Polybutadiene latex particle size distribution analysis utilizing a disk centrifuge

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Abstract: Polybutadiene latexes made in emulsifier-free emulsion polymerization with diameters ranging from 50 to 300 nm of both unimodal and bimodal particles size distributions were analyzed by the line-start (LIST) method in a Brookhaven Disk Centrifuge Photosedimentometer (DCP). A special spin fluid was designed to be able to sediment polybutadiene since the density of the polymer is $0.89 \ gcm^{-3}$ and is thus less dense than its suspending medium. Density and viscosity gradients were created simply by adding five different mixtures of ethanol, water, and emulsifier in density sequence to the spinning disk. Coagulation problems caused by diluting polybutadiene latices with ethanol were overcome by using nonionic Triton X-100 surfactant. Good agreement in the average particle size and distribution as well as polydispersity between transmission electron microscope and disk centrifuge data was accomplished. The analysis time for polybutadiene latex particle sizing thus was reduced from several days to approximately 1 h.

Key words: Disk centrifuge photosedimentometer – polybutadiene latex – particle size distribution analysis

Introduction

Polybutadiene latex (PB latex) is an important industrial emulsion polymerization product produced in enormous quantities annually. PB latex is used in a wide variety of applications in which often the particle size and distribution is an important parameter in determining the final product characteristics. PB latexes are often purposely produced to have a broad or bimodal particle size distribution (PSD).

For analysis of the average particle size of polymer latexes with a relatively narrow PSD a wide variety of commercially available equipment is at hand. However, for the analysis of broad particle size distributions accurate data is hard to obtain. Dynamic light scattering is unsatisfying for latexes with a mixture of particle sizes in a wide range due to stronger scattering of light by the larger particles. The classical way of determining the PSD of PB latices is transmission electron microscopy. However, due to the low glass tran-

sition temperature, Tg of the polymer ($-86\,°C$) cross-linking is necessary. Cross-linking of the final latex by Osmium tetroxide (OsO_4) is a tedious and dangerous practice. Counting particle sizes from electron micrographs is unimaginative and time-consuming work. The difficulty of preparing representative samples requires the counting of at least one 1000 particles. Analysis times for any TEM measurement is long (several days) and thus absolutely unfit for product control during manufacturing. TEM image analysis provides a powerful means to overcome the counting, but not the specimen preparation problems. Field flow fractionation (SF3) and hydrodynamic chromatography (HDC) provide means of particle size analysis that overcome the TEM specimen problems. However, in this paper a new way of determining particle size and distribution of PB latexes is presented, namely, the disk centrifuge photosedimentometer.

The commercially available disk centrifuge equipped with a photo electric detector, computer

and software utilized in this study for the analysis of particle size and distribution by means of sedimentation is the Brookhaven BI DCP [1] (from now on denoted as DCP). The principles of operation of the DCP are elaborately explained elsewhere [1]. The calculations are based on Stoke's law and the light-scattering theory of Mie (turbidity measurement) for homogeneous spherical particles. The DCP can be used in the particle range of 10 nm to 60 μm for a wide variety of colloids like polystyrene latexes, silver bromide colloids and titanium oxide pigments. Separation of particles is based on Stoke's law [2] for sedimentation of particles in a centrifugal force field:

$$D^2 = \frac{18 \, \eta \, \log_e (R_d/R_m)}{t \, \Delta\rho \, \Omega^2} \, , \tag{1}$$

where D is the particle diameter, η is the viscosity of the spin fluid, R_d is the radius at which the detector is positioned, R_m is the radius at which the sample enters the meniscus of the spin fluid, Ω is the rotational speed of the disk, $\Delta\rho$ is the density difference between the particles and spin fluid, and t is the time needed for a spherical particle to sediment to the detector. The theory concerning the sedimentation and detection is well described in literature [3]. The apparatus creates the necessary centrifugal force field in a hollow PMMA disk that is filled with the so-called *spin fluid*. The sample is injected near the axes of the disk and the detector is positioned near the perimeter of the hollow cavity inside the disk. This short description of the equipment shows it is designed to sediment colloids with a specific density larger than the spin fluid utilized. Generally, the criteria for disk centrifuge operation are:

1) The mean density of the suspending medium and the particles must be less than that of the spin fluid in order to prevent rapid flow of sample into the spin fluid upon injection.
2) Particle density must be higher than that of the spin fluid in order to cause sedimentation instead of creaming.
3) Viscosity of the suspending medium must be adjusted slightly higher than that of the spin fluid.
4) Spin fluid must be compatible with the suspending medium of the sample in the sense that coagulation of the colloid needs to be prevented at all cost.

