evaporation method to give a value of 95%. Extraction of the rubber-swollen organic phase with toluene for 24 h and redetermination of the solid content also gave the same value for the latter in the transferred organic phase. This showed that no free non-rubber substances were transferred to the organic

Table 4 Values obtained for the *CTC* (mol of surfactant per g of latex solid content) of the RVNRL, titrated by using benzyldimethylhexadecylammonium chloride (i) and Präpagen WK (k) in different organic solvents

No.	Solvent	δ^a ($J\,cm^{-3})^{0.5}$	CTC^b (10^{-5})	CTC^c (10^{-5})
1	Heptane	15.1	Coagulation	
2	n-Octane	15.6	Coagulation	
3	Cyclohexane	16.8	5.8 ± 0.2	5.9 ± 0.1
4	Butyl acrylate	17.0	5.8 ± 0.1	5.9 ± 0.1
5	Methyl methacrylate	18.0	5.9 ± 0.1	5.9 ± 0.1
6	Toluene	18.2	5.8 ± 0.1	5.9 ± 0.1
7	Styrene	19.0	5.8 ± 0.2	5.9 ± 0.1
8	Acrylonitrile	21.5	Coagulation[d]	

[a] δ = Solubility parameter[16] = 16.2 – 17.09 $(J\,cm^{-3})^{0.5}$ for natural rubber

[b] Determined by titration with benzyldimethylhexadecylammonium chloride

[c] Determined by titration with dialkyldimethylammonium chloride (Präpagen WK)

[d] Coagulation observed without the addition of cationic surfactant

phase and therefore, the phase transfer process could be considered as complete, i.e. all of the rubber particles were transferred, and 5% of non-rubber species were left in the aqueous phase. The results obtained were in agreement with the typical values that have been reported for the composition of the NR latex[1,17].

In contrast, coagulation of the RVNRL was observed when heptane, n-octane and acrylonitrile were used as solvents (see *Table 4*). The rubber particles were destabilized and suspended at the organic solvent/water interface. This could be explained by considering the solubility parameters of both materials. Heim[14] found that latex particles were stabilized in the organic phase after the phase transfer process has taken place as a result of polymer–solvent interactions. Hence, the optimum conditions for phase transfer should be obtained when the solvent used is a 'good solvent'.

Effect of quantity of rubber transferred and volume fraction of organic phase

The quantity of rubber transferred (%P) is defined as follows:

$$\%P = \frac{\text{weight of rubber particles before transfer}}{\text{total weight of organic phase after transfer}} \times 100 \qquad (2)$$

while the volume fraction of the organic phase (f) is given by the following:

$$f = \frac{\text{volume of organic solvent}}{\text{volume of organic solvent} + \text{volume of aqueous phase before phase transfer}} \qquad (3)$$

The effect of %P on the *CTC* values was determined by using toluene, which is a good solvent for polyisoprene. Samples were also titrated at pH 9 with aqueous solutions ($5\,g\,l^{-1}$) of the cationic surfactants (i) or (k). The *CTC* values are shown in *Table 5*, where it can be noted that these values are reproducible and do not depend on the quantity of rubber transferred for either surfactant. When the effect of the volume fraction of the organic solvent was considered, it was found that optimum conditions for phase transfer could be obtained with $f < 0.5$ for each %P, with both surfactants. At $f \geq 0.5$, there was a tendency to form an inverse emulsion of the water-in-oil type and therefore phase separation did not occur at the *CTC*.

Effect of cationic surfactants

Three types of surfactants were used in this study:

Group 1. Tetraalkylammonium halogen i.e. surfactants a–c in *Table 3*.
Group 2. Alkyltrimethylammonium halogen i.e. surfactants d–f in *Table 3*.
Group 3. Dialkyldimethylammonium halogen i.e. surfactants g–l in *Table 3*.

It was observed that the RVNRL could be transferred by titration with cationic surfactants of the third group (g–l). In this case the latex was transferred and stabilized in toluene after phase separation. By contrast, cationic surfactants of the second group (d–f) caused precipitation of the latex. Here, the rubber particles were destabilized and remained at the solvent/water interface. Surfactants of the first group (a–c) showed no effect on the latex.

