Effect of silica nanoparticles on the bulk flow properties of fine cohesive powders

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HIGHLIGHTS

- Flow properties of micrometre-sized powders with nano-additives were investigated.
- Bulk cohesion was decreased by disruption of larger powder particles by the nanoparticles.
- Smaller nanoparticles reduced friction of the larger particles more effectively.
- Internal friction increased when the direct contact of additives became dominant.
- Adding nanoparticles has a smaller effect on friction than shape of larger particles.

GRAPHICAL ABSTRACT
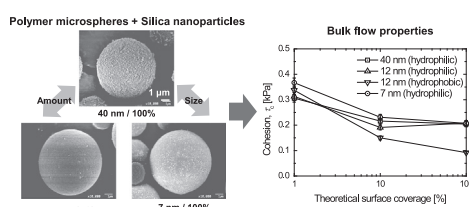
ABSTRACT

Silica nanoparticles are often used as flow regulators applied to the surface of fine industrial powder particles, such as toners for electrophotographic (EP) printing devices. In this paper, we have investigated their effect on the cohesion and internal friction of model polymer powders (poly (styrene-co-divinylbenzene) (PS-DVB), $d_{50}=7.84\,\mu m$), whose flow properties are systematically controlled by applying various different types (*e.g.* size and hydrophilicity) and amounts of silica nanoparticles under a normal consolidation stress of 2 kPa using a ring shear tester (RST). The ability of the nanoparticles to reduce the bulk powder cohesion has been confirmed to be dependent on how efficiently they can disrupt the direct contacts between the PS-DVB particles, resulting in a significant reduction of the interparticle adhesion. However, the cohesion increases when the agglomerates of the silica nanoparticles form a flat film structure which causes an increase of the effective contact area. On the other hand, the nanoparticles were found to work better as lubricants when the size of their agglomerates is smaller. Also, the internal friction becomes higher when the silica–silica contacts become dominant, *e.g.* at higher actual surface coverages, but not as high as that for irregularly-shaped particles. The variation in behaviour between nanoparticles of differing hydrophilicity can be attributed to the ease of breaking down agglomerates on mixing; the cohesion of the PS-DVB powders coated with hydrophobic silica nanoparticles is smaller due to their higher actual surface coverage whilst the internal friction becomes higher.

1. Introduction

Dry powder materials composed of micrometre-sized particles are used in a large range of industries, with various applications such as foods, ceramics (Schulze, 2008), pharmaceuticals (Aulton,

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2009), and colouring powders (*e.g.* powder coatings and toners) (Misev, 1991; Schein, 1992). In industrial dry powder materials, appropriate handling is crucial for maximising product efficiency as well as quality assurance (Rhodes, 2008). Normally, fine powder materials are highly cohesive, mainly due to the strong van der Waals interparticle attractive force. In order to improve their bulk flow behaviour, dry submicrometre- or nanometre-sized materials called 'flow regulators' or 'surface additives', playing a role of reducing the van der Waals interparticle attractive force between the particles, are applied to the surface of the powder particles (Aulton, 2009; Misev, 1991; Schein, 1992).

Various academic studies concerning how flow regulators act on the flow properties of dry cohesive powders have been carried out in the last few decades in order to obtain a deeper understanding of the fundamental mechanisms as well as more efficient control of the powder flowability. In many cases, the term 'flowability' represents the cohesive property of bulk powder materials, and it is often discussed in relation to the adhesion between the constituent particles (Kurfeß et al., 2005; Mei et al., 1997; Meyer, 2003; Meyer and Zimmermann, 2004; Müller et al., 2008; Odeku et al., 2011; Quintanilla et al., 2001; Schweiger and Zimmermann, 1999; Tomas and Kleinschmidt, 2009; Valverde et al., 1998; Veregin and Bartha, 2001; Yang et al., 2005; Zimmermann et al., 2004).

For instance, Zimmermann and colleagues evaluated the tensile strength of pharmaceutical-grade cornstarch powders in which surfaces were modified with various types of inorganic nanoparticles (*e.g.* silicon dioxide, titanium oxide and aluminium oxide) by measuring the attractive force required to separate a plate attached to the surface of bulk powder (*e.g.* Meyer, 2003; Meyer and Zimmermann, 2004; Müller et al., 2008; Odeku et al., 2011; Schweiger and Zimmermann, 1999; Zimmermann et al., 2004). They explained the effect of nanoparticles on the tensile strength by their ability to spread on the surface of the host particles and prevent the cornstarch particles from contacting directly, applying several theoretical models that will be discussed in more detail below. Yang et al. (2005) also characterised the flowability of the cornstarch powders, whose surfaces were modified using different types of silica nanoparticles, by evaluating the angle of repose (AOR) as a measure of powder flowability. They attributed differences in AOR to the changing adhesive properties of the powder particles.