5) Refractive index difference must exist between spin fluid and particle other wise photo electric detection (in principal the scattering of light by particles) is impossible.

The generally accepted way of operation of the disk centrifuge is known in literature as the *line-start method* (LIST) [4] in which a sample is injected into the spinning rotor after which the particles sediment to the detector. Another method, the *homogeneous-start method* (HOST) [4] is reported for analysis of colloids with lower specific density than the spin fluid and its suspending medium. The sample is diluted in the rotor and creams towards the axis of the spinning disk. Although this is of current interest for low-density systems like polybutadiene, the HOST method has not been explored since the available equipment is not suited for this mode of analysis.

For colloids like polystyrene latexes, silver bromide and TiO_2 pigments, literature reports spin fluids consisting of, usually, mixtures of water, sucrose, glycerol, and methanol depending on the density and viscosity needed. However, these spin fluids are not suitable for sedimentation of PB latexes. The density of polybutadiene made in emulsion is 0.89 gcm^{-3} at 25 °C, as was measured by latex flow through an Anton Paar density meter (Anton Paar DMA 401, Graz, Austria). The density and total miscibility requirements led to spin fluid mixtures of water and large amounts of alcohols like methanol, ethanol, and propanol.

Coll and Searles [5] report that a spin fluid has to be built up in density and viscosity gradients to cushion the hydrodynamic shock of the particles as they enter the spin fluid. This provides laminar flow and avoids what is called streaming. Streaming is the effect [5] that small bands of sample break through the sample layer and disturb the analysis. The causes of streaming and band broadening are well documented [2, 6]. Coll and Searles describe a method of making an external density gradient and putting this in the disk. However, many workers in the field use the so-called *buffer layer method*. In this method a layer of pure solvent is introduced on top of the solute containing spin fluid which is followed by mixing of the layer with the spin fluid by acceleration or slowing down the disk speed. In this way the layer smoothly mixes with the spin fluid and forms the required gradients. In this paper a more straight-

forward approach is used to make a density and viscosity gradient capable of analysis of the average particle size and PSD of PB latexes.

Experimental

The PB latexes used were prepared by emulsifier free emulsion polymerization. Full experimental details are given elsewhere [7]. The PB latexes were dialyzed against doubly distilled water for several days until a constant conductivity was reached equal to that of the water used. Note that the latexes used maintained their colloidal stability upon mixing with solvents like methanol, ethanol, propanol, and acetone.

The particle size and distribution were determined by TEM (Jeol 2000 FX) in combination with osmium tetroxide staining techniques. Typically, some 1000 particles were counted (Zeiss TGA-10 particle analyzer) on a set of micrographs taken from various parts of the TEM sample grid. The TEM analysis was calibrated utilizing polystyrene micro spheres of known diameter.

The solvents methanol, ethanol, and propanol were examined for use as spin fluid. Methanol and water mixture gradients seemed incapable of stabilizing the spin fluid sufficiently to prevent streaming and band broadening. The density differences between pure methanol and polybutadiene are small, thus creating ineffectual gradients. The viscosity gradients suffer from the same disadvantage. Mixtures of propanol and water were unsatisfying because relatively high viscosity prolonged the analysis time during which latex coagulation caused excessive band broadening.

