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Research Paper

Using small-angle X-ray scattering to investigate the compaction behaviour of a granulated clay

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ABSTRACT

The compaction behaviour of a commercial granulated clay (magnesium aluminium smectite, gMgSm) was investigated using macroscopic pressure-density measurements, X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray microtomography (XμT) and small-angle X-ray scattering (SAXS). This material was studied as a potential compaction excipient for pharmaceutical tabletting, but also as a model system demonstrating the capabilities of SAXS for investigating compaction in other situations.

Bulk compaction measurements showed that the gMgSm was more difficult to compact than polymeric pharmaceutical excipients such as spheronised microcrystalline cellulose (sMCC), corresponding to harder granules. Moreover, in spite of using lubrication (magnesium stearate) on the tooling surfaces, rather high ejection forces were observed, which may cause problems during commercial tabletting, requiring further amelioration. Although the compacted gMgSm specimens were more porous, however, they still exhibited acceptable cohesive strengths, comparable to sMCC. Hence, there may be scope for using granular clay as one component of a tabletting formulation.

Following principles established in previous work, SAXS revealed information concerning the intragranular structure of the gMgSm and its response to compaction. The results showed that little compression of the intragranular morphology occurred below a relative density of 0 · 6, suggesting that granule rearrangements or fragmentation were the dominant mechanisms during this stage. By contrast, granule deformation became considerably more important at higher relative density, which also coincided with a significant increase in the cohesive strength of compacted specimens.

Spatially-resolved SAXS data was also used to investigate local variations in compaction behaviour within specimens of different shape. The results revealed the expected patterns of density variations within flat-faced cylindrical specimens. Significant variations in density, the magnitude of compressive strain and principal strain direction were also revealed in the vicinity of a debossed feature (a diametral notch) and within bi-convex specimens. The variations in compaction around the debossed notch, with a small region of high density below and low density along the flanks, appeared to be responsible for extensive cracking, which could also cause problems in commercial tabletting.

1. Introduction

The work presented here demonstrates the use of small-angle X-ray scattering (SAXS) to investigate the compaction of a granular clay powder. SAXS is typically measured at scattering angles below 5° and originates from electron density variations within materials due to structure on the scale of roughly 1 to 100 nm (Feigin and Svergun, 1987; Roe, 2000). Hence, this method has been used extensively to investigate the morphologies of materials, including their responses to mechanical deformation. Nevertheless, the considerable capabilities of SAXS to investigate powder compaction behaviour were only revealed within the last few years (Laity and Cameron, 2008, 2009). It was observed that two-dimensional (2D-SAXS) patterns from various uncompacted polymeric powders were circularly symmetrical, as expected for randomly oriented granular materials. After compaction, however, the patterns became elongated in the compression direction, to an extent that increased with the applied pressure and the density achieved. This was ascribed to the Fourier transform from morphology to scattering (Feigin and Svergun, 1987; Roe, 2000), which gives a reciprocal relationship between length scales in real and scattering space. The changes in SAXS patterns were attributed to compressive strain of the intragranular morphologies, in response to the stress transmitted through intergranular

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contacts (Laity and Cameron, 2010a). Hence, by analysing SAXS patterns measured at different points across diametral sections from compacted specimens, it was possible to investigate variations in compaction behaviour associated with wall friction, specimen size and the shapes of the punches used (Laity and Cameron, 2009; Laity et al., 2010a; Han et al., 2011; Laity, 2014).

That work was largely inspired by the importance of powder compaction for pharmaceutical tabletting, which is the most popular and widely used formulation route for the majority of drugs (Aulton, 2007). Consequently, the behaviour of pharmaceutical excipients such as spheronised microcrystalline cellulose (sMCC), pre-gelatinised starch (PGS) and hydroxypropyl-methyl-cellulose (HPMC) was of major interest. Nevertheless, compaction by the application of mechanical force or hydrostatic pressure also represents an important and widely used processing method for many granular materials across various industrial sectors, including metals (Liddiard, 1984; German, 2005; Kim et al., 2013) and ceramics (Rahaman, 2003; Pizette et al., 2013). It would be interesting, therefore, to explore whether the SAXS method could also prove useful in studying the compaction behaviour of other materials.

The work reported here investigated the compaction behaviour of a commercial granulated magnesium smectite (gMgSm). Clays are important and widely-used industrial materials (Murray, 2000; Bergaya et al., 2006), with potential applications as pharmaceutical excipients, (Aguzzi et al., 2007). Hence, the present work was performed as part of a larger investigation into the feasibility of using granulated clay within tablet formulations (Asare-Addo et al., 2014). Nevertheless, the compaction behaviour of clays is also important in many other situations; examples include the manufacture of ceramics (Rahman 2003, Pizette et al., 2013); in building materials (Morel et al., 2007; Villamizar et al., 2012; Beckett et al., 2013); in geology, where compacted clay layers can trap hydrocarbon deposits (Vanorio et al., 2003, Mondol et al.2007); in soil mechanics, where compaction can affect the porosity of agricultural soil (Berisso et al., 2012; Romero, 2013) and the behaviour of foundations (Kuklíc, 2011; Prakash et al., 2013); as barrier materials for the storage of nuclear waste, where compacted clay gives low permeability (Tien et al., 2004; Ito, 2006; Villar and Lloret, 2008; Baille et al., 2010; Villar et al., 2012; Ye et al., 2012).

