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Highly filled particulate thermoplastic composites

Part I *Packing density of irregularly shaped particles*

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The packing density of irregular shaped particles greatly affects the properties of highly filled particulate composite materials. The effects of particle size distribution parameters on the packing density of fused silica powder and cristobalite flour powder of different size ranges is reported. Various size distributions, according to the log-normal function, were prepared by sieving and characterized by light scattering, using a Malvern 2600 light scattering instrument. The apparent and tap density of the various powders was used to characterize the packing density. The size distribution width was found to have a major effect on the packing density. In addition, the particle size was found to affect the packing density however, its significance depends on the size range and shape of the particles. Mixtures of powders, each having a different size distribution, behave differently.

1. Introduction

Highly filled particulate composite materials are currently being used for manufacturing a variety of products, from dental materials to rocket propellants. In such products the filler is the dominant component, with concentrations above 75 vol%, for the production of desirable chemical and/or mechanical properties. The maximum filler content is limited by its packing density, which in turn depends on particle parameters, such as shape, size, size distribution and surface properties. For example, rounded and smooth particles create denser packing than sharp edged and rough ones. Agglomeration, which is known to decrease packing density, is a common phenomenon in fine powders caused by cohesion forces which increase with increasing particle specific area. Bridging, another phenomenon of particle grouping, creates bridges and large voids which lower the packing density, in a similar way to agglomeration. Tapping is one way of breaking agglomerates/bridges and thus increasing packing density [1]. Another way to overcome these obstacles is by adding a wetting agent which reduces surface tension and friction between particles. The packing density also depends on the packing process, namely, free, vibrated or compacted powders.

Particle size measurement may seem quite simple but actually it is rather complicated due to the particle shape and size distribution. To define the size of non-spherical particles, more than one dimension is needed [2]. For example, in order to describe a needle shaped particle its length and width are needed, and for an irregularly shaped particle, a large number of dimensions are needed, which in practice are replaced by various "equivalent dimensions". Any "real" powder is composed of at least one size population of particles which can be statistically characterized. A function which was found to best suit the description of a particle population is the "log-normal" distribution. It was found to fit particle size distributions of natural powders, formed either by breakage of large particles, or by coalescence of small ones [3].

The log normal function is based on two parameters which define particle populations namely, geometric mean (median) and geometric standard deviation. The frequency distribution of the log-normal function is given by:

$$f(x) = [1/(2\pi)^{1/2} * \ln GSD]\exp[-(\ln x - \ln CMD)^2/2(\ln GSD)^2] \quad (1)$$

where GSD, (σ_g), is the geometric standard deviation and CMD, (X_g) is the median particle diameter. This expression is a direct result of normal distribution of the natural logarithms. A unique property of this distribution function is that the number and weight (or volume) distributions have the same distribution width for a given particle population [2].

According to previous studies on the packing density of powders [4–7], the particle size distribution

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width is the only parameter affecting packing density. The density increases with increasing distribution width, while the actual size of the particles has no effect. Westman and Hugil [6], however, limit this statement to cases in which electrostatic forces and air films between particles are negligible; their conclusion, though, is not based on experimental results. It should also be pointed out that the "no actual size effect" conclusion is based on studies of relatively large rounded particles.

The present work is aimed at studying of the effect of the actual particle size and particle size distribution on the packing density of relatively fine, irregularly shaped powders, which are often the case in highly filled particulate composite systems.

2. Experimental procedure

Fused silica powder, prepared by crushing and milling of a silica tube and then sieving into the appropriate size ranges, was used as the test material. The total size range obtained by sieving was 40–960 μm. In order to extend the studied size range, a cristobalite flour powder (Sibelco), another type of silica powder, of three average size fractions; represented by 29, 21 and 12 μm, was also used. The cristobalite flour was chosen as a complementary powder due to it's similarity in particle shape (Fig. 1a and b) and density to the fused silica powder. Powders of desired particle size distributions were prepared according to a log-normal distribution function, by mixing powder fractions of different size, using a double cone tumbler. Powders of three different median sizes, 56, 120 and 240 μm, each consisting of five different distribution widths, designated by the geometric standard deviation (σ_g), were prepared. The computed distribution, according to the average sieve sizes, are depicted in Fig. 2(a–f). The geometric standard deviation is calculated as follows:

$$\log \sigma_g = \log X_{84} - \log X_{50} = \log X_{50} - \log X_{16} \quad (2)$$

where:
X_{50} is the median size, X_{16} is the particle size where 16% of the particles are smaller than or equal to X_{16}, and X_{84} is the particle size where 84% of the particles are smaller than or are equal to X_{84}.