The spin fluid was prepared as a mixture of ethanol, Triton X-100 nonionic surfactant (polyethylene glycol tert-octyl phenyl ether, t-oct-C_6H_4-$(OCH_2$-$CH_2)_x$-OH, $x = 9$–10, Janssen Pharmaceutica B.V., Tilburg, The Netherlands) and water by making five different solutions of 3 ml of 68, 76, 84, 92% ethanol and 2 ml of 100% ethanol going from detector to injection level. In Table 1 the order of injection into the disk and the measured densities and viscosities of the mixtures is shown. The problem of latex coagulation was overcome by adding 5% Triton X-100 to the ethanol. The density and viscosity gradients were

formed by injecting the five mixtures in proper sequence in the spinning disk. It was not necessary to accelerate or slow down the disk speed to mix the layers, moreover, doing so evoked unsatisfying results. It is assumed that the injection of the liquids mixed the layers to an adequate degree to form a smooth uniform density gradient. After creating the gradients in the spin fluid the equipment was left spinning for 15 min to acquire a steady base line. The setup was then ready for injection of the sample.

The samples used in the disk centrifuge were dilute solutions of latex in ethanol and 5% Triton X-100, since the total density of the sample must be lower than that of the spin fluid. Approximately 0.5 ml of latex of 30% solids was added dropwise to 15 ml ethanol and soap mixture under constant mild agitation to prevent coagulation. This dilution was optimized to prevent band broadening in the DCP. The total number of particles analyzed this way is about 10^{13} times larger as compared with TEM analysis. The representability of the samples under dilution with solvent and the occurrence of any possible coagulation was checked by dynamic light scattering (Malvern IIc).

The density of the spin fluid components is determined using a density meter (Anton Paar DMA 55, Graz, Austria). The density meter was calibrated with distilled water and p.a. toluene at 20 °C.

The viscosities of the different layers of the spin fluid are determined using a viscosimeter (Ubbelohde Capillary Viscosimeter CT1450, Schott Geräte GMBH, Hofheim, BRD) which was calibrated at 20 °C. The densities measured in the density meter are used for the calculation of the viscosities according to:

$$v = \frac{\eta}{\rho} \equiv at , \qquad (2)$$

where v is the kinematic viscosity $[m^2 s^{-1}]$, η is the dynamic viscosity $[kg m^{-1} s^{-1}]$, ρ is the density $[kg m^{-3}]$, a is the calibration factor, and t is the time [s] for the liquid to flow out of the Ubbelohde capillary).

Results and discussion

The main aim of this paper is to show that the disk centrifuge method is capable of determining

Table 1. The densities [gcm⁻³], viscosities [cp] and injection order of the spin fluid components

Spin fluid component % by weight ethanol + 5% by weight Triton X-100	Density $[gcm^{-3}]$	Viscosity $[cp]$	Inject. order
100	0.806	1.358	5th
92	0.827	1.677	4th
84	0.846	2.006	3rd
76	0.866	2.309	2nd
68	0.882	2.655	1st

the PSD and average particle size of PB latexes, i.e., a colloid of lower density than its original suspending medium (serum water of the latex).

The densities of the spin fluid components are listed in Table 1. The average density of the spin fluid mixture is calculated to be: $\rho = 0.839 \, gcm^{-3}$. Introducing the densities of Table 1 in the calculation of the viscosities of the spin fluid components renders the results also shown in Table 1. The average viscosity of the spin fluid mixture is: $\eta = 1.881 \, cp$. The average viscosity and density are calculated according to Eq. (3), assuming ideal additivity of volumes:

$$\bar{Y} = \frac{2Y_{100\%} + 3Y_{92\%} + 3Y_{84\%} + 3Y_{76\%}}{11}, \quad (3)$$

where Y is either viscosity or density. The spin fluid of 68% ethanol is omitted from the average since this part of the spin fluid mixture is positioned beyond the detector in the spinning disk. This serves as a reservoir for the particles that passed the detector.

In Figs. 1a and 1b the cumulative number distributions (the Brookhaven instrument produces data in cumulative tables only) of PB latex with narrow PSD measured by TEM and the disk centrifuge are compared. Obviously, both the average particle size and PSD are in good agreement.

