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Influence of surface modification on wettability and surface energy characteristics of pharmaceutical excipient powders

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ABSTRACT

Influence of surface modification on wettability and surface energy characteristics of three micron size pharmaceutical excipient powders was studied using hydrophilic and hydrophobic grades of nano-silica. The wetting behavior assessed from contact angle measurements using sessile drop and liquid penetration (Washburn) methods revealed that both techniques showed similar wettability characteristics for all powders depending on the hydrophilic or hydrophobic nature of nano-coating achieved. The polar (γ_s^p) and dispersive (γ_s^d) components of surface energies determined using extended Fowke's equation with contact angle data from sessile drop method and inverse gas chromatography (IGC) at infinite dilution suggested a general trend of decrease in γ_s^d for all the surface modified powders due to passivation of most active sites on the surface. However, depending on the nature of the functional groups present in nano-silica, γ_s^p was found to be either higher or lower for hydrophilic or hydrophobic coating respectively. Results show that wettability increases with increasing γ_s^p. Both the techniques of surface energy determination provided comparable and similar trends in γ_s^p and γ_s^d components of surface energies for all excipients. The study also successfully demonstrated that surface wettability and energetics of powders can be modified by varying the level of surface coating.

1. Introduction

Surface characterization of the solid provides better understanding of their behavior in different processes. Surface wettability and surface energetics of powders are most critical properties to be taken into consideration during formulation and development of a solid and liquid dosage forms in pharmaceutical industry. Changes in wettability characteristics of powders can have significant effect on pharmaceutical processes such as granulation, disintegration, dissolution, dispersibility etc. Similarly, surface energy of powder plays an important role in determining the physicochemical properties such as wettability, adhesion, flowability, packing etc. Both surface wettability and energetics are prone to physical or chemical changes occurring on the solid surface. While wettability can be predominantly affected by the chemical nature of surfaces, the surface energy can be affected by various factors like powder processing or handling conditions, environmental conditions, particle size (Buckton et al., 1988; Han et al., 2013) etc.

In pharmaceutical industry, the conventional method employed for surface modification of solids includes applying solvent based functional polymer coating. Surface modification through dry coating using nano-particle is comparatively recent technique (nano-coating) where nano-particles are employed as 'guest' particle for coating the surface of bigger size 'host' particle (Pfeffer et al., 2001). It involves mechanical force where nano-particles are first de-agglomerated and then dispersed on to the surface of host particle. Dry particle coating being a solventless technique offers large number of advantages over the conventional solvent based techniques for property modification of powders. Owing to its simplicity and cost effectiveness, dry coating technique is becoming popular among the scientific community for modifying particle surface properties. Various researchers have employed this technique of particle surface modification for different applications which include improving powder flow (Jallo et al., 2012), fluidization (Ghoroi et al., 2013a), dispersion (Ghoroi et al., 2013b), aerosolization (Zhou et al., 2010), dissolution (Han et al., 2011, 2012; Tay et al., 2012) and also for modifying wettability characteristics (Lefebvre et al., 2011; Mujumdar et al., 2004;

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Ramlakhan et al., 2000) as well as surface energetics of powders (Gamble et al., 2013; Han et al., 2013).

For the assessment of wettability of solid surface, contact angle determination is one of the most commonly used methods. It can be determined using different approaches such as sessile drop technique (Luner et al., 1996), liquid penetration method (Washburn method) (Washburn, 1921), Wilhelmy method (Pepin et al., 1997), thin layer wicking method (Van Oss et al., 1992) etc. However, the two former methods are most popular. Lefebvre et al. (2011) studied the effect of surface modification on wettability and dispersibility of talc powders which were dry coated with hydrophobic silica particles in Cyclomix high shear mixer. They used sessile drop method for wettability measurement and found that concentration of nano-particle and processing time both affect the wettability. They observed that work of adhesion calculated from contact angle influenced the dispersion rate of talc powder in water. Similarly, Ouabbas et al. (2009) used Cyclomix high shear mixer for surface modification of silica gel and corn starch particles by dry coating with different percent w/w of magnesium stearate and different grades (hydrophobic and hydrophilic) of fumed silica respectively. The wettability was studied by the sessile drop method and dynamic vapor sorption (DVS) measurements. The results indicated that dry coating of silica gel powder by hydrophobic magnesium stearate resulted in improvement of its hydrophobic properties. The moisture adsorption–desorption isotherms of uncoated and coated particles obtained from dynamic vapor sorption analyzer also suggested altered moisture adsorption and desorption characteristics of powders (Ouabbas et al., 2009).

