SEM image analysis to characterize the shape of catalyst and polyethylene prepolymer particles in olefinic polymerization

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(Received 10 January 1992; revised 18 May 1992)

In a previous paper, the usefulness of SEM image analysis for the characterization of the size and shape of Ziegler-type quasi-spherical catalyst particles and polypropylene particles was shown. In the present paper, the method is extended to silica-supported and unsupported catalysts for ethylene polymerization. The shapes of these catalysts are more or less remote from a sphere. It was shown that the selected circularity index allows us to distinguish between spherical, polyhedric and more complex shapes. However, the sampling for SEM examination is more difficult the more remote the particles are from spheres. Moreover, the digitization on 512×512 pixels — necessary for non-spherical particles — leads to a four-fold increase in computer time. As far as the determination of the 'true' dispersion of a catalyst particle batch is concerned, it is not possible to obtain it from a single sample. One very interesting result is the shape evolution between silica-supported catalysts and the corresponding prepolymers.

(Keywords: catalyst; prepolymer; polymerization)

INTRODUCTION

It was shown, in a recent paper[1], that SEM digital image analysis is a useful method for the determination of the dimensions (diameter, surface, perimeter) and shape (circularity) of particles of catalyst, of coated catalyst, of prepolymer and of polymers with widely variable advancement ratios. The importance of good sample preparation before SEM examination was stressed. For such work, conducted on spheroïdal particles, the feasibility of analysis automation was demonstrated.

However, the suitability for analysis was strongly dependent on the image digitization sharpness. Indeed, due to the particle shape, digitization on a 256×256 pixels basis was found to be satisfactory. When more complicated particle shapes are considered, a sharper digitization, i.e. using 512×512 pixels (which is near the maximum sharpness easily available on routine commercial image analysis devices) might be necessary in order to obtain a better shape characterization. If so, the 'automatizability' of the method might be somewhat impaired.

The aims of the present work are:

1. to examine the influence of the digitization sharpness on the circularity values, for different particle shapes (spheroïdal and less spherical shapes).
2. to determine the 'true' dispersion of characteristic parameters of spheroïdal particle population, as announced in the conclusion of our previous paper[1].
3. to examine the feasibility of the method for particles with shapes farther and farther from the sphere.

Also considered are preparation difficulties, measurement automation and the reliability of numerical values (mainly for circularity) in relationship to the visual appearance.

INFLUENCE OF THE SHARPNESS OF IMAGE DIGITIZATION

Spheroïdal particles

Measurements were performed on a 'third generation supported catalyst', the definition of which was given in reference 1. In *Table 1* the results obtained with the 256×256 and 512×512 pixels-based digitizations are compared.

Particles with a less spherical shape

Several measurement series were performed on unsupported catalysts, the processing of which is indicated in references 2 and 3, as well as on the corresponding prepolymers. *Table 2* shows values obtained on a catalytic preparation and *Table 3* is concerned with two prepolymer granules obtained from the same catalyst.

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0032-3861/93/132720-06

Table 1 Comparison of two digitization sharpnesses for spheroïdal catalyst particles

	256 × 256 pixels image	512 × 512 pixels image
No.[a]	94	86
Diameter[b]		
Mean (μm)	30.5	30.6
SD	3.3	3.2
CV (%)	10.7	10.5
Diameter[c]		
Mean (μm)	32.4	33.1
SD	3.7	3.5
CV (%)	11.4	10.6
Circularity		
Mean	1.13	1.17
SD	0.05	0.04
CV (%)	4.50	3.61

[a] Number of measured particles
[b] Surface-based diameter
[c] Perimeter-based diameter
SD, standard deviation; CV, coefficient of variation

Table 2 Comparison of two digitization sharpnesses for non-spheroïdal catalyst particles

	256 × 256 pixels image	512 × 512 pixels image
No.[a]	56	58
Diameter[b]		
Mean (μm)	38.9	38.0
SD	12.5	12.5
CV (%)	32.1	32.9
Diameter[c]		
Mean (μm)	48.2	49.7
SD	18.3	19.8
CV (%)	38.0	39.9
Circularity		
Mean	1.54	1.71
SD	0.26	0.33
CV (%)	17.02	19.30

[a,b,c] For footnotes see *Table 1*

Figure 1 shows micrographs corresponding to *Tables 1* (*Figure 1a*) and *2* (*Figure 1b*).

