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ABSTRACT

AN EXPERIMENTAL STUDY OF DRY PARTICLE COATING: DEVICES, OPERATING PARAMETERS AND APPLICATIONS

by Michelle Ramlakhan Mohan

Dry particle coating, which mechanically coats fine guest particles onto the surfaces of larger host particles, without binders or solvents, is investigated. Several systems of host and guest particles are coated in different devices to study various aspects of dry particle coating. The devices used are Magnetically Assisted Impaction Coating (MAIC) device, Mechanofusion, and the Hybridizer.

MAIC is used to coat fine SiO_2 guest particles onto the surface of larger cornstarch and cellulose host particles. This is done to simultaneously improve the flowability of the host particles, as well as reduce their hydrophilicity. Dry particle coating is used to increase the sintering temperatures of particulate materials (host), by application of a monolayer of a highly refractory material (guest), promoting deactivated sintering. This phenomenon has not previously been reported, although activated sintering (decreasing the sintering temperatures of metallic and ceramic particles) is well established in the literature. The products analyzed in the deactivated sintering studies are coated in MAIC, Mechanofusion and the Hybridizer.

The key parameters affecting the coating performance of the dry coating devices are examined. The key parameters of MAIC are magnetic particle size, magnetic particle to powder mass ratio, frequency, current and processing time. The effects of the rotation and translation motion of the magnetic particles are also investigated. In Mechanofusion and the Hybridizer, the key parameters examined are rotation speed and processing time. The coating performance of the three devices is compared by examining contamination and adhesion of the coated products. Quantification of the contaminants on the products is achieved by measuring the amount of iron, nickel, and chromium in the sample. Adhesion of the guest to the host particles is conducted by subjecting the products to ultrasonic vibrations, to examine the amount of material that becomes detached from the surface.

Based on this work, dry particle coating is shown to be viable for the production of composites with new/improved functionalities. The coating performance of the devices as a function of their key parameters is successfully investigated. Also, the first comparative look of dry particle coating devices, in the areas of product contamination and guest-host particle adhesion is presented.

AN EXPERIMENTAL STUDY OF DRY PARTICLE COATING: DEVICES, OPERATING PARAMETERS AND APPLICATIONS

by Michelle Ramlakhan Mohan

A Dissertation Submitted to the Faculty of New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Chemical Engineering

> Department of Chemical Engineering Chemistry, and Environmental Science

> > May 2001

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APPROVAL PAGE

AN EXPERIMENTAL STUDY OF DRY PARTICLE COATING: DEVICES, OPERATING PARAMETERS AND APPLICATIONS

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 "Synthesis of Engineered Particulates with Tailored Properties Using Dry Particle Coating", Powder Technology, 117, 1-2 (2001) pp. 40-67.
- Michelle Ramlakhan, C.Y. Wu, Satoru Watano, Rajesh N. Dave and Robert Pfeffer, "Dry Particle Coating Using Magnetically Assisted Impaction Coating: Modification of Surface Properties and Optimization of System and Operating Parameters", Powder Technology, 112, 1-2, (2000), pp. 137-148.
- Michelle Ramlakhan, Rajesh N. Dave and Robert Pfeffer, "Deactivation of Sintering Temperatures of Materials by Dry Particle Coating", AIChE Meeting, Los Angeles, CA, Nov 12-17, 2000.

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NOMENCLATURE

| а | radius of the curved neck |
|---------------------------|---|
| b | size of sintered neck |
| d | diameter of guest particle |
| $\mathbf{d}_{\mathbf{p}}$ | diameter of particle |
| f | 3β/2 |
| g | gravitational force |
| h _e | distance which the centers of particles have moved closer to each other |
| ħw | Lifshiftz-van der Waals constant |
| k | Boltzmanns constant |
| m | mass of impacting guest particle |
| m _b | mass of guest particle stuck to processing bottle |
| m _m | mass of guest particles stuck to magnets |
| n, p | constants (depend on sintering mechanism) |
| q_1, q_2 | charges on particles 1 and 2 |
| r | distance between two particles |
| r _p | projected radius of the area of plastic deformation |
| t | time |
| v | impacting velocity / superficial gas velocity |
| х | radius of the neck |
| Xs | mass of guest particles remaining with host particles after processing |
| у | $x^2/4R$ |
| y _s | initial mass of guest particles |
| Zs | mass of guest particles lost during ultrasonication |
| | |
| A, B | constants |
| Co | equilibrium vacancy concentration |
| ΔC | vacancy concentration |
| D | diameter of host particle / mean particle diameter |

NOMENCLATURE (Continued)

| Do | self-diffusion coefficient |
|-----------------|--|
| D _p | granular diameter |
| Ds | diameter of sample tube |
| D_v | vacancy diffusivity of host particle |
| Ei | Young's modulus of body I |
| Felectro | electrostatic forces |
| F _p | compression force |
| F_{vw} | van der Waals forces |
| G | weight % of guest particles |
| H _p | depth of permanent deformation |
| J | instantaneous mass flux |
| К | 2π/5 |
| L | height of bed |
| ΔL | change in length of sample |
| Lo | initial length of sample |
| N | number of guest particles |
| ΔP | pressure drop |
| Po | external force to the contacting bodies |
| Qe | energy stored as elastic deformation residing in the annular region around the |
| | area of plastic deformation |
| Q _{pe} | energy stored as elastic deformation in the area of plastic deformation |
| Q _A | adhesion energy |
| Q _B | energy of attraction |
| QI | impacting energy |
| Q _P | energy dissipation in plastic deformation |
| R | radius of particle |
| R_1, R_2 | radius of host and guest particles, respectively |
| | |

R_c contact geometry parameter

NOMENCLATURE (Continued)

| $S_{D^{+}d}$ | surface area of sphere with diameter $(D + d)$ |
|--------------|--|
| S_d | cross-sectional area of guest particle |
| Т | temperature |
| Ts | sintering temperature |
| Um | adhesion due to mechanical energy |
| U_{mf} | minimum fluidization velocity |
| Us | adhesion due to surface energy |
| UT | total adhesion energy |
| V | volume |

Greek letters

| β | layer spacing |
|-------------------|---------------------------------------|
| δ | vacancy volume |
| ε | sample porosity |
| ε _o | dielectric constant |
| φ | sphericity of particles |
| γ | surface energy |
| $\Delta \gamma$ | surface adhesion energy per unit area |
| $\gamma_i{}^d$ | dispersive energy component of body i |
| η_s | viscosity |
| φ | limiting elastic velocity |
| μ | viscosity of bed |
| ν_i | Poisson ratio of body i |
| ρ | density of impacting particle |
| ρ_D | density of host particle |
| ρ_{d} | density of guest particle |
| $\rho_{\rm f}$ | density of fluid |

NOMENCLATURE (Continued)

- AAS Atomic Absorption Spectroscopy
- AOR Angle of Repose
- BET Brunaner-Emmett-Teller equation
- EDX Energy Dispersive X-Ray Spectroscopy
- FDA Food and Drug Administration
- FT-IR Fourier Transform Infrared Spectroscopy
- HB Hybridizer
- JKR Johnson-Kendall-Roberts model
- MAIC Magnetically Assisted Impaction Coating
- MF Mechanofusion
- PMMA Poly methyl-methacrylate
- RFBC Rotating Fluidized Bed Coater
- SEM Scanning Electron Microscopy
- XRF X-Ray Fluorescence

CHAPTER 1

INTRODUCTION

1.1 Dry Particle Coating

Dry particle coating to alter the surface properties and/or functionality of fine particles or powders is very important to many industries. Typically, surface modification of particles is done by wet coating methods such as pan coaters and a variety of fluidized bed coaters, or by wet-chemistry based techniques such as coacervation, interfacial polymerization, and urea/formaldehyde deposition. However, wet coating methods have become less desirable recently because of environmental concerns over the resulting waste streams and possible VOC emissions. Dry particle coating, which directly attaches tiny, sub-micron sized (guest or fine) particles onto relatively larger, micron sized (host or core) particles without using any solvents, binders or even water, is a promising alternative approach (Yokoyama *et al.*, 1987; Tanno, 1990; Naito *et al.*, 1993).

Dry particle coating processes, as opposed to wet coating processes, are relatively new. They were pioneered mostly in Japan about ten to fifteen years ago, and are still in the research and development stages. They are rarely used commercially in the United States of America. Dry particle coatings can be characterized into several categories such as deep embedding, encapsulation, filming, discrete or partial surface covering, and a loose surface coating (ordered mixture). Although all such composites can be obtained by using one of the available dry coating devices, there is a lack of understanding of the underlying physicochemical principles that govern the coating process. Also, the operating principles of each of the dry coating devices are different. Hence, the type of coating produced and the applications for which they are optimum are also different. Such an understanding is necessary to predict the choice of machines and the right combination of process variables needed to produce composite materials with desired tailored properties.

The current state-of-the-art approach is to use a trial and error procedure to determine whether the process works or not. This approach is clearly inadequate, not only because it is very time consuming, but also because it does not allow determining the conditions for obtaining the optimal quality. However, to date, very little work has been done to develop macroscopic models for these processes because the modeling of these processes is not straightforward and different devices employ different mechanical mechanisms to achieve coating.

1.2 Objectives

Due to the general lack of information on dry particle coating, this research studies several aspects of dry particle coating as well as several dry particle devices. The devices used are the Magnetically Assisted Impaction Coating device (henceforth called MAIC), Mechanofusion, and the Hybridizer. The study is divided into three main areas. These areas are: the use of dry particle coating for the synthesis of composites with improved functionalities, optimization of parameters affecting the coating performance of the devices, and the application of different dry particle coating technologies based on the degree of contamination and adhesion of the composite particles produced.

The MAIC device is used to coat soft/irregular shaped food materials to study the feasibility of simultaneously improving the flowability as well as reducing the wettability of these materials by the application of a discrete coating of silica. The MAIC is the most "gentle" of all the three devices in terms of mechanical impaction forces and therefore,

there is very little size reduction of the material during processing. As a result, this device was selected to process soft irregular shaped organic host materials, applicable to the food and pharmaceutical industries.

All three devices were used to analyze the feasibility of promoting deactivated sintering. Deactivated sintering is defined as a process whereby the surfaces of particles are coated with a monolayer of another material to delay and reduce the sintering rate of the particles. This results in an increase in the sintering temperature (temperature at which the particles begin to soften and stick together) of the particles. No information of deactivated sintering is available in the literature and it is a new term defined in this work. Based on the experimental results, a simplified model describing the mechanism of deactivated sintering, for both amorphous (glass, polymers) and crystalline (alumina) materials is presented.

Catalytic materials used in fluidized beds can undergo attrition, which causes the loss of fines resulting in the loss of active reaction sites. The feasibility of reducing particle attrition in fluidized beds by dry particle coating was investigated. Catalytic materials were coated with a discrete protective layer of SiC by dry particle coating to study the feasibility of reducing the surface attrition. The coated materials were further tested in a small fluidized bed, built to handle small batch sizes, produced by the devices.

A system of PMMA host particles coated with alumina guest particles was used to study the overall performance of the devices, as a function of system and operating parameters. The parameters examined for Mechanofusion and the Hybridizer were rotation speeds and processing times. A more in depth study was done for the MAIC due to the limited amount of data available on the performance of this device. The key system parameters examined for the MAIC were magnetic particle size, guest particle size and magnetic particle to powder (host and guest particles) mass ratio. The effects of the major operating parameters such as frequency, current (or voltage), and processing time were also investigated. The motion of the magnetic particles was examined using a high-speed digital camera to study its effect on the quality of the surface coverage obtained. Based on the optimization results and the study of the motion of the magnetic particles, a mechanism of coating is proposed for MAIC.

The coating performance of the three devices is compared by examining the contamination and the adhesion of the coated products. The identification and quantification of contaminants on the coated products are very important for the application of dry particle coating in industries such as food and pharmaceuticals. Adhesion of host to guest particles of the products is also of significant importance, as there is much concern as to the strength of the coating, since the process involves no binder or solvents. As the coating performance of each device varies for each system of materials, some simple relationships are presented to indicate good candidates of host and guest based on the calculation of adhesion energies of the systems.

The above outlined studies are presented in the chapters that follow with the hope that not only will they provide a better understanding of dry particle coating, but the numerous and diverse applications of dry particle coating will also be realized. The comparison of the coating performances of the devices strives only not to point out the limitations of the devices, but also to give an indication as to how, within which range of parameters, system as well as operating, the device can be used to its optimum.

CHAPTER 2

BACKGROUND

2.1 Advantages of Dry Particle Coating

Wet particle coating is used primarily to form a barrier or film between the host particle and its environment. The purpose of the barrier or film is to produce extended or delayed release, separation of incompatibles, protection from water vapor, light or oxygen, and in general, change the physical or chemical properties of the surface. Presently, most commercial coatings of particles, seeds, grains, granules or pellets are done using a wet process. For example, wet processes have been used in the pharmaceutical industry to coat solid dosage forms such as tablets, to create film coatings for controlled release of drugs, and for taste masking. They are used in the food industry for flavor enhancement, and for improving the appearance and stability, or shelf life, of a product, and in the agricultural industry for coating of seeds and for the sustained release of pesticides and fertilizers. While these are some of the more conventional applications of particle coating, relatively new dry coating processes are now becoming available, for which many more new and exciting applications are possible (Alonso *et al.*, 1989a to 1989d; Chaudhuri *et al.*, 1998; Watano *et al.*, 1998).

In dry particle coating process, sub-micron sized guest particles are coated onto larger, micron sized host particles in order to create value-added composite particulate materials. In contrast to wet particle coating, the guest particles are brought into close contact with the host particles through the application of mechanical forces. Since the sizes of the guest particles are so small, van der Waals interactions are strong enough to keep them firmly attached to the host particles. Thus, either a discrete or continuous coating of guest particles can be achieved depending on a variety of operating conditions including processing time, weight fraction of guest to host particles and particle properties (Figure 2.1).

Continuous coating can consist of either a particle layer (monolayer or multilayer) which is porous, or a continuous film coating, which is generally non-porous. While continuous coatings are generally preferred, the ability to create discrete coatings has some unique advantages. For example, in some applications, a coating may be required to change a specific surface property, but a complete shielding of the underlying core particle is undesirable.



Figure 2.1 Schematic of Dry Particle Coating

Sometimes, in addition to bringing the guest particles in close vicinity to the host particle, the process can either deform the guest particles or cause the guest particles to become embedded into the surface of the host particle. The increased contact area due to deformation or embedding causes the attraction between the particles to become even larger. Hence, a much stronger coating is obtained.

Apart from forming a barrier as in wet coating, dry particle coating can be used to make significant changes in the properties and/or the functionality of the original host particles, thus creating engineered particulates with tailored properties. Some examples of surface properties that can be improved or modified are flowability, dispersibility, solubility, wettability (hydrophilic/hydrophobic properties), electrostatic, electric, magnetic, optical, color, flavor, taste, particle shape/sphericity, sinterability, and solid phase reactivity. This opens up many new avenues of research and applications.

In addition to producing materials with completely different functionality, dry coating processes have an advantage of being cost effective due to the reduced use of high-priced or rare materials since the more expensive material (guest) can be coated onto the cheaper carrier material (host). Another major advantage of dry particle coating processes is that they are environmentally benign, producing none of the organic (gas or liquid) or aqueous waste streams, which usually are present in wet coating processes. Moreover, they can result in substantial energy savings because there is no need for drying the particulate products obtained.

2.2 Origins of Dry Particle Coating

The subject of dry particle coating is very closely related to the subject of dry mixing of powders. Ideally, a binary mixing process should intimately mix the two species so that any small sample taken from the mixture would contain the same proportion of the two constituents. This is hard to achieve, particularly when the powders are either cohesive,
or the two species to be mixed are quite different in size. When the powders are cohesive they naturally form agglomerates and mixing two constituents requires breaking up the agglomerates. When the constituents differ in size, there is an increased tendency for segregation, as the size difference becomes larger. However, when the two components to be mixed are very different in size (one or two orders of magnitude), then segregation may no longer be a problem. In such cases, the smaller particles tend to adhere onto the larger particles. The adhesion force between the smaller particle and the larger particle is greater than the weight of the smaller particle, and hence it is not easily removed from the host. This phenomenon is usually referred to as "ordered mixing" or "structured mixing".

In ordered mixing, a term coined by Hersey (1975), the surface of the larger particles (the first component of a binary mixture) is loosely coated/covered with smaller particles (the second component of a binary mixture). In dry particle coating, the same thing happens; however, the surface covering is more permanent because of a stronger physical (or chemical) bonding. Thus, ordered mixing and dry coating of powders are closely related, and therefore it is important to look at the literature on ordered mixing which precedes the literature on dry coating.

Initial work on ordered mixing, done by Hersey and co-workers, was mainly for the purpose of pharmaceutical applications (Hersey *et al.*, 1974, 1979, and 1981; Yip and Hersey, 1977). Orr coined the term "regimented" mix or "interactive" mix for this phenomenon [Orr and Shotton, 1973; Egermann and Orr, 1983). Staniforth and colleagues also studied ordered mixtures applicable to the pharmaceutical industry (Staniforth *et al.*, 1981 and 1982a-c; Staniforth, 1985). The main reason why this topic is interesting to the pharmaceutical industry is that, in direct tableting, it is advantageous to have a micro-fine active ingredient attached to a coarse excipient. Besides eliminating the problem of segregation, there are other advantages. The active micro-fine ingredient allows for higher dissolution rates, in some cases even making a hydrophobic drug soluble (Shah, 1990), and the coarse excipient gives the mixture better flowability and tableting properties.

The advantage of ordered mixing is that it provides a much better degree of homogeneity as long as the particle size distribution of the larger size species is not too wide (Hersey, 1975; Bannister *et al.*, 1983; Enstad, 1981). Hence in terms of subsequent segregation, ordered mixtures are more stable than ordinary mixtures (Hersey, 1975; Yip and Hersey, 1977; Staniforth, 1985; Bannister *et al.*, 1983; Bryan *et al.*, 1979; Lai and Hersey, 1981; Thiel *et al.*, 1982). It was also discussed in this literature that having a very wide size distribution of the large size species may lead to "ordered unit segregation" (Hersey and Thiel, 1979; Lai and Staniforth, 1981; Thiel *et al.*, 1983; Yip and Hersey, 1977), which should be avoided.

While there is little available in terms of quantitative modeling of the ordered mixing process (except work by Alonso *et al.*, 1989a, 1989b, 1990, and 1991), a qualitative explanation is given in Bannister and Harnby, (1983). Three stages are identified: (1) separation of the agglomerates of the fine constituent into their primary particles, (2) bonding of these fines to the carrier particles, and (3) redistribution and exchange of fines among the carrier particles until a random distribution is achieved. While the real process may not take place exactly in that order, it is clear that the deagglomeration of fines must occur in order to create such a mixture. Therefore any

mixing device, in order to achieve ordered mixing, must provide sufficient mechanical or other means of agitation to promote de-agglomeration of fines, i.e., provide a large number of particle collisions involving high normal and shear impact forces. Machines that can be used for this purpose are high intensity mixers and grinding machines such as ball and media mills.

There is another reason why ordered mixing and/or dry coating work well when using grinding type machines. It is easier to break up agglomerates into primary size particles in the presence of coarser particles in the mix when processed in a milling machine, than having fine particle agglomerates alone. While this behavior was only speculated by Yeung and Hersey, in 1977, later in 1991, Alonso showed this through statistical computer simulations. This phenomenon works to the advantage of dry particle coating when performed in a milling type machine because the host particles act as the media and help in de-agglomerating the fines.

It is likely that the earliest dry coating work may have been done using some type of milling device by researchers involved with ordered mixing applications. However, the earliest reference to a device specifically used for dry coating comes from the Japanese literature, when it was discovered (by serendipity) that a new machine developed for ultrafine grinding (Yokoyama *et al.*, 1983) could also be used for dry particle coating (Koishi, 1983). The grinding device, called the Angmill, was used for creating particulate materials with different surface properties due to the strong mechanical force acting on the particles (Koishi, 1983). Since the combination of high shear and compression forces acting on the host and guest particles actually produced some surface fusion, the treatment was termed mechanofusion, and the device, manufactured by Hosokawa Micron, is also called Mechanofusion. Several articles were published during the 1980's describing the applications of mechanofusion (Tanno, 1990; Yokoyama *et al.*, 1987; Koishi *et al.*, 1984). Another excellent review paper on mechanofusion appeared later (Naito *et al.*, 1993), and discussed the applicability of mechanofusion for powder surface modification from the perspective of comminution.

The concept of ordered mixing was also taken one step further (to dry coating) by using dry impact blending, as described in a series of papers by another Japanese group (Honda *et al.*, 1987, 1988, 1989, and 1991). They argued that an ordinary dry blending process would result in an ordered mixture, as the fine particles attach to the larger host particles through electrostatic forces (Honda *et al.*, 1991). However upon processing in an impact blending device, the large impulsive forces cause the fine particles to become firmly attached to the core particle and a coated composite particle is obtained. This device, called the Hybridizer, is manufactured by Nara Machinery of Japan. The hybridizer has proven very useful for pharmaceutical applications; for example, it accelerated aspirin dissolution when coated onto an excipient such as potato starch (Iskizata *et al.*, 1988).

The mechanofusion and hybridizer machines referred to above can produce chemical as well as physical surface interactions between the host and guest particles. While the latter machine deals with adhesion between the hosts and guests and deagglomeration of the guests, the former device deals with the change in the chemical or electronic states of the host and guest species as a result of the intimate mixing caused by the mechanical forces generated by the machines. If, in addition to physical adhesion, a chemical reaction occurs at the host-guest interface, the process is called mechanochemistry.

For example, a series of publications by Senna (1996, 1998a, 1998b, and 1999) has shown that dissimilar metallic species, notably complex oxide powders can be crosslinked by oxygen using a soft-mechanochemical process (mechanical stressing of the powders) by proton transfer through OH groups, and subsequent electron transfer. The mechanochemical reaction is not restricted to inorganic materials, but is also applicable to complex formation between inorganic-organic or organic-organic materials and can be accomplished using easily available machines for grinding or comminution. Thus, mechanochemical effects are very important considerations in the understanding of dry particle coating processes.

Both the mechanofusion device and the hybridizer produce coated particles, where the level of forces that the guest and host particles are subjected to is very high. In certain applications, these high forces are unnecessary or even detrimental to the final coated product obtained, for example, excessive size reduction of the host particles. Devices that produce "softer" coatings by applying a smaller level of forces have also been introduced. An elliptical rotor-type powder mixer, called the Theta Composer, was developed for this purpose and manufactured by the Tokuju Company in Japan. Several articles describe the operation of the theta composer, which has been found to be very useful for processing (coating) certain pharmaceutical and food products (Alonso, 1991; Shimizu *et al.*, 1997; Fukumori *et al.*, 1998; Watano *et al.*, 2000; Kawashima, 1998).

Another "softer" dry coating method uses a magnetic field to accelerate and spin larger magnetic particles mixed in with the core and guest particles promoting collisions between the particles and with the walls of the device. This magnetically assisted impaction coating (MAIC) process (Singh *et al.*, 1997; Ata *et al.*, 1998) developed by a US company, Aveka, Inc., results in very good mixing and produces mechanical stresses sufficiently large to promote adherent coating of the guest particles onto the surface of the core particles.

While most of the literature in dry coating comes from Japan, during the last few years, several concentrated activities in this area (some proprietary, and not yet described in the literature) have been initiated in the US. At New Jersey Institute of Technology (NJIT), a new device was invented based on the principle of centrifugal fluidization. This device called the Rotating Fluidized Bed Coater (RFBC) (Watano et al., 1998) can also produce soft coatings. Most recently, a novel class of coating technique has been proposed based on the concept of direct fine particle generation and subsequent coating onto host particles. In one such process, nano-sized guest particles are generated by laser ablation of a target (e.g., Ag, Y₂O₃:Eu⁺³, and TaSi₂), and the particle flux in a plasma is directed towards a small fluidized (caused by vibration) bed of micron sized host particles (Fitz-Gerald et al., 1998, 1999a and 1999b). While difficult to scale-up, this laser ablation technique can coat very fine (less than 5 µm) host particles by ultrafine guest particles, an important consideration for the pharmaceutical industry. Similar processes based on sputtering and other techniques that allow for producing a flux of nano-particles have also been proposed.

2.3 Applications of Dry Particle Coating

Dry particle coating is applicable to a variety of industrially important problems. This is due to its ability to create engineered particulates with substantial improvements of certain physical and/or chemical properties. Early work from the Japanese literature report several interesting applications. For example, 5 μ m polymethylmethacrylate (PMMA) particles coated with 10 wt. % of 0.015 μ m TiO₂ particles using mechanofusion flowed freely and had a near zero angle of repose. In contrast, both the original PMMA and TiO₂ particles did not flow well and had an angle of repose greater than 30° (Yokoyama *et al.*, 1987). It was also reported that processing of ground polystyrene resin of 10 μ m size with carbon black in mechanofusion produced easily flowing toner material of rounded shape (Yokoyama *et al.*, 1987).

