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Particle Size Distribution of Natural Rubber Latex Using Electroacoustics

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Natural rubber latex diluted to 5% solids was rapidly and accurately sized using the AcoustoSizer, an instrument that makes use of electrokinetic effects to simultaneously determine particle size distribution (PSD) and zeta potential. The results obtained are consistent with the median size and degree of polydispersity observed by Transmission Electron Microscopy, though the shape of the PSD obtained by the two methods shows some difference. The zeta potential of the latex found with the AcoustoSizer was consistent with that obtained by other methods. The measurement requires minimal sample preparation and indicates the possible application of electroacoustics to routine sizing in the processing of natural rubber latex.

At present, the only reliable method for obtaining particle size distributions (PSDs) of natural rubber latex (NRL) is Transmission Electron Microscopy (TEM) which involves extensive and laborious sample preparation, requires counting the thousands of particles for accuracy (even with image-analysis software, this is a time-consuming procedure) and may not accurately reflect the size of the swollen particles in the latex. It is theoretically possible to determine particle size distributions and zeta-potentials (potential at the hydrodynamic slip surface) by measuring the response of a latex to an electric field[1]; if successful for NRL, this would potentially allow on-line monitoring of NRL PSDs under industrial conditions.

It is important to characterise these systems in terms of PSD and stability in order to understand shear-induced coagulation and other phenomena of importance in the manufacture of NRL products. For example, we have been preparing and investigating modified natural rubber systems similar to MG rubber[2–6] which are inherently sensitive to shear-induced coagulation during preparation[7].

When an alternating voltage is applied to a colloid, the particles move back and forth at a velocity that depends on their size and zeta potential (the electrical potential at the shear radius of the particles) and on the frequency of the applied field. As they move, the particles generate sound waves. This is called the electrokinetic sonic amplitude (ESA) effect and may be measured using a pressure transducer that converts sound to electrical potential[8]. This ESA potential is given by the expression:

$$A(\omega) = \frac{\phi \mu \, \Delta\rho}{\rho} Z \qquad \dots 1$$

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where $A(\omega)$ is an instrument constant dependent on the frequency of the applied voltage ω, ϕ is the volume fraction of particles, μ is the complex dynamic mobility, ρ is the density of the solvent, $\Delta\rho$ is the density difference between the dispersed particles and the solvent, and Z is a complex acoustic impedance function.

The dynamic mobility determined in this way can be related to particle properties by the relations determined by O'Brien for dilute (<5%) and relatively concentrated (up to 20%) suspensions[1,9,10]. The general form of these expressions is:

$$\mu = \frac{\varepsilon\zeta}{\eta} G\left(\frac{\rho\omega a^2}{\eta}\right) \quad \ldots 2$$

where ε is the electrical permittivity and η the viscosity of the solvent, ζ is the zeta potential at the particle surfaces, and G is a factor representing the effect of inertia on the dynamic mobility.

The AcoustoSizer is the name given by Colloidal Dynamics to a device they have developed which measures the dynamic mobility as a function of frequency and extracting from the resultant spectra information on the particle size distribution and zeta potential of a colloid[1]. These measurements can be made in suspensions at concentrations many times greater than those accessible by light scattering and hydrodynamic fractionation methods.

MATERIALS AND METHODS

Ammoniated NRL was supplied by Nuplex Resins of Botany, Australia and used as received.

The PSD of NRL was characterised using TEM and electroacoustically using the Colloidal Dynamics AcoustoSizer which enables simultaneous measurement of PSD and zeta potential ζ[11].

TEM Method

Equal volumes of 0.2 wt% NRL and 2 wt% OsO_4 were combined, with all due care being taken to minimise exposure to the highly toxic osmium tetroxide. After ten minutes, this was microcentrifuged for 3 min at 8000 r.p.m. and the clear supernatant containing residual OsO_4 discarded. This procedure was repeated two more times using distilled water to re-suspend the latex. A dilute suspension of the stained latex particles was then dried onto a standard TEM grid and examined using the Philips CM12 120 kV electron microscope at the Key Centre for Electron Microscopy and Image Analysis, University of Sydney.

AcoustoSizer Method

NRL was diluted and placed directly into the observation chamber of the AcoustoSizer, as shown in *Figure 1*, after the device had been zeroed on distilled water. Five and fifteen vol % solutions were examined.