Several experimental studies concerning the effect of surface additives on the flowability of toner particles in printing industry have been reported by Castellanos and colleagues (*e.g.* Quintanilla et al., 2001; Valverde et al., 1998; Veregin and Bartha, 2001). Valverde et al. (1998) measured the tensile strength of various toner powders with a range of concentrations of surface additives under very low stress conditions (< 1 kPa) by applying a fluidised bed technique, in which the tensile strength of the material can be quantified by investigating the relationship between the flow rate of the gas supplied to the powder bed and the pressure drop

across the powder bed. Quintanilla et al. (2001) also investigated the effect of additives on the tensile strength as a function of the consolidation stress applied to the bulk powders as well as on the interparticle adhesive force between individual particles, which can be measured by using AFM, and found a good correlation between them. Veregin and Bartha (2001) evaluated the powder cohesion of various combinations of toner particles and surface additives, such as silica nanoparticles, by evaluating how efficiently the toners passed through a set of nested three sieves with different mesh sizes. They concluded that the interparticle adhesive force between toner particles depends on the contact radius of the surface additives on the toner surfaces; smaller additives make the contact radius smaller and therefore reduce the interparticle adhesive force more effectively.

Many attempts have been made to obtain a theoretical explanation of the effect of surface additives on interparticle adhesion (*e.g.* Kurfeß et al., 2005; Mei et al., 1997; Meyer, 2003; Meyer and Zimmermann, 2004; Zimmermann et al., 2004). Among these, Zimmermann et al. (2004) suggested a relatively simple model describing how a nanometre-sized flow regulating particle wedged in between two micrometre-sized host particles affects the van der Waals force between the host particles. They assumed the schematic arrangements shown in Fig. 1 for a flow regulating particle at low surface coverage of host particles. When a flow regulating particle is positioned directly between the centre of two host particles, (*i.e.* $\varphi = 0°$ in Fig. 1a), this produces the maximum reduction of the van der Waals force. Then, as the flow regulating particle can be displaced by an angle φ relative to the line connecting the centres of the two host particles as shown in Fig. 1a, the distance between the host particles becomes smaller than the size of a flow regulating particle. According to Zimmermann et al. (2004), the resulting van der Waals force between the host particles can be expressed as

$$F_{vdW} = -\frac{A}{6}\left[\frac{R_1 r_f}{D^2(R_1 + r_f)} + \frac{R_1 R_2}{4h^2(R_1 + R_2)}\right]. \tag{1}$$

where R_1, R_2 and r_f are the radii of the two host particles and flow regulating particle, respectively. The parameter h represents the half-distance between two host particles, $h = (R_1 + D + r_f)\cos\varphi - R_1$. The parameter A represents the Hamaker constant at a contact between two host particles and D is the distance between a host particle and surface additive at contact, which minimises the potential between the particles and is assumed to be few angstroms (Israelachvili, 2008). The predictions of Eq. (1) are shown in Fig. 2. It suggests that the van der Waals force between two host particles increases very rapidly once φ exceeds φ_{max} (Fig. 1b), whilst it does not change significantly as long as $\varphi < \varphi_{max}$. Based on this, only two distinct situations need be considered in terms of the interparticle adhesion between the host particles: strong van der Waals interaction at direct contact of the host particles, and reduced van der Waals interaction
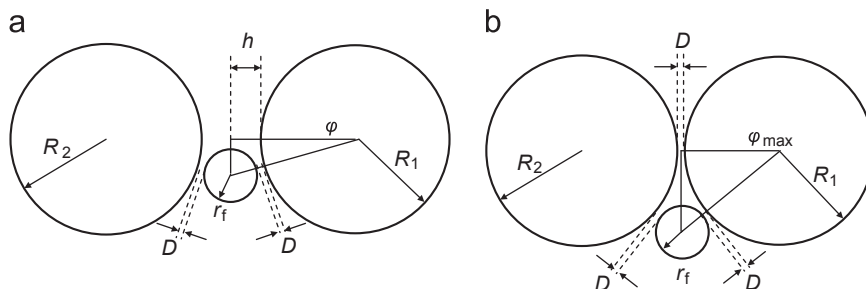

Fig. 1. Schematic arrangements, according to Zimmermann's model (Zimmermann et al., 2004), of a flow regulating particle (a) disrupting the direct contact of the two host particles with displacement angle of φ, and (b) positioned at the maximum angle of displacement φ_{max} (direct contact of the host particles is allowed when $\varphi \geq \varphi_{max}$). The other variables shown are defined in the text.