Discussion

In the case of spheroïdal particles, 512 × 512 pixels-based digitization hardly modifies numerical values measured from 256 × 256 pixels-based digitization, as far as surface-based diameters are concerned. For perimeter-based diameters and circularities, a slight increase is observed. A statistical test for mean values shows that differences are not significant for the diameters but are significant for circularities. However, the latter statement has to be taken with much caution, since the test is based on the normality of the population: as will be seen later (see *Figure 2c*), the circularity distribution is far from being normal.

In the case of non-spheroïdal particles, the same conclusion is reached as far as surface-based diameter mean values are concerned. Conversely, perimeter-based diameters and circularity mean values are significantly increased by 512 × 512 pixels-based digitization. Also in the case of the two prepolymer granules (*Table 3*), the perimeter-based diameter and circularity are greatly increased by the sharper digitization, i.e. 512 × 512 pixels.

In the case of non-spheroïdal particles, the conclusions concerning the significance of the differences between means seem less clear than would have been expected on the basis of the differences between individual figures. This is probably due to the strong dispersity of the individual figures (three to four times greater than for spheroïdal particles). If one compares, particle by particle, the values of the perimeter-based diameter and circularity one finds, in almost every case, higher figures for the 512 × 512 pixels-based image as compared to the 256 × 256 pixels-based one.

One must conclude that 256 × 256 pixels-based digitization is sufficient for the study of spheroïdal particles, whereas, for more complex particle shapes, one should rather use 512 × 512 pixels-based digitization, even though the latter would lead to a four-fold increase in computer time. This is done for the rest of this work.

Table 3 Comparison of two digitization sharpnesses for two prepolymer granules (a and b)

	256 × 256 pixels image		512 × 512 pixels image	
	a	b	a	b
Diameter[a] (μm)	589	356	588	355
Diameter[b] (μm)	802	597	858	608
Circularity	1.85	2.82	2.13	2.92

[a] Surface-based diameter
[b] Perimeter-based diameter

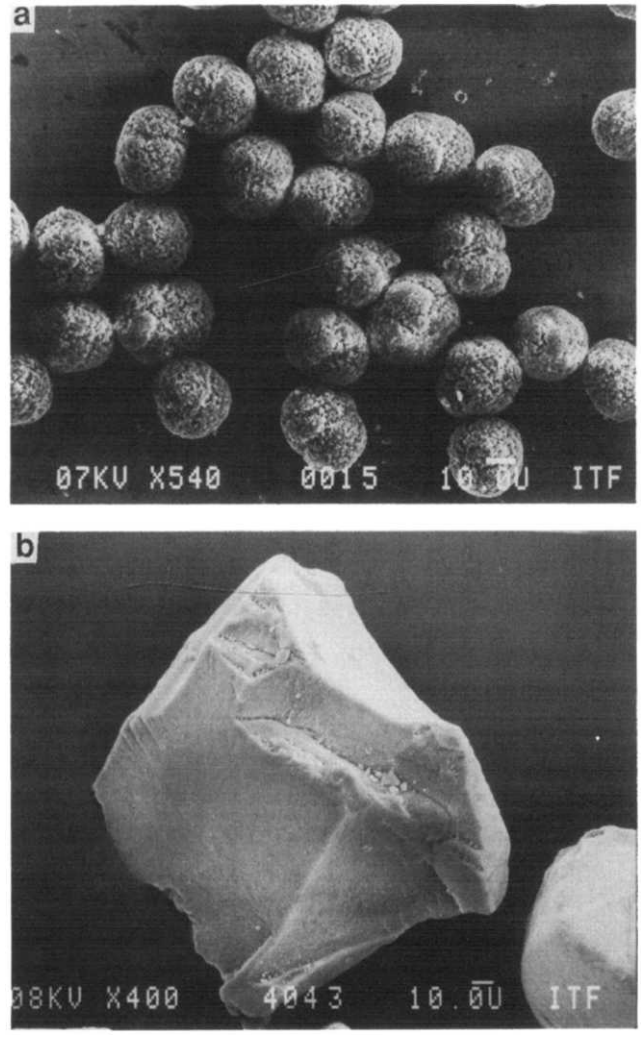

Figure 1 Micrographs corresponding to *Tables 1* (a) and *2* (b)

