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MEASUREMENT OF SHAPE AND SIZE DISTRIBUTIONS OF PVC RESIN PARTICLES BY SCANNING ELECTRON MICROSCOPY AND IMAGE ANALYSIS

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Abstract—Characterizing poly(vinyl chloride) (PVC) resin particles in terms of particulate morphology, shape and size distributions is important for various technical reasons. We describe a method that shows how these properties can be simultaneously measured using scanning electron microscopy and image analysis. A computer algorithm, which calculates the distributions, has been developed based on the present mathematical formulation, and the data generated by scanning electron microscope and image analyser. The alogorithm considers the variation in shape and size of each particle. The number of mutually exclusive particles required for these measurements, to have an acceptable level of precision, has been statistically determined to be around 430. The number- and weight-average particle diameters, of the experimental PVC resin, were estimated to be 80.4 and 114.8 μm, respectively. The particle size uniformity index was found 1.43.

NOMENCLATURE

d_{max}, d_{min} = Major and minor axes of an ellipse, respectively,
d = distance of a point on the circumference of an ellipse from the centre,
d_{av} = average diameter of a particle [equation (6)],
$\bar{d}_{av}$ = average diameter of a statistically acceptable number of PVC particles,
$\bar{d}_{max}$, $\bar{d}_{min}$ = average values of d_{max} and d_{min}, respectively,
$(d_{av})_i$ = average diameter of the ith particle,
$\bar{D}_n$ = number-average particle diameter,
$\bar{D}_w$ = weight-average particle diameter,
$g(d_{av})$, $g(s_f)$ = differential distributions of particle size and shape, respectively,
$G(d_{av})$, $G(s_f)$ = cumulative distributions of particles size and shape, respectively,
n_i = number of particles having diameter $(d_{av})_i$,
s_f = shape factor or aspect ratio of a PVC particle,
$\bar{s}_f$ = average value of s_f of a statistically acceptable number of PVC particles,
UI = particle size uniformity index,
x, y = x and y axes of a point on the circumference of the ellipse,
θ = angle with reference to the major axis of the ellipse,
σ_s^2, σ_{sh}^2 = variances of size and shape distributions, respectively,
μm = micron.

INTRODUCTION

Poly(vinyl chloride) (PVC) is a cost effective, versatile commodity polymer. Its properties can be easily modified by compounding with additives. Factors such as the type of suspending agent used during polymerization, the intensity of agitation, the mode of initiation, and the distribution of the initiator in the monomer/polymer phase cause variations in the shapes and sizes of the PVC particles [1]. Therefore, the resin particles have distributions of shapes and sizes. The significant role played by these properties is summarized below.

Compounding is a complex particulate mixing process which is influenced by the shape and size distributions of the particles. These properties also affect the packing density, particulate flow behaviour [2] and processability [3]. When PVC compounds are processed in extruders and injection moulding machines, fusion and material mixing occur together. The resin shape and size distributions affect these phenomena. Inadequate fusion causes structural defects and unacceptable performance characteristics [3–5]. Furthermore, the proper shape and size distributions are important for efficient performance of the processing machines [2].

Some of the thermal properties of particulate materials have been found to be shape-dependent [6]. During the processing of PVC resins, the shape of the particles is therefore likely to affect the heat transfer phenomenon. Particle size distribution has been reported to influence the removal of residual vinyl chloride monomer using a heated fluid-bed technique [7], and the solution shear viscosity of some polymeric composite materials [8].

The experimentally determined particle size distribution can be compared with the distribution theoretically predicted by the mathematical modeling of vinyl chloride polymerization in a reactor. Thus the predictions of the mathematical model can be evaluated.

Several methods are available for the determination of shape and size of fine particles.The shape determining methods include Fourier grain analysis, and sieve cascadograph [9]. The size determining

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techniques fall mainly into two categories, dry sieving [10, 11] and automatic particle counting. The automatic counting methods cover, according to Kaye [12], photozone and resistazone counters. The photozone counter includes laser light scattering [13] and optical particle counter [14] whereas the resistazone counters enlist Coulter counter [15] and electrical resistance particle counter [16]. The Fourier grain analysis is a cumbersome method to determine the shape. The sieve cascadograph only qualitatively separates the particles of the same size and it cannot determine the shape distribution.

