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The Influence of Water on Electrostatic Charge Retention and Dissipation in Pharmaceutical Compacts for Powder Coating

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Purpose. The electrostatic properties of five materials commonly used in tabletting were investigated to assess their suitability for the novel technique of powder coating of pharmaceutical compacts.
Methods. Powder resistivity and compact voltage decay properties were determined under dry and wet conditions using purpose built equipment.
Results. The organic materials acted as insulators having resistivities $>10^{13}$ Ωm whilst dibasic calcium phosphate showed dielectric behaviour. A clear relationship between water content and resistivity was established for all materials. Electrical conduction across powder surfaces was demonstrated as the predominant mechanism by using low concentrations of magnesium stearate. In materials absorbing significant water a bulk mechanism was also present. After charge injection, decay rates were dependent on resistivity with those having the highest values exhibiting the slowest decay. The chemical nature of the materials was unimportant except at extremely high resistivities. Conditioning of the compacts with water reduced resistivities so that decay half-lives <1 s were achieved.
Conclusions. The electrical properties of the compact materials have been modified sufficiently to enable them to be considered suitable for powder coating.

KEY WORDS: electrostatics; powder coating; powder resistivity; charge decay; water sorption.

INTRODUCTION

Powder coating is a technique which has been used widely within the automobile and electrical appliance markets. In the field of pharmaceutical technology it offers several potential advantages over liquid methods, which are used at present. These are, briefly; a less operator-dependent process which is continuous and considerably quicker, the avoidance of solvents, near 100% utilisation of the coating powder and the ability to coat one or both tablet faces with the same or different materials (1).

Electrostatics of the solid phase is important in the field of powder coating, as well as in pulmonary delivery of aerosolised products which are extensively charged, powder mixing/demixing phenomena and external lubrication in the tablet compaction process. Powder coating involves the deposition of charged powders on substrates which are positively charged or more usually neutral. The electrostatic requirements of the powder and substrate are in general opposite since they must fulfil different functions. Whilst the powder should be highly resistive i.e. once charged it should retain the charge for sufficiently long so that electrostatic forces become effective in the deposition process, the substrate must be electrically conductive so that the induced charge can be removed and further powder deposition uninhibited. The charge decay rate of a material is determined by its electrical resistivity, which is a fundamental surface and bulk property. It was the purpose of this study to relate the electrical resistivity of compact materials to their charge decay properties and to determine the sensitivity of these parameters to sorbed water.

MATERIAL AND METHODS

Dibasic calcium phosphate dihydrate (Emcompress) and microcrystalline cellulose (Emcocel) were obtained from Mendell (Redhill, Surrey, UK), sorbitol from Hopkin & Williams (Romford, Essex, UK), lactose monohydrate (Tablettose) from Forum Chemicals (Redhill, Surrey, UK) and magnesium stearate from BDH Chemicals Ltd. (Poole, Dorset, UK). Povidone K-30 was provided by GAF Chemicals Corp. (Wayne, NJ, USA).

A powder resistivity cell was designed and fabricated based on British Standard BS 5958: Part 1: 1980. It consisted of a perspex chamber in which two plane circular electrodes were positioned with guard rings being used to eliminate conduction pathways that might occur through or along the cell wall (2). Prior to use the cell was cleaned with a non-ionic surfactant solution and methanol to remove any surface contamination. Cleaning was considered satisfactory if no current could be detected flowing in the empty cell at an applied voltage of 2500 V. All measurements were made in a controlled environment whose relative humidity could be varied between 0 and 90% RH. Powder was pre-conditioned to the required RH by placing it in a rotating earthed metal drum, with the RH being monitored using an electronic gauge (Hygroscop GT probe, Rotronic, Zurich, Switzerland), before being loaded into the cell. Prior to measurements at 0% RH, the powders were dried under vacuum at 80°C for 12 hours and stored over silica gel. Experiments were carried out at 21 ± 2°C and 0, 22, 44 and 66% RH.

