REFRACTIVE INDEX OF LATEX SUSPENSIONS

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1. INTRODUCTION

Alexander *et al.* (1981) and Meeten and North (1991) used critical angle measurements to determine the refractive index of concentrated suspensions of colloidal particles. In these experiments the suspension is held in a cell either against the face of a glass prism or between glass lenses. The refractive index is shown to vary linearly with concentration and gave fair agreement with theoretical predictions using the Mie scattering models.

The objective of the experiments described in this note was to ascertain whether non-contact reflection measurements at the free suspension-air interface could also be used to determine refractive index of the suspension. This approach may be attractive in some circumstances, for example, where contact methods are undesirable. Four samples of styrene-butadiene (SB) latex suspended in water, were measured by reflectometry at a range of volume fractions from 0 – 50 vol%.

2. SAMPLE PREPARATION

The four styrene butadiene latexes were supplied at nominally 50% by volume. Particle radius (manufacturer's data) of the four samples is given in table 1. No data was available on polydispersity or styrene-butadiene ratio, but the samples were evidently reasonably monodisperse as all showed strong brown colouration in transmission (evidence of a band gap caused by particle ordering; see for example Elton *et al.*, 1998).

Table 1 Particle size data for the four SB latexes

Sample	Diameter/ nm	Measured solids/ wt%	Volume%
A	195	50.5	50.0
B	160	50.0	49.5
C	130	50.8	50.3
D	100	49.3	48.8

Each latex suspension was diluted successively from the original concentration down to nominally 37.5%, 25%, 12.5%, 5.25%, 3.125% by volume using distilled water. The density of the latex was assumed to be 1020 kg m^{-3}.

Samples were prepared for reflectomety by drawing down a smear of the suspension onto the ground back face of a glass standard (Fig 1) It was assumed that the reflection from the rough interface would be negligible (indeed, in air the ground surface produced only a barely measurable gloss).

In preparing thin smears of transparent fluids for reflectometry, it is important to eliminate as far as possible reflections from the second surface – ie. from the interface between fluid and substrate. If significant intensity is reflected from this interface, the analysis of refractive index will be compromised. This is the main reason why a rough glass block is used as the substrate. However, the rough surface also facilitates wetting and creation of a reasonable even smear.

An alternative way of presenting the samples might be in a liquid trough. In fact this method was tried, but, generally poor results were obtained owing to curvature of the surface due to meniscus forces and also to vibration of the free liquid surface.

The smears were not especially reproducible. Measurements were repeated 5 – 10 times moving the smear around. For some, additional smears were prepared and measured. The smears on the glass substrate were presented to the Reflectometer using the standard spring-loaded plunger device. In this method the glass substrate is pushed up against the reference plate which defines the measurement plane. The reference plate inevitably becomes contaminated with latex suspension, but this is easily washed off (before the suspension dries!). It is possible that this method also introduces a small height offset due to the film thickness, but the offset (if any) should be similar for all samples and this method of sample presentation is by far the quickest.

Reflectometric measurements were made using the Surfoptic SIRS 75 Imaging Reflectometer

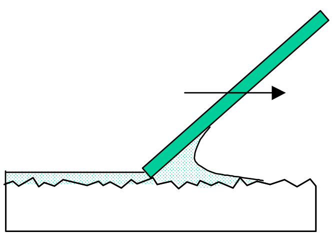


Fig. 1a – using a glass slide to draw down a smear of latex suspension.

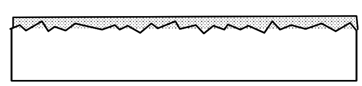
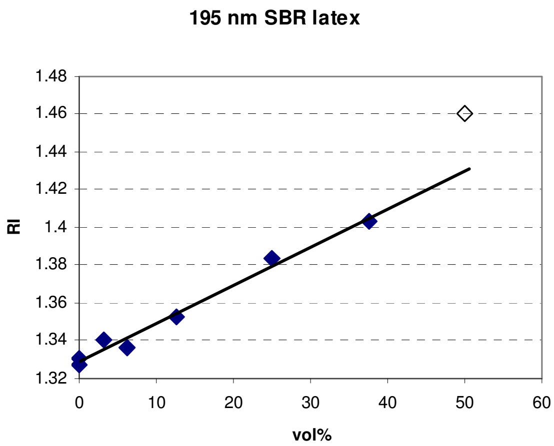


Fig. 1b – smear of latex suspension on ground glass substrate. The interface between the latex and substrate is optically rough to eliminate reflection from this surface. Only reflections from the air-latest suspension interface contribute to measurements.