Most of the above size measuring techniques, which were developed in connection with catalyst particle size characterization, have several limitations. The dry sieving method does not consider the particles individually. Hence, it cannot give a continuous particle size distribution. The other methods encounter agglomeration problems, need additional calibration and also cannot include shape factor correction. The literature shows that application of these methods to measure PVC resin particles shape and size has been limited. Besides knowing the shape and size distribution, one has also to know the particle morphology [17] and interior particle structure [18] which affect the absorption of additives [19, 20]. Scanning electron microscopy has been used for this purpose [17]. In this paper, we discuss how image analysis can be combined with scanning electron microscopy to investigate simultaneously the particle morphology, shape and size distributions. To the best of our knowledge, such a work has not been reported, especially with reference to PVC resin particles.

MATHEMATICAL FRAMEWORK

The scanning electron micrographs of commericial PVC resin particles show that these particles are approximately ellipsoids to spheroids having various sizes [17]. A spheroid is a particular case of an ellipsoid. Therefore, we shall represent the resin particles by ellipsoids so that the concept of shape factor may be used, and also the problem may be formulated generally.

Figure 1 shows the cross section along the major axis of an ellipsoid. Any point (x, y) on the circumference of this ellipsoid cross section will be given by the following equation of an ellipse:

$$x^2/d_{max}^2 + y^2/d_{min}^2 = 1 \tag{1}$$

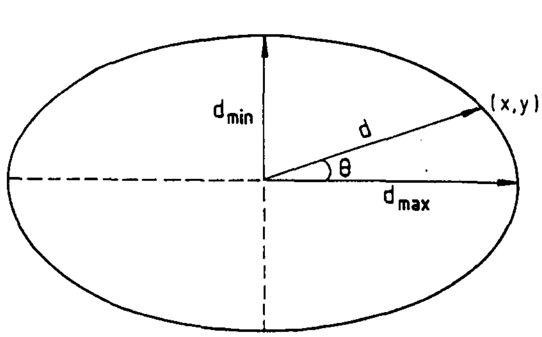

Fig. 1. Cross section along the major axis of an ellipsoid.

where d_{max} and d_{min} are the major and minor axes, respectively. They are also called object length and breadth [12], respectively.

The average diameter of the ellipse is given by

$$d_{av} = \frac{2}{\pi}\int_0^{\pi/2} d(\theta)\, d\theta \tag{2}$$

where d is the distance of any point (x, y) on the circumference from the centre of the ellipse, θ is the angle in polar coordinate (Fig. 1); it is related to x and y thus:

$$x = d\cos\theta \tag{3}$$

$$y = d\sin\theta. \tag{4}$$

From equations (1), (3) and (4), it can be shown that

$$d(\theta) = 1/\{\cos^2\theta/d_{max}^2 + \sin^2\theta/d_{min}^2\}^{1/2}. \tag{5}$$

Then d_{av} will be finally given by

$$d_{av} = \frac{2}{\pi}\int_0^{\pi/2} \{1/(\cos^2\theta/d_{max}^2 + \sin^2\theta/d_{min}^2)^{1/2}\}\, d\theta. \tag{6}$$

The shape factor will be represented by the aspect ratio or flakiness ratio, which is the inverse of elongation ratio [12] as follows:

$$s_f = d_{min}/d_{max}. \tag{7}$$

Note that for $d_{max} = d_{min}$, $s_f = 1$, and the particle becomes a sphere. d_{av} and s_f will vary from particle to particle. This variation will give rise to the distributions of d_{av} and s_f, which we wish to calculate using the experimental data. From the distributions, the average properties can be calculated as follows [21]:

$$\bar{d}_{av} = \sum g(d_{av})\, d_{av} \tag{8}$$

$$\bar{s}_f = \sum g(s_f) s_f \tag{9}$$

where $g(d_{av})$ and $g(s_f)$ are the differential distributions of d_{av} and s_f, respectively. $\bar{d}_{av}$ and $\bar{s}_f$ are the average particle diameter and particle shape, respectively for a given batch of PVC.

The cumulative or integral shape and size distributions are obtained by summing the respective differential distributions. The variance of the measured distributions will be given by [21]

$$\sigma_s^2 = \sum[(d_{av})_i - \bar{d}_{av}]^2 g(d_{av})_i \tag{10}$$

$$\sigma_{sh}^2 = \sum[(s_f)_i - \bar{s}_f]^2 g(s_f)_i \tag{11}$$

where σ_s^2 and σ_{sh}^2 are the variances for size and shape distributions, respectively. Note that variance is the measure of the width of the distributions.