In addition to powders of such size distributions, binary powder mixtures having size distributions of different medians and maximum width ($\sigma_g = 3.9$ or 3.4) were prepared. The size distribution of all powders, in every size range, obtained by sieving, of the cristobalite powder and of the prepared mixtures, were characterized, using a Malvern 2500 light scattering instrument.

The apparent and tap densities of the different powders were measured. The apparent density was determined by pouring the powder into a graduated cylinder (about 30 cm^3) and weighing. To measure the tap density, the powder in the graduated cylinder was vibrated, using a sieve vibrator. The vibration time and amplitude were set to obtain the maximum volume change and hence, the highest tap density.

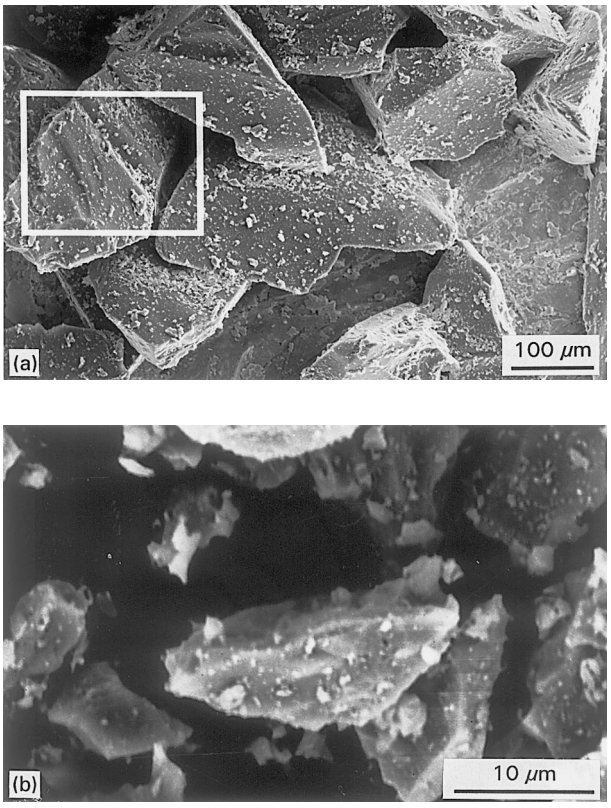

Figure 1 SEM micrograph of: (a) glass powder in the size range of $400 < x < 500$ μm. (b) cristobalite powder with median size of 29 μm.

3. Results and discussion

3.1. Particle size and shape characterization

The fused silica and the cristobalite flour particles are irregular in shape, as is shown in Fig. 1. The surface of the particles is rough and covered with both fine particles and also agglomerates (Fig. 3). Physical adherence of micronized particles onto larger particles, a common phenomenon in many powders [1], lowers the total free surface energy by lowering the total surface of the powder. A similar shape and surface appearance was observed in all the size ranges studied.

Six of the measured size distributions, obtained by using a Malvern light scattering instrument for different size ranges, are shown in Fig. 4(a–f). There is clearly a good agreement between the measured particle size distribution and the desired log-normal distribution function, in that, the particle size distribution plotted on a semi-logarithmic scale has a bell shape, typical of this distribution function [2, 3]. There is however, a deviation from the ideal symmetric bell shape which is caused by an excess of fine particles. This deviation from symmetry increases with decreasing particle size range. These fine particles are the ones adhered onto the larger particles (Fig. 3) and become separated on the sample immersion in water, a step necessary for the size analysis. The increase in measured fine particle content with decreasing particle size is caused mainly by increasing agglomeration in small particle powders. In addition, the data processing method utilized by the Malvern system does not take into consideration light reflection and refraction and deviations of the particle shape from sphericity. The Malvern data processing only takes