A stabilised power supply (Brandenburg) was used to maintain a potential difference across the electrodes with the resulting current, passing through the powder, being measured by an electrometer (model 610C, Keithley Instruments Inc., Cleveland, Ohio, USA). The usual precautions in low current measurements were taken to avoid effects from external electric fields. The voltage was increased in a stepwise manner from 500 to 2500 V, allowing 10 minutes for the current to stabilise prior to measurement. Volume resistivity, ρ, at each voltage was then calculated according to Eq. 1.

$$\rho = \frac{VA}{Id} \qquad (1)$$

where V is the applied voltage, I is the resulting current, A and d are the electrode area and separation, respectively. The voltage/current profile of each powder was determined twice using different samples of compact powders.

Four formulations were used to prepare compacts having different surface properties; (a) dibasic calcium phosphate 97% + magnesium stearate 3%, (b) sorbitol 99.5% + magnesium

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stearate 0.5%, (c) lactose monohydrate 99.5% + magnesium stearate 0.5%, and (d) microcrystalline cellulose 95.2% + povidone 4.3% + magnesium stearate 0.5%. Each formulation was compacted to provide either two smooth surfaces or one rough/one smooth surface. The rough surface was created by use of an upper punch having abrasive paper fixed to it during the compaction process. Compaction parameters were selected to allow each formulation to be made to similar relative densities.

The voltage decay characteristics of compacts were determined using equipment designed at the University of Bath (1). At the beginning of each measurement the trolley was located under the corona electrode and retained in position, against a compressed spring, by means of an electromagnet. On initiation of the timing circuit, charge injection into the compact commenced from the corona electrode (Volstatic Coatings Ltd., London, UK). After a pre-set time had elapsed the voltage supply to the corona and electromagnet was automatically switched-off and the trolley guided to a position such that the compact was located under the voltage detection probe connected to a voltmeter (Monroe Electronics Inc., New York, USA). The corona to probe transfer time was constant at 0.2 s. The voltmeter output was amplified and digitised before being fed into a computer. The data was analysed using a program written in-house to obtain various curve parameters. All measurements were made in a controlled environment of 21 ± 2°C and 0, 22, 44 or 66% RH on compacts previously conditioned to the required RH. A negative corona of 80 kV was used with charge injection times between 3 and 20 s. Five replicate measurements were made for each compact formulation using different samples.

RESULTS AND DISCUSSION

Lactose, dibasic calcium phosphate (DCP) and magnesium stearate (MS) showed no weight gain between 22 and 66%RH with water contents of 1.7, 2.8 and 17.1 mgg^{-1} respectively. Sorbitol and microcrystalline cellulose (MCC) gained weight with increasing RH having water contents of 3.7 and 30.4 mgg^{-1} at 22% rising to 15.0 and 63.8 mgg^{-1} at 66% RH respectively. The results were in good agreement with literature values (3).

After voltage application the current initially decreased owing to electrode polarisation effects as the natural dipoles relaxed and aligned with the field. The data has been plotted according to the Frenkel equation (4) which describes pre-breakdown behaviour in insulators and semi-conductors. It predicts a linear relationship between log resistivity and (applied field)$^{1/2}$ of negative slope. All materials apart from DCP were found to be insulators having field independent resistivities $>10^{13}$ Ωm (Fig. 1). In contrast DCP had a lower resistivity which decreased with field so it can, therefore, be classified as a dielectric. However, the calculated exponential term for it was considerably different to that predicted by the equation. These deviations from the Frenkel equation were probably due to the maximum applied field being 500 kVm^{-1} which may be below that required for true non-ohmic behaviour since Hirai and Naka (5) found that fields >4000 kVm^{-1} were required for insulators of 10^{15} Ωm resistivities.

Within the variation normally seen in electrostatic measurements the addition of MS to lactose and MCC at low concentrations (0.5%) had a negligible effect on their resistivity (Table I). However, at 3% concentration in DCP, resistivity increased by ~500 fold at 0%RH and 150 fold at 66%RH. Since magnesium stearate, which had a considerably higher resistivity than the other materials (Fig. 1), is adsorbed to particle surfaces the results indicated that conduction occurred by a surface mechanism. At low concentrations of MS sufficient lactose and MCC interparticle contact points existed for the conduction pathways to have been across surfaces devoid of the lubricant. In DCP where surface coverage was greater, the resistivity increase demonstrated that conduction occurred across particle surfaces rather than through them. Had this latter pathway been used resistivity would only have increased at high MS concentrations when surface coverage was complete.