Typical examples of phase transfer using members of the homologous series of cationic surfactants of the third group is presented in *Table 6*. This table indicates that the *CTC* values decrease with the increasing alkyl chain length of the cationic surfactants. A direct correlation exists between the *CTC* and the critical micelle concentration (*CMC*) values of the surfactants. These observations, which confirm the adsorption phenomena, are in agreement with Connor and Ottewill's results[13].

Table 5 The effect of the quantity of rubber transferred (%P) on the *CTC* values (mol of surfactant per g of dry latex) of the RVNRL (f = 0.3), titrated with benzyldimethylhexadecylammonium chloride (i) and Präpagen WK (k)

m^a (g)	%P	CTC^b ($\times 10^{-5}$)	CTC^c ($\times 10^{-5}$)
5	3.3	5.8 ± 0.2	5.9 ± 0.1
7	4.6	5.8 ± 0.1	5.8 ± 0.1
9	5.9	5.8 ± 0.2	5.9 ± 0.3
11	7.1	5.8 ± 0.3	5.7 ± 0.1
13	8.3	5.8 ± 0.2	5.7 ± 0.1
15	9.4	5.9 ± 0.1	5.9 ± 0.1

[a] Weight of latex (6% total solids content)

[b] Using benzyldimethylhexadecylammonium chloride (i)

[c] Using Präpagen WK (k)

Table 6 *CTC* values (mol of cationic surfactant per g of dry latex) of the RVNRL, using toluene as the organic solvent (%P = 3.3, f = 0.3), determined by titration with cationic surfactants of the third group (g–j)

Cationic surfactant	Code	*CMC* ($\times 10^{-3}$ M)	*CTC* ($\times 10^{-5}$)
Benzyldimethyloctadecylammonium chloride	j	0.12	5.7 ± 0.1
Benzyldimethylhexadecylammonium chloride	i	0.15	5.8 ± 0.1
Benzyldimethyltetradecylammonium chloride	h	1.8	6.5 ± 0.1
Benzyldimethyldodecylammonium bromide	g	3.3	7.4 ± 0.1

From these results, it is clear that only the cationic surfactants of the third group are able to transfer the NR latex. However, their *CTC* values are different depending on the alkyl chain length. Furthermore, phase transfer occurs only if the solubility parameter of the solvent used is close to that of natural rubber.

Concerning the cationic surfactants, three conditions have to be met simultaneously in order to obtain a complete transfer of latex and a homogeneous dispersion of the particles in the organic phase after transfer:

1. adsorption of the cationic surfactant on the proteins at the surface of the rubber particles;
2. neutralization of the surface charges;
3. stabilization of the rubber particles in the organic medium.

The cationic surfactants of Group 1 do not fulfil any of the above conditions, while those in Group 2 led to precipitation of the latex. Only the cationic surfactants of Group 3 meet simultaneously all three requirements. To obtain phase transfer, two hydrophobic chains seem to be necessary, with one promoting the adsorption and the other contributing to the stabilization of the particles in the organic solvent.

It is interesting to note that synthetic polyisoprene latex, stabilized with classical surfactants, i.e. of low molecular weight, can be transferred by using any of the cationic surfactants of groups 1, 2 or 3[15]. This difference in behaviour between the synthetic latex and natural latex may arise from the presence of a protein–lipid complex at the surface of the natural rubber particles. Furthermore, it is well known that cationic surfactants can cause denaturation of proteins[18]. The stability of the rubber particles in an organic medium might therefore be attributed to:

1. the second alkyl chain of the cationic surfactants;
2. the floating chain of polyisoprene on the surface of crosslinked rubber particles;
3. the denatured proteins.

CONCLUSIONS

A study of the surface characterization of γ-radiation crosslinked natural rubber latex (RVNRL) using a phase transfer technique indicated that the critical transfer concentrations (*CTC*s) were dependent on the structures of the cationic surfactants used and not on the quantity of rubber transferred, or the volume fraction of the organic solvent.

It was shown that the following conditions must be met for an optimum phase transfer process to take place:

1. The organic solvent that is used must be a 'good solvent' for natural rubber. This can be explained in terms of a steric stabilization of the rubber particles by polymer–solvent interactions after phase transfer.
2. The cationic surfactants must have either two long alkyl chains or one long alkyl chain and a benzyl group. Two hydrophobic chains seemed to be necessary, with one promoting the adsorption and the other contributing to the stabilization of the rubber particles in the organic solvent. The *CTC* values depended on the alkyl chain length, and a direct correlation existed between the *CTC* and *CMC* values of the surfactants.

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