For disk centrifuge photosedimentometry the apparent diameter measured is proportional to the square root of the viscosity of the spin fluid and to the square root of the inverse of the density difference between the particles and the suspending medium according to Eq. (1) [1]. The differences observed between the DCP and TEM measurements are therefore probably not
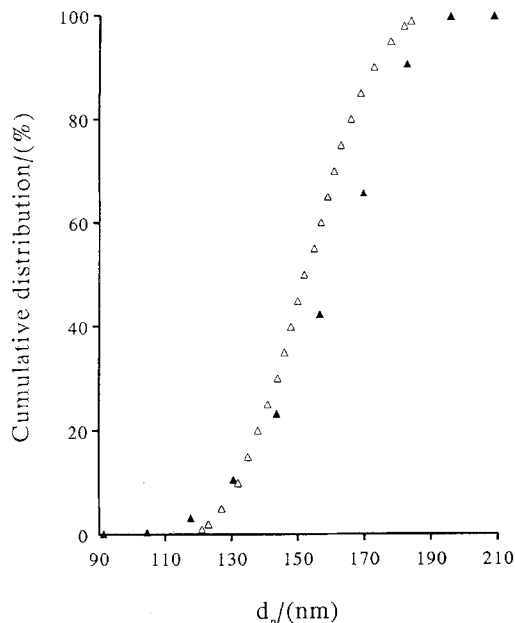

Fig. 1a. The cumulative number particle size distribution of a PB latex measured with TEM; ▲, $d_n = 159$ [nm] and $d_w = 166$ [nm], measured with DCP; △, $d_n = 152$ [nm] and $d_w = 157$ [nm]
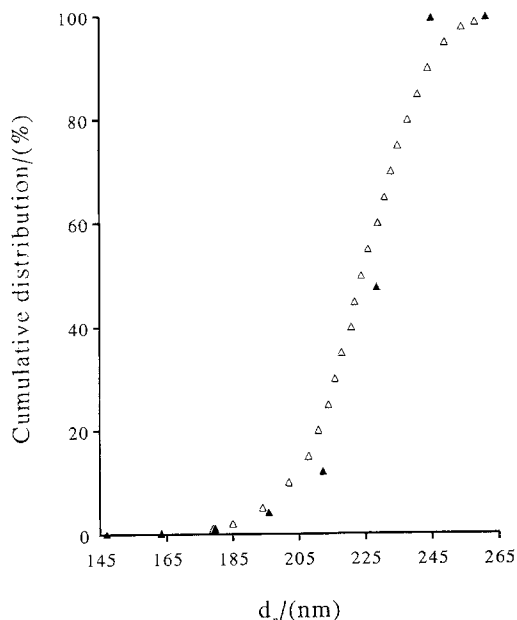

Fig. 1b. The cumulative number particle size distribution of a PB latex measured with TEM; ▲ $d_n = 226$ [nm] and $d_w = 288$ [nm], measured with DCP; △ $d_n = 224$ [nm] and $d_w = 287$ [nm].
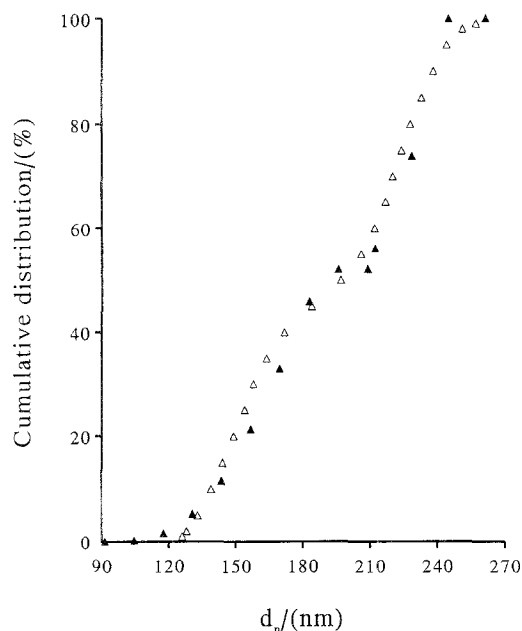
Fig. 2a. The cumulative number particle size distribution of a PB latex blend measured with TEM; ▲, $d_n = 193$ [nm] measured with DCP; △, $d_n = 191$ [nm]

