NOTE

A Novel Application of Using a Commercial Fraunhofer Diffractometer to Size Particles Dispersed in a Solid Matrix

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ABSTRACT: After a proper modification of a commercial Coulter LS230 particle size analyzer that is based on Fraunhofer principle, we have developed its novel application in directly sizing particles dispersed inside a solid matrix. Using several particle standards, we have demonstrated its validity by comparing the particle size distributions, respectively, obtained in water and directly inside different solid matrixes. In comparison with other conventional sizing methods, such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM), this novel application of Fraunhofer diffraction provides a fast, convenient, and direct way to characterize particles dispersed inside a transparent or translucent solid matrix. It can be envisioned that this application can be extended to directly size fillers inside a polymer materials, microdomains inside a polymer blends, and bubbles inside a foam. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1165–1168, 2000

Key words: Fraunhofer diffraction, particle size distribution in solid, phase transition, blends, latex particles

INTRODUCTION

Particle sizing as an active topic is important to nearly all industries, such as chemical processing, coating, ceramic materials, polymers, colloids, and food.[1–5] In the last two decades, optical particle sizing has been quickly developed into a large growing instrument market because of the availability of fast electronics.[1,6] Nowadays, commercial instruments based on dynamic laser light scattering can provide a fast and reliable particle size analysis in the small size range 2 nm – 2 μm, whereas those based on Fraunhofer diffraction and Mie scattering cover the large size range 200 nm – 2 mm. Several instrument companies, such as Brookheaven (New York, U.S.A.), ALV (Langen, Germany), Coulter (California, U.S.A.), and Malvern (London, England) are front runners in this field. The theories involved can be traced back to a long time ago, and it is not necessary to explain them in detail here.[7,8] So far, using these optical instruments, one can only measure particles in a liquid or gas dispersed media, such as polymer solution, colloidal dispersion or suspension, and aerosol. For particles dispersed inside a solid matrix, such as microdomains inside a polymer

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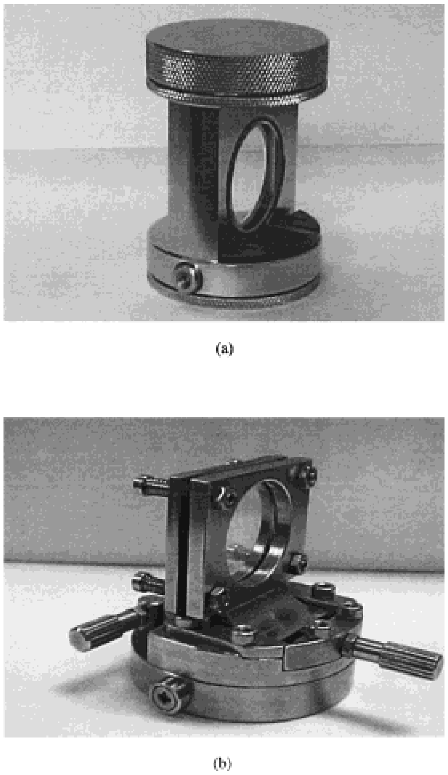

Figure 1 (a) Small volume cell used in commercial Coulter Particle Size Analyzer (LS230); (b) new sample holder developed for directly sizing particles dispersed inside a solid matrix.

blends and fillers inside a composite, optical and electron microscopic "imaging" are still the most commonly used methods. However, all the imaging methods are relatively time consuming and have a poor statistics for particles with a broad size distribution. Only for some special samples, if one can find a solvent to dissolve the solid matrix, but not the particles dispersed inside the matrix, the optical methods based on the scattering or diffraction principles can still be used. In general, directly sizing particles inside a solid matrix is still a challenging problem. In this note, we report that with a simple modification, a commercial Coulter particle size analyzer (Coulter LS230, based on the Fraunhofer diffraction and Mie scattering) can be used to directly size particles inside a solid matrix.

EXPERIMENTAL

Instrument

A commercial Coulter (LS230) Fraunhofer diffractometer with a modified sample holder was used. In a normal "Fraunhofer" instrument, an expanded parallel laser beam ($\asymp 10$ mm) is diffracted by particles enclosed between two optical windows and the diffraction pattern is recorded by a space distinguished area detector. Analyzing the diffraction pattern according to the Fraunhofer diffraction principle can result in a particle size distribution. In principle, the Fraunhofer diffraction can only be used to characterize large particles. As suggested by Van de Hulst,[9] the parameter p [$= 2\pi d|m-1|/\lambda$] should be larger than 30, where d, m, and λ are the particle diameter, the ratio of the refractive index of the particles to that of the media in which they are dispersed or suspended, and the wave length of the light in the media. In this case, particles (solid or liquid droplets or bubbles) with the same size can result in an identical diffraction pattern no matter what they are made of. For smaller particles, the Lorentz-Mie analysis have to be used, wherein one has to know the exact refractive indexes of both the media and particles.

Figure 1a shows a small volume cell used in the LS230. The dispersion is stirred by a magnetron at the bottom of the cell to prevent the particle sedimentation. In principle, there is no difference between sizing particles in a dispersion and inside a solid matrix. For directly sizing particles inside a solid matrix, the small volume cell was replaced by a solid sample holder (Fig. 1b). The thin solid film ($\asymp 0.3$ mm) can be sandwiched between the two glass plates and clipped into the sample holder. Note that the sample thickness is not very critical and the sample can be as thick as 2 mm. The sample thickness is mainly dependent on its transparency. The sample position can be adjusted by rotating and translational moving. The translational motion was used to adjust the center of the sample, which should be located at the focus plane of the detecting lens. It was fixed after the calibration and it is not necessary to adjust it afterwards.