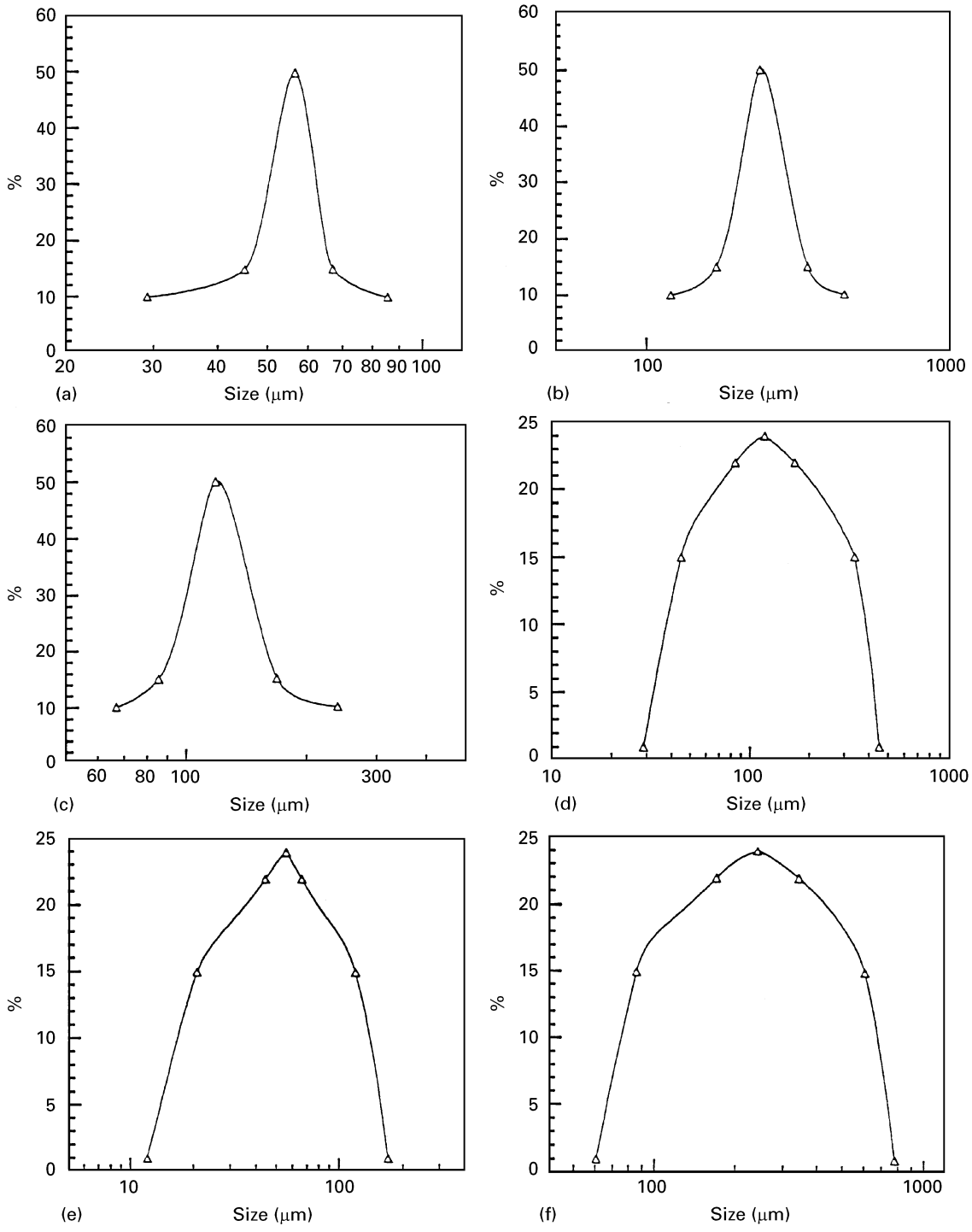

Figure 2 Frequency distribution for particles population with: (a) $X_g = 56$ μm; $\sigma_g = 1.4$ (b) $X_g = 240$ μm; $\sigma_g = 1.4$ (c) $X_g = 120$ μm; $\sigma_g = 1.4$; (d) $X_g = 120$ μm; $\sigma_g = 2.8$ (e) $X_g = 56$ μm; $\sigma_g = 2.8$; (f) $X_g = 240$ μm; $\sigma_g = 2.8$.

into account light diffraction, which tends to overestimate the relative number of finer particles [8]. Although this analysis shows a higher content of fine particles, it typically gives higher average particle size values in comparison to sieving [9]. It seems that the deviation from sphericity is one of the main reasons for a higher size reading, up to twice that of the sieving size. A similar deviation was reported by Nathier [10] for irregularly shaped particles. Fig. 5(a and b) depicts the Malvern size distributions for two size ranges of particles, 40–50 μm and 50–63 μm (according to sieve size), obtained by dry and wet sieving (wet sieving is performed under a stream of water). In general, wet sieving results in powders of a narrower size distribution than dry sieving. It seems that water acts as a dispersive agent which changes the surface energy of the particles, thereby, separating the small particles from the surface of the large ones. This effect is only possible if the fluid intimately wets the particles.