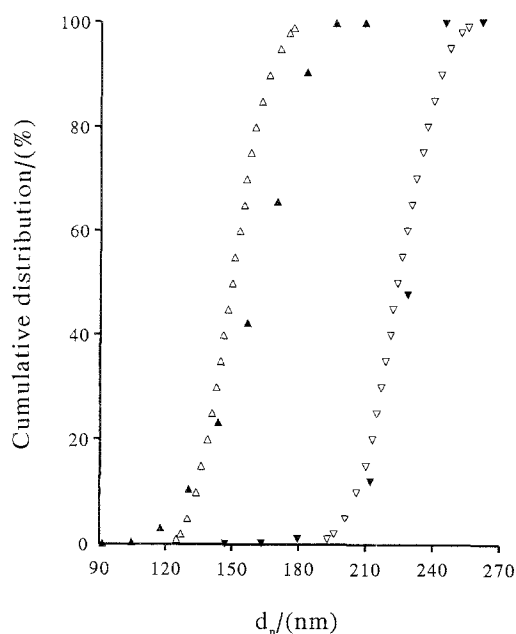Fig. 2b. The cumulative number particle size distribution of a PB latex blend measured with TEM; ▲ latex 1: ▲, $d_n = 159$ [nm] and $d_w = 166$ [nm] latex 2: ▼, $d_n = 226$ [nm] and $d_w = 228$ [nm], measured with DCP; △ latex 1: △, $d_n = 150$ [nm] and $d_n = 153$ [nm] latex 2: ▽, $d_n = 224$ [nm] and $d_w = 227$ [nm]

explained by inaccuracies in the determination of the spin fluid density or viscosity. Rather, an effect of how the measurements take into account the particle size distribution is the cause of the differences between TEM and DCP.

In Figs. 2a and 2b the analysis of a two PB latex mixture (1:1 ratio in polymer particles) resulting in a bimodal PSD is shown accompanied with the PSDs obtained via TEM analysis. In Fig. 2A the two peaks of the bimodal distribution were analyzed together and compared to TEM data. In Fig. 2B the two peaks were analyzed separately and compared with the separate sets of TEM data of the separate latices.

The disk centrifuge is capable of separating the two particle populations, provided the average particle sizes are not too close together (≈ 30 nm is the minimal required diameter difference to obtain a bimodal signal). The average particle sizes determined for both latices is in good agreement with the TEM data.

In Figs. 3a and 3b the number and weight cumulative particle size distributions of a broadly distributed PB latex are shown.

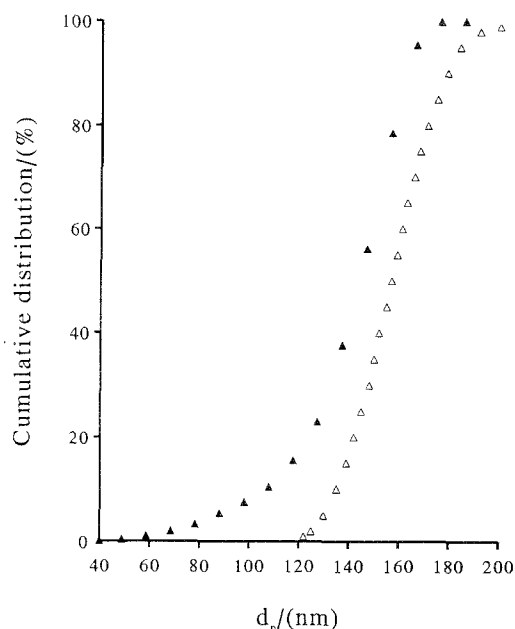Again, the agreement between both techniques is satisfying although TEM detects smaller