The mechanofusion system is also capable of promoting a high level of deagglomeration. This is evidenced by processing 10 μ m sized agglomerates of polytetrafluoroethylene (PTFE), where each individual PTFE particle had a size of about 0.1 μ m, with 5 μ m spherical PMMA host particles. When examined using SEM, the composite particles showed an even coating of individual PTFE particles over the surface of the PMMA particles indicating that the PTFE agglomerates were broken-up and well dispersed. Mechanofusion processing also resulted in a significant increase in negative polarity of PMMA particles in contrast to the uncoated PMMA, which was electrically neutral.

Most of the early work reported using the hybridizer involved processing of pharmaceutical drugs to produce controlled-release properties (Ishizata *et al.*, 1988, 1989, and 1993). As an example, fines of isoproterenol HCl, 5 % by mass, were coated onto

potato starch (~ 70 μ m) followed by a coating of carnauba wax, 5 % by mass, to achieve time released control of isoproterenol HCl. Furthermore, it has been reported that the hybridizer was useful in preparing composite and encapsulated (film-coated) particles. For instance, if inorganic fine particles were used as coating materials, they were fixed and embedded in the surface of core particles. However, if polymer or metallic fine particles were used as coating materials, they partially melted and produced a continuous film coating on the core particle (Honda *et al.*, 1994).

Many other applications of dry coated composite materials can be found in the literature (survey in Naito et al., 1993). These are: coloring and UV protection in cosmetics, production of toner particles with different colors, metal/ceramic composites, thermal spray materials, ceramic filters, solid lubricants, and electric contact materials. Other applications using mechanofusion and the hybridizer include production of yttrium-based super-conductors (Naito et al., 1989); and nano-crystalline thin films of metal oxides such as TiO₂ and SnO₂ with a highly porous structure for use in photoelectrochemical cells (Liu et al., 1995). The production of copper matrix molybdenum particle composites by hot pressing copper coated molybdenum powder to achieve improved properties such as low porosity, high hardness, and a lower coefficient of thermal expansion (Lih et al., 1995) has also been achieved. The coating of silicon nitride particles with an alumina precursor to make Si_3N_4 behave like Al_2O_3 in aqueous slurries and to achieve high packing density (Luther et al., 1995; Han et al., 1996) is also The improvement in properties of artificial bone material hydroxyapatite possible. (HAP) by coating with partially stabilized zirconia to provide high fracture toughness while preserving the original surface properties of HAP (Kawashima et al., 1997) can

also be achieved in these devices. Also, improving the performance of liquid chromatography (HPLC) by using uniform polyethylene microspheres coated with silica (Honda *et al.*, 1992). In addition, using the theta composer, softer coatings for controlled release microcapsules (Fukumori *et al.*, 1998) and food materials containing cellulose fiber (Watano *et al.*, 2000) were produced.

There are also some novel applications of dry coating not yet reported in the literature. For example, the coating of titania onto tiny glass bubbles using a dry coating process can be used to cleanup oil spills. It is believed that the glass bubbles will float over the oil spill, and titania being photo-active will react with the oil and decompose it. The glass bubbles will eventually end up on the shore as part of the sand. Fine particles of titania are very difficult to handle in such an application by themselves, but using larger hollow glass particles as carriers makes them not only floatable, but easy to handle. Another interesting example is coating nitrogen-fixing bacteria onto grass seeds. The coated seeds can provide their own fertilizer when planted in the soil. These two examples are quite different from the traditional "barrier type film coating" applications. Similarly, a novel application, requiring discrete coating as compared to film type coating, was developed in this research for promoting "deactivated sintering".

In addition to coating, it was found that these machines could also be used for other types of powder processing such as rounding of particles and precisely mixing different kinds of powders together. For example, the Hosokawa mechanofusion machine has been successfully used for mixing powder materials for superconductive oxides, multi-component targets for thin films and electric wires of Bi-based superconductive oxides (Naito *et al.*, 1990 and 1993; Asano *et al.*, 1992). The diverse examples described above indicate the huge potential market that exists for developing new particle composites for applications in foods, consumer products, cosmetics, pharmaceuticals, biomaterials, inks and toners, and ceramics.

2.4 Dry Particle Coating Devices

As already discussed in the previous section, there are numerous devices available for dry particle coating. These devices, although different in their manner of supplying the necessary mechanical forces, all strive to efficiently promote the de-agglomeration of the guest particles and their adhesion onto the surface of the host particles. In the hybridizer the ultra high rotational speed of the blades and recirculation of the powder allows the host and guest particles to violently collide with each other. In mechanofusion, the particles are also subjected to severe shear and compressive stresses as they travel between the clearance of the rotating drum and the inner piece. In MAIC, the magnetic particles spin furiously due to an oscillating electromagnetic field causing collisions between the host and guest particles, and the walls of the device. In the theta composer, the guest particles are impacted onto the host particles by the high-speed motion of an elliptical rotor in an elliptical mixer. In the RFBC, de-agglomeration and impaction of the guest particles onto the hosts occur because the bed is fluidized at very high gas velocities resulting in very good mixing and high shearing stresses. All of these devices have been used successfully by many investigators to produce composite particles with unique and improved functionality. With the exception of the theta composer, all the other devices are available at NJIT. In the next section, these dry coating devices will be described in more detail.

2.4.1 Mechanofusion

A schematic of the mechanofusion machine is shown in Figure 2.2. The device consists mainly of a rotating outer vessel, a stationary inner piece and a stationary scraper (the scraper and inner piece can be either ceramic or stainless steel). A measured amount of host and guest particles is placed into the rotating vessel. As the vessel rotates at speeds between 200 to 1600 rpm, the powder is forced outward towards the walls of the vessel. The gap between the inner piece and the rotating drum is controlled, and as a result, the particles passing through the gap are subjected to intense shearing and compressive forces. These forces generate sufficient heat energy to "fuse" the guest particles onto the surface of the host particles. The gap size between the inner piece and the walls of the vessel is very important in controlling the thickness of the desired coating. The gap between the scraper and the wall of the vessel is also controlled. The scraper breaks-up and disrupts any build-up or caking of the particles on the walls of the vessel. This is a batch-operated device.



Figure 2.2 Schematic of Mechanofusion.

There are several advantages in using the mechanofusion system. First, the shape of the inner piece, the small gap, and the high rotation speed of the drum allow the particles to be subjected to very high shear and compressive forces. Second, there is a local temperature build-up due to these strong forces acting on the particles, which can result in the fusion of the surface of the host and guest particles. This produces very strong physical and/or chemical bonds, which enhance the coating process.

2.4.2 Hybridizer

The hybridizer, shown schematically in Figure 2.3, consists of a very high-speed rotating rotor with six blades, a stator and a powder re-circulation circuit. Similar to the mechanofusion, the rotor with six blades and the powder re-circulation circuit (the inner lining) can be made with ceramic or stainless steel.



Figure 2.3 Schematic of Hybridizer.

The powder (host and guest particles) placed in the processing part of the vessel is subjected to high impaction and dispersion due to the high rotating speed of the rotor. The particles undergo many collisions, and this allows for break-up of fine agglomerates and powder coating due to the embedding or filming of the guest particles onto the surface of the host particles. Currently, this is a batch-operated device.

The hybridizer has several advantages that make it a powerful dry coating device. First, the rotor of the hybridizer can rotate anywhere from 5000 rpm to 16000 rpm. Due to the strong forces applied to the materials at these high rpm, very short processing times are required to achieve coating. Second, the device consists of a re-circulating unit that continuously moves the particles in and out of the processing vessel and against the blades of the rotor. Lastly, similar to mechanofusion, there is a temperature build-up due to the high impaction forces caused by the high rotation speeds, which aids in coating the guest particles onto the surface of the host particles.

2.4.3 Magnetically Assisted Impaction Coater (MAIC)

A schematic of the magnetically assisted impaction coating device is shown in Figure 2.4. Although MAIC can be used in a continuous mode (Hendrickson and Abbott, 1997), the small bench-scale device used at NJIT operates in a batch mode. A measured mass of both host and guest particles are placed into a processing vessel (125 ml glass bottle). A measured amount of magnetic particles is also placed in the processing vessel. The magnetic particles are made of barium ferrite and coated with polyurethane to help prevent contamination of the coated particles. An external oscillating magnetic field is created using a series of electromagnets surrounding the processing vessel. When a

magnetic field is created, the magnetic particles are excited and move furiously inside the vessel resembling a gas-fluidized bed system, but without the flowing gas. These agitated magnetic particles then impart energy to the host and guest particles, causing collisions and allowing coating to be achieved by means of impaction or peening of the guest particles onto the host particles.



Figure 2.4 Schematic of MAIC.

There are several unique features of MAIC that make it advantageous as a dry particle coating device. Firstly, the MAIC can coat soft organic host and guest particles without causing major changes in the material shape and size. Secondly, although there is some heat generated on a microscopic level due to the collisions of particles, there is negligible heat generation on a macroscopic level and hence no increase in temperature of the material during processing by MAIC. This is desirable when processing temperature sensitive powders such as pharmaceuticals. Lastly, the device can be operated both as a batch and continuous system making it versatile in the amount of material it can process.

2.4.4 Rotating Fluidized Bed Coater (RFBC)

This newly developed coating device operates on the principle of a rotating fluidized bed. The host and guest powder mixture are placed into the rotating bed and is fluidized by the radial flow of gas through the porous wall of the cylindrical distributor, as seen in Figure 2.5. Due to the high rotating speeds, very high centrifugal and shear forces are developed within the fluidized gas-powder system leading to the break-up of the agglomerates of the guest particles. Moreover, the very large flow of gas needed to fluidize the particles at high rotating speeds and the motion of bubbles when operating the bed above minimum fluidization conditions creates strong mixing and hence good coating is achieved. For example, at "100 g's", the minimum fluidization velocity can be 2 orders of magnitude greater than in a conventional "1 g" fluidized bed.



Figure 2.5 Schematic of the RFBC.

The RFBC has another advantage over a conventional fluidized bed in that very small host and guest particles belonging to Geldart group C are relatively easier to fluidize by increasing the rotating speed (Qian *et al.*, 2001). The RFBC also has the capability of being operated in a continuous mode, by feeding guest particles in with the

fluidizing gas and operating the RFBC in a vertical position so that host particles can be continuously fed into and removed from the device by gravity



Figure 2.6 Schematic of the Theta Composer

2.4.5 Theta Composer

A schematic showing the dimensions of the theta composer is shown in Figure 2.6. The theta composer consists of a slow rotating elliptical vessel (around 30 rpm) and a faster (500-3000 rpm) elliptical rotor. As the rotor rotates inside the vessel, the powder mixture consisting of host and guest particles is subjected to shear and compressive stresses as it is forced into the small clearance between the vessel and the rotor. As the rotor continues to move and the clearance between the vessel wall and the rotor becomes large, there is bulk mixing of the host and guest particles, as shown in Figure 2.6.

2.5 Devices Selected for Study

The newly developed RFBC and the theta composer are not used in this study. The RFBC is currently being analyzed by other students too create materials with new improved functionalities. The theta composer is currently not available at NJIT. NJIT is

the only institution where Mechanofusion, the Hybridizer, and the Magnetically Assisted Impaction Coating device are all available. As a result, this presents a unique opportunity whereby the coating performance of all three devices can be compared. The following chapters show a comparison of the three dry particle coating devices. The performance of the devices as a function of their key system and operating parameters are examined. Some of the numerous and diverse applications of dry particle coating are also presented.

CHAPTER 3

SURFACE MODIFICATION OF CELLULOSE AND CORNSTARCH 3.1 Dry Particle Coating with MAIC

3.1.1 Introduction

Many food and pharmaceutical ingredients, being organic and relatively soft, are very sensitive to heat and can quite easily be deformed by severe mechanical forces. Hence, soft coating methods that can attach the guest particles onto the host particles without degradation of particle size, shape and composition due to the build up of heat, are better candidates for such applications. The Magnetically Assisted Impaction Coating device can coat soft organic host and guest particles without causing much changes in the material shape and size. Furthermore, although there is some heat generated on a microscopic level and hence no increase in temperature of the material during processing in the MAIC. This is an added advantage when dealing with temperature sensitive powders such as pharmaceuticals.

Certain materials, such as cornstarch and cellulose, are important ingredients in food and pharmaceutical products. Cornstarch is frequently used as a food-thickening agent and as an inactive component of pharmaceuticals (Watano *et al.*, 1996). Cellulose is also a commonly used component in the composition of several processed foods and as a filler in pharmaceuticals. However, their cohesiveness (especially cornstarch) and hydrophilicity are undesirable. For example, cohesiveness causes problems in handling and hydrophilicity limits shelf life due to premature biodegradation or the growth of molds and other microorganisms on the surface. Also, materials can become sticky due to exposure to humid environments and there can be a loss of mechanical properties due to plasticization (Koenig *et al.*, 1994).

Fine powders are often used as flow aids by simply mixing the fines with the core material (Craik, 1958). However, simple mixing cannot change the material's hydrophilicity. Hence, the ability to modify these materials to simultaneously obtain better flow properties and also make them less hydrophilic or hydrophobic is not only advantageous, but also necessary to create composite materials with unique functionality.

Cornstarch is composed of two basic types of polymers – amylose and amylopectin. Amylose is a linear polymer where each of the monometric units (except the terminal units) contains one primary and two secondary hydroxyl groups. The hydroxyl groups impart hydrophilic properties to the polymer, which leads to an affinity for moisture, i.e., the hydroxyl groups act as sites for adsorbing moisture. Cornstarch has been chemically modified (by introducing hydrophobic ester groups at low levels of substitution), when it is desirable to impart improved flow properties to the powder (Furia, 1968). This modified cornstarch is a free flowing powder, which is also remarkably water repellant.

Cellulose fibers, similar to cornstarch, also contain hydroxyl groups (Furia, 1968) on their surfaces that are responsible for moisture absorption. To reduce the hydrophilicity of these materials, it is necessary to remove some of these hydroxyl groups either by chemical esterification or by some other surface modification process. In a series of publications, Senna (1996, 1998a, 1998b, and 1999), has convincingly shown that dissimilar metallic materials, notably complex oxide powders can be cross-linked by oxygen using a soft-mechanochemical process (mechanical stressing of the powders) by

proton transfer through OH groups, and subsequent electron transfer. The mechanochemical reaction is not restricted to inorganic materials, but is also applicable to complex formation between inorganic-organic or organic-organic materials and can be accomplished using easily available machines for grinding or comminution. Therefore, it is quite possible that particle processing by MAIC will promote a mechanochemical reaction between the almost neutral hydroxyl groups of cornstarch/cellulose and another material's more acidic hydrophilic OH groups by oxygen linkages and the removal of water molecules, to form hydrophobic groups (Figure 3.1).



Figure 3.1 Mechanochemistry effect occurring on the surface of cornstarch/cellulose to form hydrophobic groups.

Silica is one such candidate that can react with cornstarch/cellulose, as it possesses weak acidic hydrophilic silanol groups (-Si(OH)-) on its surface (Israelachvili, 1992). In addition, the fine silica particles coated onto the surface of the cornstarch can act as a flow aid by reducing the van der Waals forces between the larger host particles (Mei *et al.*, 1997). In this study silica particles have also been coated onto the surface of

cellulose (fiber-like particles with an aspect ratio of about 4 - 5) for the same purpose.

Cornstarch and cellulose were chosen as host particles for several reasons. Firstly, both materials are organic and the ability to process these materials in the MAIC without appreciably altering their properties based on shape and size will be a significant advantage. Secondly, as mentioned before, both materials are widely used commercially, but their poor flow and their high moisture absorption limit their applications. Hence, these materials are chosen to examine the feasibility of surface enhancement by MAIC as a way to broaden their usage.

3.1.2 Experimental

A schematic of the MAIC device (batch mode) was shown previously in Chapter 2 (Figure 2.4). With some modification, the device can also be operated continuously and has been scaled-up to process up to 800 lbs/hr (Hendrickson and Abbott, 1997). The device used in this study operates in a batch mode. A weighed amount of host and guest particles are placed into a processing vessel (125 ml glass bottle). The mass percentage of guest particles used in an experiment is usually calculated based on the assumption of 100% surface coverage of the host particles with a monolayer of guest particles. However, when coating with silica, only 1 weight % by mass of silica is used to conform to Food and Drug Administration (FDA) standards. Therefore, only very discrete coatings are obtained.

A measured mass of magnetic particles is also placed in the processing vessel. The magnetic particles are made of barium ferrite and coated with polyurethane to prevent contamination of the coated particles. An external magnetic field is created using a series of electromagnets surrounding the processing vessel. When a magnetic field is present, the magnetic particles are agitated and move furiously inside the vessel resembling a fluidized bed system. These agitated magnetic particles then impart energy to the host and guest particles, causing collisions and allowing coating to be achieved by means of impaction or peening of the guest particles onto the host particles.

The feasibility of the MAIC to modify the surface properties of cornstarch and cellulose host particles by coating with silica guest particles was studied. The physical properties of the materials and the experimental operating parameters are given in Tables 3.1 and 3.2, respectively. The coated cornstarch and cellulose products were examined with a Scanning Electron Microscope (SEM) to study the surface morphology and particle shape after coating. Energy Dispersive X-ray Spectroscopy (EDX) was used to study the surface composition of the coated products. In some cases, an API Aerosizer was also used to measure the particle size distribution and mean particle size of the coated sample as a function of processing time. The flowability of the products was analyzed by measuring the angle of repose (AOR) using a fixed base method.

Wettability tests were conducted by using the penetration rate method (Kaya *et al.*, 1988; Watano *et al.*, 1996) to evaluate the hydrophilicity of the coated products. In the penetration rate method, powder is filled into a column, and the change in the amount of liquid penetrating into the powder layer is measured. The powder was compacted to the same voidage by controlling the mass of powder used and the height to which the powder was compressed. The controlled voidage for both materials studied was 0.35. Fourier Transform Infrared Spectroscopy (FT-IR) was also used to study the changes in

O-H groups of the samples before and after coating to lend support to the hydrophilicity studies.

| System 1 | |
|--|---------------------|
| Host particle size: cornstarch (µm) | 15 |
| Guest particle size: silica (µm) | 0.3 |
| Agglomerate guest particle size: silica (µm) | 35 |
| System 2 | |
| Host particle size: cellulose (µm) | Aspect Ratio of 4-5 |
| | (180/40 µm) |
| Guest particle size: silica (µm) | 0.3 |

Table 3.2 Operating Parameters for Surface Modification Study

| Primary particle size: magnet (mm) | 1.4 |
|--|-----------|
| Mass susceptibility of magnetic particle (emu/g) | 24.66 |
| Mass ratio of magnets/powder | 1, 2 |
| Mass ratio of guest/host | 1% |
| Average magnetic field strength (mT) | 40 |
| Processing time (min) | 5, 10, 20 |
| Volume of processing chamber (ml) | 125 |

3.2 Results and Discussion

3.2.1 Surface Morphology and Surface Elemental Mapping

SEM micrographs of cornstarch before and after coating (10 minute processing time) are shown in Figures 3.2a and 3.2b, respectively. An elemental mapping of silicon on the

surface of the 10 minute coated product is shown in Figure 3.2c. After processing in the MAIC device, small silica agglomerates ($\leq 3 \mu m$) are observed on the surface of cornstarch. Due to the very small size of the primary particles of silica, these particles have a natural tendency to form very large agglomerates, approximately 35 μm in diameter as observed by the SEM. The absence of these large agglomerates after coating suggests that they are broken up into smaller primary sizes (deagglomeration) during the MAIC process. This observation is in contrast to using large PMMA particles (mean size of 200 μm) as the host particles and silica as the guest particles. In that study, large silica agglomerates were still seen on the surface of the PMMA particles after being subject to various processing times in the MAIC device.

The difference in these two systems shows the importance of the host to guest particle size ratio in the coating mechanism. When the primary guest particles are in the sub-micron range, the attraction forces (van der Waals, electrostatic, etc.) among the primary particles are relatively strong and require larger forces to separate them. Smaller host particles can obtain larger velocities than larger host particles from collisions with the magnetic particles, resulting in higher forces of impaction, sufficient to break the agglomerated guest particle structure. In addition to the deagglomeration of the guest particles, it should be emphasized that cornstarch still maintains its disc like shape after processing. This is also a unique feature of the MAIC device, in that after processing, soft organic materials still maintain almost their original shape and size. The elemental mapping (Figure 3.2c) confirms the small particles on the surface of cornstarch as silica.



Figure 3.2 SEM micrographs of (a) unmodified cornstarch, (b) cornstarch processed for 5 minutes and (c) EDX mapping of silicon on the surface of modified cornstarch.

A SEM micrograph of unmodified cellulose is shown in Figure 3.3a. The particles are fiber-like with an aspect ratio of 4-5. SEM micrographs showing the surface morphology of cellulose coated with silica for processing times of 5 and 10 minutes are shown in Figures 3.3b and 3.3c, respectively. Observation of cellulose coated products also showed the presence of silica on the surface (Figures 3.3b and 3.3c). As the processing time increased from 5 to 10 minutes, the area of surface coverage also increased. At a higher processing time of 20 minutes, there was no visible change in the surface coverage of cellulose as compared to the 10-minute cellulose product.



Figure 3.3 SEM micrographs of (a) unmodified cellulose, (b) cellulose coated with silica for 5 minutes and (c) cellulose coated with silica for 10 minutes.

3.2.2 Flowability

The angle of repose (AOR) is a commonly used index for flowability; hence, it is used in this work to evaluate the coating effectiveness in terms of improving flow properties. The results for the angle of repose of cornstarch products for 2 different magnetic particle to powder mass ratios are shown in Figure 3.4. The value shown for each processing time is an average of four AOR measurements obtained by a digital camera. While the humidity at which the tests were conducted was not controlled, the experiments were all performed on the same day and under the same conditions (all samples were dried in an oven before the experiments for the same time), therefore minimizing the error associated with changes in humidity. The AOR for untreated cornstarch is approximately 59°, as shown in the figure. The AOR decreases as processing time increases for both magnetic

particles to powder mass ratio, indicating improvement in the flow of cornstarch due to a surface coating of silica. For example, it is 54° after 5 minutes for a magnetic particle to powder mass ratio of 1, further decreasing to about 47° after 20 minutes. When the magnetic particle to powder ratio increases, the collision frequency of the magnets and the powders also increases. Thus, the same coating conditions are achieved at shorter processing times as seen in Figure 3.4. This is evidenced by the lower AOR at 5 minutes for the larger magnetic particle mass ratio of 2.



Figure 3.4 Flowability of cornstarch as a function of processing time for two different magnetic particle to powder mass ratios.

Craik (1958) tested several materials, including silica, as a flow aid by mixing them with cornstarch. However, the addition of silica did not improve the flowability. In the study done by Craik (1958) a similar fixed base AOR method to that used in this investigation was utilized to measure the angle of repose. In that study, large silica aggregates were observed. The presence of the large aggregates indicates that simple mixing cannot break the agglomerates due to the large attractive forces between the individual silica particles as discussed above. In contrast, in the MAIC it is possible to coat fine silica particles onto the cornstarch surface by first de-agglomerating the silica. The difference between these studies shows the importance of the size of guest particles in improving flowability.

The results for the angle of repose of the coated cellulose products as a function of processing time are shown in Figure 3.5. As was found with cornstarch, a surface coating of silica increased the flowability of the cellulose for all processing times investigated. However, a processing time of 10 minutes yielded the best flowing cellulose. Unlike the coated cornstarch product, further increases in the processing time did not improve the flowability. In fact, the flowability of the cellulose decreased after a processing time of 10 minutes suggesting that longer processing times may actually degrade the surface coating or the cellulose fiber host particles, perhaps because of their relatively high aspect ratio. While it could not be accurately determined whether the surface coating degrades, Figure 3.6 shows that for all of the processing times examined, there was a reduction in the mean particle size of the fibers. This indicated that the MAIC process is causing significant attrition of the high aspect ratio cellulose fibers. Each value given in the figure is the average of five measurements. Thus, it appears that attrition causes a decrease in flowability for a processing time greater than 10 minutes.

The ability to improve the flowability of a material by coating with fine particles has been discussed by Mei *et al.*, (1997). The authors used a discrete element simulation of powder flows between a moving and stationary plate to examine the effect of fine coatings on the surface of a larger substrate. They also developed an extended JKR (Johnson-Kendall-Roberts) particle contact model to include the effect of particle coating on the force-displacement relationship due to surface energy and elastic deformation. Their results indicated that the cohesion force between two primary particles in the presence of a fine coating is directly proportional to the size ratio of the coating particles to the host powder particle and results in drastic reduction in the cohesion forces.