Table 4 Results from the eight series of spheroïdal particles

	Surface-based diameter			Perimeter-based diameter			Circularity		
	Mean (μm)	SD	CV (%)	Mean (μm)	SD	CV (%)	Mea	SD	CV (%)
Ser. 1 ($n=217$)	30.8	3.9	12.6	32.8	4.5	13.7	1.14	0.06	5.13
Ser. 2 ($n=209$)	31.5	3.7	11.7	33.4	4.1	12.4	1.12	0.06	3.47
Ser. 3 ($n=241$)	33.2	3.3	10.0	35.8	3.9	10.8	1.16	0.06	5.57
Ser. 4 ($n=249$)	30.3	3.3	10.9	31.9	3.9	12.1	1.11	0.06	5.66
Ser. 5 ($n=274$)	31.1	3.8	12.3	33.1	4.4	13.3	1.13	0.06	5.66
Ser. 6 ($n=244$)	31.9	3.7	11.7	33.7	4.2	12.6	1.12	0.06	5.44
Ser. 7 ($n=236$)	31.9	3.6	11.2	33.3	3.9	11.8	1.09	0.04	3.75
Ser. 8 ($n=259$)	31.8	3.6	11.3	33.1	4.0	12.1	1.08	0.05	4.40
Overall results ($n=1929$)	31.6	3.7	11.7	33.4	4.2	12.7	1.12	0.06	5.60
Mean[a]	31.6	1.1	3.5	33.5	1.4	4.0	1.12	0.03	3.09

[a] Over the 40 fields

DETERMINATION OF THE 'TRUE' DISPERSION OF A POPULATION OF SPHEROÏDAL CATALYST PARTICLES (512 × 512 PIXELS-BASED DIGITIZATION)

Operating procedure

In order to try to overcome the bias arising from the manipulation, eight independent measurement series (numbered 1–8) were performed. They correspond to eight 'subsamples' collected from one and the same 'representative' sample. The latter was taken directly from the 'industrial' catalytic batch, i.e. a stirred suspension of catalyst particles in a hydrocarbon liquid: ~0.25 l of the 'industrial' suspension was collected, under nitrogen, in a 5 l vessel, and subsequently diluted, in order to obtain, at the time of the subsampling procedure, a concentration of catalyst particles compatible with a monolayer arrangement on the SEM sample holder.

To produce the eight subsamples (carried out by the same operator), the diluted suspension was stirred for 10 min, then allowed to settle, before applying the next subsampling procedure: the latter consists of drawing off with a pipette, 1 cm below the liquid surface, a very small amount of the diluted suspension, then depositing it on the SEM sample holder. After hydrocarbon evaporation, a monolayer is obtained with a suitable interparticle distance[1]. The subsampling operation was also conducted under a nitrogen atmosphere.

Results

Results corresponding to each of the eight series are reported in *Table 4*. Thus one may study the dispersion among the eight groups of means. Each series is made up of five micrographic fields and contains a total (n) of at least 209 individual particles.

The overall results from the individual results of the $8 \times 5 = 40$ fields examined are also shown, in order to obtain an estimate of the confidence intervals for the mean parameters of the population: thus, the mean circularity value may be estimated to be 1.12, with a 95% probability confidence interval of ± 0.003 (Student's 't' being close to 2, for a total number of individual measurements near 2000). In contrast, on the last line in *Table 4*, the figures arising from each of the 40 fields are considered to be individual results. As a consequence, the means, on the ninth and tenth lines in *Table 4*, are almost identical; in contrast, the dispersions are roughly three times smaller, on the last line of *Table 4*.

Figure 2 shows three distribution histograms corresponding to individual measurements for the surface-based diameter, perimeter-based diameter and circularity. Although the two diameter histograms appear substantially Gaussian, this is not the case for the circularity histogram: the latter is substantially dissymmetrical, with the mode (1.08) shifted towards smaller figures: the fact that this mode is above 1.00 indicates that the particles are somewhat different from the perfect spherical shape.

Discussion

A statistical test for the comparison of means was applied on the results in *Table 4*.

For each of the three parameters, the two most distant figures were considered, together with the corresponding standard deviation and number of measurements. The significances of the differences were computed. The results are presented in *Table 5*. It is seen that differences are significant, which clearly shows that a single subsampling with a pipette is not sufficient for an accurate evaluation of the population dispersion.

