Particle Sizing of Flocculated Latex Particles by Physisorption of Nitrogen

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SYNOPSIS

Physisorption of nitrogen at one specific pressure is used to determine the specific surface area of a flocculated polystyrene latex by applying BET theory. Assuming that a flocculated sample of polymer latex is composed of distinct spherical latex particles (i.e., there is no coagulation of particles), the volume–surface-average diameter can be calculated. The resulting diameters are compared to sizes obtained using a disc centrifuge sedimentometer, which fractionizes the particles by sedimentation. The diameters from both techniques were in good agreement, showing that physisorption of nitrogen, which is a simple technique, can be used to determine sizes of flocculated latex particles. This agreement also shows that the flocculation of the polystyrene latex produced separate nonporous spherical particles. When flocculation of a latex is done above its glass transition temperature, coagulation will occur. While other particle sizing techniques can produce particle size distributions, the physisorption of nitrogen only gives the volume–surface-average diameter. However, one advantage of the physisorption of nitrogen is that it covers a broad range of particle sizes compared to most other techniques. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Particle size analysis is important because the particle size and particle size distribution determine the physical properties and therefore the end use of a latex product. Stability and viscosity of latexes, for example, are affected by the particle size. In film formation processes particle size and particle size distributions have great influence on minimum film formation and glass transition temperature and opacity or gloss. Consequently, there is a widespread interest in methods for determining particle sizes and particle size distributions. Several techniques based on different physical phenomena have been developed. These sizing techniques all have their relative advantages and disadvantages, which ultimately determine their suitability for a particular application.

The most important and widely used techniques are electron microscopy, light scattering methods, and sedimentation methods [e.g., disc centrifuge photosedimentometry (DCP) and field-flow fractionation]. Except for electron microscopy, these techniques are in general experimentally simple, fast, and inexpensive. However, complicated mathematical analysis of the data has to be performed in order to obtain the average particle size and size distribution. In case of the light-scattering methods the wavelength of the light source restricts the application range of particle sizes. Other sizing techniques also possess inherent deficiencies that restrict their applicability.

In this work a complete different physical phenomenon is used, namely physisorption of nitrogen. Physisorption of nitrogen is normally used to determine the surface of dry particulates. It is a fairly simple analyzing method, which has been used before to analyze the sizes of inorganic particles having simple geometric shapes. To our knowledge the use of this technique to determine polymer particle sizes has only been reported on by Goodall et al.[1] They found a good agreement between the surface areas calculated by the Brunauer, Emmett, and Teller

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(BET) treatment and those determined from electron micrographs. The specific surface area of flocculated latex particles is determined with this technique by applying the BET theory.[2] Assuming that a flocculated sample of polymer latex is composed of distinct spherical latex particles (i.e., there is no coagulation of particles), the volume–surface-average diameter can be calculated. Thus particle sizing is carried out on dry latex particles instead of the suspended particles used in most other sizing methods. The authors want to show that the studied system is indeed spherical polystyrene particles as is presented with the transmission electron micrograph (TEM) (see Fig. 1).

Further it should be emphasized that the assumption of spherical particles is a crucial assumption. When the particles are not spherical, other particle size measurements (TEM, DCP) will give more reliable results than the gas adsorption method. Physisorption of nitrogen will cover a broader range of particle sizes (0.01–2 μm).

Other advantages of this method are: the technique is simple, quick, and robust; well suited to industrial application; and the technique is relatively cheap. In this way an existing technique, well known in the field of the inorganic chemistry is being extended to the colloid chemistry for the determination of particle sizes.