The size distribution of the 50–63 μm range powder, which was wet sieved, is quite narrow; the main particle population comprises 85–90% of the powder. On the other hand, in the lower 40–50 μm size range, the secondary population of fine particles still represents about 30% of the powder. This is an additional evidence for the increasing agglomeration level with decreasing particle size.

There is quite a large overlap of the size distribution curves obtained for the different size ranges (Fig. 6). This overlap is caused by powder particle effects characteristic of the sieving process and of the Malvern light scattering analysis. This overlapping in size ranges is advantageous for the preparation of powders of a desired size distribution; it enables the creation of powders of continuous particle size distribution even though they are prepared by mixing a relatively small number of powder fractions [1, 3–10], as is the case in the present work.

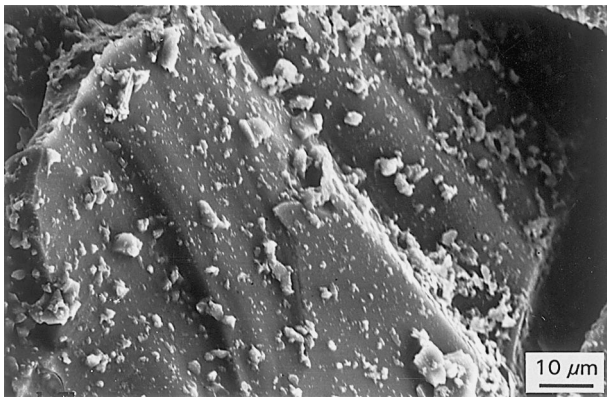

Figure 3 SEM micrograph of a glass particles surface (framed area in Fig. 1a).

3.2. Characterization of particle size distributions in mixtures containing different size ranges

The particle size distributions produced by mixing powders of different size ranges and the calculated size distributions were compared to the Malvern light scattering results. As is seen in Fig. 4, all the measured distributions are bell-shaped on a semi-logarithmic scale, and are therefore similar to the calculated

