

# Characterization of Rubber Particle Size Distribution of High-Impact Polystyrene Using Low-Angle Laser Light Scattering

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## Synopsis

A new application of low-angle laser light scattering has led to a new instrument capable of characterizing the rubber particle size distribution of high-impact polystyrene (HIPS) containing particles as small as  $0.1 \mu$ . Rubber particle size distributions of several HIPS resins have been characterized, and the particle size ranking of resins using light scattering parallels the ranking of resins using photomicroscopy. Several solvents have been employed to suspend the HIPS rubber particles for the scattering determination. Swelling of the rubber phase has been found to be relatively insensitive to variations in rubber phase crosslinking when methyl ethyl ketone is used to suspend the rubber particles. Particle swelling in methyl ethyl ketone does not detract from the usefulness of the light scattering method for HIPS rubber particle size characterization.

## INTRODUCTION

Accurate characterization of the particle size distribution of the rubber phase of high-impact polystyrene (HIPS) is essential for understanding the physical properties of the resin. Rubber particle size affects nearly all the important HIPS physical properties, and a quantitative particle size distribution is needed to correlate dependent properties to particle size and other independent resin variables.

Until recently low-angle laser light scattering was only available commercially to characterize particle sizes as small as about  $2 \mu$ . Now it is possible to classify particles as small as  $0.1 \mu$ , which is especially applicable to HIPS because its rubber particle sizes often fall in the submicron region.

Certainly no standard exists in the industry for HIPS particle size characterization. The Coulter Counter is popular, and problems initially associated with the application of that instrument to HIPS have been solved.<sup>1,2</sup> Several microscopic techniques are used to characterize HIPS rubber particle sizes. Comparison of  $500\times$  photomicrographs of HIPS samples that have been melted allows qualitative comparison of HIPS rubber particle size distributions. Dissolution of the polystyrene matrix followed by microscopic examination of the suspended rubber particles can also provide useful particle size information. Electron microscopy can reveal much detail of the HIPS rubber particles, but it is a more tedious job to obtain rubber particle size distributions by analyzing electron photomicrographs of HIPS.

## EXPERIMENTAL

### Materials Used and Preparation of Samples

Impact polystyrene resins used in this study were selected from commercial and laboratory-prepared materials that varied in rubber phase crosslinking and polybutadiene type (Table I). The laboratory method for preparing HIPS used in this study has been previously described.<sup>3</sup>

HIPS resins used in the light scattering experiment were dissolved in methyl ethyl ketone (0.6 g in 10.0 mL). For light scattering experiments in isopropanol the rubber (gel) phase of resins Ia and Ib were isolated from MEK suspensions by centrifugation. The gel phases of Ia and Ib were resuspended and centrifuged two additional times to insure complete removal of matrix polystyrene. The isolated wet gels were resuspended in methyl ethyl ketone (MEK) and stored for future particle size characterization.

In separate experiments, isolated (MEK-swollen) gel phases of all resins used in the study were weighed and placed in a vacuum oven overnight at 50°C. The ratio of the weight of the wet gel to the weight of the dry gel produced a swelling factor of each rubber phase in MEK. Swelling factors of the resins were also obtained using toluene according to the commonly used Ruffing gel test procedure.<sup>4</sup>

Resins I and II (Table I) were heat-treated to increase the crosslinking in their rubber phases. This was accomplished by extrusion at 12 g/min at 300°C using a 25:1 L:D Brabender 0.75 in. extruder.

### Determination of HIPS Rubber Particle Size Using Light Microscopy

Very small shavings of HIPS were placed between a microscope slide and coverslip. By applying heat and pressure the resin was melted and spread into a very thin film. The cooled polymer was examined under a phase contrast microscope, and 500× photomicrographs were obtained for each resin. Comparison of the photomicrographs allowed qualitative ranking of the resins in terms of rubber particle size. A quantitative measure of particle size was obtained from a photomicrograph of an MEK suspension of resin III (Table I). The size of each particle in the micrograph was measured, and a particle size histogram was constructed in a form that could be compared to data generated by light scattering as explained *vide infra*.

### Particle Size Distribution Determination Using Light Scattering

For each particle size determination, 200 mL of test solvent—MEK, toluene, *trans*-cinnamaldehyde,<sup>5</sup> or isopropanol—was circulated through a glass cell. From 0.25 to 0.5 mL of a rubber particle suspension was added to the circulating solvent. The rubber particle suspensions used were either MEK suspensions of the isolated rubber phases of resins Ia and Ib or MEK suspensions of all HIPS resins shown in Table I. The laser light scattered by the resulting dilute suspensions was collected by a lens, filtered, and focused on a light detector. The resulting detector output, which is proportional to selected functions of the particle diameter, was processed by a microprocessor to provide a 14-cell histogram plot of the particle size distribution ranging from 0.12 to 21.1  $\mu$ . Once the

TABLE I  
Solvent Effects and HIPS Rubber Particle Size Characterization Using a Laser Light Scattering Instrument