Figure 3.5 Flowability of cellulose as a function of processing time for a magnetic particle to powder ratio of 2.

This argument has been adapted to explain the improved flowability of cornstarch and cellulose in the presence of a discrete coating of silica as obtained by MAIC. The fine silica particles reduce the van der Waals attraction force between the host particles making them flow more easily. The number of guest particles on the surface of the host particles has only a minor effect on the flowability once the cohesion force is reduced by one or more coating particles. Hence, even with a very discrete coating on the surface of the host particle, there is significant improvement in the flowability of the material.



Processing time (minutes)

Figure 3.6 Volume-mean particle size of cellulose as a function of processing time.

3.2.3 Hydrophilicity

To measure the changes in the hydrophilicity of the surface of cornstarch and cellulose, wettability tests of the coated product were conducted. This was done using a rate penetration method, whereby a column was filled with the powder and a load applied to compact and control the voidage of the powder. The voidage was set at a value of 0.35 for both materials. Then, to investigate the mass percentage of water being absorbed, the column was gently submerged into a petri dish of water. The weight change of the water in the dish (that absorbed by the sample) was measured as a function of time.

The water absorption results for the coated cornstarch products (products from the magnetic particle to powder mass ratio of 2 were used for this test), together with silica alone and cornstarch alone, are shown in Figure 3.7. Silica is very hydrophilic in nature and absorbed approximately 110 % of its weight in water, during an exposure time of 5 minutes as shown in Figure 3.7. Unmodified cornstarch is also hydrophilic and absorbed

about 60% of its weight in water for the same 5 minute period of exposure. For cornstarch processed in the MAIC for a time of 5 minutes, it is observed that the water absorption is reduced to about 28% of the weight of cornstarch using the rate penetration test. A larger processing time of 20 minutes further reduced the mass percentage of water absorbed by the cornstarch to about 18%.



Figure 3.7 Wettability study of (a) silica, (b) cornstarch, (c) cornstarch processed for 5 minutes and (d) cornstarch processed for 20 minutes.

For the coated cellulose products, water absorption capacities of unmodified cellulose and coated products at 5, 10 and 20 minutes processing times are shown in Figure 3.8. The results were also obtained by the rate penetration method. The water absorption capacities decreased for all of the processing times investigated. The absorption capacity at 10 minutes, however, was lower than that at 20 minutes, again indicating deterioration of the surface coating or attrition of the host particles with increased processing time as was observed in the flowability study. This behavior was also observed for PMMA coated with alumina in the MAIC process. The surface coating

condition of PMMA deteriorated with increased processing times. It is conjectured that the continuous impaction and collisions of the magnets onto the host particles can destroy the coating integrity as well as change the size and shape of the material, after optimum processing conditions are reached.



Figure 3.8 Wettability study of (a) uncoated cellulose and cellulose processed for (b) 20, (c) 5 and (d) 10 minutes, respectively.

A reduction in hydrophilicity is believed to result from the reaction of the acidic silanol groups (-Si(OH)-) on the silica surface and the almost neutral hydroxyl groups (-(OH)-) on the cornstarch/cellulose surfaces, to form hydrophobic groups (previously shown in Figure 3.1) by releasing water molecules. The high mechanical forces arising from the particle collisions during "fluidization" enhances the reaction by mechanochemistry (Liao *et al.*, 1995). In order to confirm the hypothesis of a mechanochemical mechanism for the reduction in water absorption as described above, we used Fourier Transform Infrared Spectroscopy (FT-IR) to measure the changes in OH groups before and after coating.

FT-IR results are presented in Figures 3.9 and 3.10, for cornstarch and cellulose, respectively. In Figure 3.9, there is a reduction in the absorption caused by O-H stretching vibrations between the wavenumber of 3100 and 3650 cm⁻¹ for the coated samples as compared to the uncoated cornstarch, indicating a reduction in the O-H groups on the surface of the samples. There is also a significant reduction in absorption due to O-H stretching vibrations with an increase in processing time from 10 to 20 minutes again within the above mention wavenumber range. Figure 3.10 (for cellulose) shows that the least absorption caused by O-H stretching vibrations is obtained for the 10 minute processed sample. This appears to confirm the hydrophilicity studies for cellulose presented in Figure 3.8. This increase in absorption of the 20 minutes coated sample can be attributed to the significant attrition or reduction in the particle size of the cellulose fibers, making more O-H sited available for IR absorption due to increased surface area.



Figure 3.9 IR absorption caused by O-H stretching vibrations for (a) uncoated cornstarch, (b) cornstarch coated for 10 minutes and (c) cornstarch coated for 20 minutes.

The FT-IR results lend credence to the hypothesis that MAIC processing caused a mechanochemical surface reaction between the corn starch/cellulose host particles and the silica guest particles. This represents a new contribution, as for the first time some evidence is presented that MAIC is capable of causing mechanochemical effects.



Figure 3.10 IR absorption caused by O-H stretching vibrations for (a) uncoated cellulose, (b) cellulose coated for 10 minutes and (c) cellulose coated for 20 minutes.

3.3 Conclusions

Cornstarch and cellulose particles were both modified in the MAIC device by the application of a discrete coating of silica on their surfaces. Both materials flowed better after a coating of silica was added to the surface. At long processing times of 20 minutes, due to the size reduction of the cellulose host particle, there was a reduction in the flowability of the material. Wettability tests revealed that coated products absorbed less water after coating, indicating a reduction in hydrophilicity. Also, the wettability results were confirmed by FT-IR, which showed a reduction in OH groups for the coated materials.

CHAPTER 4

THE PROMOTION OF DEACTIVATED SINTERING BY DRY PARTICLE COATING

4.1 Introduction

Many industrial processes use particles either as starting materials, during processing or as desired end products. The food, pharmaceutical, cosmetics, toner, and catalytic industries are just some of the many examples that employ particle technology and science during mixing, granulation, compaction, coating, storage, and handling. As a result of the extensive use of particles, and the variation of their behavior as a function of material properties, the desire to understand their behavior is vital to the success as well as the optimization of their processing.

The thermal behavior of particles has generated much interest and as a result has been studied extensively by many researchers. From these studies, numerous findings of particle behavior as a function of temperature have resulted. One such finding is defined as the sintering temperature of a particle. When two particles in mutual contact form a system that is not thermodynamically stable as the total surface free energy is not a minimum, the two particles in the system if left for a period of time begin to bond (Kuczynski, 1949a). Bonding occurs in order to decrease the total surface area even though the particles are at temperatures lower than their melting temperature. This phenomenon of the bonding of two or more particles with the application of heat at temperatures below the melting point of the particles is called sintering. At the minimum sintering temperature where sintering just begins, two phenomena are observed to occur simultaneously (Bonis *et al.*, 1964). First, the contact area of the particles touching each other grows, i.e. the neck between the particles increases, as shown in Figure 4.1. Secondly, loose powder aggregates or compacts become denser by a decrease in the distance between the centers of the particles. This results in an overall decrease in the total volume of the sample, Figure 4.2, and the approach to the theoretical density of the material.



Figure 4.1 Comparison of contact area between two particles before and after sintering.



Figure 4.2 Comparison of total sample volume before and after sintering.

The first, and by now, classical experiments on the mechanism of material transport in sintering powders were presented by Kuczynski (1949a and 1949b). His study examined the driving force of sintering for metals and glass. Several investigators have gone on to present compiled works on the sintering behavior and mechanisms of ceramics and polymers (Coble, 1961). Studies have also been conducted on the sintering behavior of a two-component system, where one material is coated with about 0.01% by weight of another material to enhance the sintering rate of the material. This is referred
to as "activated sintering" whereby the sintering temperature of the material is lowered by the addition of a monolayer of a second component. For metals, nickel-activated sintering of tungsten has been reported (Brophy, 1961). The effect was pronounced, as normally tungsten sinters at temperatures around 2700°C to get near the theoretical density. However, with the addition of 0.01 wt. % nickel, the theoretical density of tungsten was obtained at about 1400°C. For the ceramic analogy, activated sintering of beryllia was found to occur with small additions of calcium oxide. With a calcium oxide addition to beryllia, the approximate temperature required to achieve high density was lowered by several hundred degrees Centigrade.

Activated sintering has also been used to describe the formation of composites whereby a low concentration of one material is added to another material to promote grain boundary segregation to increase diffusion rates. This increase in diffusion rates gives rise to faster rates of sintering, hence lowers the sintering temperatures of the material (German *et al.*, 1976a and 1976b; Li *et al.*, 1983; Panin *et al.*, 1996; Luo *et al.*, 1999). Activated sintering of materials by a surface coating or formation of uniquely tailored composites is well discussed in the literature and plays an important role in many applications.

There is however, no information on two-component systems for "deactivated sintering". Deactivated sintering can be defined as a process whereby the surface of particles are coated with a monolayer of another material to delay and reduce the sintering of the materials, hence causing an increase in the sintering temperature. The delay in sintering is believed to be caused by an increase in activation energy of the system, which gives rise to slower rates of diffusion. The question then arises as to the importance and application of increasing the sintering temperatures of materials. There are several applications in which deactivated sintering can be useful. One such application is in fluidized beds used in the petrochemical and many other industries. In these fluidized beds, the use of a catalytic material is confined to a specific temperature range, which controls the product yield. Temperature control within this range is very important, as an unmonitored increase in temperature will cause the catalytic material to soften and fuse together (sinter). As this begins to occur, the sizes of the particles change as they begin to aggregate. To keep the fluidized bed active or "alive", quick adjustments must be made to the gas velocity of the process (Siegell, 1984). If this is not done in time the bed can become inactive or "dead", resulting in a significant loss of time and money. The application of a surface coating to promote deactivated sintering of these materials can allow beds to be run at higher temperatures without fear of de-fluidization by sintering. Deactivated sintering technology can also be expanded to include glass and polymeric particles used in fluidized bed applications, where de-fluidization due to the sticking of particles to form large agglomerates is of a primary concern.

A second possible application under investigation is in the coating of polymeric materials. Many polymeric materials are used for the construction of spacecraft, but in low orbit space-flight, these polymers are subjected to destructive components, such as ionizing radiation (KeV electrons and MeV protons), vacuum ultraviolet photons and extreme temperatures. As a result, these materials suffer rapid erosion and surface roughing (Houdayer *et al.*, 1997). The polymers may undergo an irreversible degradation of their physical properties such as optical, thermal and electrical, for which they have been designed for specifically. It has been reported that a thin inorganic coating on the

polymer materials can protect the surfaces to prevent this degradation from occurring. Therefore, coating the surface of a material to promote deactivated sintering can also provide a protection layer to prevent the degradation of the polymeric material at elevated temperatures.

In 1945, to understand the mechanism of sintering, Frenkel (1945) made the first attempt to develop a theory of sintering. In this study it was assumed that the process was due to a slow deformation of the crystalline particles under the influence of surface tension, which reduces to a viscous flow. Kuczynski (1949a) then went on to discuss several possible mechanisms of sintering and, unlike other researchers, presented experimental data to define the predominant mechanism. Here, the four possible mechanisms for the transport of material to form a bond between two particles were defined as surface diffusion, volume diffusion, viscous flow, and evaporation.

Surface and volume diffusion is produced by the motion of atoms from one place to an adjacent place in the lattice structure. This occurs from regions of high density to porous sections of the material. Surface diffusion has been reported to be only important during the initial stage of sintering and is caused by the initial adhesion between the particles. Surface diffusion cannot promote substantial densification. Volume diffusion is chiefly responsible for densification. Surface and volume diffusion mechanisms are the predominant mechanisms of sintering in crystalline and metallic particles.

Unlike diffusion mechanisms of sintering, sintering by viscous flow involves the movement of lattice planes from high to low vacancy concentration areas, which is initiated by the effects of surface tension an external forces (Tardos *et al.*, 1984). Sintering by a viscous flow mechanism is the predominant means of material transport

for the sintering of polymeric, glassy and non-metallic materials. The evaporation or condensation mechanism of sintering involves transport in the vapor phase. This is considered the least important mechanism of sintering.

Johnson and German (1996) went on to expand the volume mechanism presented by Kuczynski (1949a) and the three stages presented by (Coble, 1961) to derive a theoretical model for activated solid-solid sintering. Activated sintering described by Johnson and German (1996), involved the formation of composites with small additions of transition elements to metals aimed at accelerating the sintering rate by decreasing the activation energy for diffusion at the grain boundary, resulting in higher diffusion rates. The three stages used to define sintering in this model are the initial, the intermediate and the final stage. In the initial stage, there is neck growth and densification as the distance between the centers of particles in contact decreases. After some time, when the neck region has decreased sufficiently, the equations for initial sintering are no longer valid. The intermediate stage involves the rounding and smoothing of the inter-connective pores at the grain boundaries. In the final stage, as densification continues, the pores begin to close and the microstructure of the particles are then defined by spherical pores at the grain boundaries (Coble, 1958).

Here dry particle coating is used to synthesize materials for the promotion of deactivated sintering, i.e. a reduction of sintering rates to increase the sintering temperatures of particulate materials. Several host particles are coated with small amounts of the highly refractory SiC (guest particles) in three dry particle coating devices. The three devices used are MAIC, Mechanofusion (MF), and the Hybridizer (HB). The host particles chosen are PMMA, glass beads, a high purity γ -alumina, a

thermally stabilized γ -alumina (3% Lanthanum), and a composite of alumina and silica. The properties of these particles as well as the properties of the SiC guest particles are given in Table 4.1. Glass beads and PMMA are chosen as host particles, as they are perfectly spherical, non-porous surfaces, and can be coated quite uniformly with silicon carbide guest particles. They are excellent model systems to study deactivated sintering. Alumina-Silica, γ -alumina, and 3% Lanthanum thermally stabilized γ -alumina are chosen as host particles as they represent true systems of interest, in that they are porous particles, irregular in shape and most importantly are actual catalytic support materials commercially available. SiC is chosen as the guest particle for all of the host particles as it has a very high melting point and thus a corresponding high sintering point.

| Samples | Density | Size (µm) | Description |
|---------------------|---------|--------------|-------------------------------|
| | (g/cm) | | |
| PMMA | 1.19 | 200 | Spherical, smooth, non porous |
| Glass beads | 2.5 | 300 | Spherical, smooth, non porous |
| Alumina-Silica | 3.6 | 40 | Irregular, porous |
| High Purity Alumina | 3.9 | 80 | Irregular, porous |
| La Enhanced Alumina | 3.9 | >63 (Sieved) | Irregular, porous |
| SiC | 3.2 | 0.5 | Irregular |

Table 4.1 Properties of Host and Guest Particles

In this investigation, the coated products are analyzed to compare the coating performance of each device and to examine the changes in the sintering rates of the materials for the promotion deactivated sintering. Several characterization techniques are used to fulfill these objectives. Particle size analysis (API Aerosizer) is conducted to measure changes in the size of the materials after processing. A Scanning Electron Microscope (SEM) and an Optical Microscope are used to examine the surface morphology and neck growth of sintered particles. EDX is used to show the presence of silicon (from silicon carbide) on the surface. BET surface area analysis is used to measure changes in the surface area of the host particles after coating and after sintering. A modified vertical Dilatometer (Figure 4.3) is used to measure the sintering temperatures of the materials (Compo *et al.*, 1987). In this device, the samples, before and after being coated, are individually heated in the dilatometer, and the expansion/contraction of the material as a function of temperature is plotted. From these curves, the minimum sintering temperature, defined as the lowest temperature at which the surface of the particles begin to soften and the sintering process begins (represented by a sharp drop in the dilation versus temperature curve), is obtained (Compo *et al.* 1987).

A simple model to explain the phenomenon of deactivated sintering is proposed based on the previous works of Kuczynski (1949a), Coble (1958), Johnson and German (1996), and Tardos *et al.*, (1984). The model highlights the fact that by the addition of a surface layer of SiC, there is a significant reduction in the diffusion rates at the initial stages of sintering for alumina-SiC samples. For coated glasses and polymers, an increase in the surface viscosity of the particles with a coating of SiC is postulated as the mechanism of deactivated sintering.



Figure 4.3 Schematic of the modified vertical dilatometer.

4.2 Experimental

Measured amounts of host and guest particles are processed in the three dry coating devices. The mass percentage of guest particles to be used in an experiment is usually calculated based on the assumption of 100% surface coverage of the host particles with a monolayer of guest particles. The assumptions for the calculation are that all guest particles are of the same size, the host and guest particles are spherical, and the guest particles do not undergo deformation. From these assumptions, the number of guest particles N, required to coat 1 host particle with a continuous monolayer is derived from the following expression:

$$N = \frac{S_{D+d}}{S_d} = \frac{\pi (D+d)^2}{\frac{\pi d^2}{4}} = \frac{4(D+d)^2}{d^2}$$
(4.1)

where S_{D+d} is the surface area of the sphere with diameter (D+d), S_d is the cross sectional area of a guest particle, D is the diameter of a host particle and d is the diameter of a guest particle. The mass ratio of host to guest particle for a given system is derived as follows:

| Number ratio: | 1 | Host | : | Ν | Guest |
|---------------|----------------------------|------|---|--------------------------------|-------|
| Volume ratio: | $1 \ge D^3$ | Host | : | $N \ge d^3$ | Guest |
| Mass ratio: | $1 \ x \ D^3 \ x \ \rho_D$ | Host | : | $N \; x \; d^3 \; x \; \rho_d$ | Guest |

Therefore for any give batch size, based on 100% surface coverage, the weight percentage of guest particles to be used is:

$$Gwt\% = \frac{\left(N \times d^3 \times \rho_d\right)}{\left(D^3 \times \rho_D\right) + \left(N \times d^3 \times \rho_d\right)} \times 100$$
(4.2)

where, N is given by Equation 4.1, ρ_D is the density of the host material, and ρ_d is the density of the guest material.

For the MAIC, a measured amount of magnets is also placed in with the host and guest particles, at a predefined mass ratio (usually 2). The schematics of the three dry particle coating devices were previously shown in Chapter 2. The mass percentages of guest particles used in each experiment are listed in Tables 4.2 to 4.4. The processing times, batch size (amount of material processed in each device) and rotational speeds at which the devices are operated at, are also shown in Tables 4.2 to 4.4.

| Samples | Processing Time | e Wt % Guest Total Batch Siz | | |
|---------------------|-----------------|------------------------------|----|--|
| | (minutes) | | | |
| PMMA/SiC | 10 | 3 | 10 | |
| Glass beads/SiC | 10 | 0.8, 8 | 10 | |
| High purity alumina | 10 | 2 | 10 | |
| La-alumina | 2, 5 | 2 | 10 | |
| Alumina/SiC | 2.5, 5, 10 | 2 | 10 | |

 Table 4.2 Operating Parameters for MAIC

 Table 4.3 Operating Parameters for Mechanofusion (600 RPM)

| Samples | Processing Time | Wt % | Total Batch Size (g) |
|---------------------|-----------------|--------|----------------------|
| | (minutes) | Guest | |
| PMMA/SiC | 10 | 3 | 50 |
| Glass beads/SiC | 10 | 0.8, 8 | 100 |
| High purity alumina | 10, 20 | 2 | 50 |
| La-alumina | N/A | N/A | N/A |
| Alumina/SiC | N/A | N/A | N/A |

| Table 4.4 Operating Parameters for Hydrolizer (0000 KFM | Table 4.4 | Operating | Parameters | for Hybridize | r (6000 RPM |
|--|-----------|-----------|------------|---------------|-------------|
|--|-----------|-----------|------------|---------------|-------------|

| Sample | Processing | Wt % | Total Batch Size (g) |
|---------------------|----------------|-------|----------------------|
| | Time (minutes) | Guest | |
| PMMA/SiC | 5 | 3 | 20 |
| Glass beads/SiC | N/A | N/A | N/A |
| High purity alumina | 2 | 2 | 20 |
| La-alumina | 2 | 1 | 20 |
| Alumina/SiC | 2 | 2 | 50 |

4.3 Results and Discussion

4.3.1 PMMA

The glass transition temperature of uncoated PMMA is approximately 105°C (Lide, 1998) and the softening temperature is approximately 110°C. The weight percentage of guest particles used is 3%, and is based on the assumption that 100% of the surface of the PMMA host particle is covered with a monolayer of SiC (Equation 4.2). The coated samples obtained from the three devices, as well as uncoated PMMA, were heated to different temperatures in the dilatometer to examine the degree of sintering as a function of temperature. The temperatures used were 130°C and 150°C, respectively. Optical micrographs of the uncoated samples and the coated samples, at room temperature are shown in Figure 4.4a to 4.4d. At 130°C, the uncoated sample showed beginning signs of sintering, whereas the coated samples from all three devices showed no signs of neck growth or fusion between particles. Optical micrographs for the uncoated and the MAIC coated sample are shown in Figure 4.5a and Figure 4.5b, respectively.

At 150°C, the uncoated PMMA was a solid fused mass (Figures 4.6a). The MAIC, MF and HB coated samples showed initial signs of sintering at 150°C (Figures 4.6b to 4.6d), but were mainly loose individual particles. SEM micrographs of uncoated PMMA and PMMA coated in the MAIC, MF and HB at room temperature are shown in Figures 4.7a to 4.7d, respectively. The samples coated in all three devices were uniformly coated with a layer of SiC. The MAIC and the MF samples were discretely covered, while the HB samples were more densely coated. The contraction as a function of temperature for the uncoated as well as the coated samples heated to 150°C in the

dilatometer is shown in Figure 4.8. There was a larger shrinkage of the uncoated than the coated samples when heated to 150°C, as shown in Figure 4.8.



Figure 4.4 Optimal micrographs of (a) uncoated PMMA (b) HB coated PMMA (c) MAIC coated PMMA and (d) MF coated PMMA, at room temperature.



Figure 4.5 Optimal micrographs of (a) uncoated PMMA and (b) MAIC coated PMMA heated to 130°C in the dilatometer.



Figure 4.6 Optimal micrographs of (a) uncoated PMMA (b) HB coated PMMA (c) MAIC coated PMMA and (d) MF coated PMMA, heated to 150° C in the dilatometer.



Figure 4.7 SEM micrographs of (a) uncoated PMMA (b) HB coated PMMA (c) MAIC coated PMMA and (d) MF coated PMMA, at room temperature.



Figure 4.8. Contraction of PMMA samples heated to 150°C in the dilatometer.

4.3.2 Glass Beads

Glass bead samples processed in the HB were crushed due to their brittle nature. The samples prepared in the MAIC and MF used two different weight percentage of guest particles, 0.8% and 8%, respectively. This was done to examine the degree of sintering as a function of guest weight percentage. The amount of guest particles required to cover 100% of the surface a glass bead with a monolayer, from Equation 4.2, is 0.8 wt. % of SiC. The coated samples, as well as the uncoated glass beads were heated to 600, 700 and 800°C in the dilatometer, respectively. The minimum sintering temperature of uncoated glass beads is approximately 575°C (Tardos *et al.*, 1984).

The results for the MAIC coated samples are presented as follows. Optical micrographs of the uncoated and 0.8 wt. % and 8% wt. coated samples, at room temperature are shown in Figure 4.9. At 600°C, the uncoated sample showed beginning signs of sintering with some increases in contact area. This increase in contact area was

not visible with the 0.8 and 8 wt. % guest coated samples, Figures 4.10a to 4.10c. At 700°C, most of the uncoated sample was fused together, whereas the 0.8 and 8 wt. % coated samples remained individual particles, as shown in Figures 4.11a to 4.11c. At 800°C, both the uncoated and the 0.8 wt. % coated samples were completely fused, as shown in Figures 4.12a and 4.12b, respectively. However, the 8 wt. % guest coated sample still remained individual particles with just a small amount of neck growth visible, Figure 4.12c. Similar results were obtained for the MF processed particles. This clearly showed that a thicker, more continuous coverage coating results in better promotion of deactivated sintering. SEM micrographs of glass beads uncoated and 4.13b, respectively. A thick uniform coating of SiC on the surface is clearly visible for the MAIC coated sample.



Figure 4.9 Optical micrographs of (a) uncoated glass beads (b) 0.8 wt. % SiC coated glass beads and (c) 8 wt. % SiC coated glass beads, at room temperature.



Figure 4.10 Optical micrographs of (a) uncoated glass beads (b) 0.8 wt. % SiC coated glass beads and (c) 8 wt. % SiC coated glass beads, heated in the dilatometer to 600°C.



Figure 4.11 Optical micrographs of (a) uncoated glass beads (b) 0.8 wt. % SiC coated glass beads and (c) 8 wt. % SiC coated glass beads, heated in the dilatometer to 700°C.



