Characterization of Rubber Particle Size Distribution of High-Impact Polystyrene Using an Image Analysis Method

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Synopsis

Accurate characterization of high-impact polystyrene (HIPS) rubber particle size distribution has been achieved using an automatic image analysis system. The new method involves preparation of a microscope slide consisting of a dilute suspension of HIPS particles in a polymer matrix. Images of silhouetted rubber particles of true diameter are obtained using an image processor and particle size calculations can be made with a minimum of editing of the binary image. The new method provides measurement of true rubber particle diameters because the particles in the prepared slide are not swollen by any solvent.

INTRODUCTION

Characterization of high-impact polystyrene (HIPS) rubber particle size distribution is necessary for HIPS product/process research. In the past few years we have used a Microtrac Small Particle Analyzer, a laser light-scattering instrument, for characterization of the HIPS rubber particle size distribution.[1] While the light-scattering method provides size distribution data that correlate with HIPS physical properties, the particles are swollen in methyl ethyl ketone (MEK) solvent used to suspend the particles. Recently, we have developed a new method that measures the size of many individual particles in the unswollen state. The new method offers an alternative to an existing procedure for characterization of unswollen HIPS rubber particles.[2]

Automatic image analysis systems are available for accurate characterization of particle size distributions if a representative image of the particles can be supplied to the image processor. Making these systems useful for characterization of the HIPS rubber particle size distribution depends on preparation of a specimen containing clearly visible silhouetted rubber particles of true size.

A technique has been devised for obtaining a microscope slide containing a dilute suspension of HIPS rubber particles imbedded in a polystyrene matrix. The slide preparation method and the equipment used for capture and evaluation of the particle image are discussed. The image analysis and Microtrac methods for HIPS particle size determination are compared.

EXPERIMENTAL

Sample Selection and Microtrac Particle Size Determination

The technique for particle size determination using the Microtrac instrument has been described previously.[1] Repeat analyses of samples evaluated in

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1981 were carried out using a new Microtrac instrument and the results from the two instruments were in close agreement. A few more recent samples of interest were added to expand the data set.

Computer-Controlled Micropolymerization for HIPS Rubber Particle Microscope Slide Preparations

Several pieces of equipment were used to prepare a suitable microscope slide that would enable the capture of good binary images of HIPS rubber particles. A slide jig was made in our shop to hold a coverslip to a glass slide using low spring tension. In each micropolymerization the jig, holding the glass slide, was placed on a surface where the temperature of the slide was carefully controlled. The heating surface consisted of a small aluminum heating block containing a 1000 W heater which was computer controlled to $\pm 1.0°C$ using a control system developed in our laboratory.

In the preparation of each suspension of particles for the slide preparation, HIPS (0.250 g) and Amoco R2 general purpose crystal polystyrene (1.750 g) were dissolved in styrene (8.000 g). An aliquot (0.010 mL) of the suspension was placed on a microscope slide. A 0.0010-inch shim was fixed to one edge of a 0.01-inch thick cover slip used to make the mount. The combination was heated for 2 h at 110, 2 h at 142, 1 h at 170, and 1 h at 210°C with 15 min linear ramps between plateaus.

The HIPS particles were thus embedded in a polystyrene matrix and spread enough to see each particle clearly to obtain the binary image. Good control of the polymerization was essential for good reproducibility in the preparation of the slide specimens.

Particle Size Determinations Using Image Analysis

An image processor made by Image Technology Corporation (ITC) was used in the particle size determination. Our set-up consists of a phase contrast microscope fitted with a solid-state video camera for transfer of images to the ITC image processor. ITC software was run on an IBM PC to obtain particle size measurements from the binary image provided by the image processor. A macro program was written to automatically evaluate samples with a small amount of editing of the binary image required.[3] The data collected consisted of four measurements per particle considered (height, width, length, and breadth).[4] Since rubber particles in HIPS are spherical, the four parameters were usually equal. About 400 particles were measured per sample. A minimum particle diameter of 0.13 μm could be detected using a 100 $\times$ objective (1000 $\times$ total magnification through the microscope). However, a 40 $\times$ objective lens was found to be acceptable for most samples. Polystyrene occlusions sometimes caused voids in the binary image of particles, particularly at the higher magnification. The "fill" function in the ITC software converted images of particles containing voids to solid particles.[5]

The data were up-loaded to a host computer in which the calculations were made. Columns of data were easily manipulated using available software and number- and volume-average diameter calculations were made on each sample.

