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A small-angle X-ray scattering study of local variations within powder compacts

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ABSTRACT

This work used two-dimensional small-angle X-ray scattering (2D-SAXS) to investigate the compaction behaviour of pre-gelatinised starch (PGS) and microcrystalline cellulose (MCC), which are commonly used as pharmaceutical excipients. By analysing azimuthal variations in scattering intensity, reproducible relationships were found between the compaction pressure, relative density and changes in the shapes of 2D-SAXS patterns for each material. These results indicated differences in the compaction mechanisms between PGS and MCC.

The relationships also provided a means for investigating local variations in compaction behaviour within specimens prepared using different materials and compaction conditions. Relative density results from 2D-SAXS were consistent with expectations based on the effects of friction during compaction and appeared similar to data from other methods. In addition, however, 2D-SAXS measurements revealed local variations in the effective direction in which compaction occurred, with significant radial components observed near the die walls. This appeared to be consistent with the transfer of some compaction pressure to friction on the die wall. These observations represent an important advance, since other experimental methods do not easily reveal the direction of force transmission within the powder compact.

1. Introduction

Powder compaction is an important industrial process, which is widely used in many manufacturing sectors. In addition to producing moulded engineering parts from ceramics, metals or polymers, powder compaction provides the basis for manufacturing pharmaceutical tablets, while the behaviour of soils and other granular materials is important in civil engineering. This has stimulated a considerable body of research; consequently, the general principles of powder compaction are well known. It is generally accepted that granule movement and reorientation within the powder bed at low packing fractions are followed by deformation and fracture at higher compaction loadings [1–6]. This results in greater contact area and bonding between granules, such that the strength of the compact increases with the relative density.

More precise analyses of the various mechanisms operating at different stages during powder compaction are considerably harder to obtain, however. The balance between movement, reorientation, deformation and fracture depends on the material properties of the powder granules, such as modulus and strain behaviour (i.e. brittle fracture, elastic or plastic deformation), as well as geometric factors such as surface rugosity, shape and size distribution. It also depends on friction, both between granules and with the compaction die surfaces. The combination of these factors leads to significant variations in compaction behaviour and the resulting density within compacts [7–20]. Moreover, in spite of extensive research, in terms of both experimental studies and numerical simulation, there is relatively little direct evidence of densification mechanisms [16] and a complete understanding of compaction physics still eludes us [2].

We reported recently that small-angle X-ray scattering (SAXS) could provide a novel and useful technique for studying powder compaction [21]. Investigations on three materials commonly used as pharmaceutical excipients: hydroxypropyl-methyl-cellulose (HPMC), microcrystalline cellulose (MCC) and pre-gelatinised starch (PGS), revealed azimuthal variations (i.e. intensity changes around the direction of the incident beam) in the 2D-SAXS patterns, with stronger scattering over larger angular ranges parallel to the applied compaction force compared with the transverse direction.

In general terms, X-ray scattering in the small-angle range (between approximately 0.1 and 3°) originates from electron density variations on the scale of roughly 1 to 100 nm [22–24]. This makes SAXS a very useful method for studying the nanometre-scale morphology of materials. At present, however, the structural origins of the scattering observed from the compacted powders studied have not been identified conclusively. Electron density variations associated with the molecular architecture or intragranular pores have been suggested as possible sources [21], although these hypotheses remain conjectural, at present. Nevertheless, it was found that the magnitude of the azimuthal variations varied between materials and increased with the compaction pressure, which suggested that 2D-SAXS could be used for investigating the local variations in force transmission within a powder compact.

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The work presented here used 2D-SAXS to investigate local variations in compaction behaviour within flat-faced cylindrical tablets of PGS and MCC. Of the materials previously investigated [21], HPMC gave the strongest effect; however, the granules of this powder appeared significantly anisometric (elongated or lamellar), which allowed the possibility of granule reorientation as an explanation for the changes in 2D-SAXS patterns. By contrast, both PGS and MCC exhibited smaller changes in their 2D-SAXS patterns. The granules of these materials appeared roughly spherical, however, removing any significant effects of reorientation during die filling or compaction. Hence, it was likely that the changes observed in the 2D-SAXS patterns for PGS and MCC could be attributed to deformation or rearrangement of the nanometre-scale morphologies within the granules, in response to compaction stress.

The present work is reported in two sections. The first part established some empirical relationships between average upper punch pressure, relative density and changes in 2D-SAXS patterns for PGS and MCC. These relationships were then used in the second part of the work to investigate the local variations in compaction behaviour both within and between specimens prepared using both materials under different conditions.

2. Experimental

Experiments were performed using PGS (1500, Colorcon Ltd. Kent, UK) or MCC (Celphere SCP100, Asahi-Kasei, Japan). Both materials were stored under ambient conditions and used without further modification.