Figure 4.12 Optical micrographs of (a) uncoated glass beads (b) 0.8 wt. % SiC coated glass beads and (c) 8 wt. % SiC coated glass beads, heated in the dilatometer to 800°C.



Figure 4.13 SEM micrographs of (a) uncoated glass beads and (b) 0.8 wt. % SiC coated glass beads (c) 8 wt. % SiC coated glass beads, at room temperature.

4.3.3 High Purity γ-Alumina

SEM micrographs of the uncoated and the MF coated samples are shown in Figure 4.14. The EDX mappings of silicon on the surface of the coated samples obtained from the three devices are shown in Figure 4.15. The weight percentage of guest particles used in the coating devices was 2, based on Equation 4.2



Figure 4.14 SEM micrographs of (a) alumina uncoated and (b) alumina coated for 10 minutes in the MF, at room temperature.



Figure 4.15 SEM micrographs with corresponding EDX mapping of silicon for (a) HB coated alumina (2 min., 6000 rpm), (b) MAIC coated alumina (5 min.), and (c) MF coated alumina (10 min., 600 rpm).

The BET measured specific surface area and the average pore size of the uncoated and coated samples before sintering are shown in Figures 4.16 and 4.17 respectively. It can be seen that by placing a coating of SIC on alumina did not decrease the surface area or reduce the average pore size by clogging and blocking the pores, which were initial concerns.



Figure 4.16 BET specific surface area at room temperature.

Figure 4.17 BET average pore size at room temperature.

The dilatometry results of contraction as a function of temperature for uncoated alumina, and alumina processed in the MAIC (5 minutes), MF (10 minutes, 600 rpm) and the HB (2 minutes, 6000 rpm) heated to 1550°C are shown in Figure 4.18. Where the greatest change in gradient occurs for each curve is a measure of the minimum sintering temperature. It can be seen that all coated samples had a higher minimum sintering temperature than the uncoated sample, with the MF sample showing the highest. The percentage of shrinkage as a function of temperature is shown in Figure 4.19. The uncoated samples had an overall shrinkage of about 9%, while the coated samples had overall shrinkage less than 3%. The mechanofusion samples had the lowest shrinkage of about 0.75%.



Figure 4.18 Elongation-contraction vs. temperature for (a) uncoated alumina, (b) alumina coated in MAIC (5minutes), (c) alumina coated HB (2 minutes, 6000 rpm) and (d) alumina coated in MF (10 minutes, 600 rpm).



Figure 4.19. Shrinkage as a function of temperature for (a) uncoated alumina, (b) alumina coated in MAIC (5minutes), (c) alumina coated HB (2 minutes, 6000 rpm) and (d) alumina coated in MF (10 minutes, 600 rpm).

SEM micrographs of the samples after being heated to 1550° C confirmed the dilatometry results, by showing fully sintered uncoated particles and partially sintered coated samples obtained from the HB, MAIC, and MF, Figures 4.20a to 4.20d, respectively. The specific surface area and the average pore size of the uncoated and coated samples after sintering are shown in Figures 4.21 and 4.22, respectively. As expected, after being heated to 1550° C in the dilatometer, there was a drastic reduction in the specific surface area of the material due to the phase change from γ to α (Hong *et al.*, 1997). A subsequent increase in the average pore size is to be expected for phase change due to the changes in the crystalline structure of the material. However, when the samples were heated to 1550° C (a very high temperature), the results showed both increases and decreases, which can be due to the changes in the structure of the material, as well as sintering of the pores of the material.



Figure 4.20 SEM micrographs of (a) uncoated, (b) MAIC coated (c) HB coated and (d) MF coated samples, heated to 1550°C in the dilatometer.



Figure 4.21 BET specific surface area of samples heated to 1550°C in the dilatometer.



Figure 4.22 BET average pore size of uncoated and coated samples heated to 1550°C in the dilatometer.



Figure 4.23 BET specific surface area of uncoated and coated samples as a function of temperature.

A close looker at phase transformation was observed by heating the uncoated and MAIC coated sample to 800, 1000, and 1250°C in the dilatometer and then measuring the specific surface area. The specific surface area of the uncoated and coated samples as a

function of temperature is shown in Figure 4.23. It can clearly be seen that the phase change from γ to α takes place around 1000°C, much lower than the sintering temperature of the uncoated material. Therefore, by coating high purity γ -alumina with SiC promotes deactivated sintering at elevated temperatures, i.e. prevents the sticking and softening of the surfaces. However, the reduction in surface area due to the phase change from γ to α , makes the material unattractive as a catalytic support at high temperatures.

4.3.4 Thermally Stabilized High Purity γ-Alumina

The desire to promote deactivated sintering in a material that could maintain its surface area at elevated temperatures, lead to the use of a 3% lanthanum (La) thermally stabilized alumina (manufactured by Alcoa). The use of thermally stabilized catalytic supports to ensure that there is minimum phase change, allowing a maximum maintenance of specific surface area is well documented (Arai and Machida, 1996). The La thermally stabilized alumina was a very weak composite material. This material was coated with 1% and 2 % SiC in both MAIC and the HB, respectively. There were tremendous size changes in the material when processed in both devices, even for very short processing times of 1 and 2 minutes. The size changes were evident from the reduction in the flowability of the material and from SEM micrographs. SEM micrographs of uncoated stabilized alumina, and coated stabilized alumina processed in the MAIC (1 minute, 2 %) and HB (2 minutes, 1%, 6000 rpm), are shown in Figures 4.24a to 4.24c.



Figure 4.24 SEM micrographs thermally stabilized alumina at room temperature for (a) uncoated alumina, (b) MAIC coated (1 min.) and (c) HB coated (2 min., 6000 rpm).

The dilatometry results of the samples heated to 1300° C are shown in Figure 4.25. The dilatometry results showed the minimum sintering temperature of uncoated and coated materials were very similar, approximately 1100° C. SEM micrographs of the uncoated and the coated MAIC and HB samples heated to 1300° C are shown in Figure 4.26a to 4.26c. The sintering temperature of a material is a function of its size and in general, smaller the size of the material, the lower the sintering temperature. The lack of change in the sintering temperature of the coated from the uncoated material may be due to the severe size reduction of the material during processing. The specific surface area of the uncoated and coated samples as a function of temperature is shown in Figure 4.27. There is still a significant reduction in the surface area of the material (due to a size change), but relative to the high purity γ -alumina, the decrease in surface area is much smaller so that the catalytic properties may still be effective for high temperature applications.

150 µm



Figure 4.25 Elongation-contraction of (a) uncoated alumina (b) MAIC coated alumina and (c) HB coated alumina, heated to 1300°C in the dilatometer.



150 µm

Figure 4.26 SEM micrographs of thermally stabilized alumina heated to 1300°C in the dilatometer for (a) uncoated alumina (b) MAIC coated (1 minute) and (c) HB coated (2 minutes, 6000 rpm).

4.3.5 Alumina-Silica

The alumina-silica catalytic support was not run in the MF due to the large batch size required to run the device and the small amount of material available. The volume-mean particle size of the coated samples from the MAIC and HB, as well as the uncoated sample is shown in Figure 4.28. There was severe size reduction in the HB processed

sample and hence the sample was not used in the dilatometry analysis. A large change in the mean particle size is not desirable, since this will not only affect the dilatometry results but can also affect the function of the catalytic support material.



Figure 4.27 Specific surface area of samples heated to different temperatures in the dilatometer.



Figure 4.28 Volume-mean particle size of (-+a) uncoated alumina (b) coated in MAIC for 2.5 minutes (c) coated in MAIC for 5 minutes, (d) coated in MAIC for 10 minutes and (e) coated in HB for 2 minutes (6000 rpm).



Figure 4.29 SEM micrographs of (a) alumina-silica uncoated and (b) alumina-silica coated for 2.5 minutes in MAIC, at room temperature.

Further analysis of the MAIC samples showed that the surface coverage of the sample processed for 10 minutes was about 50 %, compared to 11% and 14 %, for the samples processed for 2.5 and 5 minutes, respectively. Though, a large surface coverage is desirable to help promote deactivated sintering, the desired coating for these particles is that it should not be large enough to reduce the surface area of the catalytic material by clogging the pores. Hence, only dilatometry analysis of the samples processed for 2.5 and 5 minutes, as well as the uncoated support, was conducted.

The results of the sample processed for 2.5 minutes and the uncoated sample are presented in Figure 4.29. Both the coated and uncoated samples were heated to 1250°C and 1550°C. The dilatometry results of the samples heated to 1550°C are shown in Figure 4.30. The minimum sintering temperature of the uncoated and the coated samples were found to be approximately, 1180°C and 1320°C, respectively. SEM micrographs of the samples at 1250°C are shown in Figure 4.30a showed an increase in the neck growth of the uncoated sample at 1250°C,

whereas the coated sample remained individual particles at 1250°C in Figure 4.31b, agreeing with the dilatometry results.



Figure 4.30 Elongation-contraction of uncoated and coated samples heated to 1550°C in the dilatometer.



Figure 4.31 SEM micrographs of (a) uncoated alumina-silica and (b) alumina-silica coated in the MAIC for 2.5 minutes, heated to 1250°C in the dilatometer.

4.4 Mechanism of Deactivated Sintering

The mechanism of sintering can be due to viscous flow, evaporation-condensation, volume diffusion and surface diffusion, as previously mentioned. These mechanisms are distinguished by the relationship of radius of "neck" growth x (Figure 4.32), of two particles of the same size, as a function of time. These relationships have been discussed by numerous investigators and have been used to describe the sintering mechanism of different materials. The relationships are as follows (Kuczynski, 1949b):

| Viscous flow | $x^2 \sim t$ |
|--------------------------|--------------|
| Evaporation-condensation | $x^3 \sim t$ |
| Volume diffusion | $x^5 \sim t$ |
| Surface diffusion | $x^7 \sim t$ |



Figure 4.32 Schematic of neck growth during sintering for two spheres of similar sizes.

4.4.1. Alumina

When two particles of the same material and relatively same size are in contact, densification depends of the curvature gradient between the curved neck region and the grain boundary. Based on the model of Kuczynski (1949a) where the volume diffusion

mechanism of sintering was described using a vacancy concentration theory at the interface, the increase in vacancy concentration ΔC can be estimated from the Kelvin equation as follows (Kuczynski, 1949a):

$$\Delta C = \frac{\gamma Co \ \delta^{3}}{\kappa T} \left(\frac{1}{a} - \frac{1}{x} \right)$$
(4.3)

where Co is the equilibrium vacancy concentration, γ is the surface energy, δ is the vacancy volume, x is the radius of the neck, a is the radius of the curved neck, k is the Boltzmann constant, and T is the absolute temperature. Since x >> a, the equation reduces to:

$$\Delta C = \frac{\gamma Co \ \delta^{3}}{\kappa T} \left(\frac{1}{a}\right)$$
(4.4)

As the uncoated alumina and the SiC coated alumina undergo both neck growth and skrinkage, the volume of the host material arriving at the surface of the guest/host particles is given by (Coble, 1958):

$$\frac{dV}{dt} = \pi x^2 \frac{dy}{dt} \tag{4.5}$$

where $y = x^2/4R$, and R is the radius of the host particle. The instantaneous mass flux J of the vacancies leaving the neck is given by Fick's first law.

$$J = D_{v}A\frac{\Delta C}{x} \approx 4Dv\Delta C(2\pi x)$$
(4.6)

where D_v is the vacancy diffusivity for atoms, ions or molecules of the host particles. Therefore, the volume diffused is given by:

$$\frac{dV}{dt} = \frac{\pi x^3}{2R} \frac{dx}{dt} = J\delta^3 = 4D_v \Delta C(\pi x)\delta^3$$
(4.7)

Equating the vacancy diffusivity D_v in Equation 4.7, and the self diffusion coefficient D_D , such that $CoD_v = D_D\delta^3$, and substituting $\Delta C = C_o(\gamma\delta^3/\kappa Ta)$ and $a = x^2/(4R)$ results in the following expression:

$$\int x^4 dx = \int \frac{64 D_D \gamma \delta^3}{\kappa T} R^2 dt$$
(4.8)

Integrating Equation 4.8 results in the following expression:

$$\left(\frac{x}{R}\right)^n = A \frac{D_D \gamma \delta^3}{R^3 \kappa T} t$$
(4.9)

where for this instance n = 5, and A is a constant, and can be different depending on the mechanism of sintering (Coble , 1958). The sintering model can then be written in terms of the shrinkage of the length of the sample.

$$\left(\frac{\Delta L}{L_0}\right)^p = B \frac{D_D \gamma \delta^3}{R^3 \kappa T} t$$
(4.10)

where ΔL is the change in the length of the sample, L_o is the initial legth of the sample, p=n/2, is determined by the mechanism of sintering, and B is a constant. Using a modified vertical dilatometer (Compo *et al.*, 1987), $\Delta L/L_o$ can directly be measured as a function of time, isothermally. From these plots, the diffusivity of the uncoated and coated particles can be calculated. However, first the mechanism of sintering is determine by plotting a log-log plot of $\Delta L/L_o$ as a function of time t, from which the slope of the line determines 1/p.

Plots of log (Δ L/Lo) as a function of log (t), for the uncoated and SiC coated alumina processed in the MAIC, Mechanofusion and the Hybridizer, at 1250°C are shown in Figure 4.33. The slopes of all lines were between 0.43 and 0.53. Therefore, p is assumed to be approximately 2.5, indicating that the constant B is 10 (Coble, 1958), and that the sintering mechanism is based on a bulk diffusion path where the vacancy sink is the grain boundary. For Equation 4.9, if p = 2.5, then n = 5, indicating that volume diffusion is the predominant mechanism of sintering, based on the discussion by Kuczynski (1949a). The slope of $(\Delta L/Lo)^{2.5}$ as a function of time t, is used to calculate the diffusivity of the uncoated and coated samples according to Equation 4.10. The slopes obtained for the uncoated and coated materials are shown in Figures 4.34 and 4.35, respectively.



Figure 4.33 Contraction as a function of time at a temperature if 1250° C for (\Box) uncoated alumina (\triangle) HB coated sample (2 minutes, 6000 rpm) (\circ) MAIC coated sample (5 minutes) and (x) MF coated sample (10 minutes, 600 rpm).

The diffusivities of the uncoated and coated alumina samples are listed in Table 4.5. The ratio of the diffusivity of the coated to uncoated samples are also listed in Table 4.5. The values listed clearly indicate that the diffusivity of the uncoated alumina (alumina-alumina system) is much higher that the coated material (alumina-SiC system). The lower diffusivity for the coated sample results in a reduction in the rate of sintering, which causes an increase in the sintering temperature of the material with a surface coverage of SiC.



Figure 4.34. Contraction to the 2.5 power as a function of time, at an isothermal temperature 1250°C.



Figure 4.35 Contraction to the 2.5 power, as a function of time at an isothermal temperature of 1250°C for (\triangle) HB coated samples (\bigcirc) MAIC coated samples and (x) MF coated samples.

| Sample | Diffusivity(cm ² /s) | Ratio |
|--|----------------------------------|-------|
| Uncoated high purity γ-alumina | 7.69 x 10 ⁻¹⁴ | 1.000 |
| MAIC coated sample (5 minutes) | 1.22 x 10 ⁻¹⁵ | 0.016 |
| HB coated sample (2 minutes, 6000 rpm) | 8.11 x 10 ⁻¹⁶ | 0.011 |
| MF coated sample (10 minutes, 600 rpm) | 2.84 x 10 ⁻¹⁶ | 0.004 |

Table 4.5 Diffusvities of Uncoated and Coated Samples

4.4.2 Glasses and Polymeric Materials

Frenkel (1945) presented a general expression for the neck growth between two similar size spheres of the same material where viscous flow is the predominant mechanism of coating.

$$\left(\frac{x}{R}\right)^2 = \frac{3\Gamma t}{2R\eta} \tag{4.11}$$

where x is the neck growth, R is the original radius of the particle, Γ is the effective surface energy of the two surfaces, t is the sintering time, and η is the viscosity coefficient.

Tardos *et al.*, (1984) later used the dilatometer to measure the surface viscosities of glass and polymers at high temperatures. The theory and equations they presented are briefly outline below. The contraction of the sample can be expressed as a function of the flattened contact point b (radius of the sintered neck), by the following equation:

$$\left[\frac{b}{D_{p}}\right]^{2} \cong \left[f\frac{\Delta L}{2L_{o}}\right]$$
(4.12)

where ΔL is the contraction of the sample, L_o is the initial length of the sample, D_p is the granule diameter and f is related to the layer spacing and the voidage of the arrangement of particles, such that for small particles:

$$f = \frac{3\beta}{2} \tag{4.13}$$

$$\beta = \sqrt{\frac{2}{3}} \left[\frac{\pi}{3\sqrt{2}(1-\varepsilon)} \right]^{\frac{1}{3}}$$
(4.14)

and

where β is the layer spacing and ϵ is the porosity of the sample.

The general relationship between the size of the sinter neck b, the compression force F_p , the time t, and the viscosity η_s , neglecting the compression force by surface tension and van der Waals forces, discussed by Rumpf (1977) can be expressed by the following equation.

$$\left[\frac{b}{D_p}\right]^2 = \left[\frac{KF_p t}{D_p^2 \eta_s}\right]$$
(4.15)

The derivative of Equation 4.15 is taken with respect to time t, such that the contraction of the sample (at an isothermal temperature) can be related to the surface viscosity as a function of time by the following expression:

$$\frac{\partial \left(\frac{f\Delta L}{2L_o}\right)}{\partial \left(t^{\frac{1}{p}}\right)} = \left[\frac{KF_p}{\eta_s D_p^2}\right]^{\frac{1}{p}}$$
(4.16)

Using the dilatometer, a log-log plot of the change in contraction of the sample $f(\Delta L/L_o)$], is plotted against time t. Provided that the slope 1/p of this relationship is 1, Equation 4.16 can be reduced to:

$$\eta_{s} = \frac{KF_{p}D_{p}^{-2}}{\frac{\partial}{\partial}\left(f\frac{\Delta L}{2L_{0}}\right)}$$
(4.17)

where $K = (2/5)\pi$ and $F_p = 4\epsilon (D_p)^2 L/[\pi (1-\epsilon)(D_s)^2]$. The load L, used for all the experiments was 35 grams. The diameter D_s , of the sample tube was 4 mm. The slope of $[f(\Delta L/2L_o)]$ as a function of time t, yields the denominator of Equation 4.17, from which the surface viscosity of the material can be calculated. The porosity used for the calculations was 0.4, resulting in a value of 1.31 for f.

In this study, Equations 4.16 and 4.17 were used to calculate the surface viscosity of the uncoated and the coated materials, for both glass beads and PMMA. This calculation is based on the assumption that the mechanism of sintering, with and without a surface coating is via a viscous flow. First, Equation 4.16 is used to obtain the slope 1/p. The majority of the results are presented in APPENDIX A.

The results for glass beads uncoated and coated with 8 wt. % SiC in the MAIC, at an isothermal temperature of 620°C, are shown in Figure 4.36. The slope 1/p, for the uncoated and the coated samples is found to be 0.87 and 1.01, respectively. This indicates that Equation 4.17 can be used to calculate the surface viscosity of the uncoated area of both the uncoated and coated samples. It is believed that the surface viscosity of the glass beads at a given temperature does not changed. However, the amount of coverage of SiC on the surface of the beads, affects the viscous flow mechanism, resulting in a higher " effective" surface viscosity. The relationships of the contraction as a function of time at an isothermal temperature of 620°C, for the uncoated and coated samples, are shown in Figure 4.37. The slope of the uncoated sample is lower that the slope of the coated sample, indicating that the effective surface viscosity of the coated sample is higher than the uncoated sample. A layer of SiC lowers the sintering of the glass beads by preventing the material from undergoing a viscous flow, hence resulting in a higher effective surface viscosity for the coated material.



Figure 4.36 Contraction as a function of time at 620° C for (a) uncoated glass beads and (b) glass beads coated with 8 wt. % of SiC.



Figure 4.37 Contraction as a function of time at 620° C for (a) uncoated glass beads and (b) glass beads coated with 8 wt. % of SiC.
Similar plots were constructed for glass beads, uncoated and coated, for an isothermal temperature of 600°C. Plots were also constructed for PMMA, uncoated and coated in the MAIC for 5 minutes with 3 wt. % SiC, at two isothermal temperatures of 105 and 120 °C. The slope 1/p, from the log-log plot of $[f(\Delta L/2L_o)]$ has a function of time t, yielded values between 0.80 and 1.20 (APPENDIX A), again indicating that viscous flow is the dominant mechanism of sintering..

The surface viscosity of the samples was calculated and is presented in Figures 4.38 and 4.39, for glass beads and PMMA, respectively. In all cases the surface viscosity of the coated particles was higher than the uncoated particles. This is due to the discrete coating of SiC that slows the sintering mechanism, by preventing the viscous flow of the surfaces of glass beads and PMMA, promoting deactivated sintering. The ratio of the surface viscosity of the coated material to the uncoated material at each temperature is given in Table 4.6.



Figure 4.38 Surface viscosity of glass beads, uncoated and coated as a function of temperature.



Figure 4.39 Surface viscosity of PMMA, uncoated and coated as a function of temperature.

| | Surface vis | Ratio | |
|-------------|------------------------|------------------------|--------|
| | Uncoated | Coated | Coated |
| Glass Beads | | | |
| 600 | 6.93 x 10 ⁹ | 9.53 x 10 ⁹ | 1.4 |
| 620 | 4.67 x 10 ⁹ | 7.62×10^9 | 1.7 |
| PMMA | | | |
| 105 | 0.93 x 10 ⁹ | 1.97 x 10 ⁹ | 2.1 |
| 120 | 0.56 x 10 ⁹ | 1.79 x 10 ⁹ | 3.2 |

 Table 4.6 Ratio of Surface Viscosity of Coated to Uncoated Material

4.5 Conclusions

It was possible to obtain individual particles of PMMA at 150°C, about 45°C ($T_s \sim 105^{\circ}$ C), above the minimum sintering temperature of the uncoated PMMA using all three devices with a surface coating of SiC. At this temperature uncoated PMMA particles were totally sintered. For glass bead samples, it was also possible to obtain individual

particles of coated glass beads at 700°C, about 125° C (Ts ~ 575°C), above the minimum sintering temperature of uncoated glass beads. An increase in deactivated sintering is observed with an increase in guest weight percentage and/or increased time of operation. With the use of 0.8 wt. % of SiC guest particles, with was possible to obtain individual glass beads at 700°C. With the use of 8 wt. % of SiC, it was possible to obtain individual particles even at 800°C.

For the high purity and lanthanum-enhanced alumina, phase and size changes, prevented the proper analysis of both materials. However, for the high purity γ -alumina there was an increase in the sintering temperature of the coated materials. MAIC gave the best results for the alumina-silica catalyst support study based on changes in the volume mean particle size of the samples after processing. With the MAIC coated samples, there was an increase in sintering temperature of the coated sample by almost 140°C, after only 2.5 minutes of processing in the MAIC. SEM micrographs clearly supported the dilatometry studies.

The mechanism of deactivated sintering for both crystalline (alumina) and amorphous (glass and polymers) materials was successfully investigated. For crystalline materials, it was found that the neck growth and shrinkage of the material was due a volume diffusion mechanism. The application of a surface coating of SiC on the alumina particles provides a deactivated layer. This deactivated layer causes a significant reduction in the diffusivity of Al^{+3} in the volume diffusion mechanism. The diffusivity of the Al^{+3} for the uncoated material was much higher than the alumina processed in all three devices. This reduction in the diffusivity for the coated material results in a delay in the sintering of the material. Hence, deactivated sintering was successfully achieved.

For the case of amorphous (glass and polymers) materials, the mechanism of sintering was caused by a viscous flow mechanism. The deactivated layer of SiC on the surface of glass beads and PMMA caused an increase in the effective surface viscosity of the material. The effective surface viscosity of the coated material was 1.5 times larger than the uncoated material for glass beads. For PMMA, the effective surface viscosity for the coated material was more than 2 times larger than the uncoated PMMA. The increase in the surface viscosity is caused by the surface coverage of the SiC preventing the flow of the softened PMMA or glass.

CHAPTER 5

OPTIMIZATION STUDY OF PARAMETERS AFFECTING DRY PARTICLE COATING

Dry particle coating is a new technique for achieving particle coating that is currently under investigation. Due to the absence of solvents and binders, this technology can prove to be beneficial to numerous industries, especially in the food and pharmaceuticals. However, very little is known about the operating parameters and the effects of these parameters on the overall coating process. The following sections introduce the key parameters affecting the coating performance of the MAIC, the Mechanofusion and the Hybridizer. A system of PMMA coated with alumina is investigated. Each device will produce surface coatings of varying characteristics based on the properties of the host and guest particles (hardness, shape, size, etc.). However, this introductory study gives the general trends of surface coverage achieved by varying the key operating parameters.