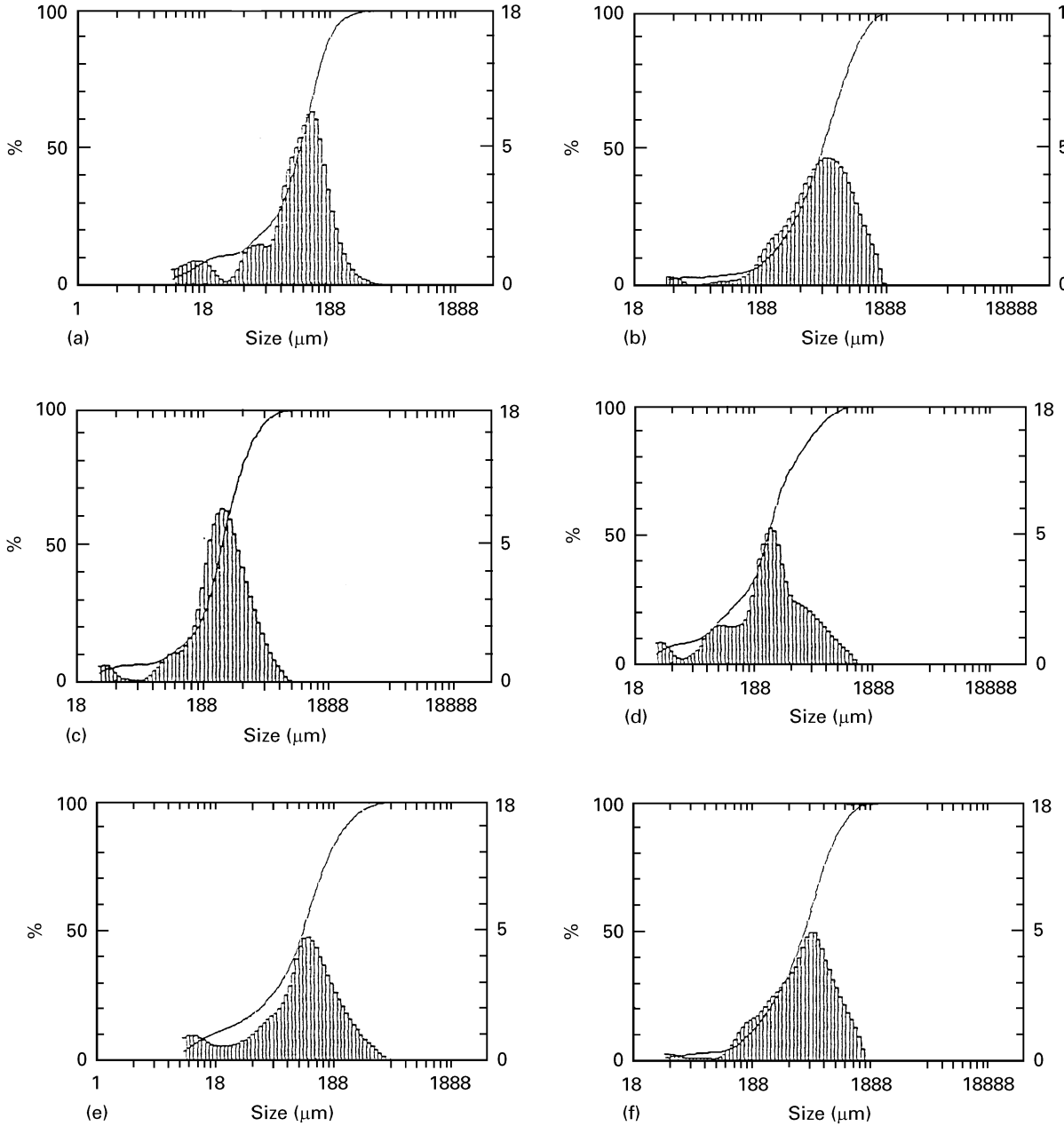

Figure 4 Size distributions, obtained by Malvern light scattering analyses for powder mixtures characterized by: (a) $X_g = 56$ μm; $\sigma_g = 1.4$ (b) $X_g = 240$ μm; $\sigma_g = 1.4$ (c) $X_g = 120$ μm; $\sigma_g = 1.4$ (d) $X_g = 120$ μm; $\sigma_g = 2.8$ (e) $X_g = 56$ μm ; $\sigma_g = 2.8$ (f) $X_g = 240$ μm; $\sigma_g = 2.8$.

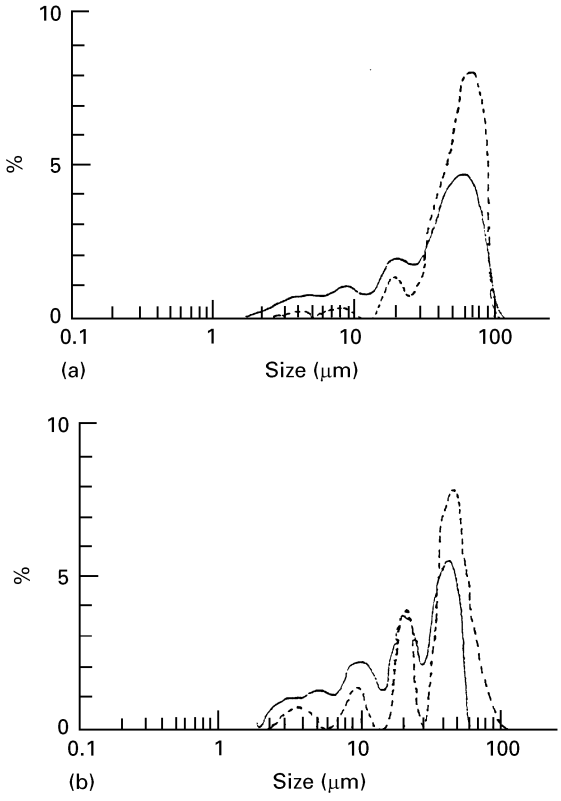

Figure 5 Size distribution obtained by Malvern light scattering analyses for glass powder in the range; (a) $50 < x < 63$ μm (b) $40 < x < 50$ μm. – – – dry sieving, —— wet sieving.

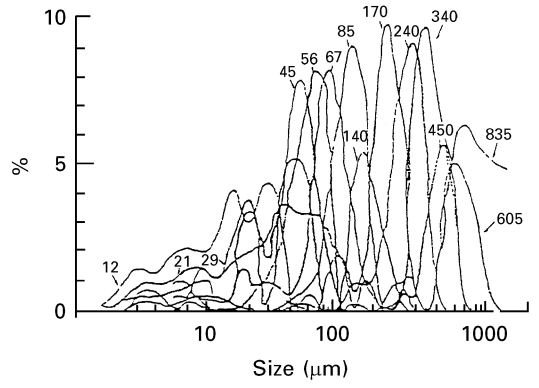

Figure 6 Size distributions, obtained by Malvern light scattering analysis for the different sieve fractions. The numbers denote the average particle size of two adjacent sieves in each fraction.

log-normal distributions. The overlapping of the sieved size ranges (Fig. 6) causes the smoothness and continuity of the "real" size distributions characterizing the powder mixtures. Still, the measured distributions are somewhat different from the calculated ones in details such as distribution width and the exact bell shape. The binary mixtures of powders, with different size distributions, have a wider distribution width than a single powder (see Fig. 7). Hence, forming a binary mixture did not generate a new kind of distribution consisting of two particle populations; it only broadened the single population distribution. This observation is important for the discussion of packing density of binary mixtures.