3. RESULTS

Figure 2 shows plots of refractive index versus volume percentage for the four latexes. In each case, the refractive indices increase linearly with volume percentage up to 40 vol%. The refractive index for the 50 vol% samples lies significantly off the line for all latexes. The smears at 50 vol% samples were difficult to prepare – they tended to be slightly coagulated and bubbly, so the results may be less trustworthy… however, the measurements on the 50% samples were nonetheless fairly repeatable and the trend is similar for all four samples. This result is discussed further below in section 5.

Extrapolating all four plots to 100 vol% yields a predicted RI for SBR latex of 1.532 ± 0.005. The RI for water from the intercept is about 1.329 (c.f. ~1.331 for λ = 635 nm). This value is within expected errors.



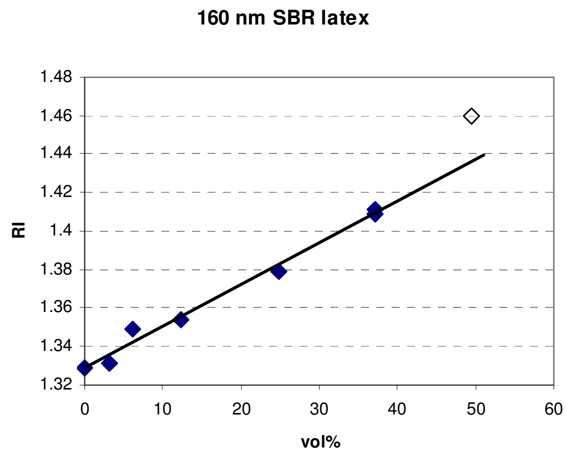
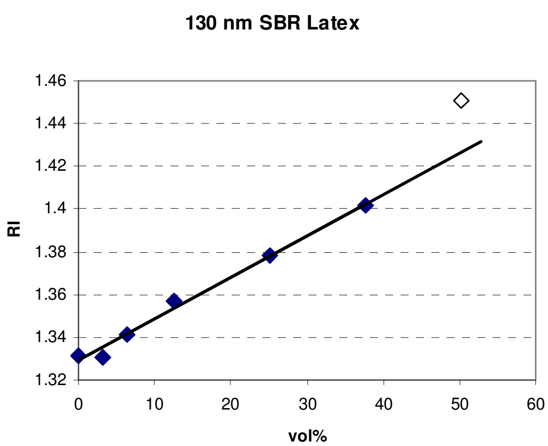


Fig 2a Refractive index vs Vol% for sample A. Note error bars are not shown as they are generally of the same size as the point marker.

Fig 2b Refractive index vs Vol% for sample B



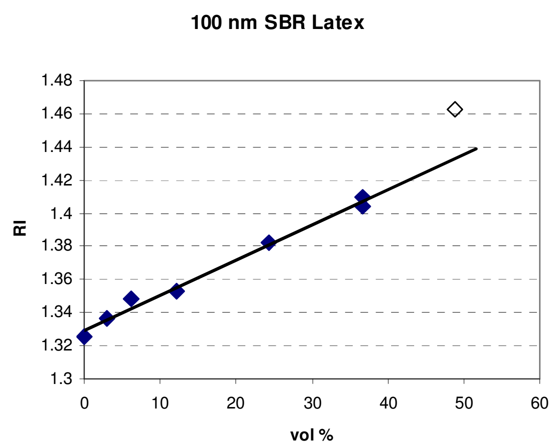


Fig 2c Refractive index vs Vol% for sample C

Fig 2d Refractive index vs Vol% for sample D

In all cases, measurements of microroughness and macroroughness were small or negligible. Figure 3 shows the observed glosses of the latex suspensions. The measured gloss (3° acceptance angle, G3) increases fairly linearly over the 0 – 40 vol% range. The results for the 50 vol% samples were very variable, probably because of variability and clumping in the film. The Reflectometer also measures gloss over nominally 20° acceptance angle (G20). Generally G3 = G20 for these samples. However, for the 50 vol% samples, G20 > G3 indicating that some light was being scattering outside the 3° acceptance of the usual gloss measurement for the high volume fraction samples.