If two different means, taken at random from the eight available ones, are not to significantly differ from each other, the gaps (or 'deltas') should be as follows: delta (mean perimeter-based diameter) $\leqslant 0.6$ μm (mean: 35.6 μm; SD: 3.5; $n=250$); delta (mean circularity) $\leqslant 0.01$ (mean: 1.12; SD: 0.06; $n=250$).

The above requirements are indeed fulfilled for a number of pairs arising from the eight series examined. The latter remark explains the statement made in our previous paper[1] about the precision of measurements.

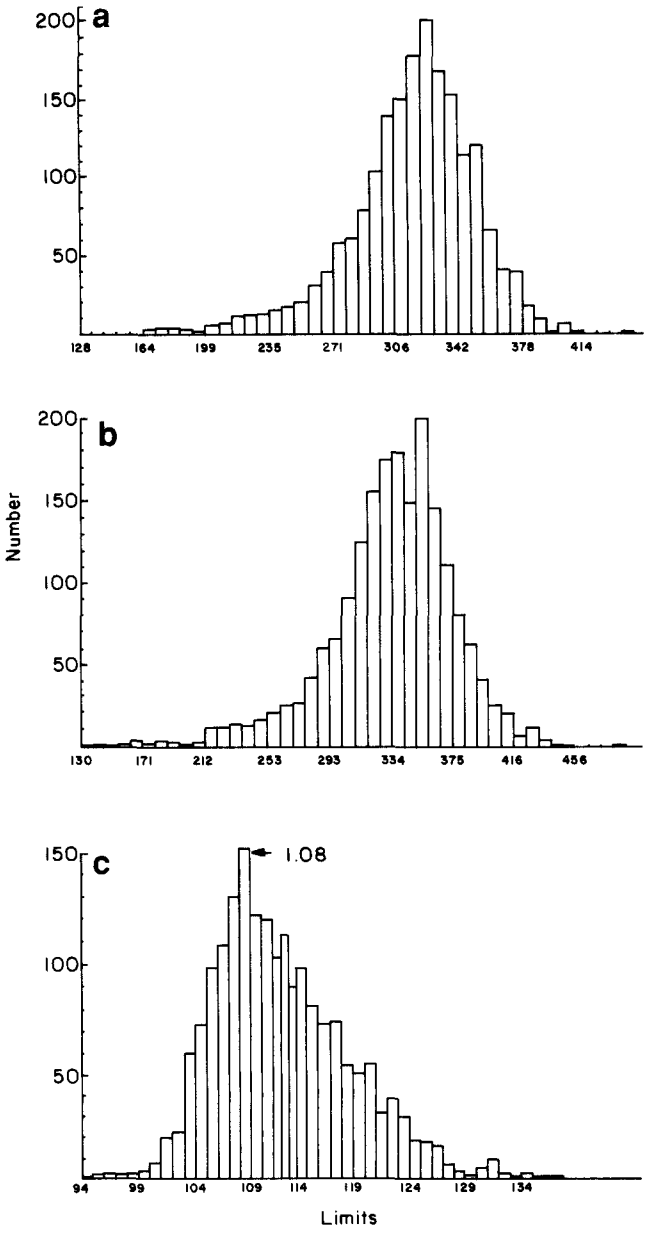

Figure 2 Histograms corresponding to individual measurements for (a) the surface-based diameter, (b) the perimeter-based diameter and (c) circularity for a population of spheroïdal particles

COMPARISON BETWEEN CATALYSTS AND PREPOLYMERS WITH A POLYHEDRAL-LIKE SHAPE

Several series of SiO_2-supported catalysts were examined.

Catalyst support (silica), catalysts and prepolymers of Cr/SiO_2 type

Figure 3a shows the morphology of: granular silica from Crosfield (ref. EP10). *Figures 3b* and *c* show EPA0 silica-supported catalyst, treated according to reference 4.

Figure 3d shows polyethylene prepolymer with an advancement ratio of ~90 g/mmol Cr obtained from the above catalyst[4].

Visual examination of these micrographs clearly shows that EP10 SiO_2, the corresponding catalyst and the prepolymer prepared therefrom have polyhedral shapes. In addition, the catalyst support (silica) and catalyst particle surfaces look smooth, whereas the polymer particle surface looks much coarser.