TABLE I
Rubber Particle Size Distribution Parameters Using Image Analysis and Laser Light Scattering Methods

Number	HIPS resin type	Average Diameter (μm)			
		Image analysis method		Microtrac method	
		Number	Volume	Number	Volume
I	Commercial	1.98	2.51	2.03	4.24
II	Commercial	2.47	3.22	2.54	4.99
III	Pilot plant	2.16	3.59	2.77	5.72
IV	Pilot plant	2.03	3.34	2.74	5.79
V	Pilot plant	2.24	4.46	2.80	7.25
VI	Commercial	1.17	1.37	0.90	3.22
VII	Commercial	1.14	1.37	0.68	1.42
VIII	Commercial	1.63	2.05	1.51	3.63
IX	Lab-prepared	0.61	0.87	0.38	1.55
X	Lab-prepared	1.37	1.62	1.18	2.76
XI	Lab-prepared	1.46	1.72	1.13	2.63
XII	Lab-prepared	1.46	1.83	1.24	3.46
XIII	Lab-prepared	1.68	2.39	1.99	4.69
XIV	Lab-prepared	1.66	1.95	1.22	2.72
XV	Lab-prepared	1.74	2.09	1.42	3.74
XVI	Lab-prepared	1.75	2.23	1.51	4.07
XVII	Lab-prepared	1.64	2.01	1.19	2.78
XVIII	Lab-prepared	1.54	1.98	1.24	3.62
IXX	Lab-prepared	2.12	2.72	2.67	5.12
XX	Lab-prepared	1.63	2.36	1.65	3.39
XXI	Lab-prepared	2.28	2.85	2.39	4.79
XXII	Lab-prepared	1.94	2.41	1.58	3.36

RESULTS AND DISCUSSION

A summary of the particle size distribution parameters obtained using image analysis and Microtrac methods is shown in Table I. The raw data from the image analysis method contain much information about the particle size distribution. Compared to the Microtrac, which provides a 16-cell histogram over a range of 0.12 to 42 μm, the ITC data can be assembled in a much more refined histogram (Fig. 1) since the size of individual particles is obtained using the image analysis method. The total time required to do the sizing is less than 20 min per sample. Duplicate determinations, counting about 400 particles per test, have shown reproducibility and counting more particles per sample does not change the distribution parameters appreciably.

A good correlation exists between the image analysis and Microtrac particle size methods. Volume average diameter (M_v) as measured by the Microtrac is determined from MEK solvent-swollen particles, but the image analysis method gives the true volume average diameter. Swelling of the rubber particles in MEK solvent has been determined to be about 4.4-fold by volume[1] which corresponds to an increase in diameter by a factor of 1.64. Applying this factor to the image analysis M_v data gives calculated diameters of swollen particles and allows a direct comparison of the Microtrac and image analysis methods (Fig. 2). Accounting for swelling in MEK solvent ties the two methods together very well.

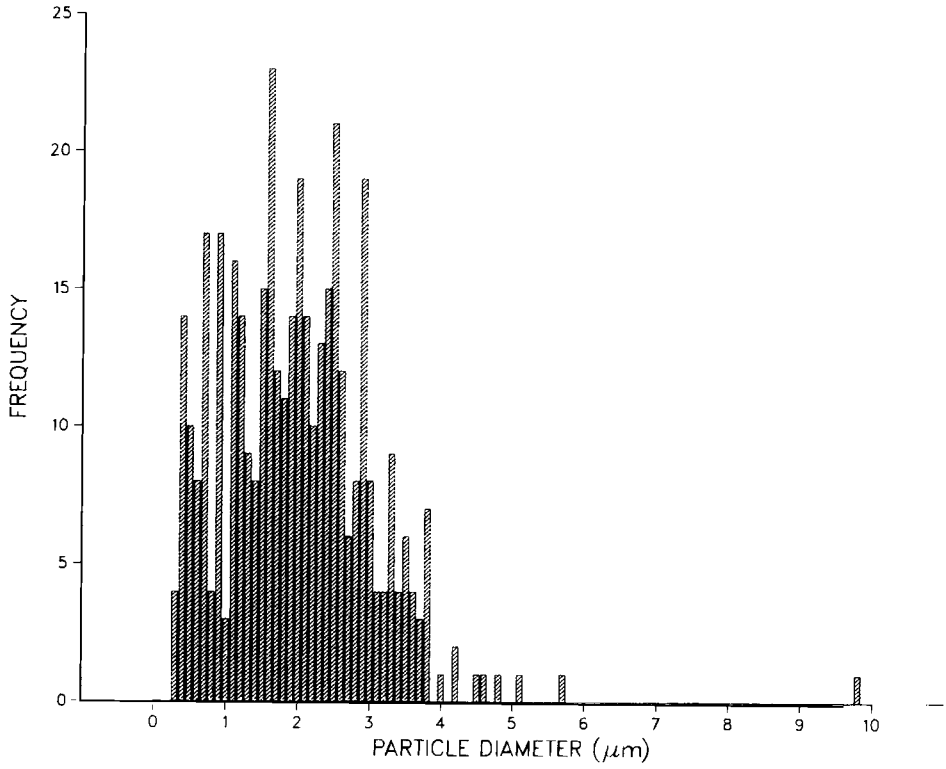

Fig. 1. Particle size distribution for HIPS Sample I.