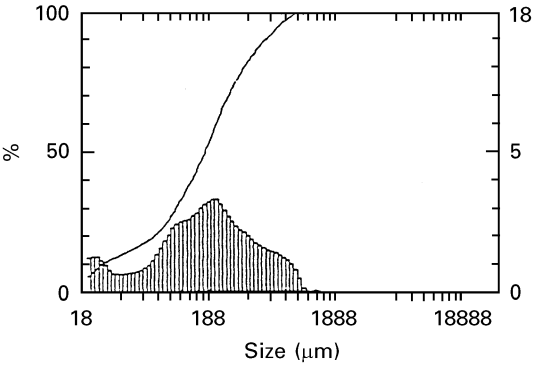

Figure 7 Frequency distribution obtained from Malvern light scattering for a binary mixture of size distributions with: $X_g = 56$ μm; $\sigma_g = 3.9$ and $X_g = 120$ μm; $\sigma_g = 3.9$.

3.3. Influence of particle size and size distribution on packing density

The tap and apparent density of powders with different particle size distributions are presented as a function of median size and distribution width in Fig. 8(a–c). Each data point represents an average of three measurements. The scatter is within $\pm$ 1.9% of the measured value, resulting largely from the error in volume reading.

A similar general behaviour of the powder packing density (tap and apparent) as a function of σ_g is observed for the three powders of different median sizes, however, the packing density values are affected by the median size. The packing density monotonically increases with increasing the distribution width, and tapping, as expected, causes a significant increase in the packing density. The relatively large effect of tapping is a result of the irregular shape and the rough surface of the powder particles; tapping destroys bridging and disintegrates agglomerates [1]. The shapes of the density versus σ_g curves are quite surprising. For the lower values of σ_g, up to 2, there is a large increase in density with increasing σ_g. In the range of $\sigma_g = 2 - 2.8$ the density is almost constant, whilst further increase in the size distribution width, from 2.8 to 3.4 or 3.9, causes a large increase in density. The expected behaviour is a monotonic increase in density with σ_g, which gradually reaches asymptotically the theoretical maximum density (TMD) [11]. The distribution width effect presented in Fig. 8(a–c), which differs from other reports in the literature, is suggested to stem from the particles irregular shape. Additional explanations are required to fully understand this phenomenon, but to date none are available. The effect of the powder particles median value on the tap density is depicted in Fig. 9; packing density increases with median size. There is a large increase in packing density from $X_g = 56$ μm to $X_g = 120$ μm and then, only a small increase in packing density upon further increasing X_g to 240 μm. These results clearly show that although theoretically [5–7, 11, 12] the packing density is not expected to be affected by the particle size, but only by the size distribution width, the particle size does significantly