5.1. Magnetically Assisted Impaction Coating Device

There are several critical system and operating parameters affecting the coating performance of the MAIC device. Once the host and guest particles are specified, the key system parameters are magnetic particle size and magnetic particle to powder (host and guest particles) mass ratio. The major operating parameters are frequency, current (or voltage), and processing time. To study the effects of these parameters on the coating efficiency, a model system consisting of 200 μ m spherical PMMA host particles and several sizes of alumina guest particles was chosen. Experiments were conducted which systematically varied all of the parameters mentioned above. PMMA was chosen as the

host material in our "model system" because the particles are both spherical and smooth, and therefore the added variable of surface irregularities is eliminated in evaluating coating performance. In addition, several investigators (Ata *et al.*, 1998) have used the PMMA (host particles) coated with alumina (guest particles) system to an advantage for dry particle coating studies because of the favorable difference in hardness between the two materials (soft-hard spheres). The motion of the magnetic particles was also examined using a high-speed digital camera. This was done to study the effect of the motion of the magnetic particles on the quality of the surface coverage obtained. Based on the results of the optimization and the magnetic particle motion studies, a preliminary mechanism of coating by MAIC is proposed.

The physical properties of PMMA and alumina and the variations in experimental system and operating parameters are given in Tables 5.1 and 5.2, respectively. The parameters examined were processing time, current, frequency, magnetic particle to powder mass ratio, magnetic particle size and guest particle size. The speed and the behavior of the magnetic particles, during processing in the MAIC device, were obtained by using a Kodak EktaPro1000 high-speed digital camera with an intensified imager (capable of recording at up to 1000 frames per second) to capture the motion. The movement of magnetic particles was examined as a function of the frequency of the external field. By combining the results of the speed and the parameter optimization studies, the surface coverage as a function of the magnetic particle speed was obtained.

The coated products obtained were evaluated using several characterization techniques. Surface morphology micrographs for all the coated products were obtained using a Scanning Electron Microscope (SEM). The micrographs were quantitatively

analyzed by a statistical technique. In this technique, the number of guest particles on the surface of the host particles is individually counted by counting the number of particles that lay on several randomly chosen lines. The average of these values are calculated as a percentage and reported as the area of surface coverage obtained. A sample calculation is shown in APPENDIX B. The results for each parameter studied are presented in the following sections.

| Properties | РММА | Alumina |
|----------------------|------|--------------------------|
| Size (µm) | 200 | 0.05, 0.2, 0.4, 0.7, 1.0 |
| Density (g/cm) | 1.9 | 3.96 |
| Hardness (Knoop-GPa) | 21 | 2100 |

Table 5.1 Physical Properties of Materials.

 Table 5.2 Variations in the System and Operating Parameters.

| Magnetic particle to powder mass ratio | 0.5, 0.75, 1.0, 1.5, 2.0 |
|--|--------------------------|
| Magnetic particle size (µm) | 180, 800, 2700 |
| Processing time (minutes) | 1, 3, 5, 7, 10 |
| Current (amperes) | 1, 2, 3, 4, 5 |
| Frequency (hertz) | 45 to 110 |

5.1.1 Processing Time

The processing time was investigated by conducting experiments at 1, 3, 5, 7 and 10 minutes, respectively. The size of alumina used for this study was $0.2\mu m$. The mass percentages of alumina guest particles used were based on the assumption of 100% surface coverage of the host particles with a monolayer of guest particles (Equation 4.2,

Chapter 4). The surface coverage of the coated products as a function of processing time is shown in Figure 5.1. An increase in processing time from 1 to 5 minutes showed a corresponding increase in the percentage of surface area covered. After 5 minutes, the amount of surface coverage achieved fluctuated slightly. A previous study as shown that it is possible for the magnetic particles to detach and reattach the guest particles after an optimum processing time is reached. The small fluctuations after 5 minutes can be due to small differences between detachment and reattachment, where an "equilibrium" between both is reached. The surface morphology of PMMA coated with alumina for processing times of 1 and 5 minutes are shown in Figures 5.2 and 5.3, respectively. In Figure 5.2, for a processing time of 1 minute, a very discrete and relatively small amount of surface coating of alumina is seen as compared to a processing time of 5 minutes (Figure 5.3), where the coating appears thicker and much more uniform.



Figure 5.1 Surface coverage as a function of processing time.





Figure 5.2 SEM micrograph of PMMA coated with alumina for a processing time of 1 minute.

Figure 5.3 SEM micrograph of PMMA coated with alumina for a processing time of 5 minutes.

5.1.2 Current and Frequency

The effect of current on the coating efficiency was examined by varying the current at a fixed frequency of 45 Hz. The current was varied from 1 to 5 amperes and each experiment was conducted for a processing time of 5 minutes, with a guest particle size of $0.2\mu m$. It was found that the surface coverage increased linearly with increased current and the results are shown in Figure 5.4. The maximum current which could be attained by the Triathalon Power Control, which we used in our experiments, was 5.0 amperes.

Using an optimum current of 5.0 amperes and a processing time of 5 minutes, the frequency of the system was varied from 45 Hz to 100 Hz. An unusual behavior was observed as shown in Figure 5.5. At 45 Hz, the surface coverage obtained was about 66%, then from 45 to 70 Hz, the surface coverage decreased with increasing frequency. After 70 Hz, the surface coverage of the coated product increased gradually with increasing frequency, where it again peaked in surface coverage at a frequency of 90 Hz.

This suggests that the variations in the frequency cause a periodic fluctuating behavior in the amount of surface coverage obtained.



Figure 5.4 Surface coverage as a function of current at a fixed frequency of 45 Hz.



Figure 5.5 Surface coverage as a function of frequency at a fixed current of 5A.

5.1.3 Magnet to Powder Mass Ratio

The motion of the magnetic particles is responsible for coating guest particles onto the host particles by a vigorous "fluidized" type motion causing collisions between host particles and the host and guest particles. Therefore, the mass of magnetic particles used in the system significantly affects the surface coverage obtained. The magnetic particle to powder mass ratio was varied to determine the optimum mass of magnetic particle needed. Several ratios were investigated and the results obtained are shown in Figure 5.6. It can clearly be seen that as the magnetic particle to powder mass ratio is increased, the percentage of surface area covered also increased. For ratios larger than 2, it has been shown that there is not much change in the coating efficiency, and in some cases coating is even poorer than at lower ratios.



Figure 5.6 Surface coverage as a function of magnetic particle to powder mass ratio.



Figure 5.7 Surface coverage as a function of magnetic particle size.

5.1.4 Magnetic to Host Size Ratio

Three sizes of magnetic particles were used to investigate the effect of size on coating in the MAIC system. The percentage of surface coverage achieved for each size is shown in Figure 5.7. As seen in the figure, the largest magnets with a mean size of 2.7 mm gave the best surface coverage results.

5.1.5 Guest to Host Size Ratio

The size effect of guest particles on the coating efficiency was investigated using four sizes of alumina guest particles: 0.05, 0.2, 0.4, and 1 micron. Based on complete coverage with a monolayer of alumina particles, the percentage of alumina by weight for each of these 4 sizes was as 0.25, 1.0, 2.0, and 5.0, respectively. As the guest particles size increased, the area of coverage decreased as shown in Figure 5.8. The two smallest sizes gave the best coating results. However, careful examination of the surface

morphology of the products coated with 0.05 micron and 0.2 micron alumina, Figure 5.9 and 6.10, respectively, showed that the PMMA particles coated with 0.2 micron alumina were more uniformly coated than the PMMA particles coated with 0.05 micron alumina. Many more agglomerates of alumina were observed on the surface of PMMA for a guest size of 0.05 micron. This is due to the inability of the MAIC device to efficiently deagglomerate the 0.05 micron size guest particles. This conclusion was based on the study of several additional SEM micrographs (not shown). Therefore from these observations, the 0.2 micron sized guest particles were considered to be the better guest particle size for obtaining a more uniform surface coverage.



Figure 5.8 Surface coverage as a function of guest particle size.





Figure 5.9 Surface morphology of PMMA coated with 0.05 micron Al₂O₃ guest particles.



Figure 5.10 Surface morphology of PMMA coated with 0.2 micron Al₂O₃ guest particles.

5.1.6 Magnetic Particle Speed and Behavior Studies

A small experimental system consisting of magnets, host and guest particles was assembled similar to that used for the parameter studies. Using the Kodak camera, the movement of the magnetic particles was recorded at different frequencies at a fixed current of 5 amperes. The first important observation made was that, in addition to the magnetic particle moving haphazardly in all directions (translation), they were also spinning furiously (rotation). The movement of the magnetic particles at different frequencies was measured and recorded. These recorded images were further analyzed to obtain approximate values for the translational and rotational motions. The translational and rotational speeds as a function of frequency. Thus, the relationships of the surface coverage as a function of translational and rotational speed were obtained (Figures 5.11 and 5.12). The second important observation (obtained from the figures) showed that the rotational speed of the magnetic particles influenced the coating efficiency much more significantly than the translational speed.



Figure 5.11 Surface coverage as a function of the rotational speed of the magnetic particles.



Figure 5.12 Surface coverage as a function of translational speed of the magnetic particles.

The combination of parameter and magnetic particle motion studies suggest that the primary motion due to the magnetic field is the spinning of the magnetic particles, promoting deagglomeration of the guest particles, as well as the spreading and shearing of the guest particles onto the surface of the host particles. However, the effect of the translational speed is also significant as it allows for the impaction of one particle onto another promoting coating. A schematic diagram of a proposed mechanism of coating in the MAIC device derived from this study is shown in Figure 5.13.



Figure 5.13 Mechanism of coating in the MAIC process (a) excitation of magnets (b) distribution of guest particles (c) shearing and spreading of guest particles on the surface of the host particles (d) magnetic-host-host particle interaction (e) magnetic-host-wall interaction and (f) coated particles.

The guest particles exist as agglomerates. The rotation of the magnetic particles helps in the de-agglomeration of the guest particles, which are then distributed on the surface of the host particles. Both distribution and de-agglomeration can occur simultaneously. A combination of the translation speed and the host-guest-wall interactions, as well as the spin of the magnets help to evenly distribute and coat the guest particles onto the surface of the host particles. The proposed mechanism of coating for the MAIC is clearly supported by experimental data. PMMA host particles were coated in the MAIC for varying times of 2.5, 5, and 10 minutes using a guest particle size of 0.7 μ m. SEM micrographs of the coated samples as function of time were taken and are shown in Figure 6.15. At 2.5 minutes, large agglomerates of alumina are visible on the surface of the PMMA. After 5 minutes of processing time, the alumina is more uniformly distributed on the surface of the PMMA host particles (via de-agglomeration by the rotational motion of the magnetic particles). At a longer time of 10 minutes processing time, the PMMA host particles are uniformly coated with PMMA (combination of host-magnet-wall interaction). This is supported by an EDX mapping of aluminum of the surface of the PMMA host particle (Figure 5.15).







Figure 5.15 EDX mapping of alumina on the surface of PMMA processed in the MAIC for (a) 5 minutes and (b) 10 minutes.

5.2 Mechanofusion

Critical parameters affecting the performance of the Mechanofusion are the rotating speed of the drum, the processing time and the clearance between the arm head and the rotating drum. The rotational speeds can vary from 400 to 1500 rpm. Long processing times from 10 to 40 minutes are required to obtain a significant surface coverage. A system of PMMA host particles with alumina guest particles was processed in the Mechanofusion. The coated products were analyzed by the use of several techniques to compare the performance of the device as a function of rotating speed and processing times. The processing times and the rotational speeds used are given in Table 5.3. The clearance for all the experiments was fixed at a value of 1 mm. The clearance between the drum and the arm head could vary from 1 to 6 mm. Results of surface coverage as a

function of rotational speed and processing time are presented for the products using both the stainless steel and ceramic arm head and scraper (Figure 5.16).



Figure 5.16 Schematic of the Mechanofusion with stainless steel and ceramic arm head and scraper.

 Table 5.3 Variations in the Operating Parameters for the Mechanofusion.

| Rational speed (rpm) | 600, 800 |
|---------------------------|------------|
| Processing time (minutes) | 10, 20, 40 |

5.2.1 Rotational Speed

SEM micrographs of PMMA coated in the Mechanofusion with the stainless steel arm head and scraper (henceforth collectively called inner pieces), for 600 and 800 rpm, are shown in Figures 5.17a and 5.17b, respectively. A processing time of 40 minutes was

used. Larger processing times were not used due to the visible levels of contamination of the powder from the stainless steel of the rotating drum.



Figure 5.17 SEM micrographs of PMMA coated with alumina for 40 minutes at (a) 600 rpm and (b) 800 rpm using stainless steel inner pieces.

SEM micrographs of PMMA coated in the Mechanofusion using the ceramic inner pieces for 600 and 800 rpm are shown in Figure 5.18a and Figure 5.18b. Again, the processing time used was 40 minutes. The SEM micrographs at high magnification, shown in APPENDIX B, were used to calculate the surface of the host particles covered by the guest particles (surface coverage). The technique used to count the particles is the same as the technique used in Section 5.1 for the MAIC samples. The surface coverage as a function rotational speed for both the ceramic and the stainless steel inner pieces is shown in Figure 5.19.

In comparing the surface coverage achieved at different rotating speeds, it can clearly be seen that higher rotational speeds gave better surface coverage. This is evident by the increased distribution of alumina on the surface of the host particles with increased rotational speeds. Higher rotation speeds results in larger shear stresses responsible for the deagglomeration and spreading of guest particles onto the surface of the host particles. From the results presented in Figure 5.19, the stainless steel inner pieces gave higher surface coverage than the ceramic inner pieces. This is a result of the higher adhesion of alumina to the ceramic inner pieces in preference to the stainless steel inner pieces, thereby, reducing the amount of alumina available to coat the PMMA host particles. The attachment of alumina guest particles to the inner pieces was clearly visible during the experimental runs.



Figure 5.18 SEM micrographs of PMMA coated with alumina for 40 minutes at (a) 600 rpm and (b) 800 rpm using ceramic inner pieces.



Figure 5.19 Surface coverage as a function of rotation speeds for (\diamond) stainless stain and (\triangle) ceramic inner pieces.

5.2.2 Processing Times

SEM micrographs of samples processed for 10, 20 and 40 minutes in the Mechanofusion at 600 and 800 rpm are shown in Figures 5.20 and 5.21, respectively. These samples were processed with the stainless steel inner pieces. The SEM micrographs of samples processed with the ceramic inner pieces at 800 rpm, for 10 and 40 minutes are shown in Figure 5.22. The surface coverage as a function of processing time for both the stainless steel and ceramic inner pieces is shown in Figure 5.23.



Figure 5.20 SEM micrographs of samples coated with stainless steel inner pieces at 600 rpm for (a) 10, (b) 20 and (c) 40 minutes.



Figure 5.21 SEM micrographs of samples coated with stainless steel inner pieces at 800 rpm for (a) 10, (b) 20 and (c) 40 minutes.



Figure 5.22 SEM micrographs of samples coated with ceramic inner pieces processed at 800 rpm for (a) 10 minutes and (c) 40 minutes.



Figure 5.23 Surface coverage as a function of processing time for products coated using Mechanofusion.

Overall, results indicate than longer processing times and higher rotational speeds give the best surface coverage, as would be expected. However, longer processing times produced particles with unfavorable level of contamination, and hence are best avoided. The stainless steel inner pieces produced the best overall surface coatings, though contamination of the products is more than for the ceramic coated samples (discussed in detail in the next chapter). The ceramic inner pieces gave poorer surface coverage results due to the tendency of alumina particles to adhere to the head of the ceramic inner piece and scraper as discussed previously. Higher rotation speeds were not investigated with the ceramic inner pieces, due to the fracture of some of the PMMA particles at 800 rpm. While for the stainless steel inner pieces, higher rotation speeds were not examined due to the increased level of contamination with increased rotation speed. Significant fracture of PMMA, due to high shear force at 800 rpm for samples processed with the ceramic inner pieces for 40 minutes, is shown in Figure 5.24.



Figure 5.24 SEM micrographs of samples coated with ceramic inner pieces at 800 rpm showing fracture of samples.

5.3 Hybridizer

The Hybridizer device is relatively simple to operate and has very few operating parameters, once the host material and guest particles are specified. The key parameters are the rotation speed and the processing time. The rotation speeds can be varied from 5000 to 15000 rpm. Due to the very higher rotation speeds of the device, very short processing times are required to get significant surface coverage on a host particle. The atmosphere of the processing chamber can also be changed to different gases. In this study only air was used. The temperature of the cooling water can be varied to allow the

processing chamber to work at different temperatures, which can sometimes help in the adhesion of the guest to host particles, in the coating process. Again, this parameter was held constant by using only tap water.

The variations in operating parameters are given in Table 5.4. Similar to Mechanofusion, the Hybridizer has both stainless steel and ceramic fittings. However, unlike the mechanofusion device, the entire vessel is lined with ceramic and not just a few pieces. The entire re-circulatory tube and the chamber are made lined with ceramic, while the rotor with the six blades, is made completely of ceramic. The discharge vessel and the connecting tubes, where the powder is released via a control valve after processing, however, are not made of ceramic.

 Table 5.4 Variations in Operating Parameters for the Hybridizer.

| Rotating speed (rpm) | 5000, 6000, 8000, 10000 |
|---------------------------|-------------------------|
| Processing time (minutes) | 2, 4, 5 |

5.3.1 Rotation Speed

A SEM micrograph of uncoated PMMA is shown in Figure 5.25a. SEM micrographs of products coated in the Hybridizer for 2 minutes at different rotation speeds of 6000, 8000 and 10000 rpm are shown in Figures 5.25b, 5.25c and 5.25d, respectively. The samples were processed in the ceramic lined device. SEM micrographs of samples processed in the stainless steel device for 2 minutes, at rotation speeds of 5000, 6000, and 8000 rpm are shown in Figures 5.26b and 5.26c, respectively. Surface coverage as a function of rotational speed for the ceramic and stainless steel devices are shown in Figure 5.27.

There was an increase in the surface coverage with increased rotation speeds, for both the ceramic lined and the stainless steel Hybridizer. The samples processed in the stainless steel Hybridizer were dark gray in color due to the severe contamination of the samples. Again, the natural tendency of alumina to adhere to the ceramic parts of the device lowers the efficiency of the coating processing, by reducing the amount of alumina available to coat the surface of the host particles.



Figure 5.25 SEM Micrographs of (a) uncoated PMMA and samples coated in the Hybridizer for 2 minutes at (b) 6000 rpm, (c) 8000 rpm and (d) 10000 rpm.

5.3.2 Processing Time

SEM micrographs of PMMA coated with alumina for 2, 4, 5 minutes at 6000 rpm, using ceramic inner pieces are shown in Figures 5.28a to 5.28c. It can clearly be seen that there is an increase in the surface coverage of PMMA with increased processing time. Samples were not processed in the stainless steel device, as long processing times increases the level of contaminants.



Figure 5.26 SEM Micrographs of samples coated with stainless steel lined Hybridizer for 2 minutes at (a) 5000 rpm, (b) 6000 rpm and (c) 8000 rpm.



Figure 5.27 Surface coverage as a function of rotational speed for samples processed in the Hybridizer for 2 minutes, using both the ceramic and the stainless steel lined devices.



Figure 5.28 SEM micrographs of samples processed at 6000 rpm for (a) 2 minutes, (b) 4 minutes and (c) 5 minutes.

5.4 Conclusions

The optimum parameter studies showed that there is an optimum processing time for the MAIC device, dependent on the materials being coated. An increase in magnetic particle size increased the coating efficiency, with an optimum magnetic particle to host size ratio of approximately 10. The coating efficiency increased with decreasing guest size. However, with very small guest particles the uniformity of coating is poor due to severe guest particle agglomeration.

As observed in the experiments and preliminary simulations, the magnetic particles in the MAIC system spin furiously during the coating process. The rotational speed (spinning motion) is more dominant than the translational speed in its influence on particle coating. Therefore it is proposed that the mechanism of coating is the deagglomeration of the guest particles, followed by the shearing and spreading of the guest particles onto the surface of the host particle, coupled with host-magnet-wall collisions and interactions.

In the mechanofusion process, increases in the processing time and the rotation speeds result in an increase in the surface coverage of the host particles. However, there is an increase in contamination of the samples due to the abrasion and erosion of the rotating vessel. For brittle, soft materials such as PMMA, increases in rotation speeds can cause the material to fracture. The stainless steel inner pieces gave much better surface coverage than the ceramic inner pieces, but with a higher contamination.

In the hybridizer, increases in the rotation speeds and the processing times, result in an increase in the surface coverage of the host particles. Similar to mechanofusion, the stainless steel inner pieces gave higher surface coverage of the host particles. Also, with increases in the operating conditions, there is a corresponding increase in the contamination of the products processed in the stainless steel device.

CHAPTER 6

A COMPARATIVE STUDY OF DRY PARTICLE COATING DEVICES

Dry particle coating by mechanical impaction, can be achieved by the Magnetically Assisted Impaction Coater (MAIC), Mechanofusion, and the Hybridizer. These three devices have been used successfully to produce particulates with unique or improved functionalities. The type of coating achieved by these devices can either be discrete or continuous. The mechanical forces of the devices and the physical properties of the materials determine the type of coating achieved by the devices. Pioneered in Japan, dry particle coating is slowly making its way into the United States. There is, however, reluctance to use of dry particle coating, due to the many mysteries surrounding this new technology. Chapters 3 and 4 have successfully shown the use of dry particle coating in the synthesis of materials with improved functionalities. Chapter 5 has shown the key parameters affecting the coating performance of each device and the effect of each parameter on the surface coverage achieved. This chapter strives to compare the coating performance of the three devices by looking at two key issues: contamination and adhesion.

The contamination of the coated products is of significant importance as the two largest potential users are the food and pharmaceutical industries, both of which require high levels of product purity. This information is not only vital to various areas of possible applications, but also in the modification of the device to achieve desired end products. Adhesion of the coating to the host particles, is another area where numerous questions have arisen contesting the strength of the coating, due to the absence of binders

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or solvents. Here we look at the strength of the coating by testing the coated products in an ultrasonic bath to examine the amount of material that remains adhered to the surface of the host particles after being subjected to ultrasonic vibrations.

6.1 Contamination

6.1.1 Introduction

Contamination of powders during processing has been reported since the beginning of times in the area of size reduction of materials. Today, most of the work presented on contamination in the field of particle technology in the literature, comes from the manufacture of semiconductors and from ball milling studies (particle size reduction or comminution).

The study of particular contamination on surfaces of semiconductors is very important, as the contaminants are known to have adverse effects on the device topography, performance, reliability, and yield. As a result, great care is required during handling and manufacture (Selwyn *et al.*, 1989). Though the device fabrication is done within the confines of a clean room, particle contamination is still possible. For semiconductors, contamination is possible by many ways during dry processing steps, such as from deposits on the chamber walls, during handling, and by chemical sources.

In ball milling, abrasive and erosion forces are responsible for the contamination of products as well as the life of the tool. As a result, the mechanism of wear of the tool is very important. The mechanism of ball wear in conventional tumbling mills has been systematically studied since the early 1970's. Studies have also looked at dry grinding (Gundewar *et al.*, 1990) and wet grinding (Iwasaki *et al.*, 1988), and the difference in the mechanism of wear due to the presence of water and other liquids.

There is no information present on contamination or the mechanism of wear of dry particle coating devices. Dry particle coating processes, which originated from grinding, are very similar to dry grinding processes. Hence, contamination studies and the mechanism of wear of a dry particle coating device can be related to studies on dry grinding devices, where abrasion and erosion forces are predominant in the wear mechanism.

In dry particle coating devices, particles undergo severe abrasion forces as they are forced to collide with each other and also with the walls of the vessel. In MAIC, the motion of the magnetic particles influences the entire coating process, and as a result the host and guest particles collide randomly with the irregular shape magnetic particles. The irregular shape favors the attrition of the edges of the magnetic particles. These can contaminate the product if they are not carefully removed after processing. The elemental composition of the magnetic particles used in this study is shown in Figure 7.1. The magnetic particles are made up mostly of barium (14%) and iron (84%), with the remaining 2% being trace elements.

In Mechanofusion, as the outer vessel rotates, the host and guest particles are pushed into the gap between the inner piece and the vessel. In this region they undergo severe shear forces, promoting the wear of the lining of the outer vessel and the inner piece, by abrasion and erosion. In the Hybridizer, the movement of airflow through the device causes the dispersion of the guest and host particles against the blades of the rotor, as well as the lining of the re-circulation tube. Again, the mechanism of wear can be attributed to the abrasion and erosion of the vessel caused by the rubbing motion of the particles.