RESULTS AND DISCUSSION

The AcoustoSizer afforded reproducible PSDs for NRL within a few minutes. The device outputs three parameters: a ζ potential, a median size, and a spread of particle sizes equivalent to the standard deviation of a log-normal distribution. Results obtained for two samples of NRL are shown in *Table 1*. *Sample 2* was a sample of NRL that had been stored for some months and had been found to coagulate more readily than the newer material of *Sample 1*.

The Smoluchowski ζ potential found with the AcoustoSizer was within 5% of the value

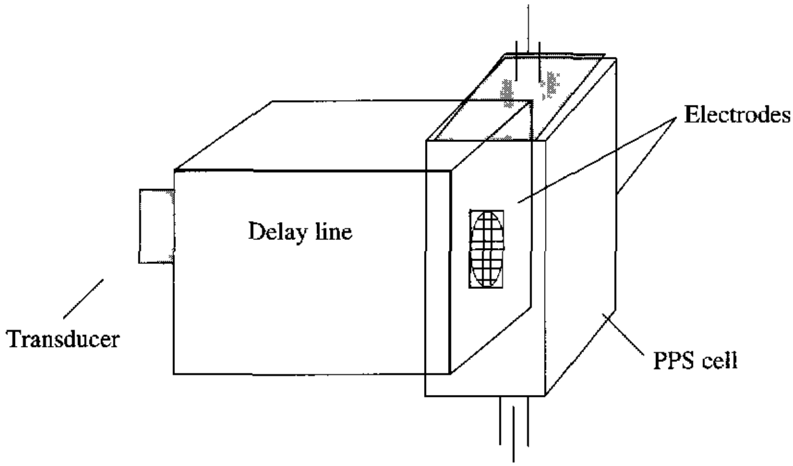

Figure 1. The AcoustoSizer.

TABLE 1. ACOUSTOSIZER RESULTS FOR NATURAL RUBBER LATEX

Parameter	*Sample 2*	*Sample 1*
Density (g cm^{-3})	0.913	0.913
Temperature (°C)	24.2	26.5
*p*H	10.28	10.10
Volume fraction solid (%)	5.0	5.0
Smoluchowski ζ^a (mV)	–66.2	–71.8
ζ potential (mV)	–80.9	–87.0
Median diameter (μm)	0.528	0.630
68% size range (μm)	0.238–1.172	0.305–1.303

[a]The Smoluchowski ζ potential is an approximation valid for particles with relatively thin double layers[12].

measured with a Brookhaven Instruments PALS (Phase Analysis Light Scattering) device.

PSDs from AcoustoSizer and TEM are best compared as cumulative distributions on a log (diameter) scale: the AcoustoSizer assumes that the cumulative distribution is log-normal, while the distribution seen with TEM is nearer to a normal distribution. The agreement between the PSDs determined by TEM and the AcoustoSizer for *Sample 1* is shown in *Figure 2* as a cumulative distribution, and as an actual particle size distribution in *Figure 3*. As can be seen, less physically reasonable polydispersities were obtained at larger volume fractions of solids, but the median values of particle size remained close to the value determined by TEM.