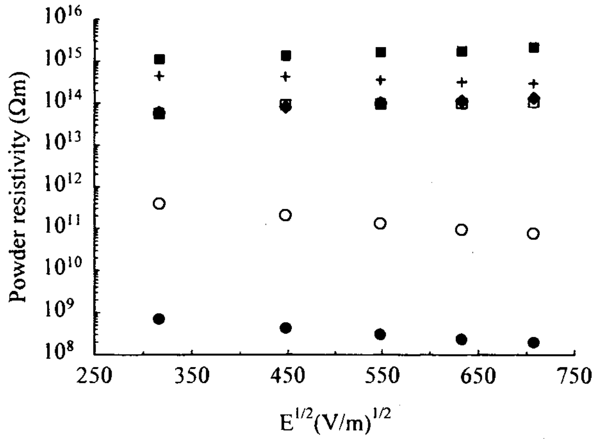

Fig. 1. The effect of applied electric field on powder resistivity at 0% RH (■ magnesium stearate (MS), + lactose, ◆ MCC, □ sorbitol, ○ dibasic calcium phosphate and 3% MS, ● dibasic calcium phosphate).

The resistivity of all materials, other than magnesium stearate, decreased as the storage RH was increased (Fig. 2) with the largest reduction being observed for sorbitol and MCC, the two materials which sorbed the greatest weights. Whilst the resistivity of magnesium stearate decreased between 0 and 22% RH, due to significant water gain, no further reduction occurred at higher RHs despite further water gain. The resistivity of lactose decreased to a similar extent between 0 and 22% RH despite its water content being one tenth that of magnesium stearate. It also showed a further reduction in resistivity between 22 and 66% RH although no additional water gain occurred. These effects arose from the hydrophilic and ionic nature of lactose which promoted conduction pathways at low water contents whereas magnesium stearate, being hydrophobic, did not. The reduction in DCP resistivity with RH also indicated that conduction occurred by a surface mechanism since it was more likely that at these RHs water was sorbed onto the surface rather than internally. These results, therefore, provide experimental evidence for the hypothesis that solid state conduction occurs by a surface mechanism (6, 7).

The experimental evidence also indicated that conduction could occur through particles. At high storage humidities the weight gain in sorbitol and MCC was primarily due to water absorption rather than adsorption since the powder surfaces were already saturated. Thus the observed decrease in resistivity must have arisen from conduction through the particles due to alteration of its bulk conductivity. No break was noted in the

Table I. The Effect of Magnesium Stearate on the Resistivity of Compact Materials at 0 and 66% RH (determinations at 200 kVm^{-1})

Powder Resistivity (Ωm × 10^9)							
0% RH		66% RH					
DCP	DCP +3% MS	DCP	DCP +3% MS	Lactose	Lactose +0.5% MS	MCC	MCC +0.5% MS
0.442	215	0.002	0.3	3.6	9.1	1.0	0.3

Note: MCC—microcrystalline cellulose, DCP—dibasic calcium phosphate, MS—magnesium stearate.

resistivity/RH relationships, unlike results previously described, which might have indicated a change in sorption mechanism (8).

All the compact materials, apart from DCP, had resistivities $\geq 10^{13}$ Ωm after drying and storage at 0% RH, which we consider too high for powder coating. This would result in significant charge retention of the deposited layer after powder coating, so reducing the electric field between corona electrode and compact and ultimately charge repulsion of incoming powder. However, this undesirable effect can be prevented, and the functionality of the compact materials enhanced, by increasing water content of the compacts to achieve resistivities which are high enough for a rapid charge dissipation rate to be achieved. Other workers have made similar use of water to reduce resistivity (9–10).

Compaction has been shown previously to have no effect on electrical resistivity (11). It was, therefore, considered that for this study the resistivities of the powder samples were identical to those of the compacts. Surface voltage was measured for 200 s (slow decay) or until it fell below a threshold of 50 V (fast decay) with the initial voltage decay data being fitted to the exponential relationship developed by Inoue and Kokado (12), Eq. (2)

$$V = V_0 e^{-at^{0.5}} \qquad (2)$$

where V and V_0 are the voltages at time t and $t = 0$ respectively and a is a constant. V_{max}, the maximum measured voltage, will be lower than V_0 since it was determined after the corona to probe transit during which charge decay has already occured.