Calibration samples were prepared essentially as described previously [21], by single-sided, uniaxial compaction in a nominally 5 mm diameter stainless steel pellet die (Specac Ltd. Smiths Industries, Kent, UK), at 1 mm min^{-1} to the desired loading using a mechanical testing rig (type 5567, Instron Ltd. High Wycombe, Buckinghamshire, UK).

The following method was developed for filling the die evenly and consistently. The empty die was supported 'upside-down', the push-rod was inserted to the required extent, then the upper (driven) punch was allowed to rest on the end of the push-rod. The required powder charge was poured in and scraped level with the bottom of the die. The upper pellet and the powder charge were then retracted into the die barrel, by moving the push-rod, to allow the lower (static) punch to be inserted without compressing the powder significantly. Finally, the die was inserted into the base and the assembly was turned the 'right way up', to perform the compaction experiment.

In each case, the maximum loading was maintained for 1 min before unloading, also at 1 mm min^{-1} and ejecting the sample in the compaction direction. The force, $F(t)$, and apparent displacement, $x_a(t)$, were recorded during each compaction experiment. Machine deformation under load (compliance, $\xi\{F(t)\}$, as a function of the applied force) was determined using an empty die and fitted by an empirical function, which was used to correct the apparent displacement, in order to obtain the actual displacement of the upper punch:

$$x(t) = x_a(t) - \xi\{F(t)\}. \tag{1}$$

The length (h_T) and diameter (d) of the compact were measured to ± 0.01 mm, using a micrometer gauge, within about 1 min of releasing the compaction force; its weight (m) was subsequently determined to ± 0.0003 g using an electronic top-pan balance. The initial length (h_0) was obtained from h_T and the total displacement recorded. Thus, the average relative density, ρ_R, of the powder bed could be calculated throughout the experiment:

$$\rho_R(t) = \frac{4m}{\rho_0 \pi (h_0 - x(t)) d^2} \tag{2}$$

where ρ_0 is the true density of the material. The average upper punch pressure during compaction was calculated from $F(t)$ and the diameter of the compact, which was assumed to be equal to the internal diameter of the die and remain constant throughout the experiment:

$$P(t) = \frac{4F(t)}{\pi d^2}. \tag{3}$$

Samples for mapping studies were prepared in an analogous manner, except that larger dies (nominally 10 or 13 mm diam) were used.

Diametral sections were prepared from the calibration or mapping samples, using a sharp scalpel to shave away the unwanted parts of the compacts, as demonstrated in Fig. 1. Reasonably thick (approximately 2 to 3 mm) sections were prepared deliberately, so that any surface damage caused by the scalpel would constitute only a small fraction of the irradiated sample volume.

SAXS measurements were performed as described previously [21], using a Nanostar camera (Bruker AXS GMBH, Karlsruhe, Germany), fitted with a sealed microbeam source, which was run at 40 kV, 35 mA and filtered to give $Cu_{K\alpha}$ radiation (wavelength, $\lambda_X = 0.154$ nm). The sample to detector distance was set at approximately 1.05 m and the entire optical path, including sample chamber, was evacuated to minimise 'air scattering'. A circular lead 'beamstop' was suspended on transparent polymeric wires just in front of the detector and centered on the incident beam, to prevent overloading and damage to the detector from unattenuated X-rays. The centre of the 2D-SAXS pattern was found and the scattering angle (2θ) was calibrated using a silver behenate reference standard. The modulus of the scattering vector was calculated using:

$$q = |q| = \frac{4\pi}{\lambda_X} \sin\theta. \tag{4}$$

Sample sections were mounted in the SAXS camera, with the compaction axis vertical and the compacted surface uppermost. In order to collect scattering from calibration samples, the X-ray spot was located near the centre of the cross-section, where median values of the relative density were expected. Mapping experiments were performed by first locating the corners of the cross-section (with respect to the x and y co-ordinates of the sample stage), then programming a series of target co-ordinates to move the X-ray spot in

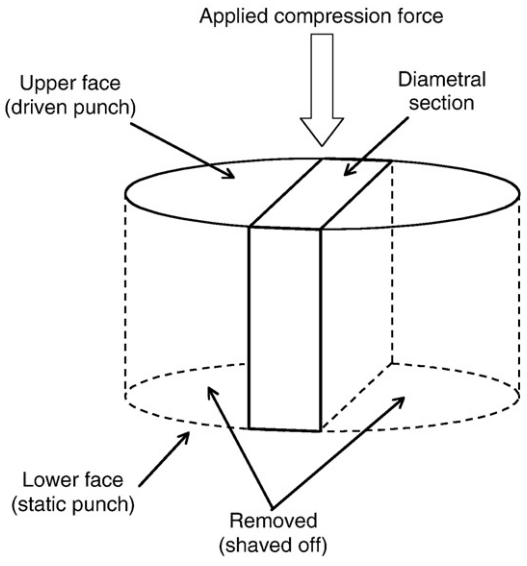

Fig. 1. Geometry of diametral sections with respect to compacted specimens.