To compare the degree of uniformity of the PVC particle size, we define the uniformity index as follows [22]:

$$\mathrm{UI} = \bar{D}_w/\bar{D}_n \tag{12}$$

$$\bar{D}_n = (\sum n_i d_i)/\sum n_i \tag{13}$$

$$\bar{D}_w = (\sum n_i d_i^4)/(\sum n_i d_i^3) \tag{14}$$

where $\bar{D}_n$ and $\bar{D}_w$ are the number- and weight-average diameters, respectively.

EXPERIMENTAL PROCEDURES

The experimental PVC was a commercial, suspension-polymerized particulate material having a K value of 70. It had a number-average molecular weight of 52,900 and glass

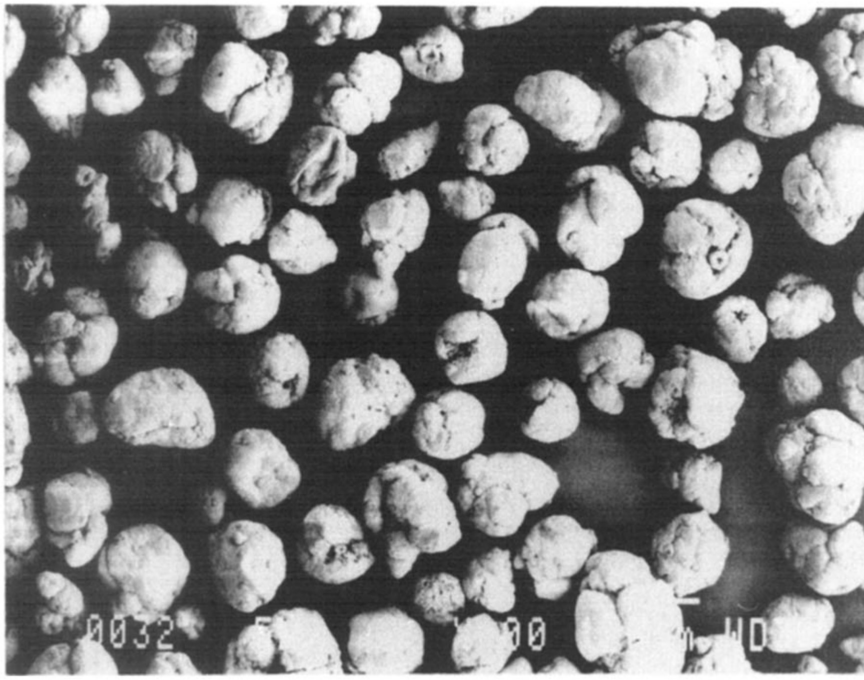

Fig. 2. Scanning electron micrograph of the experimental PVC resin particles, taken at 100 magnification.

transition temperature of 90°. The number-average molecular weight had been measured by a Knauer membrane osmometer. The osmometry experiments were done at 31° using reagent grade tetrahydrofuran (THF) as solvent. The glass transition temperature was determined by a Perkin–Elmer differential scanning calorimeter (Model DSC-4). The sample weight was 10 mg, and the scanning rate was 20°/min. The calorimeter was calibrated using standard procedures.

The PVC resin particles were spread as a monolayer on the sample holder using double sided scotch tape. Then the surface was gold sputtered to make it conductive and prevent charging in the electron beam. Using a Jeol 840 scanning electron microscope, micrographs were taken at magnifications of 100 and 500. The magnifications were varied by varying the scanned length on the surface of the experimental sample. Several independent 100-magnification micrographs (Fig. 2), covering mutually exclusive particles, were taken. All the samples were run at zero tilt. Figure 3 shows a typical micrograph taken at 500 magnification, which illustrates the microporous surface morphology of a PVC grain.