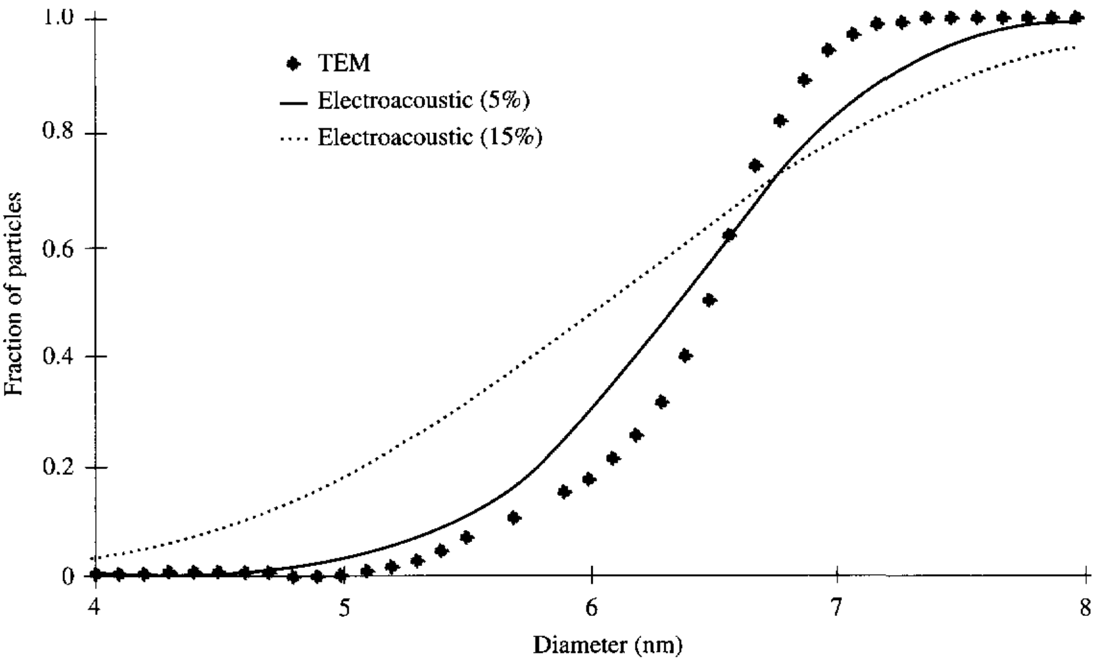

Figure 2. Comparison of cumulative particle size distribution obtained by TEM and ESA.

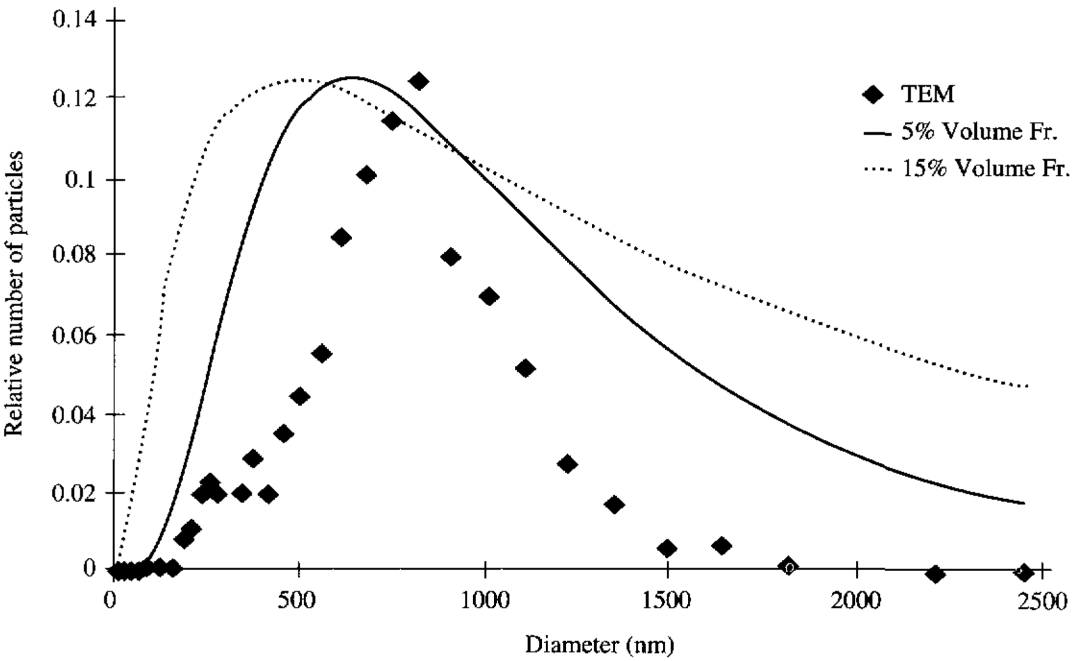

Figure 3. Data of Figure 2 *as (non-cumulative) particle size distributions; for convenience of comparison, all distributions have been normalised to have the same maximum value.*

Previously, electroacoustic effects have been of limited utility in the analysis of polymer latices, due to the fact that polymers tend to have densities relatively close to that of water, which has limited the sensitivity of the technique (from *Equation 1*, the magnitude of the ESA is dependent on the density difference between the disperse and continuous phases). New developments in the technology of the AcoustoSizer have increased its sensitivity, enabling its use in systems where the density difference is less pronounced.

CONCLUSION

The AcoustoSizer was found to be an excellent method for rapid PSD measurement for natural rubber latex. The agreement between TEM and AcoustoSizer was very satisfactory, particularly for low volume fraction samples (~5%).

There is considerable potential for the device in the rapid and reliable characterisation of dispersions such as NRL which have hitherto been very hard to investigate. Although the AcoustoSizer is not yet suitable as a direct in-line sizing instrument, only a relatively small step remains before this is a real option.

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