During the charging process ions are generated as a result of collisions between electrons produced by the high voltage and neutral molecules in air. On being deposited on the compact surface these ions may be neutralised by electron loss to the conduction band of materials near the surface (13). The electron is subsequently trapped in a surface state and moves into the bulk if given sufficient activation energy. Lateral spreading of charge occurs across the compact surface since the electric field will seek to reduce itself. Since the voltage probe has a limited area of detection this charge movement will result in voltage reduction. The surface voltage will also decay as a result of interaction with neutral molecules in the air, particularly water due to its polarity.

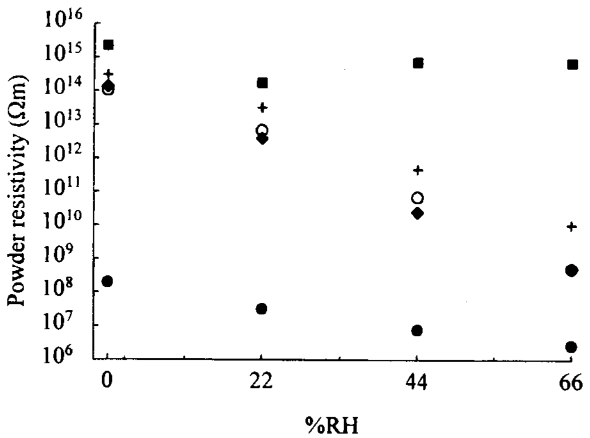

Fig. 2. The relationship between relative humidity and powder Resistivity at 500 kVm^{-1} (■ magnesium stearate, + lactose, ○ sorbitol, ◆ MCC, ● dibasic calcium phosphate).

Varying the charge injection time between 3 and 20 s had no effect on V_{max} or $t_{1/2}$. Thus all subsequent measurements were carried out at 80 kV corona voltage and 3 s charge injection time. Similar insensitivity to charging times up to 30 s has been previously noted for polyethylene films (14). No differences in V_{max} and $t_{1/2}$ were observed between compacts having rough or smooth surfaces.

At 0% RH, sorbitol, lactose and MCC compacts had similar values of V_{max} whilst DCP had a considerably lower value (Table II). The values were broadly in line with material resistivities (Fig 1) although V_{max} was insensitive to resistivities $>10^{14}$ Ωm. MCC compacts showed the slowest decay rate whilst lactose compacts, which had similar resistivities, decayed more rapidly. This anomalous behaviour indicated the complexity of the electrostatic interactions and that material resistivities were not absolute predictors of the electrical behaviour of materials. Other factors, such as molecular structure, electronic traps (15) and crystal form which can also influence electronic conduction were likely to be important. The decay rates of all compacts at 0% RH were too slow for use in powder coating since incoming charged particles would be repelled by the surface potential and not deposited. In order to increase surface conduction, the RH was increased which resulted in a dramatic reduction in V_{max} and $t_{1/2}$ (Table II and Fig. 3) although V_{max} for lactose remained >2000 V. Indeed the increase in decay rate of sorbitol compacts was such that at 66%RH no decay curve could be obtained since the voltage dropped rapidly following charging. Again the values were broadly in line with material resistivity and relative permittivity (unpublished data). Half-lives <5 s were attained which were sufficiently short for powder coating to be considered a feasible process. The decay behaviour of PVA, PVC and polyester powders was also found to be in agreement with Eq. (2), with the decay rate increasing with water content (16). Surface conductivities of polypropylene and PFA powders were found to be relatively unaffected when water was absorbed into them but very sensitive to humidity across the entire range when water remained on the surface (8).

Table II. The Effect of Relative Humidity on Compact Voltage Decay After Charge Injection at 80 kV for 3 Seconds (mean with 95% C.I.)