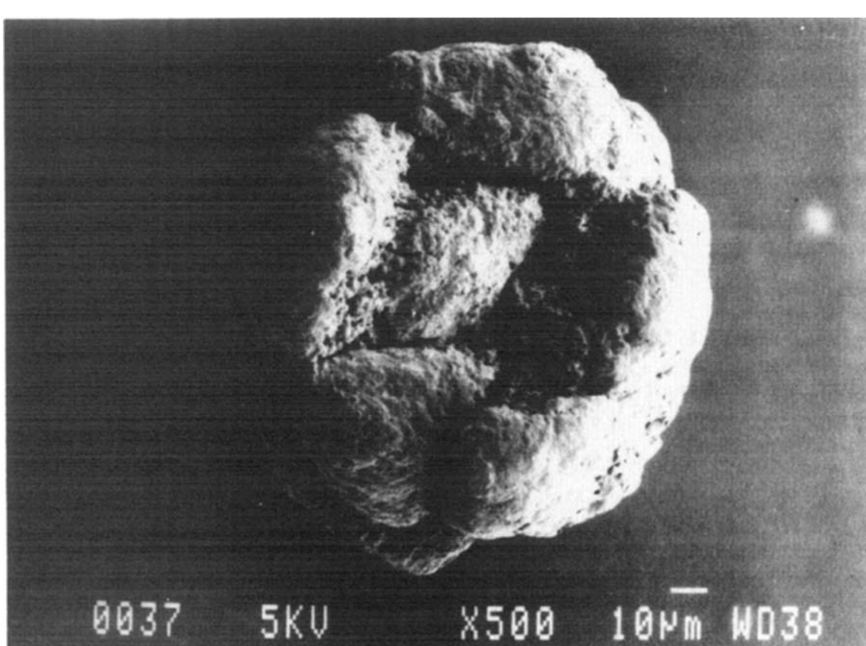

Fig. 3. Scanning electron micrograph of a typical PVC resin particle, taken at 500 magnification.

The micrographs taken at 100 magnification were placed on the measuring tablet of a Zilog IBAS image analyser. The perimeter of each particle was digitized using a stylus to trace the periphery of the particle. Then d_{max} and d_{min}, corresponding to an ellipsoid geometric configuration were calculated using the areal moment of interia. The Zilog IBAS1 interactive computer software was used for this purpose.

The data (d_{max} and d_{min}) generated by the image analyser, were stored in the computer. Then d_{av} and s_f were calculated for each particle using equations (6) and (7), respectively. A computer algorithm was developed to calculate the differential distributions, considering individually the resin particles. The alogrithm considers the variation of d_{av} and s_f from one particle to another and keeps account of the number of particles having the same d_{av} and s_f. The cumulative distributions were obtained by summing the differential distributions.

RESULTS AND DISCUSSION

Figure 4 shows the effect of the number of PVC particles on the breadth and smoothness of the cumulative size distributions. The distributions become narrower and smoother as the particle number increases. Also, note that the distributions corresponding to particle populations of 391 and 467 nearly overlap each other. The variances [equation (10)] corresponding to these two values are fairly close to each other. Therefore, around 430 mutually exclusive PVC resin particles, which is an average between 391 and 467, is a reasonable number for the calculated distributions to be statistically acceptable.

Figure 5 demonstrates the influence of the PVC particle population on the width and smoothness of the cumulative shape distributions. The variance of these distributions does not significantly differ with increasing number of PVC particles, showing that particle population hardly affects cumulative shape distribution.

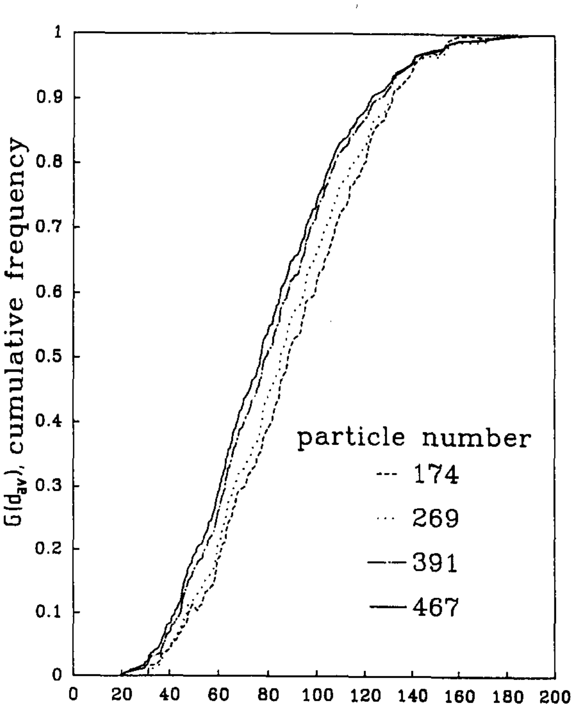

Fig. 4. Effect of the number of PVC particles on the breadth of the cumulative particle size distributions.