Table 6 gives the measured diameters and circularities of the above samples. The following observations can be made:

1. Silica and the catalyst particles have different diameters (the significance is demonstrated by a statistical test). The fact that the catalyst diameter is smaller (notice the different magnifications in *Figures 3b* and *c*, on the one hand, and *Figure 3d*, on the other), suggests that, during catalyst treatment, the coarser silica particles were fragmented (see *Figure 3a*).
2. Circularity is not significantly modified between the support and catalyst particles. The 1.32 value must be considered to be quite significantly different from that obtained for spheroïdal particles (see *Figure 2c*, with 1.08 modal circularity).
3. The mean circularity of prepolymer particles is again farther from the spheroïdal shape value, since it reaches 1.50, with a high dispersity, which suggests that there is no replication between the catalyst particle and the prepolymer particle shape.

Catalyst support (silica), catalysts and prepolymers of Ziegler–Natta type

Figure 4 shows the morphology of granular silica from Grace (ref. SG 332) and of polyethylene prepolymer (40 g/mmol Ti), made from a SG 332 silica-supported catalyst.

Visual examination of the micrographs clearly shows that the 'granular' SG 332 silica particles and the corresponding prepolymer particles have a polyhedral shape.

Table 7 shows the diameter and circularity values obtained for four samples. The following remarks can be made:

1. The microspheroïdal support particles and those of the corresponding catalysts have very similar diameters and circularities
2. Granular silica circularity, although apparently not very far from 1.00 (mean value: 1.22) is most probably significant of a non-spheroïdal shape (note that the square has a circularity of 1.27). Prepolymer made from a catalyst on a granular silica has a shape farther from that of the sphere (mean circularity: 1.51), with a high dispersion. The latter observation suggests that, once more, there is no replication between support and polymer shape.

Table 5 Comparison of means for the most distant series in *Table 4*

	n	Mean (μm)	SD	q^a	thr 95%	thr 99%
Surface-based diameter						
Ser. 3	241	33.2	3.3	16	2	2.6
Ser. 4	249	30.3	3.3			
Perimeter-based diameter						
Ser. 3	241	35.8	3.9	9.7	2	2.6
Ser. 4	249	31.9	3.9			
Circularity						
Ser. 3	241	1.16	0.06	11	2	2.6
Ser. 8	259	1.08	0.05			

[a] q is the figure which should be below the threshold (thr)