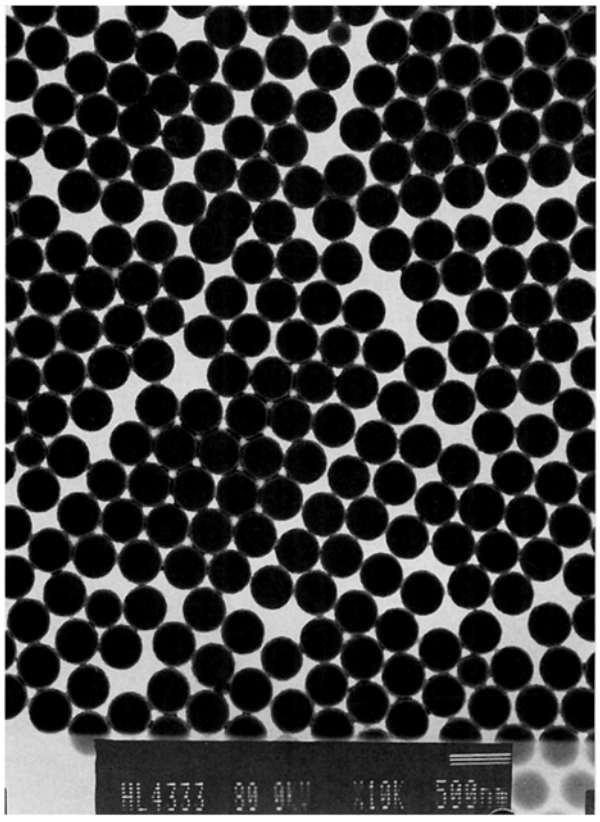

Figure 1 TEM-micrograph of styrene latex particles, prepared by surfactant free emulsion polymerization.

The disc centrifuge photosedimentometer uses the fractionating technique based on sedimentation of particles and their difference in extinction. From the signal of the optical detector, the particle size distribution can be calculated with the help of light-scattering theory. In this short communication disc centrifuge measurements are compared with the results from physisorption experiments.

The sizes measured by physisorption are in good agreement with the sizes measured by the disc centrifuge method. This means that physisorption of nitrogen can be used as a simple and relatively fast method to determine volume–surface-average particle sizes.

EXPERIMENTAL

Materials

A series of standard monodisperse polystyrene latexes in a particle size range from 0.01 to 1 μm was used. These latexes were prepared by surfactant-free emulsion polymerization using a persulfate initiator system in a batch reactor. The method of preparation of these seeds will be reported elsewhere (Zirkzee et al. in preparation). One polystyrene–divinylbenzene latex with a diameter of around 2 μm was added to this series. $Al(NO_3)_3$ nonahydrate (Merck, extra pure) was used as the coagulant and H_2SO_4 (Merck, 95–97% p.a.) to adjust the pH of the latex.

Methods

DCP

The Brookhaven Bi-Disc Centrifuge Photosedimentometer was used to determine the surface-average diameter of the standard latexes. Theory and experimental procedure of the disc centrifuge method can be found in the literature.[3]

Flocculation

The latices were flocculated by a dropwise addition of the coagulant $Al(NO_3)_3$ ($1M$) under careful stirring. As soon as aggregates of latex particles were formed, stirring was stopped and the latex was left to flocculate completely. To prevent deposition of aluminum oxide, the pH of the latex was raised to 3–4 with H_2SO_4 before flocculation. The flocculated latex particles were filtered over a Buchner funnel and dried in a vacuum stove at 50°C.

Physisorption of Nitrogen

The Carlo Erba Instruments Sorpty 1750 was used to determine the surface area by physisorption of nitrogen. The Sorpty 1750 is a fully automated instrument for rapid surface area determinations based on a static volumetric principle. The adsorbed gas volume is calculated by measuring the pressure change resulting from adsorption of a known volume of gas (nitrogen). The physisorption of nitrogen by a sample is measured at a single relative pressure P/P_0 of 0.17, within the linearity of the BET theory.[1] P_0 is the saturated vapor pressure of nitrogen (795 mmHg).

The whole procedure was started by weighing a sample of about 2 g of the flocculated latex in a glass burette.

Before actual physisorption of nitrogen was measured, it was very important to purify the sample by outgassing. Outgassing was carried out at 50°C until the pressure dropped below 0.04 mbar. The outgassed sample was weighed again in the burette under vacuum. After this outgassing procedure the burette was connected to the gas outlet and a thermos flask filled with liquid nitrogen was placed over the burette.

A blank analysis with inert helium gas must be performed with the sample in the burette in order to calibrate the measurement circuit. This method was used to check the volume of burette and circuitry. Helium was directed from a variable volume chamber at a pressure of 795 mmHg into the evacuated burette until a preset pressure of 135 mmHg was reached. When equilibrium was established a piston compressed the helium in the volume chamber to the original pressure of 795 mmHg to counterbalance the volume of gas that had passed into the measurement circuit and burette. From the new position of the piston the volume of gas added to the burette was calculated, and thus the surface area of the burette and circuitry could be calculated.

The physisorption of nitrogen was carried out with the same procedure as described above for the blank measurement. The blank measurement was subtracted from the value obtained by the physisorption of nitrogen. The specific surface area of the sample was calculated by dividing the surface area by the sample weight.