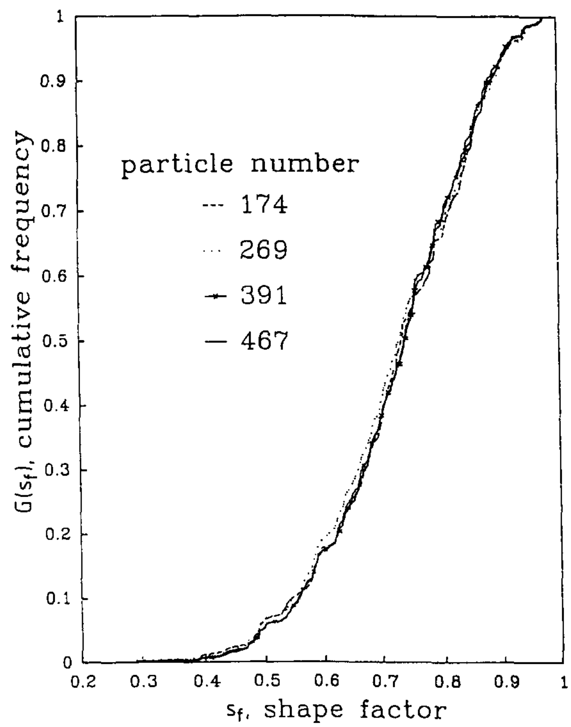

Fig. 5. Effect of the number of PVC particles on the breadth of the cumulative particle shape distributions.

The cumulative shape distributions (Fig. 5) particularly show that the PVC resin particles have varying shapes which lie, from a geometric view point, between an ellipsoid and a sphere. The average shape factor $\bar{s}_f$ of the experimental PVC resin particles was found to be 0.73 μm, whereas the average particle size $\bar{d}_{av}$ was 80.4 μm. This value lies between $\bar{d}_{min} = 69.3$ μm and $\bar{d}_{max} = 95.7$ μm. Note that the present mathematical treatment enables calculation of $\bar{d}_{min}$, $\bar{d}_{av}$ and $\bar{d}_{max}$ which can be used to find the approximate signature waveform [12] of a given lot of PVC resin particles.

Figure 6 compares the average particle size distribution of $\bar{d}_{av}$ with that of d_{min} and d_{max}. Note that $\bar{d}_{min}$ is the parameter that is measured by sieve analysis [12]. The distribution of d_{av} lies between that of d_{min} and d_{max}. This figure also shows that the experimental PVC resin consisted of particles which fall under the category of subgrains and grains as defined by Geil [23]. From the above figures, also notice that the cumulative shape and size distributions are elongated ∫-shaped curves.

CONCLUSION

The PVC resin particles can be simultaneously characterized in terms of particulate morphology, shape and size distributions using scanning electron microscopy and image analysis. Using the developed computer algorithm, which is based on the

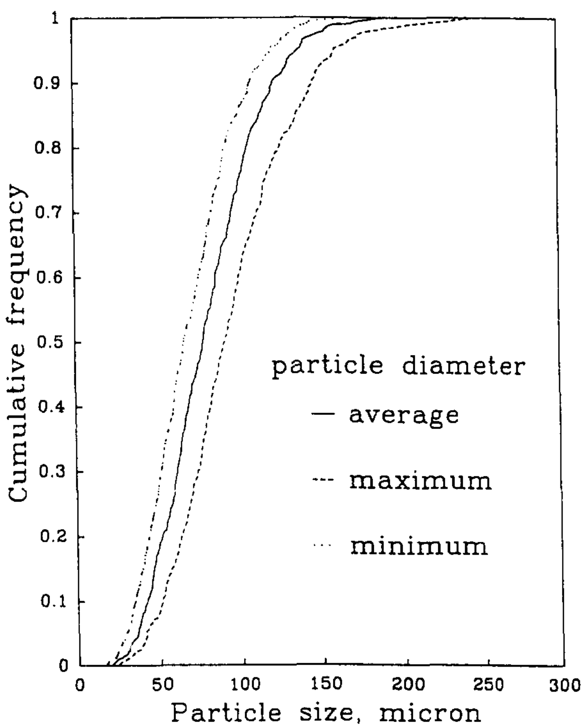

Fig. 6. Comparison of the average particle size distribution with minimum and maximum particle size distributions.

mathematical approach explained in this paper and which considers each particle, the output information from the image analyser can be readily converted into the continous shape and size distributions. Based on the statistical analysis, the number of particles required for the measurement to have an acceptable degree of precision was concluded to be around 430. From the distributions, the average properties can also be obtained. For the experimental PVC, the average values of the particle diameter and aspect ratio were 80.4 μm and 0.73, respectively. The number- and weight-average particle diameters were estimated as 80.4 and 114.8 μm respectively. The particle size uniformity index was found to be 1.43. Both the cumulative shape and size distributions were found to be elongated ∫-shaped curves.

The above alogorithm is versatile in the sense that it can also compute shape distributions involving classic shape factors which are based on particle area, perimeter, and object length. The details will be shown in a future publication.

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