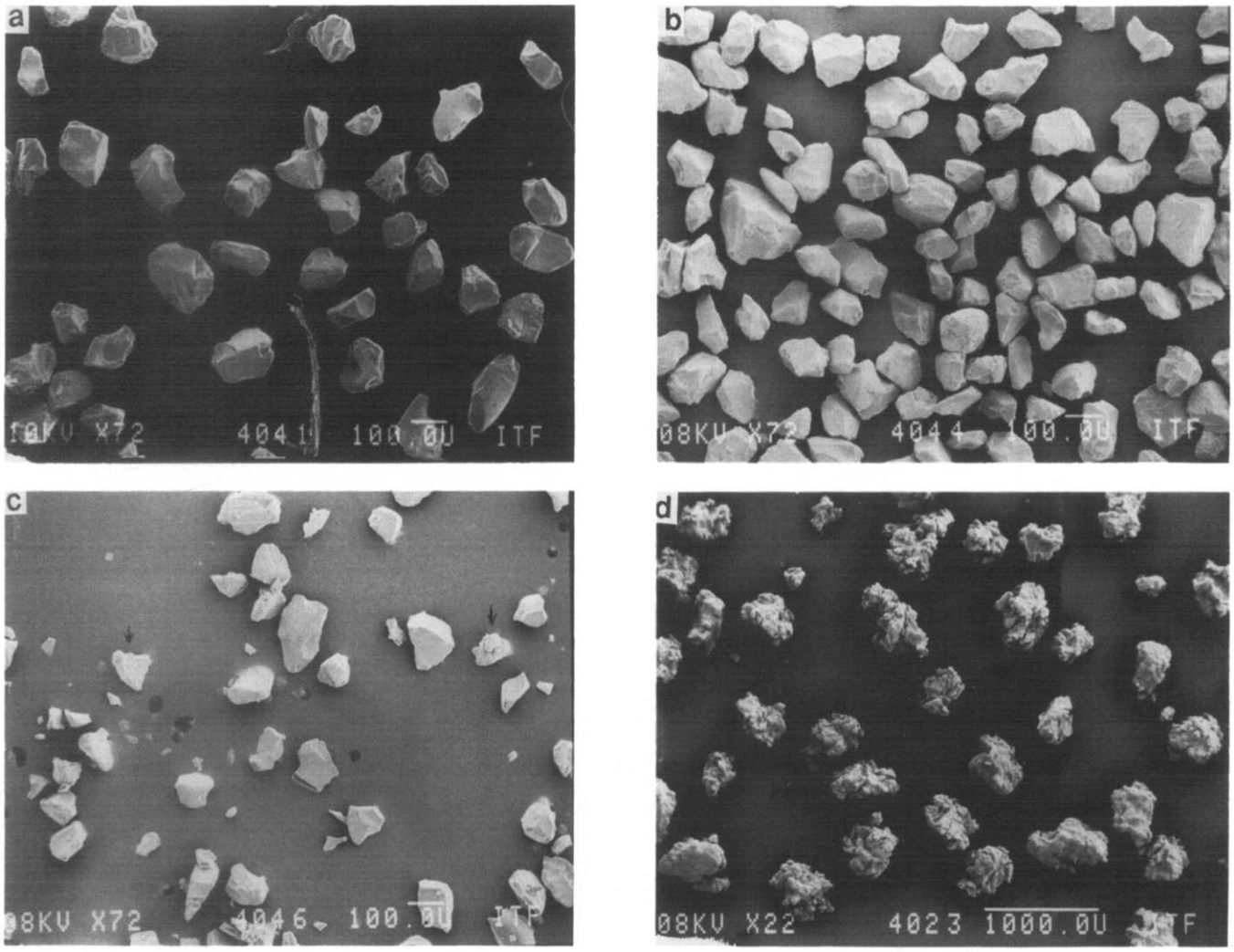

Figure 3 Micrographs of (a) granular silica, (b, c) silica-supported catalyst and (d) prepolymer from a Cr-based catalyst

Table 6 Measured diameters and circularity of EP10 silica, catalyst and prepolymer (Cr/SiO_2)

	EP10 silica	Catalyst	Prepolymer
No.[a]	137	171	133
Diameter[b]			
Mean (μm)	136.2	101.9	432.9
SD	36.4	27.5	105.4
CV (%)	26.7	27.0	24.4
Diameter[c]			
Mean (μm)	156.6	116.7	530.1
SD	41.8	32.7	135.8
CV (%)	26.7	28.0	25.6
Circularity			
Mean (μm)	1.33	1.31	1.50
SD	0.11	0.12	0.20
CV (%)	8.6	8.9	13.3

[a,b,c] For footnotes see *Table 1*

Discussion

As observed earlier, for particles with shapes very different from spherical, 512 × 512 pixels-based digitization permits a reasonably good characterization of the polyhedral shape of silica particles. Polyhedral catalyst particles supported on granular silica or elongated particles supported on microspheroïdal silica have a mean circularity of 1.3 (compared to spheroïdal catalyst particles with a mean circularity of 1.1 on the one hand, and to catalyst particles with shapes very different from spherical, with a circularity which may reach values of over 2, on the other hand).

In addition, for polyethylene prepolymers made over catalysts with granular particles, both for chromium and for Ziegler (titanium) catalysts, their mean circularity tends to increase with an increasing dispersion. This suggests that the replication between supported catalyst and prepolymer is no longer the rule and, consequently, that the catalyst lacks homogeneity (anisotropic growing of the polymer particle) and/or strength (fragmentation).

CONCLUSIONS

The attempt to apply the previously described[1] method to particles with shapes very far from spherical, proves feasible and, in addition, allows us more specifically to measure the shape of particles: the circularity is 1.1 for a spheroïdal shape, and 1.3 for a polyhedral shape. When one moves to catalyst or polymer particles with more complex shapes, the circularity may reach values equal to or above 2. However, the automation of the method is somewhat impaired by the necessity to digitalize the images on 512 × 512 pixels instead of 256 × 256 pixels. As a consequence, the computer time is multiplied by 4.