Similarly, for assessment of surface energetics of solids, there are various techniques available such as techniques based on wettability determination like contact angle determination using sessile drop method (Luner et al., 1996; Puri et al., 2010) or liquid penetration method (Siebold et al., 1997), techniques based on gas adsorption phenomenon like inverse gas chromatography (IGC) (Das et al., 2011; Newell et al., 2001) and based on thermodynamic principles like microcalorimetry (Buckton and Beezer, 1988). While contact angle method has been widely used (mostly compressed disc technique) to evaluate the surface characteristics of solids (James et al., 2008; Luner et al., 1996), in recent years IGC has been considered as a more accurate and sensitive alternative for surface energy determination (Buckton and Gill, 2007).

Different studies comparing the surface energy determined from these two methods suggested a great degree of agreement for dispersive component of the surface energy (Dove et al., 1996; Heng et al., 2006; Planinsek et al., 2001). Dove et al. (1996) studied the wettability and surface energetics of theophylline and caffeine powders from contact angle and inverse gas chromatography (IGC) methods respectively. They found that dispersive component of surface energies obtained from IGC was almost identical to that from contact angle method. Dispersive surface energies of pharmaceutical powders were also compared from these two different approaches by Planinsek et al. (2001). They also suggested that a good correlation of results for these methods can be obtained provided diiodomethane or bromonaphthalene is used to determine the non-polar components in contact angle studies.

In all these studies, the dispersive component of surface energy was found to be comparable from both the techniques. However, analysis based on polar component of surface energy has still not been discussed in literature. Thus, a direct comparison of polar component of surface energy, which otherwise has a great significance for complete characterization of solid surface energetics is missing in the literature. Although numerous studies have reported the comparative accounts for wettability property from different methods, a comprehensive study of wettability and surface energetic properties together from different methods and their interrelation is lacking in open literature. This work is planned to compare wettability and surface energy of powders separately from two different techniques. A comprehensive analysis of these results based on the morphological aspects and chemical nature of particle surfaces is also planned.

With this aim, the influence of surface modification on wettability and surface energetics of three commonly used excipient powders viz. Avicel PH 105, lactochem fine powder and corn starch was assessed before and after their surface modification using hydrophilic and hydrophobic colloidal silica nano-particles. Also, the effect of surface morphology on quality of the surface modification for these fine powders was studied. The wettability of coated and uncoated powders was evaluated through contact angle measurement using sessile drop and liquid penetration methods. The wettability characteristics were also explained in terms of work of adhesion and spreading coefficient. Surface energy of these powders was determined using contact angle data from sessile drop method and from IGC at infinite dilution. Results for both wettability and surface energy determined from different methods were then compared and correlated. The extent of surface modification and its effect on wettability and surface energetics of the powder was also studied using corn starch powder with different percentage of hydrophobic nano-silica coating.

2. Experimental

2.1. Materials

Microcrystalline cellulose (Avicel PH105, FMC Biopolymers), lactose monohydrate (Lactochem fine powder, Domo Friesland) and corn starch (Suru Pharma, India) were used as 'host' powders for nano-coating. Hydrophilic fumed silica grade (Aerosil 200P) and hydrophobic fumed silica grade (Aerosil R972 Pharma) having mean particle size of around 12 nm and 16 nm respectively were obtained as a gift sample from Evonik/Degussa Industries, USA and were selected as 'guest' particle for nano-coating. De-ionized water (Milipore, USA) and glycerol (Merck, USA) were used as polar test liquids; and diiodomethane (National Chemicals, India) and *n*-hexane (Merck, USA) were used as non-polar probe for contact angle determination studies. For inverse gas chromatography experiments Decane (Spectrochem, India), Nonane (Merck, USA), Octane (Spectrochem, India) and Heptane (RANKEM, India) were used as non-polar alkane probes whereas dichloromethane (Finar, India) and ethyl acetate (Finar, India) were used as polar probes.

2.2. Dry coating process

Dry coating of excipient powders was performed in a Co-mill (Prism Pharma Machinery, India) using hydrophilic and hydrophobic grades of nano-silica following a method described in the literature (Mullarney et al., 2011). Co-mill provides intensive mixing between the host (excipient) and guest (nano-silica) particles with the help of impellers resulting in coating of the host surfaces with guest particles. Prior to coating experiment, the excipient powder and nano-silica were co-sifted through 30 mesh BSS sieve and pre-mixed in V-blender at 15 ± 1 rpm for 10 min. The blend was then passed through Co-mill operating at 1800 ± 1 rpm to achieve the required coating. Based on the bulk property characterization previously performed in the lab, about 0.5% w/w level of Aerosil R972 (hydrophobic) and 1.0% w/w level of Aerosil 200P (hydrophilic) were used for coating all three excipients. Further, to study the effect of percentage of surface area coverage on wettability and surface energy, only corn starch was coated with 0.25%, 0.5% and 1% w/w of Aerosil R972. All the experiments were performed at room conditions of $40 \pm 5\%$ RH and $25 \pm 2\,^{\circ}$C.