Figure 6.1 Elemental composition of magnetic particles using XRF.

The host and guest particles are subjected to very high impaction forces and as a result the coated products are contaminated due to abrasion and erosion of the wall of the vessel. The objectives here are to identify and quantify the contaminants in the products processed in each device, and examine the effect of the key parameters on the level of contamination. The systems chosen for study are PMMA host particles coated with alumina guest particles and cellulose host particles coated with silica guest particles. PMMA and alumina are chosen as they comprise an ideal system of a soft-hard system and many investigators have used them. Cellulose and silica are chosen as cellulose was previously coated with silica (Chapter 3) to improve its flow as well as reduce its hydrophilicity, making it a system with real applications. Also, cellulose is commonly used in the food and pharmaceutical industries and as a result this knowledge can be of value to potential users of dry particle coating technology. Several analytical tools are

used to help identify and quantify the contaminants. X-ray fluorescence is used for the PMMA and alumina system. Atomic absorption is used for the cellulose and silica system. A Minolta Spectrophotometer is used to detect the changes in the color of the material due to increasing levels of contamination.

The properties of PMMA, alumina, cellulose and silica have been given in previous chapters. The operating conditions of the three devices for the PMMA (200 μ m)-alumina (0.7 μ m) system investigated are given in Table 6.1. The size of the magnetic particles used for the MAIC was approximately 1.5 mm. The operating conditions of the three devices for the cellulose-silica system are shown in Table 6.2.

| Table 6.1 O |)perating | Conditions | for | PMMA-A | lumina |
|--------------------|-----------|------------|-----|--------|--------|
|--------------------|-----------|------------|-----|--------|--------|

| MAIC | | | |
|---------------------------------|-------------------------|--|--|
| Processing time (minutes) | 5, 10, 15, 20 | | |
| Mechanofusion (Ceramic) | | | |
| Processing time (minutes) | 20, 40 | | |
| Rotating speed (rpm) | 600 | | |
| Mechanofusion (Stainless Steel) | | | |
| Processing time (minutes) | 20, 40 | | |
| Rotating speed (rpm) | 600 | | |
| Hybridizer (Ceramic) | | | |
| Processing time (minutes) | 2 | | |
| Rotating speed (rpm) | 5000, 6000, 8000, 10000 | | |
| Hybridizer (Stainless Steel) | | | |
| Processing time (minutes) | 2 | | |
| Rotating speed | 5000, 6000, 8000 | | |

| MAIC | | |
|---------------------------|------------|----------|
| Processing time (minutes) | 10, 20 | |
| Mechanofusion (Ceramic) | | |
| Processing time (minutes) | 10, 20, 40 | <u> </u> |
| Rotating speed (rpm) | 600, 800 | |
| Hybridizer (Ceramic) | | |
| Processing time (minutes) | 1 | |
| Rotating speed (rpm) | 6000, 8000 | |

 Table 6.2 Operating Conditions for Cellulose-Silica

6.1.2 MAIC (PMMA-Alumina)

The kilo counts per second (kcps) as a function of energy (KeV), obtained from the XRF for the MAIC coated products are shown in Figure 6.2a and 6.2b, respectively. The graphs show the results of samples processed for 10 and 20 minutes, and clearly indicate the presence of Fe in both samples. There was an increase in the concentration of Fe with an increase in the processing time of the samples, evident by the increase in the height of the peak for Fe. Longer processing time allow the particles to undergo more agitation, promoting increased attrition of the magnetic particles. This gives rise to larger amounts of fine iron particles in the samples. The results obtained from this characterization technique can be interpreted in two ways. PMMA is a highly reflective material. An increase in surface coverage of PMMA particles with alumina particles causes a decrease in the reflectance of the material as a function of wavelength. On the other hand, when contamination is examined, lower reflectance indicates darker samples corresponding to

more contaminated samples. A combination of the XRF elemental analysis and the spectrophotometer results together with knowledge of surface coverage obtained are needed to accurately determine the best coating with the least contamination. The XRF can be used to quantify the concentration of contaminants in the samples; while the spectrophotometer can be used to measure a reduction in the reflectance of the sample either due to surface coverage or due to increases in the contamination (darker sample).



Figure 6.2 XRF results for MAIC samples processed for (a) 10 minutes and (b) 20 minutes.

Based on the XRF results (see Table 6.3 for actual values) the 20 minutes processed sample was more contaminated than the 10 minutes processed sample. The spectrophotometer results showed that the 10 minutes processed sample had a higher reflectance than the 20 minutes processed samples, indicating either less contamination or poorer surface coverage. In Chapter 5, it was shown that it was possible to obtained
uniformly coated PMMA in MAIC for a processing time of 10 minutes. Therefore, it can be deduced from the spectrophotometer results that the high reflectance for the 10 minutes processed sample as a function of wavelength, is due to less contamination and not poorer surface coverage. PMMA processed in the MAIC achieved the best surface coverage with alumina and least contamination from the magnetic particles at a processing time of 10 minutes.



Figure 6.3 Spectrophotometer results for uncoated PMMA and PMMA coated in the MAIC for varying processing times.

6.1.3 Mechanofusion (PMMA-Alumina)

The kilo counts per second (kcps) as a function of energy (KeV) for the products coated in Mechanofusion with the stainless steel inner piece and scraper are shown in Figure 6.4. The figure shows the presence of Fe, Ni and Cr, for the samples processed for 40 minutes at 600 and 800 rpm, respectively. All three elements were present in the samples, showing an increase in concentration with increasing rotation speeds.

Similar results were obtained for samples processed in Mechanofusion with ceramic inner piece and scraper, for 40 minutes at 600 and 800 rpm, respectively. The

results are shown in Figure 6.5. From the height of the peaks (the intensity) of Fe, Cr, and Ni obtained from the graphs (different scales), it was observed that the use of a ceramic inner piece reduced the contamination of the products with stainless steel by almost 50% (refer to Table 6.4). Higher rotation speed results in particles being subjected to higher shear forces against the wall and inner piece. These higher forces aid in the abrasion and erosion of the walls of the vessel, as a part of the wear mechanism.

The Minolta spectrophotometer results of the reflectance of the products as a function of wavelength are shown for the stainless steel samples processed at 600 and 800 rpm, at 20 and 40 minutes, in Figure 6.6. The reflectance results for samples processed with the ceramic inner piece at 600 and 800 rpm, for 20 and 40 minutes are shown in Figure 6.7.



Figure 6.4 XRF results for samples processed in the Mechanofusion with the stainless steel inner piece and scraper for 40 minutes.



Figure 6.5 XRF results for samples processed in the Mechanofusion with the ceramic inner piece and scraper for 40 minutes.



Figure 6.6 Spectrophotometer results for samples processed in the Mechanofusion with the stainless steel inner piece and scraper.



Figure 6.7 Spectrophotometer results for samples processed in the Mechanofusion with the ceramic inner piece and scraper.

The XRF results showed that the samples processed with the stainless inner pieces for a processing time of 40 minutes, at 600 and 800 rpm were both significantly contaminated with Fe. The spectrophotometer results also showed the contamination of the samples, evidenced by the reduction in the reflectance of the samples with increases in rotation speed and processing time. For the stainless steel device, the least contaminated sample was processed for 20 minutes, at a rotation speed of 600rpm.

The XRF results for the samples coated with the ceramic inner pieces showed that the samples were less contaminated than the stainless steel inner pieces coated samples. As most of the collisions take place between the gap of the vessel and the arm head, the fact that the arm head is made of ceramic minimizes abrasion of the particles. The spectrophotometer results indicate that the samples processed at a rotation speed of 600 rpm, for processing times of 20 and 40 minutes were not severely contaminated as the sample processed for 40 minutes at 800 rpm. This is evident by the higher reflection of the samples processed at 600 rpm, compared to the sample processed for 40 minutes at 800. Based on the spectrophotometer results, the level of contamination of the sample processed for 20 minutes, at 800 rpm were comparable to that of the samples processed at 600 rpm

6.1.4 Hybridizer (PMMA-Alumina)

The kilo counts per second (kcps) of the elements of contamination as a function of energy for the products coated in the Hybridizer (stainless steel) are shown in Figure 6.8. The samples were processed for 2 minutes at 5000, 6000, and 8000 rpms, respectively. There were larger amounts of Fe, Ni, and Cr present in the samples, which increased with increasing rotational speeds. The XRF result0s for the Hybridizer with ceramic lining coated samples are shown in Figure 6.9 for 6000, 8000, and 10000 rpms. Again, the samples were processed for 2 minutes at rotational speeds of 5000, 6000, 8000 and 10000 rpms, respectively. There was very little iron present in the sample. The cause of iron being present in the ceramic samples can be due to the very high velocity at which the processed materials enter the discharge chamber via stainless steel pipes.

The spectrophotometer results for the stainless steel and ceramic lined Hybridizer are shown in Figures 6.10 and 6.11, respectively. The stainless steel samples were highly contaminated compare to the ceramic samples, indicated by their low reflectance. There was a significant decrease in reflectance with increased rotational speeds.



Figure 6.8 XRF results for samples processed in the Hybridizer with stainless steel inner pieces for 2 minutes.



Figure 6.9 XRF results for samples processed in the Hybridizer with ceramic inner pieces for 2 minutes.



Figure 6.10 Spectrophotometer results for samples processed in the Hybridizer with stainless steel inner pieces.



Figure 6.11 Spectrophotometer results for samples processed in the Hybridizer with ceramic inner pieces.

Photographs of the ceramic and the stainless steel samples processed for 2 minutes, at 8000 rpm are shown in Figure 6.12. It can clearly be seen that the stainless steel sample is dark gray compared to the white ceramic sample. The extreme forces that the particles undergo cause them to violently hit the walls of the vessel, the rotor, and the

re-circulation pipes. As a result, the blades of the rotor undergo severe wear via abrasion and erosion. This becomes visible after continuous processing in the device.

The least contaminated samples were processed in the ceramic lined Hybridizer. The stainless steel device gave very poor results. The increase in contamination from the discharge with increases in processing time, suggested that the sample processed at 8000 rpm was least contaminated and had the best surface coverage (see Chapter 5).



Figure 6.12 Photograph of samples processed in the Hybridizer at 8000 rpm using (a) ceramic lined and (b) stainless steel inner pieces.

6.1.5 Quantification of Contaminants using XRF

Assuming that the samples are uniformly mixed during coating, the amount of Fe, Ni and Cr in the sample can be calculated using XRF intensity given by counts per second. A fixed mass of coated samples was used in each XRF analysis (2 grams). The amount of alumina added to the sample before coating is known. Therefore, the amount of alumina in 2 grams of sample can be calculated, assuming that the samples are uniformly mixed. A sample calculation is given in APPENDIX C.

Carbon and hydrogen in the PMMA are not detected. The signals obtained are based on the presence of alumina and any contaminants in the sample. The XRF gives the percentage of each element present and also the intensity of the signal for each element (in counts per second). By calculating the mass of element per gram of sample, a calibration curve of counts per second as a function of concentration can be constructed. The data can then be fitted by least squares method, where R^2 is the root mean squared of the fit (R^2 =1 would be a perfect fit). A calibration curve for Fe concentrations in the Hybridizer with stainless steel pieces is shown in Figure 6.13.



Figure 6.13 XRF calibration curve for the concentration of Iron in the stainless steel lined Hybridizer.

The amount of contaminants, as a result of using the three devices for the examined conditions are shown in Tables 6.3 to 6.5, respectively. The overall results suggest that the ceramic lined Hybridizer produced the least contaminated samples, the stainless steel Hybridizer produced the most contaminated samples. The presence of the magnetic particles in the MAIC process did not significantly affect the contamination of the processed samples. No barium was detected in the samples since the magnet particles are made up of mostly iron. The concentration of barium present in the sample would

probably be parts per billion. The contamination of the samples processed in the MAIC can be lower if a more stringent method is used for the removal of the magnetic particles after processing.

| Table 6.3 Concentrations of Contami | inants in MAIC Processed Sample | S |
|-------------------------------------|---------------------------------|---|
| | | |

| Samples | Iron (ppm) |
|----------------------------|------------|
| Processing time 5 minutes | 47 |
| Processing time 10 minutes | 67 |
| Processing time 20 minutes | 80 |

Table 6.4 Concentrations of Contaminants in Mechanofusion Processed Samples

| Samples | Iron | Nickel | Chromium | |
|---------------------------------------|-------|--------|----------|--|
| | (ppm) | (ppm) | (ppm) | |
| Stainless steel (40 minutes, 600 rpm) | 59 | - | 7 | |
| Stainless steel (40 minutes, 800 rpm) | 197 | 33 | 27 | |
| Ceramic (40 minutes, 600 rpm) | 35 | - | 3 | |
| Ceramic (40 minutes, 800 rpm) | 92 | 10 | 13 | |

| Samples | Iron | Nickel | Chromium |
|---------------------------------------|-------|--------|----------|
| | (ppm) | (ppm) | (ppm) |
| Stainless steel (2 minutes, 5000 rpm) | 260 | 30 | 39 |
| Stainless steel (2 minutes, 6000 rpm) | 465 | 60 | 71 |
| Stainless steel (2 minutes, 8000 rpm) | 1000 | 134 | 128 |
| Ceramic (2 minutes, 6000 rpm) | 13 | - | - |
| Ceramic (2 minutes, 8000 rpm) | 27 | - | - |
| Ceramic (2 minutes, 10000 rpm) | 40 | - | - |

Table 6.5 Concentrations of Contaminants in Hybridizer Processed Samples

The results of contamination obtained from the XRF were checked using Atomic Absorption. The sample processed with the ceramic lined Hybridizer for 2 minutes at 10000 rpm were digested with nitric acid and filtered. The Atomic Absorption results indicated that the concentration of Fe in the sample was approximately 25 ppm. This value, though lower than the results (40 ppm) obtained from the XRF analysis shows that the values obtained are in the same range.

6.1.6 Contamination Studies of Cellulose Coated with Silica Samples

The identification and quantification of contaminants in the cellulose samples processed in the three devices were done using the Atomic Absorption Spectrophotometer (Perkin Elmer 370). The samples were first digested using nitric acid and hydrogen peroxide. Standards of iron, nickel, and chromium were made, ranging from 1 to 5 pmm. These standards were then run in the AAS 370 to obtain the absorbances. The samples were then run in the AAS 370 to calculate the concentration of the contaminants, by using predetermined standards. The results showed the concentration of Fe, Ni, and Cr for all the examined samples to be less than 1 pmm.

At first these results were a little puzzling. However, on careful consideration of the system of cellulose and silica and the operating conditions, the results seemed quite reasonable. First, very mild processing conditions were used (e.g. for the Hybridizer, a processing time of 1 minute was used) to prevent severe size reduction of cellulose. Second, cellulose being a fiber has an aspect ratio and this structure allows the material to more easily broken than PMMA. Therefore, abrasion and erosion of the vessel due to the rubbing motion of the host particles is more with PMMA than with cellulose. Last, alumina is much more abrasive than silica and 5 wt. % of alumina was used in comparison to 1 wt. % of silica. This amount of alumina can severely aid in the abrasion and erosion of the vessel and magnetic particles than 1 wt. % of silica. More stringent operating conditions of the silica and cellulose system will lead to contaminated powders and significantly reduce the size of the cellulose material.

6.2 Adhesion

6.2.1 Introduction

The adhesion of fine particles to substrates is a topic of great interest in many fields of technology. Good adhesion is desirable for surface coatings, as well as for the adhesion of medicinal particles to specific sites, in the pharmaceutical industry. Undesirable adhesion occurs in cases where unwanted particles adhere to the surfaces of food, drugs, and semiconductors, resulting in severe product contamination. In adhesion, the adhesive forces generally refer to the minimum force needed to separate particles adhering to one another. Adhesion forces can be broadly classified into the following:

- Electrostatic forces
- Van der Waals forces
- Liquid bridges (capillary forces)
- Solid bridges

Electrostatic forces can occur when two solids, in contact with each other, charge each other electrostatically (triboelectrication). The electrostatic force can be calculated from the following expression:

$$F_{electro} = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2}$$
[6.1]

where q_1 and q_2 are the charge of the two particles, r is the distance between the two particles and ε_0 is the dielectric constant of the medium.

The van der Waals force can be considered a short-range electromagnetic force interacting between two molecules (atoms). The force can also exist between macroscopic bodies, such as particle-particle and particle-wall. An expression for the van der Waals force between a sphere and a plane, based on microscopic theory is given by:

$$F_{vvv} = \frac{Ad_p}{6z^2}$$
[6.2]

where A is the Hamaker constant (which depends on the surface properties of the material and has a value of the order of 10^{-19} Nm), z (m) is the particle separation distance at the co-ordination point (where 0.4 nm is the smallest separation distance) and d_p (m) is the particle diameter.

The relationship for the intensity of the van der Waals force between macroscopic bodies calculated by Lifshitz-Landau is given by:

$$F_{vw} = \frac{\hbar\omega}{16\pi z^2} d_p$$
 [6.3]

where $\hbar\omega$ is the "Lifshitz-van der Waals" constant which has values on the order of 10^{-19} nm.

Liquid bridges have different properties depending on the amount of liquid present in the bond. They can be immobile or mobile bonds. Mobile liquid bridging between solids is the sum of the forces due to capillary suction pressure and the surface tension of the liquid. Immobile liquid bridging are formed when thin layers of a viscous binder are introduced between the solids. Solid bridges occur as a result of sintering, chemical reaction, melting, hardening and crystallization. The strength of the bond formed is dependent upon the strength of the material forming the bond and the conditions at which the bond is formed.

In dry particle coating, with the absence of liquid and binders, van der Waals forces are the most predominant forces responsible for the adhesion of the guest particles to the host particles. The small guest particles that come into contact with the larger host particles by various mechanical impactions adhere to the surface via van der Waals forces. For each device, larger forces of impaction, result in higher surface coverage of the host particles. There is no direct way to quantify the adhesion of the guest particles onto the surface of the host particles after processing. Hence, several novel methods were examined to help determine the strength of the surface coating and quantify the amount of guest particles that were firmly attached to surface of the host particles.

First, an attempt was made to directly measure the amount of guest material that was not coated onto the surface of the host particle to calculate a term called the "sticking ratio". Before an experiment, the amount (weight) of guest and host particles was accurately measured. After processing, the total powder that was retrieved and collected was again weighed. The loss of any particle was assumed to be guest particles that got stuck onto the walls of the processing chamber or onto the magnetic particles (for the MAIC). It was assumed that no host particles were lost. The entire batch of coated product was then placed into a mesh basket of openings of 45 μm. The mesh basket was submerged into an ultrasonic bath filled with about 4.5 inches of distilled water for 1 minute with the ultrasonic bath turned on (Figure 6.14). Ultrasonic forces have been proven to be very effective in the removal of fine particles from surfaces. As it is a very extreme force, a short time of 1 minute was used.

The powders were then removed, dried in an oven at 70°C for 24 hours and then weighed. The change in mass was attributed to the loss of guest particles. Hence, knowing the amount of guest particles that was initially weighed, the amount of guest particles that remained with the host particles after being processed in the dry coating device, and the amount of guest particles remaining after ultrasonication, it was possible to calculate the "sticking ratio" as defined below:

$$stickingratio = \frac{x_s - z_s}{x_s} \times 100$$
[6.4]

and

$$x_s = y_s - m_b - m_m \tag{6.5}$$

where y_s is the initial mass of guest particles, m_b is the mass of guest particles stuck to processing bottle, m_m is the mass of guest particles stuck to the magnets, x_s is the mass of guest particles remaining with the host particles after processing, and z_s is the mass of guest particles lost during ultrasonication.

However, it was only possible to calculate the sticking ratio using Equation 6.3 for MAIC processed samples. Both host and guest particles were lost during processing in the Mechanofusion and the Hybridizer. In the Mechanofusion, as much as 3 grams of the total powder were lost, and for the Hybridizer, about 2 grams. As a result, SEM micrographs were used to assess the samples before and after they were subjected to ultrasonic forces. Again, the statistical technique used and described in Chapter 6 was used to calculate the surface coverage before and after ultrasonication (with the use of SEM micrographs). The surface coverage of the samples after ultrasonication was used to show the strength of the coating, and compare the adhesion of each device based on the operating parameters.





6.2.2 Particle Adhesion in the MAIC

The adhesion of the samples based on the calculation of the sticking ratio (Equation 6.4) for the MAIC processed samples, is shown in Figure 6.15. Surface coverage based on SEM micrographs as a function of processing time, before and after ultrasonication is shown in Figure 6.16. The average percentage of alumina adhering to the host particles is very similar in the two cases though the method of calculation is completely different.



Figure 6.15 Sticking Ratio as a function of processing time for MAIC samples, before and after ultrasonication.



Figure 6.16 Surface coverage as a function of processing for MAIC samples, before and after ultrasonication.

The average value of particle adhesion in the MAIC after ultrasonication was found to be around 40 %. SEM micrographs of PMMA coated with alumina for a processing time of 20 minutes, before and after ultrasonication is shown in Figures 6.17a and 6.17b, respectively. The MAIC can be classified as the gentlest of all the three coating devices. This is evident by the very low surface coverage achieved in this device. Almost 50% of the initial coating (for the case of 20 minutes processing) was washed away in the ultrasonic bath.



Figure 6.17 SEM micrographs of MAIC samples processed for 20 minutes (a) before ultrasonication and (b) after ultrasonication.

6.2.3 Particle Adhesion in Mechanofusion

The surface coverage of the Mechanofusion samples as a function of processing time, for PMMA coated with alumina at 600 and 800 rpm, before and after ultrasonication is shown in Figure 6.18. These samples were processed using the stainless steel arm head and scraper. SEM micrographs of PMMA coated with alumina for 40 minutes, at 800 rpm with the stainless steel arm head and scraper, before and after ultrasonication are shown in Figures 6.19a and 6.19b, respectively.

The stainless steel mechanofusion processed samples showed an overall loss of about 25 to 30 % of the original amount of alumina on the surface, for both rotation speeds. There was an overall decrease in the amount of alumina lost from the surface during ultrasonication, with increasing processing time, as well as with increasing rotation speed. At longer processing times, the guest particles have longer times to collide and get spread over the host particles, becoming more firmly attached to the surface. At higher rotation speed, the particles are subjected to high shear forces which again aids in the adhesion of the guest to host particles. This improves the adhesion of the host and guest particles, due to the embedding of the guest particles into the surface of the host particles. The embedding increases the contact area between the host and guest particles, and as a result, the van der Waals forces that hold the particles together after impaction increases.



Processing time (minutes)

Figure 6.18 Surface coverage as a function of processing time for PMMA coated with alumina, for different rotation speeds, before and after ultrasonication.



Figure 6.19 SEM micrographs of Mechanofusion samples processed for 40 minutes, at 800 rpm (a) before ultrasonication and (b) after ultrasonication.

6.2.4 Particle Adhesion in the Hybridizer

The surface coverage of PMMA with alumina in the ceramic lined Hybridizer as a function of rotation speed, before and after ultrasonication, is shown in Figures 6.20. The processing time was 2 minutes. Similarly, the surface coverage as a function of rotation speed for the stainless steel Hybridizer, before and after ultrasonication, is also shown in Figure 6.20. SEM micrographs of the samples processed at 8000 and 10000 rpm, with the ceramic lined Hybridizer, before and after ultrasonication is shown in Figures 6.21, and 6.22, respectively.

There was a decrease in the amount of alumina lost with increased rotation speed for both the ceramic lined and the stainless steel processed samples. There was an overall 3 to 12 % loss of alumina for all the samples analyzed, with the products processed at the higher rotation speeds having minimum loss of alumina. At higher rotation speeds, there are more collisions and better dispersion of the guest onto the surfaces of the host particles, which helps in the overall adhesion of the guest particles to the surface of the host particles.

At very higher impaction velocity it is even possible for the alumina guest particles to become embedded into the softer surface of the PMMA host particles. Similar to mechanofusion, when alumina particles become embedded into the surface of the host particles, the area of contact between the host and guest particles increases, resulting in an increase in the van der Waals forces between particles. An increase in the van der Waals force, the predominant adhesion force between the host and guest particles, gives better adhesion in the dry particle coating process.



Figure 6.20 Surface overage as a function of rotation speed, for HB processed samples (2 minutes), using both the ceramic lined device and the stainless steel device, before and after ultrasonication.



Figure 6.21 SEM micrographs of PMMA processed in the ceramic lined Hybridizer for 2 minutes, at 8000 rpm (a) before ultrasonication and (b) after ultrasonication.



Figure 6.22 SEM micrographs of PMMA processed in the ceramic lined Hybridizer for 2 minutes, at 10000 rpm (a) before ultrasonication and (b) after ultrasonication.