Moreover, the preparation of monolayers of non-

Table 7 Measured diameters and circularity of SD 3217, supported catalyst, granular-type silica and prepolymer (Ziegler/SiO_2)

	SD 3217 (microspheroïdal)	SD 3217 supported catalyst	SG332 (granular)	Prepolymer
No.[a]	32	38	30	32
Diameter[b]				
Mean (μm)	60.7	58.9	161.9	395.8
SD	15.3	12.8	41.8	96.5
CV (%)	25.2	21.8	25.8	24.4
Diameter[b]				
Mean (μm)	68.1	67.3	179.2	490.3
SD	17.3	16.7	46.6	151.7
CV (%)	25.4	24.8	26.2	30.9
Circularity				
Mean (μm)	1.27	1.30	1.22	1.51
SD	0.20	0.14	0.09	0.22
CV (%)	16.01	10.64	7.65	14.40

[a,b,c] For footnotes see *Table 1*

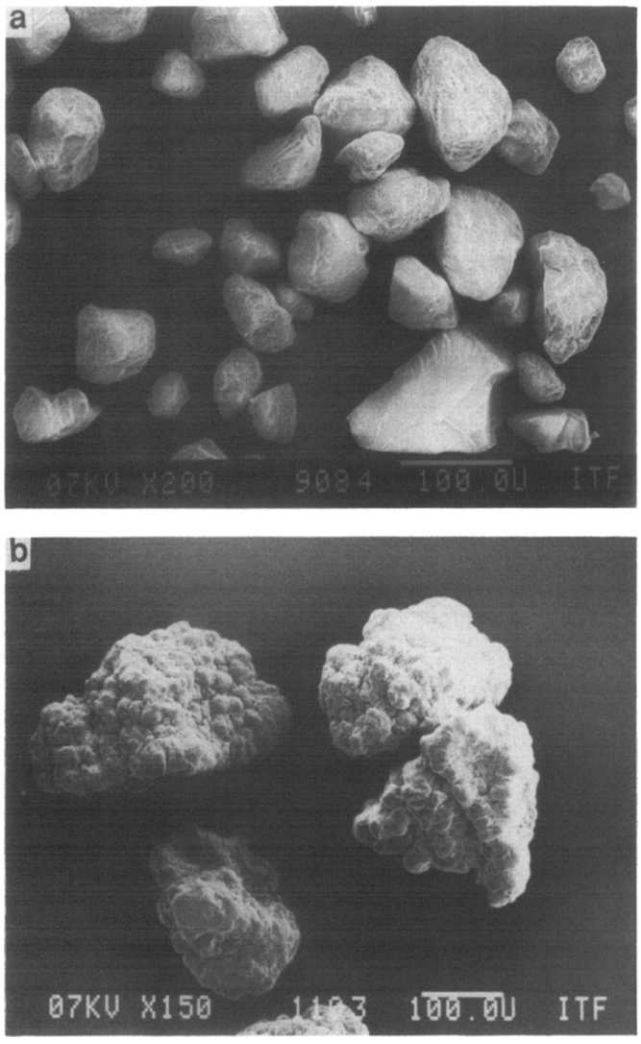

Figure 4 Micrographs of (a) granular silica and (b) prepolymer from granular silica

spheroïdal particles, without overlapping is less easy to obtain; this is particularly true in the case of catalyst particles, which have to be handled under nitrogen. One must work with more diluted suspensions of particles, giving photographic fields with less particles. As a consequence, one has to analyse a greater number of fields.

As far as spheroïdal particles are concerned, the determination of the 'true' population dispersion proves more difficult than expected: dilute suspension analysis from only one sample taken with a pipette does not allow the 'true' dispersion to be obtained, since, among the eight samples analysed, some give significantly different results. However, it should be pointed out that observed differences between the eight groups of mean values remain within quite acceptable limits. A better, although more cumbersome, way to proceed would be to do several (at least three) independent dilutions from the initial sample.

In the case of spheroïdal catalysts for suspension polymerization of propene monomer[1] no significant shape modification from catalyst to polymer particles with varying yields was observed. This is not true when polymerization is performed with silica-supported catalyst particles for ethylene polymerization. In fact, starting from polyhedral catalyst particles with a circularity near 1.3, one obtains prepolymer particles with a more complex shape (circularity 1.5).

It would be worthwhile to examine whether such a difference between silica-supported catalyst shape and polymer shape increases with polymerization yield. Also, it would be interesting to evaluate the relationship between the polymerization processes (batch/continuous and suspension/gas phase) and the particle shape evolution during processing.

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