It should be emphasised that SAXS measurements are generally performed at smaller angles than typical X-ray diffraction (XRD) measurements from crystalline materials. From the reciprocal relationship between scattering angle and length, this means that SAXS generally informs on structural features larger than typical crystalline spacings. Hence, the present work used measurements below 3° to investigate the larger scale structures within gMgSm granules and their responses to compaction. A distinction can be drawn between this and the study reported previously by Villar et al. (2012), which used measurements around 5° to investigate changes in the basal spacing of bentonites following compression at different water contents.

Although powder compaction may appear conceptually simple, a complete explanation of the underlying mechanics must address the frictional effects between granules and against the compaction tooling, the stochastic nature of intergranular contacts and the responses of granules to applied contact forces. Even in the simplest example of a flat-faced cylindrical specimen produced by single-ended compaction (*i.e.* the volume reduction occurs through displacement of one driven punch, while the other punch is static), local density variations occur due to friction against the tooling and the consequent granular flow pattern. The largest variations occur along the sides in contact with the die wall, with the highest density in a rim adjacent to the driven punch and the lowest density in a rim adjacent to the static punch. Smaller variations occur within the compact, with a high density zone in the centre of the compact just above the static punch and a low density zone below the centre of the driven punch.

This phenomenon was first explained by Train (1956), based on the movement of coloured layers within compacted magnesium carbonate powder beds. Similar results have also been obtained in many subsequent studies, using diverse materials and methods. These include further applications of the coloured layer method (Briscoe and Rough, 1998), hardness measurements (Kandeil et al., 1997), autoradiography of radioactive materials (Macleod and Marshall, 1977), magnetic resonance imaging (MRI) after perfusing with a non-swelling liquid (Nebgen et al., 1995) and X-ray microtomography (XμT) (Busignies et al., 2006).

The density variations obtained depend on the characteristics of the powder used – in particular, the friction coefficient and whether the granules respond by brittle fracture or plastic deformation. Consequently, powder formulations for compaction often involve mixtures of materials, including lubricants, binding agents and porogens. The situation is even more complex in pharmaceutical tabletting, which may also involve diluants and drugs with difficult compaction behaviour (Aulton, 2007; Sinka et al., 2009).

The patterns of density variations depend on the shapes of the dies used and the profiles of the punch surfaces. Significant differences can be observed between flat-faced and convex punches, while dramatic effects can be produced by embossed features (Sinka et al., 2004; Djemai and Sinka, 2006; Wu et al., 2008; Mc. Donald et al., 2009; Laity et al., 2010a; Han et al., 2011; Laity, 2014). The density variations can also be affected by the compaction method; friction against the die walls during single-ended compaction causes distinct asymmetry between the static and driven faces, while double-ended compaction (*i.e.* the displacement is applied equally through two opposing punches) produces more symmetric patterns.

Density variations within compacted artefacts are important for several reasons. Generally, low density is linked to poor strength and an increased likelihood of mechanical failure. Large local variations in compaction behaviour can also lead to crack formation (Mc. Donald et al., 2009). Clearly, these effects are undesirable where significant load-bearing is a crucial element in the desired function (*e.g.* in some engineering parts or the foundations of buildings), but may also affect how easily products become damaged in subsequent handling (*e.g.* chipping of pharmaceutical tablets during packaging and transportation). Moreover, where compaction occurs as part of a sintering process, low density equates to high porosity, which may be linked to dimensional instability during subsequent processing. Conversely, however, maintaining adequate porosity may also be an important property (*e.g.* for aeration and drainage of agricultural soil; permeability of catalytic supports, filters and 'self-lubricating' bearings). In the case of pharmaceutical tablets, low porosity may impede disintegration and delay the drug delivery (Aulton, 2007; Laity and Cameron, 2010b).

In view of the wide diversity of situations where powder compaction is important, this presents enormous scope for scientific investigation and has resulted in numerous publications, although a comprehensive review is well outside the scope of this paper.

The present work examined the compaction behaviour of gMgSm at several levels. Firstly, XRD was used to reveal the crystal structure of gMgSm and the granule structure was investigated by SEM. Bulk compaction behaviour was examined through measurements of average punch pressure against relative density and the structures of the compacted specimens were examined using XμT. The main part of the work used SAXS to relate macroscopic compaction behaviour to morphological responses of granules at the nanometre scale. This was based on methods developed previously using polymeric excipients, but provided a 'proof of principle' for studies on gMgSm, which has a very different chemical composition. Having established relationships between compaction behaviour and changes in SAXS patterns, local variations were explored by spatially resolved SAXS mapping measurements.

2. Experimental

The work reported here was performed using a commercial granulated clay (Veegum G®, R.T Vanderbilt Co. Inc.), extracted from Arizona,