6.3 Adhesion Model for Dry Coating Studies

6.3.1 Introduction

The various dry coating processes are difficult to model because dynamics at several different length and time scales, that differ by several orders of magnitudes, are important. The largest length scale is the device scale, while the smallest length scale is the molecular scale. Only by considering the molecular scale, can one truly understand particle adhesion and the bonding between the guest and host particles. The intermediate scales are those of the host and guest particles. Since the sizes of host, guest and the device differ substantially, the problem of modeling needs to be broken up into a set of simpler problems.

Dry particle coating devices impart energy to systems of host and guest particles by the application of mechanical forces, causing the particles to impact each other. Impacting guest particles can either adhere to the host particle or rebound becoming detached from the host particle, depending on the magnitude of the adhesion forces between the host and the guest particles after impaction. Therefore, the objective is to theoretically calculate the adhesion energy between different systems of materials (used in the experimental study). With this information, it would be possible to predict the likelihood of the two materials (host and guest) adhering to each other after an impaction.

The preliminary idea to satisfy this objective is to use a model presented by Roger and Reed (1984). These authors presented a model to describe adhesion of particles due to elastic-plastic impacts with a surface. The model considers elastic deformation in the two impacting bodies and plastic deformation in the softer of the two bodies. For a guest particle G, impacting on a host particle H, the criteria which allows the particle to rebound is given by:

$$(Q_1 + Q_B - Q_p) > Q_A \tag{6.6}$$

where Q_I is the impacting energy due to an impacting velocity v, Q_B is the energy of attraction as G approaches H, Q_P is the energy dissipation in plastic deformation, Q_A is the adhesion energy between G and H, after collision. It is further assumed that $Q_I >> Q_B$, so that Equation 6.6 reduces to:

$$(Q_I - Q_p) > Q_A \tag{6.7}$$

The energy due to plastic deformation Q_p , is based on a model by Bitter (1963). The model proposed by Bitter is based on elastic and plastic deformations on one of the impacting bodies, with only elastic deformation occurring in the other.

There are two stages of the first phase for the interaction between the impacting bodies. The first stage is characterized by the purely elastic deformations of the two bodies due to impaction. The impact progresses until the pressure between the two bodies reaches the elastic yield limit of the softer of the two bodies. The elastic yield limit can only be reached if the impacting velocity is greater than the limiting elastic velocity φ , given by the following expression.

$$\varphi = \left(\frac{2\pi}{3K}\right)^2 \left(\frac{2}{5\rho}\right)^{0.5} y^{2.5}$$
(6.8)

where y is the elastic yield limit of the softer of the two bodies, ρ is the density of the impacting particle and K is defined by the following expression:

$$K = \frac{4}{[3\pi(k_1 + k_2)]} \tag{6.9}$$

with,

$$k_i = \frac{(1 - v_i^2)}{(\pi E_i)} \tag{6.10}$$

where v_i is the Poisson ratio and E_i is the Young's modulus of body i.

The second stage continues until the two bodies have zero relative velocity. During this stage, there is growth of a region of plastic deformation of the softer of the two bodies. This area of plastic deformation is surrounded by an annulus in which only elastic deformation occurs. The energy stored as elastic deformations in the area of plastic deformation is given by the following expression:

$$Q_{pe} = h_e \pi r_p^2 y / 2$$
 (6.11)

where, h_e is the distance which the centers of the two particles have moved closer together and r_p is the projected radius of the area of plastic deformation. The energy used up to produce this deformation is given by:

$$Q_p = \int_0^{Hp} \pi r^2 y dH \tag{6.12}$$

where Hp is the depth of the permanent deformation resulting from the impaction. With the use of Equations 6.9 to 6.12, Equation 6.11 reduces to:

$$Q_{pe} = \left(\frac{15}{4} - Q_e Q_p\right)^{\frac{1}{2}}$$
(6.13)

where Q_e is the energy stored as elastic deformations in the annular region around the area of plastic deformation. Using conversation of energy, the total kinetic energy of the impaction Q_I , can be expressed as follows:

$$Q_I = \left(\frac{v^2 m}{2}\right) = Q_e + Q_{pe} + Q_p$$
 (6.14)

where v is the impacting velocity and m is the mass of the impacting guest particle. From Equation 6.13, the energy used to produce the plastic deformation and the energy stored

as elastic energy in the area of plastic deformation can be expressed by the following expressions.

$$Q_{p} = \left(\frac{(2mv^{2} - \frac{1}{8}m\varphi^{2})^{0.5} - (\frac{15}{8}m\varphi^{2})^{0.5}}{2}\right)^{2}$$
(6.15)

and

$$Q_{pe} = \left(\frac{15m\varphi^2}{8}\right)^{0.5} \left(\frac{(2m\nu^2 - \frac{1}{8}m\varphi^2)^{0.5} - (\frac{15}{8}m\varphi^2)^{0.5}}{2}\right)$$
(6.16)

The adhesion energy of the two bodies that holds the bodies together after impaction is found from the expression:

$$U_T = U_M + U_S \tag{6.17}$$

where U_T is the total adhesion energy and is equal Q_A , U_M is the adhesion due to mechanical energy and U_S is the adhesion due to surface energy. U_M and U_S are defined by the following expressions:

$$U_{M} = P_{0} \left(\frac{P_{1}^{2/3} + 2P_{0}P_{1}^{-1/3}}{3K^{2/3}R_{c}^{1/3}} \right)$$
(6.18)

$$U_s = \Delta \gamma \pi \left(\frac{R_c P_1}{K}\right)^{2/3} \tag{6.19}$$

where P_0 is the external force applied to the contacting bodies ($P_0 = mg$), m is the mass of the guest particle, g is the gravitational force, $\Delta \gamma$ is the surface adhesive energy per unit area (Equation 6.20), and R_c is the contact geometry parameter given by Equation 6.21, and P_1 is defined by Equation 6.22.

$$\Delta \gamma = 2(\gamma_1^d \gamma_2^d)^{0.5} \tag{6.20}$$

where γ_i^d is the dispersive energy component of body i.

$$\frac{1}{R_c} = \frac{1}{R_1} + \frac{1}{R_2} \tag{6.21}$$

where R_1 is the radius of the host particle and R_2 is the radius of the guest particle.

$$P_{1} = P_{0} + 3\Delta\gamma\pi R_{c} + \left[(P_{0} + 3\Delta\gamma\pi R_{c})^{2} - P_{0}^{2} \right]^{1/2}$$
(6.22)

The projected radius of plastic deformation the particle undergoes is found by the following expression:

$$r_{p} = \left(\frac{2Q_{pe}}{\pi yR}\right)^{\frac{1}{2}} \left(\frac{3K}{2\pi y}\right)$$
(6.23)

Using the values calculated for U_T (= Q_A), Q_I and Q_P , and Equation 6.6, it is possible to predict for chosen systems of host and guest particles, whether the guest particles would adhere to or rebound from the surface of the host particles. The systems of host and guest particles used for the calculations are shown in Table 6.6. The properties of the materials are given in Table 6.7. A sample calculation that determines whether a guest particle rebounds from, or adheres to the surface of a host particle is given in APPENDIX D.

| Host Particles | Guest Particles |
|------------------|--------------------------|
| PMMA (~200 μm) | Alumina (0.7 µm) |
| PMMA (~200 μm) | Silica (0.25 µm) |
| PMMA (~200 μm) | Silicon Carbide (0.5 µm) |
| Alumina (~80 μm) | Silicon Carbide (0.5 µm) |

Table 6.6 Systems of Host and Guest Particles

| Properties | PMMA | Alumina | Silica | SiC |
|--|----------|----------|---------------|---------------|
| Elastic Yield Limit (Pa) | 10000000 | 70000000 | Not needed | Not needed |
| Density (kg/m ³) | 1190 | 3970 | 2200 | 3200 |
| Poisson's Ratio | 0.5 | 0.26 | 0.4 | 0.19 |
| Young's Modulus (MPa) | 3300 | 345000 | 300000 | 400000 |
| Hardness (GPa) | 21 | 2100 | 1250 | 2500 |
| Dispersive Surface Energy (mJ/m ²) | 41 | 100 | 72 | 214 |

 Table 6.7 Properties of Materials

6.3.2 Results and Discussion

The limiting elastic velocity φ , which must be achieved for plastic deformation of the host particles to occur, is given in Table 6.8 for each system. With all the three guest particles, the PMMA host particles required a much smaller limiting elastic velocity to undergo plastic deformation, than the alumina host particle impacted with SiC guest particles. The PMMA particles are much softer than the alumina particles (see Table 6.7). Therefore, less energy is required for the surface of PMMA to undergo plastic deformation.

The initial kinetic energy Q_I , of the impacting guest particles as a function guest size is shown in Figure 6.23. The values are calculated at an impacting velocity of 1 m/s. The initial kinetic energy is based on the density of the particles. Therefore, alumina with the highest density impacts the host particles with the largest impaction velocity. As the size of the guest particle increases and the impaction energy increases, the kinetic energy for the initial impaction increases.

| Host Particles | Limiting Elastic Velocity (m/s) |
|----------------|---------------------------------|
| PMMA-Alumina | 0.00042 |
| PMMA-Silica | 0.00056 |
| PMMA-SiC | 0.00047 |
| Alumina-SiC | 0.00935 |

Table 6.8 Limiting Elastic Velocity Required for Plastic Deformation



Figure 6.23 Initial kinetic energy Q_I , as a function of guest size at an impaction velocity of 1 m/s.

The energy dissipated in plastic flow Q_p , as a function of guest size, at an impaction velocity of 1m/s is shown in Figure 6.24. The guest particles are impacting a PMMA host particle. The energy dissipated for plastic deformations of PMMA, is highest in the case of alumina, due to the higher kinetic energy of the alumina guest particles. This is supported by the values obtained for the projected radius of plastic deformation, r_p . For alumina guest particles, larger deformations were achieved than for the SiC and silica guest particles, of the same guest sizes, and at the same impaction

velocity. Larger projected radius of plastic deformation results in larger surface deformation of the host particles due to the impacting guest particles. Larger the area of deformation results in a larger contact area between the host and guest particles, and hence, stronger the adhesion of the guest particles to the surface of the host particles. Therefore, better surface coverage is obtained for PMMA coated with alumina guest particles, based on impaction energy.



Figure 6.24 Energy dissipated for plastic deformation, Q_p , as a function guest size, at an impaction velocity of 1 m/s.



Figure 6.25 Projected radius of plastic deformation r_p , as a function guest size, at an impaction velocity of 1 m/s.

The total adhesive energy, Q_A , calculated using Equation 6.17, as a function of guest size, at an impaction velocity of 1 m/s is shown in Figure 6.26. The total energy is the energy that keeps the guest particles adhering to the host particles after initial impaction. The total adhesive energy, Q_A , is greatly dependent of the surface adhesive energy per unit area, $\Delta\gamma$. The surface adhesive energy of SiC is much higher that the values for silica and alumina. These values were estimated using the Hamaker constants of each guest particles. The larger surface adhesive energy for the PMMA-SiC system results in higher total adhesion energy than for silica and alumina guest particles.



Figure 6.26 Total adhesive energy as a function of guest particle size, at an impacting velocity.

The total adhesion energy as a function of guest particle size for SiC with PMMA and SiC with alumina is shown in Figure 6.27. The total adhesion energy is much higher for the PMMA-SiC system than for the alumina-SiC system. This was also confirmed by experimental results. A SEM micrograph of PMMA coated with SiC, for a processing time of 10 minutes in Mechanofusion, is shown in Figure 6.28a. A SEM micrograph of alumina coated with SiC using Mechanofusion, for a processing time of 10 minutes is shown in Figure 6.28b. It can clearly be seen that the PMMA host particle had a much higher surface coverage of SiC guest particles, than the alumina host particles. The wt. % of guest particles used in each study is 3% and 2%, for PMMA and alumina, respectively.



Figure 6.27 Total adhesion energy as a function of guest particle size, at an impacting velocity of 1 m/s.



Figure 6.28 Surface coverage of (a) PMMA and (b) alumina, coated with SiC in Mechanofusion for processing time of 10 minutes.

The overall objective of this comparison of the experiments, with the study of Roger and Reed (1984) is to predict whether an impacting guest particle would adhere to or rebound from the surface of a selected host particle. For all the case studies investigated, $Q_I - Q_p$ was much less than Q_A . This indicates that the guest particles would adhere to the host particles in all instances. The actual values and a sample calculation are given in APPENDIX D.

6.4 Conclusions

Contamination studies for PMMA coated samples have shown that there are parts per million (ppm) trace amount of Fe present in samples processed in all the devices, with the stainless steel Hybridizer producing the largest concentration of Fe. Mechanofusion and Hybridizer processed samples also have traces of Cr and Ni present, characteristic of the presence of stainless steel. With the use of the ceramic inner pieces in Mechanofusion, there was approximately a 50 % reduction of contamination of the samples. In the ceramic lined hybridizer, the presence of Fe at 10000 rpm indicates that the discharge tube plays a role in the contamination of the products at high rotation speeds.

In the adhesion studies, the strength of the coating achieved of each device is clearly demonstrated. The MAIC is the "gentlest" of all devices. Almost 50 % of its initial surface coverage was washed away during ultrasonication. The best surface coverage achieved was about 40%. In Mechanofusion, about 30% of the initial surface coverage was washed away during ultrasonication. The best surface coverage achieved was about 60% for the conditions examined. The hybridizer produced the strongest coating. Only about 5% of the initial surface coverage was washed away during ultrasonication in some of the experiments. The best surface coverage achieved was about 80% for the conditions examined.

The initial kinetic energy and the projected radius of plastic deformation, suggests that the PMMA-alumina system will undergo more surface deformation due to the higher

density of alumina and higher kinetic energy of this system. Silica, with the lowest density and lowest initial kinetic energy of the three guest materials studied, resulted in the smallest plastic deformation of the surface of the PMMA host particle. The total adhesion energy of the systems indicates that the best combination of host and guest particles would be PMMA host particles coated with SiC. This is evident by the difference in the hardness of both materials (see Table 6.7). For the cases of host-guest systems studied in this analysis, the rebounding energy (Q_I - Q_P) was much less than the total adhesion energy after impaction, Q_A . Therefore, the three different guest particles adhered to the surface of PMMA, and SiC adhered to the surface of alumina host particles. This is strongly supported by the experimental studies. In Chapter 4, both PMMA and alumina were coated with SiC to successfully promote deactivated sintering. In Chapter 5, almost 80 % of the surface of PMMA was covered with alumina.

CHAPTER 7

SYNTHESIS OF ATTRITION RESISTANT PARTICULATES BY DRY PARTICLE COATING

7.1 Introduction

Fluidized beds are used successfully in a multitude of processes that can be both catalytic and non-catalytic. Common catalytic uses are hydrogen carbon cracking of petroleum and reforming, and oxidation of naphthalene to phthalic anhydride. A few non-catalytic uses are roasting of sulfide ores, coking of petroleum resides, calcination of limestone, drying, coating, and particle classification (Perry and Green, 1984).

Fluidized beds provide efficient gas-solid contacting, good bed-to-wall transfer, and excellent temperature homogeneity. The beneficial properties of fluidized beds are all related to the mobility of the particles in the fluidized state. During fluidization the particles become an expanded, suspended mass that has many properties of a liquid. It has been observed that particles with distributions from 10 μ m to 150 μ m are the best for smooth fluidization with the least bubble formation.

Geldart (1973) characterized four groups of solids that exhibit different properties when fluidized by a gas. These groups are A, B, C and D. Group A particles are between 50 to 100 μ m and are readily fluidized. Group B particles do not show a particulate fluidization regime and are generally larger than 100 μ m. Group C particles are usually less than 30 μ m, cohesive and difficult to fluidize. Group D particles are larger than 1 mm and are fluidized by forming a fountain or spout with particles rising up at the center and falling down at the periphery of the "spouted bed".

150

As gas is passed upwards through the bed of fluidized particles, friction causes a pressure drop across the bed. As the gas velocity increases, the pressure drop increases until it equals the weight of the bed divided by the cross sectional area of the bed. This velocity is called the minimum fluidization velocity, U_{mf} . At this point, a bed of group A particles will expand uniformly as the velocity is increased (particulate fluidization). At a higher velocity, gas bubbles will develop in the system and this is known as the bubbling regime, also called the aggregative fluidization regime, as the bubbles, induce vigorous motion and mixing of the particles. For Group B particles, bubbles form immediately after minimum fluidization is reached.

As the velocity is further increased, the bed will expand, the density of the bed will decrease and turbulence will increase. This is known as the turbulence regime of the bed. In smaller diameter beds, especially with group C and D powders, slugging will occur as the bubbles in the bed increase in sizes and can become greater than half the diameter of the bed. The size of the bubbles in the system continues to increase as the gas velocity is further increased. Further increase in the velocity results in dilute-phase pneumatic transport of the two-phase system.

One of the major drawbacks of fluidized beds is the attrition particles undergo at higher gas velocities than the minimum fluidization regime, especially in the bubbling and turbulent regime. These collisions are due to particle interaction and bed-to-wall impacts. As a result, catalyst attrition has been a major obstacle in the development of new fluidized bed processes (Werther and Reppenhagen, 1999). The generation of fines is the main consequence of particle attrition. These fines are lost by entrainment in the gas and are collected by the dust recovery system, resulting in an overall loss of valuable
material. Due to the loss of fines by attrition, the remaining catalyst particle size distribution can change appreciably. It is therefore often necessary to add fresh make-up catalyst to maintain the system at the required particle size distribution.

The study of attrition of catalyst has been reported in the literature in two main areas. The first area is a study of the attrition of catalyst in different types of fluidized beds, different flow regimes and different regions of the bed (Werther and Reppenhagen, 1999; Weekes and Dumbill, 1990; Ghadiri *et al.*, 1992 and 1994; Zhao *et al.*, 1999). Several ASTM standards have been developed to help standardized the attrition of catalyst, based on the size of the materials used (ASTM D5757-95, ASTM D4058-96). The second area of study concentrates on making materials attrition resistant by different modification or manufacturing techniques (Wei *et al.*, 2000 and 2001).

This study focuses on the surface modification of catalyst supports by dry particle coating, to investigate the feasibility of making the material more attrition resistant. A high purity γ -alumina (~ 80 µm), used commercially as a catalytic support is coated with SiC (~0.5 µm) in several dry particle devices. The devices used are the MAIC, Mechanofusion, and the Hybridizer. The uncoated and coated particles are fluidized in a conventional vertical fluidized bed at velocities higher than minimum fluidization velocity for various times, to promote the attrition of the particles. The API Aerosizer is then used to measure the changes in the particle distribution, to investigate changes in size of the uncoated, as well as, the coated samples as a function of time run in the fluidized bed. SEM is also utilized to examine changes in the surface coverage, as well as the overall shape of the material as a function of time of fluidization in the bed.

7.2 Experimental

7.2.1 Dry Particle Coating

Measured amounts of host (alumina) and guest (SiC) particles were processed in the three dry particle coating devices. A measured amount of magnetic particle was also placed in with the host and the guest particles for the MAIC. The magnetic to powder mass ratio used was 2, and the size of the magnets was approximately 1.4 mm. The amount of guest particles used was 2 wt. %. The properties of alumina and SiC were given in the previous chapter (Table 4.1). The alumina used is a high purity γ -alumina. Due to changes in the size of the materials during processing in the dry coating devices, alumina without SiC, was run in the devices to provide controls for the investigation. The operating conditions for the devices are given in Table 7.1.

| Samples | Conditions | | |
|-----------------------------|---------------------|--|--|
| MAIC (without SiC) | 10 minutes | | |
| MAIC (with SiC) | 10 minutes | | |
| Mechanofusion (without SiC) | 40 minutes, 600 rpm | | |
| Mechanofusion (with SiC) | 40 minutes, 600 rpm | | |
| Hybridizer (without SiC) | 4 minutes, 6000 rpm | | |
| Hybridizer (with SiC) | 4 minutes, 6000 rpm | | |

| Table 7.1. Oberating Conditions for the Device | ole 7.1. Operating Con | ditions for | the Devices |
|---|------------------------|-------------|-------------|
|---|------------------------|-------------|-------------|

After processing, the particles (uncoated as well as coated) were sieved using a 38 μ m sieve to remove all the alumina under 38 μ m, as well as, any uncoated SiC sitting loosely in the system. A vibration sieve was used and the sieving time for all the runs

was 25 minutes. The uncoated and coated samples were then run in a plexi-glass fluidized bed of diameter of 1 inch. The sieved alumina particles belong to Geldart Group A.

7.2.2 Fluidized Bed

The batch size of powders processed in the dry coating devices varies from 10 grams for the MAIC, to 100 g for Mechanofusion, with 25 grams for the Hybridizer. The fluidized bed for attrition analysis had to be small enough to fluidize such small masses of particles. As a result a small system was built in-house. The fluidized bed constructed was a simple conventional vertical bed with a distributor made of wire mesh with openings of 45 μ m (labeled A on Figure 7.1). A schematic of the bed is show in Figure 7.1. Two types of distributor were used, a simple mesh that covered the entire bottom of the bed and a plate with a smaller diameter hole of 0.5 inches covered with mesh (Figure 7.2). The second distributor was used to provide a jet region. A photograph of the actual system is show in Figure 7.3.



Figure 7.1 Schematic of the Fluidized Bed.



Figure 7.2 Schematic of (a) full screen and (b) plate with small-hole distributors, used in the fluidized bed design.



Figure 7.3 Photograph of the fluidized bed.

The bed was fitted with a top screen (labeled B on Figure 7.1) made of a mesh of 20µm openings. This prevents a majority of the fines produced by attrition from leaving the system, allowing changes in the particle size distribution of the original feed to the

bed to be easily measured. Fine particles smaller than 20 μ m produced by attrition that leave the bed, were captured in the flask of distilled water (label C on Figure 7.1).

The bed was calibrated to measure the minimum fluidization velocity of the powder. A graph of pressure drop across the empty bed is shown in Figure 7.4. A graph of experimental pressure across the bed (height 2.1 inches) as a function of gas velocity is shown in Figure 7.5. The minimum fluidized velocity U_{mf} , is approximately 0.017 m/s. The theoretical pressure-drop across the bed as a function of gas velocity is also shown in Figure 7.5. The theoretical pressure drop was calculated using the Ergun Equation given by Equation 7.1.

$$\frac{\Delta P}{L} = \frac{150\mu\nu(1-\varepsilon)^2}{\phi^2 D_{\rho}^2 \varepsilon^3} + \frac{1.75\rho_f \nu^2(1-\varepsilon)}{\phi D_{\rho} \varepsilon^3}$$
7.1

where L is the height of the bed of powder, μ is the viscosity of the fluid, ρ_f is the density of the fluid, D_p is the mean particle diameter, v is the superficial gas velocity, ε is the voidage of the bed (assumed to be 0.4) and ϕ is the sphericity of the particles, assumed to be 0.8. A bed of 25 grams of powder, 2.1 inches in height is shown at rest in Figure 7.6a. Bubbles in the sample during fluidization appeared at gas velocities of approximately $2U_{mf}$. As a result, attrition tests were conducted at about $4U_{mf}$. A photograph of the bed at $4U_{mf}$ is shown in Figure 7.6b. The bubbles in the bed at $4U_{mf}$ could not be easily photographed and hence, are not shown. The coated and uncoated samples were processed in the fluidized bed at $4U_{mf}$ for various times given in Table 7.2.



Figure 7.4 Pressure drop (ΔP) across the empty fluidized bed as a function of superficial gas velocity (u) using the full screen distributor.



Figure 7.5 Theoretical and experimental pressure drop (ΔP) as a function of superficial velocity (u) using full screen distributor.



Figure 7.6 Photographs of the fluidized bed (a) at rest and (b) at $4U_{mf}$.

| Samples | Distributor | Mass (g) | Run Times (hours) |
|------------------------------|----------------|----------|-------------------|
| MAIC (without SiC) | Partial Screen | 10 | 2, 18 |
| MAIC (with SiC) | Partial Screen | 10 | 2, 18 |
| Mechanofusion (without SiC) | Partial Screen | 20 | 2, 18 |
| Mechanofusion (with SiC) | Partial Screen | 20 | 2, 18 |
| Mechanofusion (without SiC)* | Full Screen | 20 | 120 |
| Mechanofusion (with SiC)* | Full Screen | 20 | 120 |
| Hybridizer (without SiC) | Full Screen | 20 | 1.5 |
| Hybridizer (with SiC) | Full Screen | 20 | 1.5 |

* - the top screen at position B was removed to let the fines escape.