Compact Material	0% RH		44% RH		22/66% RH	
	V_{max} (V)	$t_{1/2}$ (secs)	V_{max} (V)	$t_{1/2}$ (secs)	V_{max} (V)	$t_{1/2}$ (secs)
Sorbitol	2260 (350)	63.5 (14.6)	1040 (180)	0.5 (0.2)	1863 (258)	2.48 (0.69)
DCP	1190 (280)	2.0 (1.6)	660 (310)	0.8 (0.1)	141 (30)	0.35 (0.18)
Lactose	2310 (330)	39.0 (9.0)	2020 (170)	1.7 (0.6)	1176 (182)	1.32 (0.54)
MCC	2160 (140)	82.5 (10.6)	710 (230)	0.4 (0.5)	1497 (114)	2.75 (0.28)

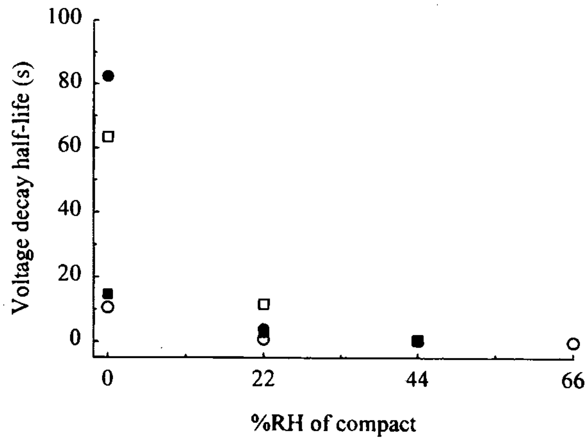

Fig. 3. Variation in voltage decay half-life with compact relative humidity. (● MCC, ○ sorbitol, □ lactose, ■ dibasic calcium phosphate).

A relationship between resistivity and voltage decay rate has been derived by Coelho (17) which is complex due to the dependence of resistivity on applied field. However, whilst ρ cannot be calculated directly from the Coelho equation, $dV/dT \propto 1/\rho$, i.e. low resistivities yield fast decay rates. The influence of ρ on $t_{1/2}$ is given in Fig 4 with the material resistivities having been determined at $V_{max} \cdot t_{1/2}$ was independent of the compact material at resistivities $<10^{12}$ Ωm with differences between materials only becoming apparent above this value. These differences have previously been discussed. Use of Fig 4 does not imply that there is a simple relationship between ρ and $t_{1/2}$ but rather their interdependence.

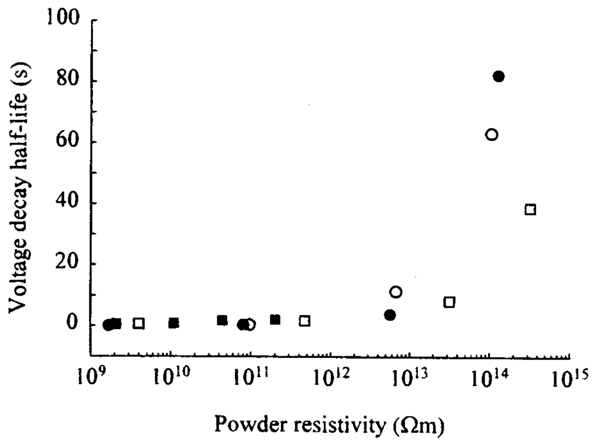

Fig. 4. The relationship between powder resistivity and $t_{1/2}$ for compact Materials (● MCC, ○ sorbitol, □ lactose, ■ dibasic calcium phosphate).

Since many drugs and compact materials are water sensitive, storage at 44% RH may be unacceptable; thus the voltage decay characteristics of compacts stored at 22% RH were tested at 66% RH. Half-lives <3 s were observed for all compacts (Table II) indicating the rapid sorption of water in the 10 s exposure time prior to measurement and the feasibility of this approach in making compact surfaces more conductive for powder coating.

CONCLUSIONS

The resistivities of dried materials, apart from dibasic calcium phosphate, were too high for use in powder coating. Deposition of charged particles on these compact surfaces would rapidly increase their electrostatic potential and reduce the electrical field between the corona electrode, used for powder coating, and the substrate. Hence only thin powder layers (<30 μm) would deposit before repulsion of incoming particles occurred and the process became self-limiting. This powder layer is unlikely to be thick enough for a continuous film to form during the next stage of the process when it is exposed to IR radiation. However, conditioning of the compacts, either by pre-storage at elevated humidities or powder coating in a high humidity environment, increased their charge decay rates making this technique feasible. Exposure of compacts to high humidities, or in the extreme case wetting with a mist, should not cause stability problems since the IR radiation would rapidly evaporate any water.

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