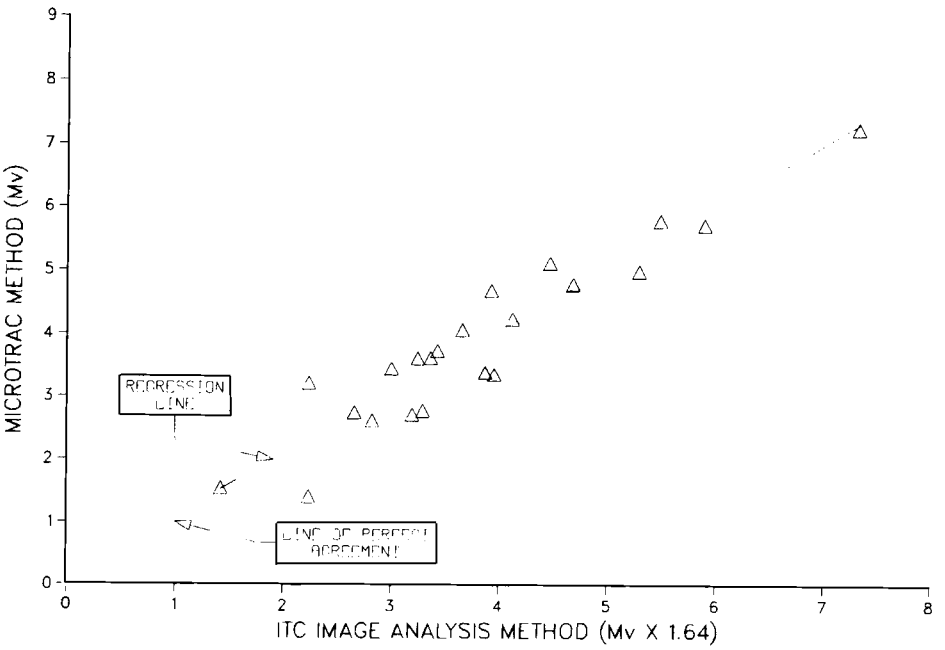

Fig. 2. Comparison of particle measurement methods.

The differences in number-average diameters obtained by the two methods cannot be reconciled by accounting for solvent swelling. Some assumptions must be made to calculate the number-average diameter from the Microtrac instrument output and the Microtrac number average diameter is proportional to, but not an accurate measure of the number average diameter of particles swollen 4.4-fold in MEK. Since the image analysis method measures diameters of individual unswollen particles a more accurate measure of the number average diameter of particles in HIPS is provided.

SUMMARY AND CONCLUSIONS

The preparation of a suitable specimen containing HIPS rubber particles sufficiently diluted in a polymer matrix allows the measurement of true particle diameters using an image analysis system. Implementation of several ideas has led to the microscope slide preparation method that produces the specimen: (1) the construction of a microscope slide jig to hold a coverslip on a slide under low spring tension; (2) accurate, reproducible computer control of a small heat block (linear ramps and plateaus) for styrene micropolymerization on a microscope slide; and (3) the use of a one-mil shim on one side of a coverslip to give a suitable thickness gradient of polymer containing imbedded rubber particles once the micropolymerization has been carried out on the slide.

An ITC image processor fitted to a phase-contrast microscope obtains a binary image of silhouetted rubber particles contained in the prepared slide and the true diameters of unswollen particles can be measured. Once the diameters of many individual particles are known, it is easy to obtain accurate size distribution parameters such as number- and volume-average diameters.

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References

1. R. A. Hall, R. D. Hites, and P. Plantz, *J. Appl. Polym. Sci.*, **27**, 2885–2890 (1982).

2. T. O. Craig, R. M. Quick, and T. E. Jenkins, *J. Polym. Sci., Chem Ed.*, **15**, 433(1977); **15**, 441(1977).

3. Editing can include artifact deletion, filling of particles, separation of overlapping particles, etc.

4. The four features were nearly always equal for a given particle since rubber particles in HIPS are spherical. Length is the longest of height, width, and two 45-degree diagonals. Breadth is the shortest of the four measurements.

5. The "fill" function was shown later to be unnecessary. Using ITC feature-specific image analysis, the measured diameter of a detected particle is the same whether or not the particle contains voids as long as the voids are completely surrounded by detected rubber.

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