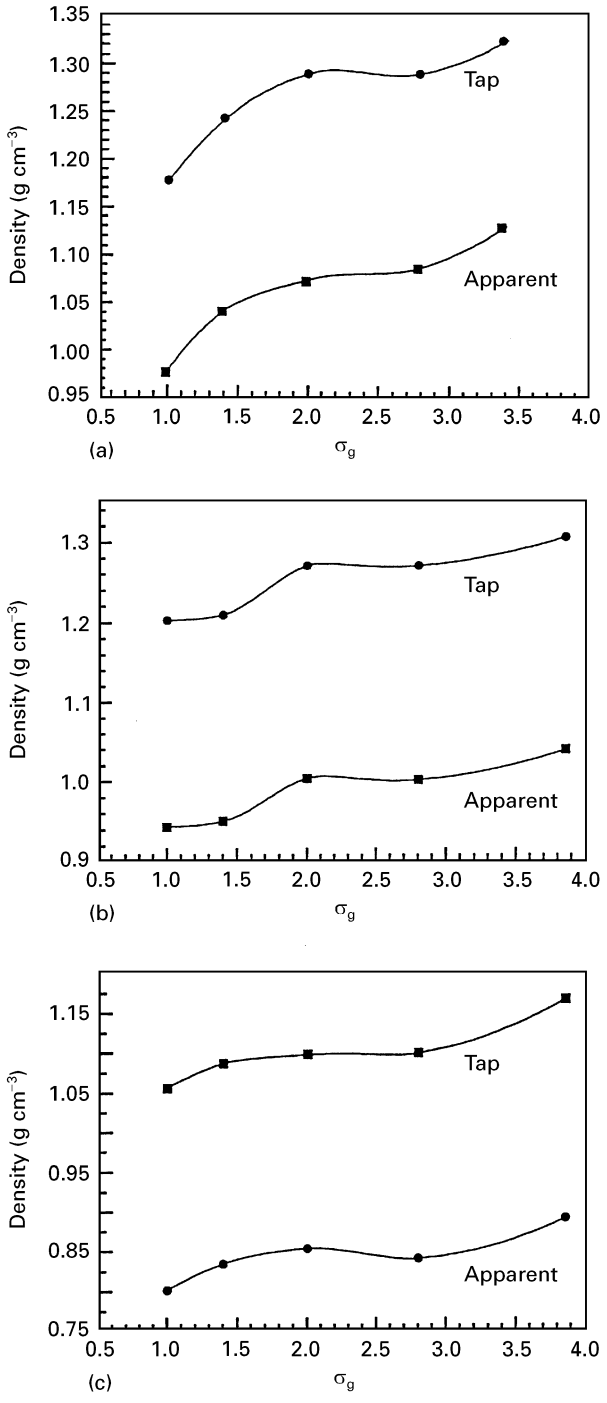

Figure 8 Tap and apparent density as a function of σ_g for powders with: (a) $X_g = 240$ μm (b) $X_g = 120$ μm (c) $X_g = 56$ μm.

affect the packing density of relatively fine powders. The particle size effect is thus expected to diminish for larger particle size powders. The effect of particle size on packing density is a result of agglomeration and bridging, which is common in fine powders but becomes less severe as the particle size increases. This is also the explanation for the change in the Hausner ratio (tap/apparent density) [12] as a function of median size, as is depicted in Fig. 10.

To investigate the effect of an additional particle size distribution powder on the packing density, binary mixtures, having σ_g values of 3.4 or 3.9, were prepared. The effect of the additional population median size on the packing density was studied. As is shown in Fig. 11, the packing density is improved by

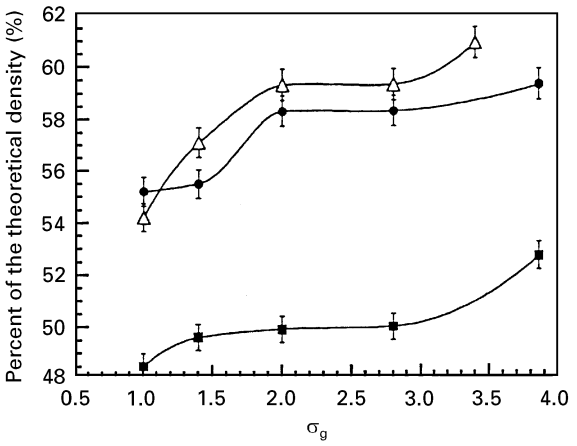

Figure 9 Tap density, expressed as per cent of theoretical density, as a function of particle size distribution width for powders with three medians (■) $X_g = 56$ μm, (●) $X_g = 120$ μm (△) $X_g = 240$ μm.

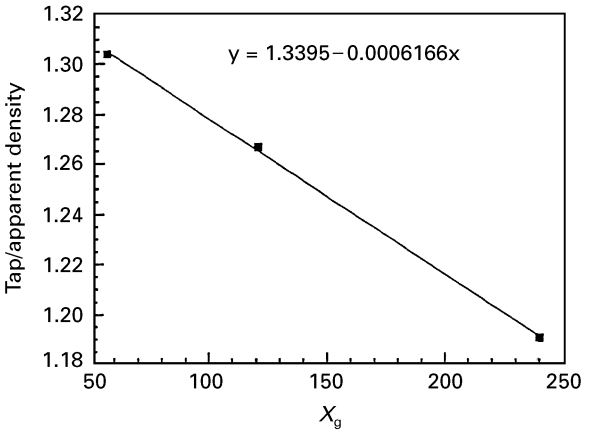

Figure 10 The average Hausner, tap/apparent density ratio, as a function of median size.