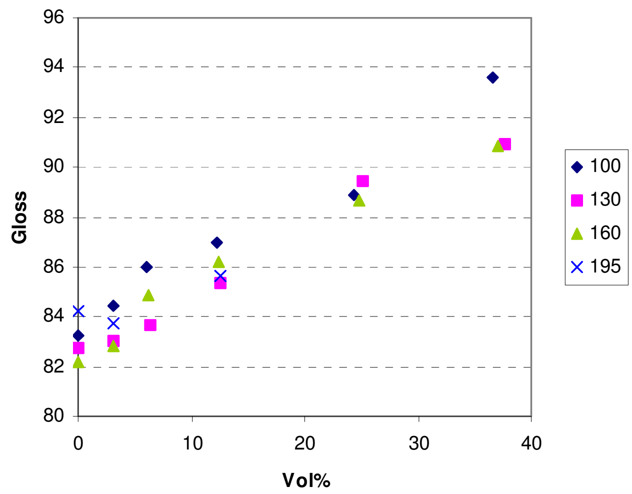


Fig 3. Observed glosses for the various latex suspensions

4. COMPARISON WITH THEORY

In their various papers, Alexander *et al.* (1981), Killey and Meeten (1981), Meeten and North (1991) (and references therein) used two methods for measuring the refractive index of concentrated colloidal suspensions. One method was to use a modified Abbé refractometer to perform critical angle measurements by reflectance. The second was using a specially designed transmission apparatus. In each case they observed that refractive index increased linearly with volume fraction up to about 0.5. The extinction coefficient, by contrast, tended to peak, then fall with increasing volume fraction owing to multiple scattering and particle crowding.

Champion *et al.* (1978) and Meeten (1980) developed theory for calculating the refractive index (and extinction coefficient) from various scattering theories. To first order, the refractive index of a homogeneous mixture of two components can be described as a linear combination of the individual refractive indices of the each component (e.g. Meeten, 1986):

$$n = n_1 v_1 + n_2 v_2$$

where n_1 is the refractive index of component 1 and v_1 its volume fraction in the mixture, etc. The idea can readily be extended to mixtures of many components.

In the case of colloidal paricles whose size is comparable with the wavelength of light, the particle size also has an influence on the measured refractive index. Latexes are ideal spherical particles with which to investigate the theoretical predictions. Following the theory set out by Killey and Meeten (1981) (and references therein), the refractive index of the latex suspensions used in this study have been calculated using Mie theory to obtain the refractive and scattering efficiencies for the spherical particles. It has been assumed that the refractive index of the bulk styrene-butadiene latex is 1.532 (as determined by extrapolation of experimental results here).

Table 2 shows dn/dv - the observed slope of the RI vs vol% graph compared to the same slope obtained from theory. Also shown is the observed intercept of the data which indicates the refractive index of water.

Table 2 The slope and intercept of the refractive index versus volume percent graph for the four latex samples, together with the slope calculated using Mie theory.

Sample diam/nm	dn/dv Observed x 1000	dn/dv Mie x 1000	Intercept (RI of water)
100	213 ± 11	201	1.330 ± 0.002
130	194 ± 9	204	1.329 ± 0.002
160	216 ± 11	206	1.329 ± 0.003
195	202 ± 14	208	1.329 ± 0.003

The agreement is reasonable given the difficulty in preparing reproducible samples.

5. DISCUSSION AND CONCLUSIONS

This short study demonstrates that the Imaging Reflectometer can be used successfully to measure the refractive index of colloidal suspensions by reflection at the air-colloid interface. Latex has neutral buoyancy in water, so particles are expected to be evenly distributed through the film or bulk suspension. In the case of a sedimenting dispersion, it is possible that the measurements would be biased to the liquid phase and the method would consequently work less well.

Refractive index measurement precision by reflectometry is about ± 0.001. Results here are generally more variable than this owing to difficulties in preparing reproducible smears and the average standard deviation based upon repeat measurements on smears is around ± 0.006. Meeten & North (1991), give ± 0.003 as the approximate precision of their transmission critical angle method.

The change in refractive index with volume fraction is linear up to about 40 vol%. Results for 50 vol% show higher refractive index than expected, and a variable, but generally lower gloss. At this high volume fraction, scattering is evidently becoming more significant (as shown by the relative drop in 3° and increase in 20° acceptance angle glosses), and it is also likely that some particle ordering is occurring at the air-suspension interface. It was noted that the bulk 50 vol% samples showed a characteristic colour in transmission indicative of the formation of regular arrays of particles, and such ordering often occurs preferentially at interfaces. Ordering of particles at the surface layers may lead to interference effects and perhaps a local increase in particle volume fraction which could contribute to the anomalously high refractive index results for the 50 vol% samples.

The measured slope of refractive index with volume fraction agrees quite well with that calculated using Mie theory. The refractive index for bulk SB latex will depend on the precise composition which is not known here. However, the extrapolated value of 1.532 is within the expected range. The refractive index of water as determined by these measurements agrees within errors with the expected value. It is perhaps systematically slightly low, but within expected systematic errors of calibration and instrument geometry.

ACKNOWLEDGMENTS

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