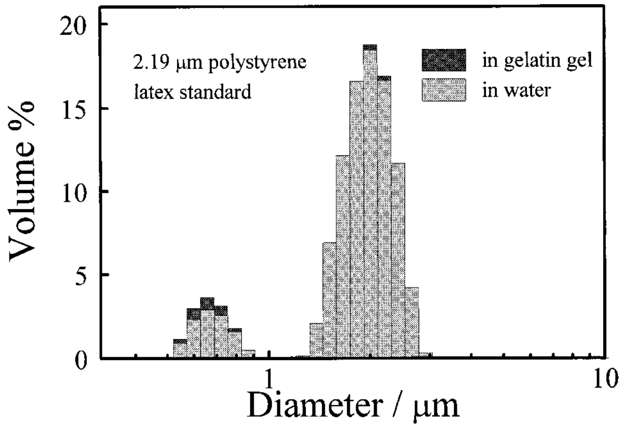

Figure 2 Particle size distributions of the polystyrene latex standard (diameter = 2.19 μm) determined inside a gelatin matrix and in water.

Table I Comparison of Average Particle Size and Particle Size Distribution of Particle Standards, Respectively, Determined in Water and Inside a Solid Matrix

Sample	Nominal Diameter μm	Volume Mean Diameter/μm In Water	Volume Mean Diameter/μm In Solid Matrix	Standard Deviation/μm In Water	Standard Deviation/μm In Solid Matrix
PS latex 2	2.19	1.92	1.95	0.56	0.54
PS latex 13	13	12.9	13.1	5.8	6.0
PS latex 45	44.5	45.0	43.0	11	12
Garnet 35	35	36.0	34.8	12	9.5

Samples

Uniform polystyrene latex particles dispersed inside a gelatin gel network matrix and garnet powders dispersed in a cross-linked poly(α-cyanocrylate) network matrix were used to test the method of directly sizing particles inside a solid matrix. Three polystyrene latex standards (diameter = 2.19, 12.9, and 45 μm) and one garnet powder (diameter = 35 μm) were used. Note that for each kind of the samples, we also prepared an identical solid matrix without the particles and used it as the blank background. In a typical measurement, we first place the background matrix into the sample holder to record the background for 30 s and then exchange the background with the sample to repeat measurements. The analysis of the particle size distribution by using the program in the instrument took only ≍1 min or less. The typical total time of sizing a sample was less than ≍5 min.

RESULTS AND DISCUSSION

Figures 2 shows the size distributions of the 2.19 μm latex particles respectively determined inside the gelatin matrix and in water. In water, the measurement was still conducted by using the small volume cell; whereas for the solid matrix, the distribution was determined by using the new sample holder. Table I shows a comparison of the particle sizes of three polystyrene latex samples, respectively, obtained in gelatin matrix and in water. It is clear that the measurements of each sample, respectively, dispersed inside the solid matrix and in water resulted in a nearly identical particle size distribution, showing that a Fraunhofer diffractometer, such as Coulter LS230, can be used to directly size particles dispersed inside a solid matrix. The error from the repeated measurements was no more than 10%.

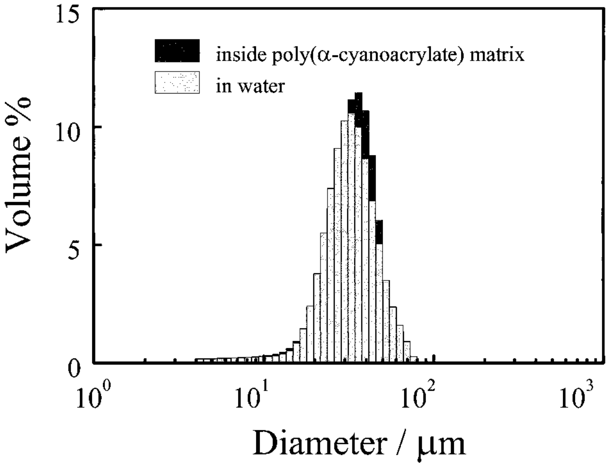

Figure 3 Particle size distributions of the garnet particles (diameter = 35 μm) dispersed inside a poly(α-cyanocrylate) solid matrix and in water.

Figure 3 shows a comparison of the particle size distributions of the garnet sample respectively dispersed inside a poly(α-cyanoacrylate) solid matrix and in water. Once again, it shows that we can directly characterize particles inside a solid matrix. In practice, if a sample can not be directly sandwiched between the two glass sheets, one can slice the sample into a thin transparent or translucent sheet and insert it between the two glass plates with a very small amount of refractive index-matching liquid between each sample/glass interface.

In summary, with a proper modification, a commercial particle sizing instrument can be used to size particles dispersed inside a solid matrix. Such a sample can be fillers inside a plastic material, microdomains inside a blends material, and bubbles inside a foam-type material as long as the particles and the solid matrix have different refractive indexes. In comparison with an optical or electron microscopic imaging methods, the method proposed here enjoys a simple sample preparation, a better statistics, and a fast measurement. This method is ready to be used as a complimentary method to scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for the characterization of particle size distribution inside a solid matrix.

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