Number	Resin Description	Polybutadiene type <sup>a</sup>		Swelling index		Particle size evaluation				Particle size ranking	
		Low <i>cis</i>	High <i>cis</i>	MEK	Toluene	Solvent	Vol avg diameter ( $\mu$ )	No. avg <sup>b</sup> diameter, calcd ( $\mu$ )	Poly dispersity (vol avg/no. avg)	LALLS <sup>c</sup> micrograph <sup>d</sup>	500X Photo
Ia	Commercial HIPS	Low <i>cis</i>		3.7	9.2	MEK	5.7	2.8	2.0	11	11
Ia						Toluene	8.8	—	—		
Ia						Cinnamaldehyde	5.9	—	—		
Ia						Isopropanol	5.4	1.1	4.9		
Ib	Heat-treated Ia	Low <i>cis</i>		3.7	8.5	MEK	5.8	2.7	2.1	10	10
Ib						Toluene	8.4	—	—		
Ib						Cinnamaldehyde	5.5	—	—		
Ib						Isopropanol	5.6	1.0	5.6		
II	Lab-prepared HIPS	High <i>cis</i>		4.8	14.1	MEK	4.6	1.6	2.9	9	9
III	Commercial HIPS	High <i>cis</i>		5.0	14.3	MEK	3.6	1.5	2.4	8	8
IVa	Lab-prepared HIPS	Low <i>cis</i>		4.9	13.3	MEK	2.8	1.2	2.3	7	6
IVb	Heat-treated IVa	Low <i>cis</i>		4.7	11.7	MEK	2.6	1.1	2.4	6	7
V	Commercial HIPS	High <i>cis</i>		4.6	13.6	MEK	2.0	0.9	2.2	5	5
VI	Commercial HIPS	High <i>cis</i>		3.8	12.1	MEK	3.2	0.9	3.6	4	4
VII	Commercial HIPS	High <i>cis</i>		3.8	10.9	MEK	1.4	0.7	2.0	3	3
VIII	Lab-prepared HIPS	High <i>cis</i>		4.7	13.6	MEK	1.8	0.6	3.0	2	2
IX	Lab-prepared HIPS	Low <i>cis</i>		5.4	15.2	MEK	1.6	0.4	4.0	1	1

<sup>a</sup> Firestone Diene-type (low *cis*) and Polysar (high *cis*) Taktene-type polybutadienes were employed.

<sup>b</sup> Calculated from the volume average diameter histograms, assuming that all particles in a given cell have the diameter of the midpoint of the cell; number average diameter is defined as the sum of the diameters of the particles divided by the total number of particles.

<sup>c</sup> Based on calculated number average diameter.

<sup>d</sup> Size ranking was done independently by two individuals.

histogram was obtained, various distribution parameters were calculated. For example, volume average diameter was given directly by the instrument's microelectronics. Dow's poly(vinyl toluene) ( $2.0 \mu$ ) and polystyrene ( $0.5 \mu$ ) calibration standards were run prior to test samples; in general, the observed diameters were within 10% of the known diameters of the standard particles.

A Leeds and Northrup Microtrac Small Particle Analyzer (range of  $0.12$ – $21.1 \mu$ ) was used for most of the evaluations. However, for evaluating HIPS with relatively large rubber particle size in toluene where swelling of the rubber particles is substantial, a standard range Leeds and Northrup Microtrac (range of  $1.9$ – $176.0 \mu$ ) was employed.

## RESULTS AND DISCUSSION

The swelling of the HIPS rubber phase in organic liquids is well known. Gel tests commonly used to determine rubber phase crosslinking measure the amount of swelling the rubber phase exhibits in a solvent such as toluene.<sup>4</sup> The degree of swelling of the rubber phase that a HIPS resin exhibits may differ from solvent to solvent. Polystyrene nonsolvents such as methanol or water do not swell the rubber phase.

HIPS rubber particle size distribution can be characterized by the Microtrac Particle Size Analyzer using any nonviscous medium that will suspend the particles. As summarized in Table I, several solvents have been employed. Rubber particles swell markedly in toluene, and the volume average diameters of resins Ia and Ib (heat-treated Ia) differ more in toluene than in MEK. The rubber phase of Resin Ib is crosslinked more than that of Ia, but the difference in swelling in MEK is negligible and does not greatly affect the particle size distribution measurement when MEK is the solvent.

The relative insensitivity of rubber phase swelling in MEK, compared to sensitivity of rubber phase swelling in toluene, is illustrated by Figure 1, a plot of the swelling factor data shown in Table I. The difference in rubber phase crosslinking from resin to resin would in most instances not cause incorrect light scattering ranking of resin particle size when MEK is used as the solvent. Other

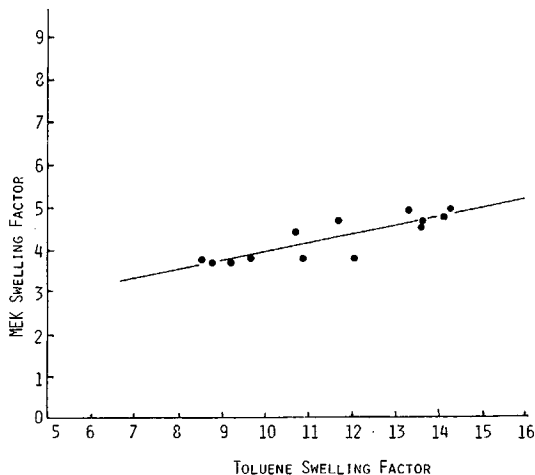


Fig. 1. Swelling of the rubber phase in MEK and toluene.

things being equal, toluene would cause incorrect ranking of the resins due to swelling. The hypothesis is supported by the observation that when MEK is the solvent, the ranking of HIPS resins according to size by the scattering experiment matches the qualitative ordering by the comparison of photomicrographs. The particle size distributions from low-angle scattering when MEK is the solvent can be used for correlating particle size to physical property data such as ESCR, toughness, gloss, etc.