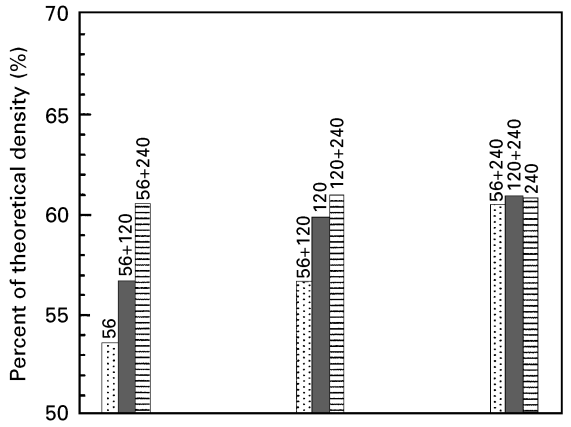

Figure 11 Tap density expressed as a per cent of the theoretical density, for single and binary mixtures of size distributions. The mixtures with median sizes of 56 and 120 μm have $\sigma_g = 3.9$; the mixture with $X_g = 240$ μm has $\sigma_g = 3.4$.

adding a powder with a larger median. This improvement further increases with an increase in median size of the added powder. On the other hand the addition of a powder with a smaller median, lowers the packing density which is probably due to an increase in agglomeration and bridging. A similar result is reported by Sohn [11] and Bierwagen [4], however, they refer

to two separate populations whilst in the present work, a mixture of two powders still produces only one population although with a much wider size distribution. Therefore, it seems that widening the size distribution, rather than the existence of two populations, causes the increase in packing density. It was, however, concluded [11,12] that any increase in distribution width results in an increase in the packing density whilst according to the present study of powder mixtures, increasing the width by adding particles with a smaller median, decreases the packing density. The explanation of this controversy could be related to the quantitative proportions of the two powders with different particle size distributions in the mixture. In the presently studied binary mixtures the ratio is 1:1 and the agglomeration and bridging which exists in the finer powder could be dominant in determining the packing density of the mixture. Further investigation is needed if a better understanding of this behaviour is to be obtained.

4. Summary and conclusions

4.1. Particle size and size distribution

(a) Particle size distribution in powder fractions obtained by dry sieving has a wider range than the size range between two adjacent sieves. The efficiency of dry sieving decreases with decreasing particle size due to agglomeration. Therefore, wet sieving, in addition to dry sieving, is recommended for particles under 60 μm.

(b) In general, the glass particle size distribution follows a log normal distribution function.

(c) The difference between size analysis by sieving and light diffraction is a consequence of different particle size definitions and particle shape effects. In light scattering analysis, the particle composition also affects the size measured due to refraction and reflection effects.

(d) Distribution width and median size obtained by a Malvern light scattering instrument are larger than those obtained by sieving. Very small particles cannot be detected by sieving since they are adhered to larger particles. In the Malvern light scattering analysis those small particles are separated from the larger ones and can, therefore, be detected.

4.2. Packing density

(a) Packing density increases monotonically with distribution width at a constant median size. Packing density also increases with median size. This increase becomes gradual with increasing median size; for $X_g > 100$ μm, median size has only a minor effect on packing density.

(b) Packing density of binary distribution mixtures is higher than that of a single distribution with a smaller size range, only if the added distribution's median is larger than the median of the "basic" distribution.

(c) Vibration improves the packing density of powders. It's effect increases with decreasing particle size due to vast agglomeration and bridging in fine powders.

References

1. R.M. GERMAN, "Particle Packing Characteristics", 1st edn. (MPIF. Princeton, 1980).
2. T. ALLEN, "Particle Size Measurement", 4th edn. (Chapman and Hall, London, 1990).
3. D.W. COOPER, *J. IES* **34** (1991) 21.
4. G.P. BIERWAGEN, *Powder Tech.* **10** (1974) 111.
5. H.W. KUHLMAN, *SPE Trans.* **5** (1965) 101.
6. A.E.R. WESTMAN and H.R. HUGIL, *J. Amer. Ceram. Soc.* **13** (1930) 767.
7. R.J. WAKEMAN, *Powder Tech.* **11** (1975) 297.
8. G. ROY and P. TESSLER, *J. Aerosol.* **21** (1990) 515.
9. N.G. ORFANOUDAKIS, *Part Syst. Charact.* **9** (1992) 223.
10. D. NATHIER, *Powder Tech.* **76** (1993) 191.
11. H.Y. SOHN and C. MORELAND, *Canadian J. Chem. Engng.* **46** (1968) 162.
12. G.S. REILEY and G.P. MAM, *Mater. Res. Bull.* **7** (1972) 163.

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