Fig. 3a. The cumulative number particle size distribution of a PB latex measured with TEM; ▲, $d_n = 139$ [nm], and measured with DCP; △, $d_n = 157$ [nm]
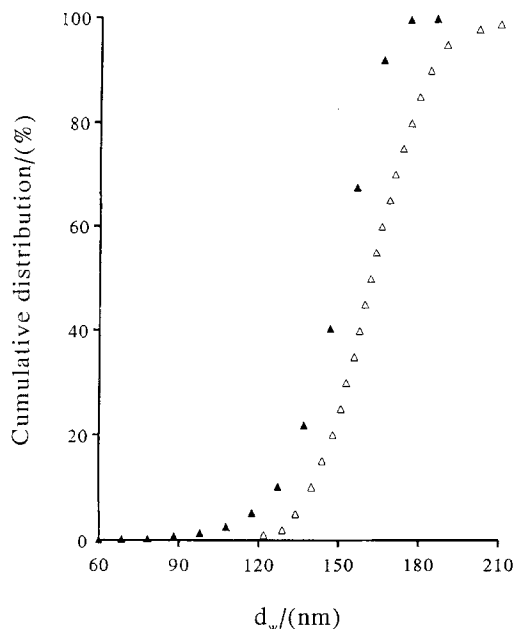
Fig. 3b. The cumulative weight particle size distribution of a PB latex measured with TEM; ▲, $d_w = 148$ [nm], and measured with DCP; △, $d_w = 162$ [nm]

Table 2. Number average diameter, d_n [nm], weight average diameter, d_w [nm], and polydispersity, d_w/d_n, determined by the disk centrifuge, DCP and by transmission electron microscopy, TEM

Figure	DCP			TEM		
	d_n [nm]	d_w [nm]	d_w/d_n	d_n [nm]	d_w [nm]	d_w/d_n
1A.	152	157	1.033	159	166	1.044
1B.	224	227	1.013	226	228	1.009
2B latex 1	150	153	1.020	159	166	1.044
2B latex 2	224	227	1.013	226	228	1.009
3A&B.	157	162	1.032	139	148	1.065

Figs. 1–3. The agreement between TEM and disk centrifuge is excellent.

Conclusions

The conclusions of this work can be summarized as follows.

It is possible to create a spin fluid with adequate density and viscosity gradients by sequentially filling the spinning disk with five different layers. The value of the densities of the layers should be slightly lower than the density of the particles, but higher than the density of the sample to avoid streaming.

It is possible to analyze a colloid of a density lower than that of its original suspending medium (in this case the water of the PB-latex) by diluting this medium with a completely miscible solvent with a density lower than that of the original suspending medium and colloid.

The overall agreement in analysis between TEM in combination with OsO_4 staining techniques and the disk centrifuge using the above-mentioned spin fluids is satisfying in average particle size, PSD, and polydispersity.

The analysis time of a disk centrifuge measurement including the preparation of the samples is about 1 h, depending on the particle size of the sample at hand. This is a considerable advantage over complicated and time-consuming TEM analysis.

The representability of the polybutadiene latex samples, made in emulsifier-free emulsion polymerization, is not affected by dilution in the different solvents used, as was shown by dynamic light scattering. Moreover, the amount of particles analyzed by the disk centrifuge is 10^{13} times larger as compared with TEM analysis.

particles than the disk centrifuge. This effect obviously is less pronounced in the weight average diameter. The disk centrifuge seems to underestimate the small particles with a diameter below 100 nm. This phenomena was observed on several occasions. The problems of detection of small particles in the presence of large particles is well known [3]. The broadness of the distribution also makes the TEM data less accurate even if the Osmium staining and cross-linking techniques applied are widely accepted in the literature [8–10] as the best way of determining polybutadiene latex particle size distributions which does not affect the particle size measured. Although about 1000 particles are counted from the micrographs, this is a very small amount as compared with the particle number concentration of such a latex. The effect of the use of Triton X-100 in the spin fluid on the DCP operation is accounted for by the measurement of the density and viscosity in the presence of this emulsifier. The true distribution is therefore hard to obtain and probably lies between the values provided by TEM and DCP.

In Table 2 the average particle size and polydispersity are given of the distributions depicted in

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