7.3 Results and Discussion

7.3.1 MAIC

SEM micrographs of alumina as received from the manufacturer, at two different magnifications are shown in Figure 7.7. The rough edges of the particles are clearly visible. SEM micrographs of alumina processed in the MAIC for 10 minutes, without SiC, as a function of processing time in the fluidized bed is shown in Figure 7.8. SEM micrographs of alumina coated with SiC in the MAIC for 10 minutes as a function of time run in the fluidized bed is shown in Figure 7.9. A rounder shape for the particles after being processed in the MAIC is observed. There is little change in the overall shape of the material, before and after being fluidized. The one important observation made was that the coated particles retained a significant amount of surface coverage of SiC after fluidization of 2 hours (Figure 7.10).



Figure 7.7 SEM micrographs of alumina as received (unprocessed) at (a) 235 x and (b) 500 x.

The cumulative volume distributions of the samples run for 0 and 2 hours, uncoated and coated, are shown in Figure 7.11. There is not much difference in the particle size distributions of the samples. The volume-mean particle size ranged from 59 to 70 microns. However, the preliminary results in Figure 7.11 show that the coated alumina particles were more attrition resistant than the uncoated material. The figure

shows attrition of the uncoated (50% mean diameter), but no attrition of the coated. Longer processing times in the fluidized were used but not analyzed, because during the runs the distributor at position B became clogged due to the fines produced by attrition.



Figure 7.8 SEM micrographs of alumina uncoated processed in MAIC for 10 minutes and fluidized in the bed for (a) 0 hours and (b) 2 hours.



Figure 7.9 SEM micrographs of alumina coated with SiC in MAIC for 10 minutes and processed in the fluidized bed for (a) 0 hours and (b) 2 hours.



Figure 7.10 SEM micrographs of (a) uncoated alumina, and alumina coated with SiC in MAIC and processed in the fluidized bed for (b) 0 hours and (c) 2 hours.



Figure 7.11 Cumulative volume-distribution of the uncoated and coated alumina, before and after fluidization.

7.3.2 Mechanofusion

SEM micrographs of alumina, without SiC, processed by Mechanofusion for 40 minutes at 600 rpm, before and after fluidization are shown in Figure 7.12. The particles were then fluidized for 2 and 18 hours, respectively (Figure 7.12) using the partial screen distributor. SEM micrographs of alumina coated with SiC using Mechanofusion for 40 minutes, at 600 rpm, before and after fluidization are shown in Figure 7.13. Again, the fluidization times were 2 and 18 hours. SEM micrographs of alumina, uncoated and coated, processed in the fluidized bed for 5 days are shown in Figure 7.14. The top screen (label B in Figure 7.1) was removed to prevent the upper screen from becoming clogged with fines during the five-day period.



Figure 7.12 SEM micrographs of alumina, without SiC, processed in Mechanofusion for 40 minutes at 600 rpm, and fluidized for (a) 0 hours, (b) 2 hours and (c) 18 hours.



Figure 7.13 SEM micrographs of alumina coated with SiC in Mechanofusion for 40 minutes at 600 rpm, and fluidized for (a) 0 hours, (b) 2 hours and (c) 18 hours.



Figure 7.14 SEM micrographs of alumina (a) uncoated and (b) coated with SiC, processed by Mechanofusion for 40 minutes at 600 rpm and fluidized for 5 days.



Figure 7.15 Cumulative volume distribution of alumina, without SiC, processed by Mechanofusion and fluidized for different times.

The cumulative volume distributions of alumina, uncoated and coated, before and after fluidization are shown in Figures 7.15 and 7.16, respectively. The fluidization times examined were 2 and 18 hours, respectively. The cumulative volume distributions of alumina, uncoated and coated, and fluidized for 5 days are shown in Figure 7.17.



Figure 7.16 Cumulative volume distribution of alumina coated with SiC in the Mechanofusion and fluidized for different times.



Figure 7.17 Cumulative volume distribution of alumina, uncoated and coated with SiC, fluidized for 5 days.

These preliminary results again indicate that the uncoated alumina is less attrition resistant than the SiC coated alumina. This is evident from the SEM micrographs in Figure 7.12 and Figure 7.13. At 2 and 18 hours after being fluidized, the uncoated particle appeared much more smoothed than the coated alumina. The cumulative volume distributions also suggested that the uncoated particle had undergone a larger size reduction that the coated material. Based on the mean particle size at 50%, the uncoated sample underwent a size reduction of about 5 microns after 18 hours, compared to 2 microns for the SiC coated alumina, after 18 hours. For the 5 days fluidized samples, the uncoated underwent a size change of about 7 microns, compared to the coated material that underwent a size change of about 3 microns.

The number based distribution did not show as much fines in the Mechanofusion processed samples compared to the MAIC samples. It was possible to fluidize the particles for extended periods of time without the distributor being clogged (with the screen at point B removed). This indicates that the Mechanofusion coated particles held up better that the MAIC coated particles, which was to be expected.

7.3.3 Hybridizer Samples

A SEM micrograph of alumina, without SiC, processed in the Hybridizer for 4 minutes at 6000 rpm, is shown in Figure 7.18a. A SEM micrograph of alumina coated with SiC in the Hybridizer for 4 minutes, at 6000 rpm is shown in Figure 7.18b.



Figure 7.18 SEM micrographs of alumina (a) uncoated and (b) coated with SiC, processed in the Hybridizer for 4 minutes at 6000 rpm.

The particles, both uncoated and coated appeared round and smooth. The Hybridizer is known for its spheroidization feature. These samples were fluidized in the bed. However, at very short processing times less than 0.5 hours, the distributor became clogged with fines. This occurred with both types of distributors. The strong impaction forces in the Hybridizer can cause materials to undergo severe size reduction (as see previously in Chapter 4, Section 4.3.5. The number based cumulative distributions of alumina after being processed in the Hybridizer, showed the presence of a large percentage of fines in the samples. For alumina, processed without SiC, the percentage of particles below 45 µm was 70 %, and for alumina coated with alumina, 80 % of the particles were below 45 µm.

7.4 Conclusions

The idea of the making gamma alumina catalytic support particles attrition resistant by dry particle coating the surfaces with SiC, resulted from the work on deactivated sintering (Chapter 4). It is a relatively new area of study in this research. The results presented are preliminary results and are somewhat inconclusive. However, the investigation has provided valuable information needed for the continuation of the project. From the studies, it has been learned that the fluidized bed currently being used does not provide a strong enough fluidization jet region that will allow the particles to undergo significant attrition in short periods of time. Originally, the idea was to duplicate the conventional fluidized beds used commercially. However, with this method very long processing times are required for the particles to undergo significant attrition. Therefore, the fluidized bed should be re-designed to provide a jet region. This can easily be done, by re-constructing the distributor to comprise of a few small holes rather using a full or partial screen distributor, as in these experiments.

Dry particle coating of alumina with SiC, in all the three dry coating devices, reduces the size of the alumina. To provide uncoated control particles, alumina without SiC, was run in the devices for the same operating conditions as alumina with SiC. However, the presence of SiC in the system contributes to the size reduction of alumina. Therefore, to overcome this additional size reduction problems, smaller guest particles sizes, as well as smaller amounts of guest particles should be used to minimize the size reduction of the alumna in the dry particle coating devices. The samples can also be sieved within a narrower size distribution. Also the top mesh, with openings of 20 μ m,

used to retain the fines should be removed as it becomes clogged during the experiments, and by preventing the elimination of fines results in clogging the distributor as well.

The preliminary results however, do provide some indication as to robustness of the coating. For MAIC and Mechanofusion, SEM micrographs show that there is still a significant amount of SiC on the surface of alumina after 2 hours of processing in the fluidized bed. For Mechanofusion processed samples processed in the fluidized bed for 18 and 5 days, much of the initial surface coverage of SiC on the surface remained attached.

CHAPTER 8

CONCLUSIONS

8.1 Closing Remarks

Dry particle coating used for the synthesis of materials with new/improved properties has been successfully demonstrated. The key parameters, affecting the coating performance of three dry coating devices (MAIC, Mechanofusion, and Hybridizer) were examined for a system of PMMA coated with alumina. A more in depth study was done for MAIC, as very little information was previously available for this device. A comparative study of the three devices, again for a system of PMMA coated with alumina, has shown the strengths and weaknesses of the devices.

MAIC was found to be the gentlest of all the devices. The flowability and wettability of cornstarch was successfully modified with the use of this device, without undergoing severe size changes. Cellulose, consisting of fibers with an aspect ratio of about 4 to 5, did show some attrition (breakage) for long processing times. These materials were tested in the Hybridizer, but due to the intense impaction forces in this device, the materials underwent severe size reduction. It was also impossible to coat glass beads in the Hybridizer, as the material was ground, even at the lowest rotation speed and the shortest processing time. However, it was possible to coat glass beads in Mechanofusion. Using very short processing times (10 minutes) and also low rotation speeds (400 rpm) in Mechanofusion, it was possible to process cellulose in the device, without severe size changes. However, studies have shown at these gentle operating conditions, the desired surface coverage could not be achieved.

The phenomenon of deactivated sintering is defined in this research for the first time. There is no literature on deactivated sintering, though there are numerous examples of activated sintering of metals and ceramics available in the literature. Fundamental studies have been done to show that deactivated sintering can indeed be obtained by a discrete coating of various host particles with SiC guest particles, which has a very high melting point (~2700°C). The mechanisms of deactivated sintering have been investigated for both crystalline and amorphous materials, and experiments conducted to verify these mechanisms.

In the contamination studies, it has been shown that there is a significant amount of abrasion and erosion of the processing chamber, inner pieces and magnetic particles. This is inevitable, as mechanical impaction provides the energy for the surface coverage, which will also contribute to the abrasion and erosion of the components of the coating device. Overall, the Hybridizer (with ceramic inner parts) can be considered the system with the least contamination, followed by MAIC and then Mechanofusion. In the Hybridizer, the contribution of the discharge pipes to the contamination of the products is presented for the first time. With Mechanofusion, a limitation was that a ceramic lined vessel was not available for this study, as this would definitely have reduced the contamination of the powders. Therefore, for a desired coating, where contamination is a major concern, both Mechanofusion and the Hybridizer can be used (with ceramic parts) and with the proper operating conditions. MAIC will cause contamination from the magnetic particles, however these can be precoated with polymers to limit the contamination. In the Hybridizer, the particles are subjected to strongest impaction forces as observed from the ultrasonic studies. Only about 5% of the initial surface coverage was washed away in the ultrasonic bath. The ultrasonic bath is an extreme method for testing the adhesion of the guest particles to the surface of the host particles. Nevertheless, it has provided a method by which the coating strength of the devices can be compared. Mechanofusion was second to the Hybridizer in providing a strong surface coating. MAIC was the "gentlest" of all the devices.

The adhesion model of Roger and Reed (1984), for a particle impacting another particle, whereby there is an elastic-plastic deformation has been used to investigate whether guest particles rebound from or adhere to the surface of host particles. It has been shown that for dense particles, which possess higher inertia than lighter particles, there is a larger area of plastic deformation. Also, for the total adhesion energy, systems (host and guest particles) with larger surface adhesive energy per unit area will have a higher adhesion force after impaction. In this study, the systems (host and guest particles) of materials investigated all adhered to the surface of the host particles. This is verified by the experimental results.

The study of the production of attrition resistant particles by dry particle coating is introduced in this research. Though the results are somewhat inconclusive, it has provided vital insights for the continuation of the project. Preliminary results have indicated that after several hours of fluidizing the particles, there still remains a significant surface coverage of SiC on the surface of the host particles.

8.2 Recommendations

In this research, dry particle coating has been successfully used for the synthesis of particles with improved flowability, reduced wettability, and increased sintering temperatures. There are however many other applications where dry particle coating technology can be utilized for the production of improved composites. One such area is in the activated sintering of metals and ceramics. Though, activated sintering is well documented in the literature, it has been achieved by other coating techniques. Activated sintering has many potential applications, for which dry particle coating can be a cheaper, and a more environmental friendly way of producing coated materials.

In the promotion of deactivated sintering, more experiments need to be conducted to examine the surface viscosity as a function of temperature, for both the uncoated and coated material. It is believed that surface viscosity of the uncoated PMMA or glass beads does not change at a given temperature. However, the surface coverage of SiC hinders the viscous flow mechanism, resulting in a higher effective surface viscosity. Therefore, the "effective" surface viscosity of the coated material needs to be correlated as a function of surface coverage achieved.

The effect of the key parameters on the coating performance of the devices has been studied for a system of PMMA coated with alumina. Though, these conditions may vary for different systems of materials, (e.g. the best coating conditions for cornstarch coated in MAIC was at a processing time of 20 minutes, but for alumina and PMMA it was between 5 and 10 minutes, depending on the size of guest particles), the overall trends remain the same. However, there are two important parameters that need to be analyzed in the subsequent research studies; these are the upper and lower size limit of host particles that can be processed in each device. With guest particles, the lower limit is controlled by the ability of the device to de-agglomerate the guest particles. The upper limit depends on the size ratio of the host to guest particles.

In the area of particle adhesion, there are numerous factors that still need to be addressed. First, guest particles in the sub-micron range exist as agglomerates. The ability of the dry coating to de-agglomerate and effectively disperse the guest particles should be investigated both experimentally and theoretically. In the study of surface coverage as a function of guest particle sizes, an uneven coating of the surface of PMMA with the 0.05 micron guest particles was observed. With the use of 0.2 micron guest particles a more uniform coating was observed. The ability to model and thus predict whether a guest particle would de-agglomerate based on the forces they are subjected to in the devices would greatly simplify the amount of experiments that need to be conducted.

The total adhesion energy of a system of host and guest particles can also be calculated to give an indication of the strength of the adhesion forces between the materials. This can provide a theoretical base to determine whether the coating would be strong enough to remain attached during processing and handling. The model of Roger and Reed (1984) can also be used to calculate whether particles would rebound from or adhere to the surface of a host particle. In this study an impaction velocity of 1 m/s was randomly chosen. The most precise calculation would result from a combination of the numerical stimulation and experimental studies. For example, the collision energy which the particles, undergoes can be obtained from numerical simulations, and adhesion information such as strength of adhesion and depth of deformation can be obtained from

Atomic Force Microscope (AFM) experiments. From this information, a correlation can be developed which can accurately predict the likelihood of materials adhering during impaction, the deformation of the host particles upon impaction, and the total adhesion energy after impaction.

APPENDIX A

CALCULATION OF SURFACE VISCOSITY

The following plots were used to calculate the surface viscosity of uncoated PMMA and glass beads, as well as the "effective" surface viscosity of PMMA and glass beads coated with SiC. The slopes of the lines constructed are used in Equation 4.17. The log-log plots verify the mechanism of sintering.



Figure A1 Log-log plot of contraction as a function of time, at an isothermal temperature of 105°C, for uncoated PMMA.



Figure A2 Contraction as a function of time, at an isothermal temperature of 105°C, for uncoated PMMA.



Figure A3 Log-log plot of contraction as a function of time, at an isothermal temperature of 105°C, for PMMA coated with 3wt.% of SiC.



Figure A4 Contraction as a function of time, at an isothermal temperature of 105°C, for PMMA coated with 3wt.% of SiC.



Figure A5 Log-log plot of contraction as a function of time, at an isothermal temperature of 120°C, for uncoated PMMA.



Figure A6 Contraction as a function of time, at an isothermal temperature of 120°C, for uncoated PMMA.



Figure A7 Log-log plot of contraction as a function of time, at an isothermal temperature of 120°C, for PMMA coated with 3wt.% of SiC.



Figure A8 Contraction as a function of time, at an isothermal temperature of 120°C, for PMMA coated with 3wt.% of SiC.



Figure A9 Log-log plot of contraction as a function of time, at an isothermal temperature of 600°C, for uncoated glass beads.



Figure A10 Contraction as a function of time, at an isothermal temperature of 600°C, for uncoated glass beads.



Figure A11 Log-log plot of contraction as a function of time, at an isothermal temperature of 600°C, for glass beads coated with 8wt.% of SiC.



Figure A12 Contraction as a function of time, at an isothermal temperature of 600°C, for glass beads coated with 8wt.% of SiC.

APPENDIX B

CALCULATION OF SURFACE COVERAGE

A sample calculation is presented to show how the surface coverage of the host particles is obtained using SEM micrographs. SEM micrographs of the coated particles at very high magnification are taken, and then lines drawn randomly on the picture. The same magnification is always used. The lines are 8 cm in length. The length of the line that crosses guest particles is measured using a scale, and expressed as a percentage of the original length of the line. The following figures give examples of how this is done.



Figure B1 SEM micrograph used to calculate the surface coverage of the guest particles. Example 1:

Line 1: 5 mm cross guest particles (surface coverage = $5/80 \sim 6\%$ coverage)

Line 2: 35 mm cross guest particles (surface coverage = $35/80 \sim 44\%$ coverage)

An average of all the lines is taken and presented as the surface coverage. In this case the surface coverage was found to be $\sim 20\%$



Figure B2 SEM micrograph used to calculate the surface coverage of the guest particles

Example 2:

Line 1: 75 mm cross guest particles (surface coverage = $75/80 \sim 94\%$)

Line 2: 40 mm cross guest particles (surface coverage = $38/80 \sim 48\%$)

The average of all the lines is taken as the surface coverage of the particles. In this case the surface coverage was found to be 75%.

APPENDIX C

CALCULATION OF CONTAMINATION

Sample Calculation

The following sample calculation shows how the concentrations of the contaminants are calculated using the results from the XRF. The samples processed in the Hybridizer device are used to construct the calibration curve.

| Total powder used in the Hybridizer | == | 20 grams | | |
|-------------------------------------|----|----------|---|-------------|
| Amount of PMMA | = | 95 wt. % | = | 19.00 grams |
| Amount of Alumina | = | 5 wt. % | = | 1.00 grams |

Assuming perfect mixture of PMMA and alumina, and using 2 grams for XRF analysis.

| Amount of PMMA | - | 95 wt. % | = | 1.90 grams |
|-------------------|---|----------|---|------------|
| Amount of Alumina | = | 5 wt. % | = | 0.10 grams |

The XRF identifies the elements present in the sample based on a weight percentage.

e.g. Sample processed in the Hybridizer for 2 minutes at 8000 rpm in the stainless steel device.

Elemental composition is given as follows

| Amount of alumina present in sample | = | 95.908 wt. % |
|-------------------------------------|---|--------------|
| Amount of iron present in sample | = | 01.925 wt. % |
| Amount of chromium in sample | = | 00.498 wt. % |
| Amount of Silica in sample | = | 01.669 wt % |

Therefore for Iron:

If 95.908 wt. % of sample = 0.10 grams

| Then, 01.925 wt. % | = . | (0.1/0. | 95908): | x 0.01925 |
|-------------------------------|----------|---------|---------|---------------|
| Concentration of iron | = | 0.002 | grams/2 | grams sample |
| | = | 0.001 | grams/g | ram of sample |
| Concentration of iron in part | s per mi | llion | = | 0.001mg/1000 |
| | | | = | 1000 ppm |

Similarly this was done to calculate the concentration of iron in the samples processed in the stainless steel Hybridizer for 2 minutes, at 5000 and 6000 rpm. The concentrations of iron in the samples in parts per million were plotted as a function of intensity. The points are fitted by a least square methods, where the equation of the line is given as follows:

$$y = 66.81x \ (R^2 = 0.996) \tag{C1}$$

where x is the intensity of the of the element in the sample, and y is the concentration (ppm) of the element in sample. The intensity of alpha iron (FEKA) is then measured from the graph obtained from the XRF analysis and substitute into Equation C1 to calculate the measure the concentration in parts per million.

e.g. Sample processed in the Hybridizer for 2 minutes, at 10000 rpm in the ceramic lined device.

| The intensity of FEKA in the sample | | 0.6 kcps |
|---|---|--------------------|
| The concentration of iron in the sample | = | 0.6 x 66.81 |
| Concentration of iron in the sample | = | 40 ppm (Table 6.5) |

Similarly for chromium and nickel, the intensity of the elements detected by XRF was used in Equation C1 to calculate the concentrations of these elements in the samples.

APPENDIX D

CALCULATION OF ADHESION ENERGY

The following sample calculation shows for a system of PMMA and alumina, whether the impacting guest particle (alumina ~ 0.7 microns) will adhere to or rebound from the surface of the host particles.

| Properties | ΡΜΜΑ (200 μm) | Alumina (0.7 μm) |
|--|------------------|---------------------|
| Elastic Yield Limit (Pa) | 10000000 | 7000000 |
| Density (kg/m ³) | 1190 | 3970 |
| Poisson's Ratio | 0.5 | 0.26 |
| Young's Modulus (Mpa) | 3300 | 345000 |
| Hardness (Knoop) | 21 | 2100 |
| Dispersive Surface Energy (mJ/m ²) | 41 | 68 |

For rebound to occur:

$$(Q_I - Q_p) > Q_A$$

where QI is the initial kinetic energy, Qp is the energy dissipated in particle deformation and QA is the adhesion energy after impaction. For the model to be valid the impaction velocity v, must be larger than the elastic limiting velocity φ :

$$\varphi = \left(\frac{2\pi}{3K}\right)^2 \left(\frac{2}{5\rho}\right)^{0.5} y^{2.5}$$
$$K = \frac{4}{[3\pi(k_1 + k_2)]}$$

with,

$$k_i = \frac{(1 - v_i^2)}{(\pi E_i)}$$

where v_i is the Poisson ratio and E_i is the Young's modulus of body i.

$$k_{1} = \frac{1 - 0.5^{2}}{\pi (3.3 \times 10^{9})} = 7.23 \times 10^{-11}$$
$$k_{2} = \frac{1 - 0.26^{2}}{\pi (3.45 \times 10^{11})} = 8.61 \times 10^{-13}$$
$$K = \frac{4}{3\pi (k_{1} + k_{2})} = 5.8 \times 10^{9}$$

Therefore the elastic limiting velocity is:

$$\varphi = \left(\frac{2\pi}{3 \times 5.8 \times 10^9}\right)^2 \left(\frac{2}{5 \times 3970}\right)^{0.5} (10 \times 10^6)^{2.5} = 0.00042 \text{ m/s}$$

The initial kinetic energy is given by:

$$Q_{I} = \left(\frac{v^{2}m}{2}\right) = Q_{e} + Q_{pe} + Q_{p} = \left(\frac{1^{2} \times (3970) \times (\frac{4}{3}\pi \times (3.5 \times 10^{8})^{3})}{2}\right) = 3.6 \times 10^{-16} J$$

Where the impacting velocity v, is chosen as 1 m/s. The energy used to produce the plastic deformation and the energy stored as elastic energy in the area of plastic deformation can be expressed by the following expressions.

$$Q_{p} = \left(\frac{(2mv^{2} - \frac{1}{8}m\varphi^{2})^{0.5} - (\frac{15}{8}m\varphi^{2})^{0.5}}{2}\right)^{2} = 3.56 \times 10^{-16} J$$

Energy for rebound:

$$Q_I - Q_P = 4 \times 10^{-18} J$$

The total adhesion energy is given by:

$$Q_A = U_T = U_M + U_S$$

where, U_T is the total adhesion energy and is equal Q_A , U_M is the adhesion due to mechanical energy and U_S is the adhesion due to surface energy. U_M and U_S are defined by the following expressions:

$$U_{M} = P_{0} \left(\frac{P_{1}^{2/3} + 2P_{0}P_{1}^{-1/3}}{3K^{2/3}R_{c}^{1/3}} \right)$$

$$U_{S} = \Delta \gamma \pi \left(\frac{R_{c}P_{1}}{K} \right)^{2/3}$$

$$P_{0} = mg = \left(\frac{4}{3} \pi (3.5 \times 10^{-8})^{3} \right) \times 3970) \times 9.8 = 7.0 \times 10^{-15} N$$

$$\Delta \gamma = 2(\gamma_{1}^{d} \gamma_{2}^{d})^{0.5} = 2(38 \times 68)^{0.5} \div 1000 = 0.106 \frac{J}{m^{2}}$$

$$\frac{1}{R_{c}} = \frac{1}{R_{1}} + \frac{1}{R_{2}} = \frac{1}{0.0001} + \frac{1}{0.000000035} = 3.48 \times 10^{-7}$$

$$P_{1} = P_{0} + 3\Delta \gamma \pi R_{c} + \left[(P_{0} + 3\Delta \gamma \pi R_{c})^{2} - P_{0}^{2} \right]^{1/2} = 6.9 \times 10^{-7} N$$

$$U_{M} = 6.78 \times 10^{-24} J$$

$$U_{S} = 4.01 \times 10^{-16} J$$

$$U_{T} = 4.01 \times 10^{-16} J$$

Therefore the alumina guest particle adhere to the surface of the PMMA host particle as,

$$Q_{I}-Q_{P} < Q_{A}$$

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