In order to measure the particle size distributions in the nonswelling solvent isopropanol, the gel phases of Ia and Ib had to be isolated to avoid precipitation of dissolved matrix polystyrene that would occur upon transferring the suspensions to alcohol solvents. The particle size distributions are much broader in isopropanol than in MEK, as indicated by a higher polydispersity of Ia and Ib in isopropanol (Table I). This is explained by a combination of little or no swelling in the isopropanol, causing a low number average diameter, and agglomeration of some particles, causing a high volume average diameter. Microscopic examination of the isopropanol suspensions revealed the presence of grapelike clusters along with many single particles.

It has been demonstrated that *trans*-cinnamaldehyde selectively dissolves matrix polystyrene in HIPS, giving a suspension of rubber particles suitable for microscopic examination.<sup>5</sup> Either resin Ia or Ib has about the same volume average diameter in MEK or *trans*-cinnamaldehyde. This indicates that *trans*-cinnamaldehyde and MEK swell the rubber particles to nearly the same extent for a given degree of rubber phase crosslinking. No advantage is seen to using *trans*-cinnamaldehyde as solvent in the light scattering analyzer.

The scattering instrument is accurate, as indicated by close agreement between Microtrac size measurements of calibration standards and the known sizes of the standards obtained by electron microscopy. As a further check of accuracy relative to the HIPS application, a particle size histogram generated by the scattering instrument has been compared to a histogram constructed from measurements taken from a 500 $\times$  photomicrograph of an MEK suspension of resin III (Table I). As summarized in Table II, fairly close agreement exists comparing the instrumental method to the photomicrographic analysis.

The precision of the scattering instrument is demonstrated by an experiment performed on two of the resins shown in Table I. Resin VII was divided into three vials and dissolved (suspended) in methyl ethyl ketone on the first day of the evaluation. The distributions of rubber particle sizes within each vial were

TABLE II  
Comparison of Particle Size Histogram Data Obtained by LALLS and Photomicrograph Analysis

Particle size diameter ( $\mu$ )		Relative volume (%)	
Cell center	Cell upper limit	Photomicrograph	LALLS
0.55	0.66	0	0
0.80	1.01	1	2
1.30	1.69	2	7
2.22	2.63	14	18
3.14	3.73	32	31
4.44	5.27	41	30
6.28	7.46	10	12
8.88	10.55	0	0

TABLE III  
 Variability in the HIPS Particle Size Determination Using Low-Angle Laser Light Scattering

Sample	Test variable	Volume average diameter statistical data ( $\mu$ )	
		$\bar{X}$	$S$
VII	All determinations <sup>a</sup>	1.36	0.034
VII	Tested day 1, vials 1, 2, and 3	1.38	0.006
VII	Tested day 2, vials 1, 2, and 3	1.37	0.009
VII	Tested day 3, vials 1, 2, and 3	1.34	0.057
VII	Vial 1, tested days 1, 2, and 3	1.37	0.003
VII	Vial 2, tested days 1, 2, and 3	1.38	0.006
VII	Vial 3, tested days 1, 2, and 3	1.34	0.055
II	0.5-mL sample size	4.51	0.350
II	0.25-mL sample size	4.64	0.155

<sup>a</sup> Particle size determinations on three vials of resin VII, each tested in triplicate on 3 consecutive days.

measured in triplicate (three measurements on each instrument loading) on each of 3 consecutive days. As summarized in Table III, the envelope of error for all determinations of resin VII is quite small. Furthermore, the mean diameters of the samples calculated by day or by vial do not differ significantly from one another or differ significantly from the mean of all determinations of resin VII. Resin II was used to evaluate the effect of sample size on the particle size determination. No significant difference is observed when 0.25 mL or 0.5 mL of the MEK suspension of resin II is used to obtain the particle size data.

### SUMMARY AND CONCLUSIONS

The use of low-angle light scattering has been shown to be a precise, accurate, and convenient means to determine the rubber particle distribution of HIPS. Methyl ethyl ketone, used to dissolve the polystyrene matrix, adequately suspends the rubber particles for the scattering determination. In comparing the particle size distributions of a group of HIPS resins that vary in rubber phase crosslinking, the use of MEK is not likely to cause incorrect ranking of the resins, since swelling of the rubber phase in MEK is relatively insensitive to changes in rubber phase crosslinking.

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Received December 15, 1981

Accepted January 22, 1982