RESULTS AND DISCUSSION

From the specific surface area S, measured by physisorption of nitrogen, the volume–surface-average diameter d_s can be obtained for monodisperse spheres with density ρ_s according to Eq. (1).

$$S = \frac{6}{\rho_s d_s} \tag{1}$$

where the density of polystyrene is 1.05 g/cm^3. The limit of particle sizing is dependent on the accuracy of the surface area measurement. Areas that can be measured with the Sorpty 1750 lie between 1 and 1000 m^2/g, as claimed by the manufacturers. This compares with particles sizes ranging from 2 to 0.01 μm. However, for samples with small surface areas (1–3 m^2/g) or less, more polymer sample may be required in order to perform accurate measurements. One final assumption that has to be made is that the cross-sectional area of an adsorbed nitrogen molecule is constant (0.162 nm^2). This assumption is necessary because the cross-sectional area of the adsorbate may vary from one polymer to another.

The results of the measurements done by the disc centrifuge method and the physisorption method are shown in Table I. The left part of Table I contains the volume–surface-average diameters and the dispersities measured by the disc centrifuge method according to surface areas, calculated by Eq. (1). The right part of Table I lists the specific surface areas of the flocculated latex particles measured by the physisorption of nitrogen and the according to diameters, calculated by Eq. (1).

The diameters determined by the disc centrifuge method and by physisorption of nitrogen show a good agreement. From this agreement can be concluded that there is negligible coagulation during this process. Polystyrene has a glass transition temperature of 100°C. One of the flocculated polystyrene latexes (sample 2) was heated at 120°C and the specific surface area decreased from 16.8 to 2.3 m^2/g. The particles obviously underwent coagulation, thus reducing their specific surface area. We can conclude from this that latices with a low glass transition temperature should be flocculated below their glass transition temperature in order to avoid coagulation

Table I Comparison between Disc Centrifuge and Physisorption Results

	Disc Centrifuge			Physisorption	
Sample	d (nm)	Dispersity d_w/d_n	S (m^2/g)	S (m^2/g)	d (nm)
1	91	1.011	62.8	55.4	103
2	342	1.018	17	16.8	340
3	487	1.366	11.7	15.3	373
4	774	1.014	7.4	7.7	742
5[a]	2061	—	2.8	2.9	1970

[a] Styrene divinylbenzene latex.

and erroneous particle sizes. This can be achieved by freeze drying techniques. Also note that physisorption of nitrogen together with other particle sizing techniques can give information on the physical state of the latex particles (whether or not particle coagulation occurs at a particular temperature, etc.).

Physisorption of nitrogen as a particle sizing technique *only* gives a surface-average diameter. Utilizing Eq. (1) assumes that the latex particles are monodisperse. Therefore, experiments on polydisperse latices will give average diameters with larger deviations from the true values.

This can be seen in Table I, where the latex with the highest polydispersity gives the biggest deviation from the DCP value (the DCP technique measures the full particle size distribution). This limitation is common to many techniques utilized for measuring latex particle sizes and must be kept in mind when using these techniques.

The authors want to clarify that it is quite possible that a sample containing two different materials can have the same surface area but two totally different particle size distributions. In this case, the average particle size as determined by gas adsorption will have a limited value. Obviously, the more monodisperse the latex sample the more accurate the measured diameter.

CONCLUSIONS

Physisorption of nitrogen can be used to measure the volume–surface-average diameter of flocculated latex particles, if the flocculation and physisorption measurements are carried out below the glass transition temperature of the polymer. This conclusion follows from the fact that diameters calculated from physisorption of nitrogen measurements are in good agreement with the diameters obtained by the disc centrifuge method. Physisorption is an easy technique that can measure a broad range of particle sizes. A size distribution, however, cannot be produced using this technique.

The main advantages of the physisorption of nitrogen technique are that a large range of particle sizes can be measured: this is often a limitation of other techniques. Physisorption does not suffer from overcomplicated mathematical analysis of the measured result, which renders the results of techniques like light scattering difficult to interpret. The physisorption technique is simple, quick, cheap, and very robust, and hence very suited to many industrial applications.

Further work will include measurement of latex particles with low glass transition temperatures and measurement of full BET adsorption isotherms for various latices in order to establish where the basic theory utilized in this work is valid.

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