

Microencapsulation of Finely Divided Ceramic Powders

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Abstract

Polymer coated alumina particles have been prepared by spray drying alumina powder with a polymer emulsion. Powders containing a maximum of 50% wt. were obtained. The coated particles were compared to mixtures of alumina and polymer. Oven sintering tests show the coated material to compact more than the mixed and pure polymer materials. Strong, well defined parts with layer thicknesses of 0.002" were produced from both coated and mixed materials by the Selective Layer Sintering process.

Introduction

Microencapsulation is a method by which minute particles of fluids or solids are encased in a shell of polymeric material. Microencapsulation finds uses in many everyday applications ranging from carbonless copy paper and scented tissues to time released pharmaceuticals and electrostatographic toners. Microencapsulation is envisioned as a means of adapting the Selective Layer Sintering (SLS) process to the production of ceramic and metal products. By taking advantage of low melting point polymers as encapsulating materials and ultimately as intermediate binders it is hoped that full utilization of the SLS process will be achieved without the need for high temperature modifications otherwise required for normal ceramic and metal processing.

Many methods exist for the encapsulation of small particles (Kondo, 1979). Of these methods, spray drying was chosen due to its availability. Since spray drying is an evaporative process it is possible to make use of water soluble polymers and water based polymer emulsions. The studies focus on polymer emulsions due to wide variety of materials available with a broad spectrum of properties.

Materials and Methods

Samples of polymer latex emulsions were obtained from BF Goodrich Corp. and Union Carbide Corp. These samples were Geon 151, Geon 460x49 and Hycar 26256 from BF Goodrich Corp. and UCAR 148, UCAR 430, and UCAR 133 from Union Carbide Corp. Table 1 lists polymer constituents. Finely divided alumina (mean particle size $< 10\mu\text{m}$) was obtained from Aldrich Chemical Company.

Table 1. Polymer emulsions

Emulsion	Polymer type	T _g (°C)
UCAR 148	Styrene, Methacrylic Acid Copolymer	45
UCAR 430	Styrene, Methyl Methacrylate, Butyl Acrylate, Methacrylic Acid Copolymer	50
UCAR 133	Vinyl Acetate	1.5
Geon 151	Vinyl Chloride Copolymer	82
Geon 460x49	Vinyl Chloride Copolymer	40
Hycar 26256	Acrylic Ester Copolymer	45

The experimental apparatus used for spray drying is a "Pulvis Mini-Spray" spray drier, Model GA-31. This apparatus consists of a main drying chamber with cross-sectional area of 182.4 cm² and height of 71 cm, a nozzle type atomizer with 0.4 mm-diameter orifice and pressure capability of 0 to 70 psi, a liquid feed peristaltic pump capable of 0 to 40 ml/min, a bypass-type aspirator providing airflows of 0 to 700 L/min, and a 2 kW heater for heating inlet drying air in the range 40 to 200°C.

Emulsion Solids Determination

The reported emulsion solids contents were verified by drying a weighed sample of emulsion in an oven at 50°C for 8 hr. The resulting solid was again weighed to determine the emulsion solids weight percentage.

Preparation of Spray Dried Material

Pure dried polymer material was obtained by processing the polymer emulsion as received or, if the emulsion was too viscous, first diluting the emulsion with water to lower the viscosity. To produce alumina particles coated with polymer the emulsion solids content was maintained at the determined value by adding alumina to the emulsion in an amount to effect a 1:1 ratio of polymer to alumina and then adding water to restore the percent solids. This was done to maintain the flow characteristics of the emulsions and to reduce the amount of settling of alumina from the fluid. The details of polymer emulsion, alumina, and water amounts used are presented in Table 2. Spray drying conditions were maintained so that complete drying resulted. Typical drying conditions are presented in Table 3. Alumina contents of the spray dried products were determined by ashing a sample at 650°C for 2 hours.

Table 2. Details of polymer emulsion and alumina mixtures prepared

Emulsion	Solids Content, (wt%)	Mass of emulsion, (g)	Mass of alumina, (g)	Mass of water, (g)
UCAR 430	43	35.5	16.2	27.0
Hycar 26256	52.2	50.1	25.0	25.7

Table 3. Spray drying conditions

Emulsion	Fluid flow, (ml/min)	Drying air flow, (L/min)	Nozzle pressure, (psi)	Inlet temperature, (°C)
UCAR 133	7.1	225	42.6	100
UCAR 148	8.5	275	45.5	110
UCAR 430	11.0	300	45.5	115
Hycar 26256	12.1	340	45.5	120
Geon 460x49	12.1	275	45.5	120
Geon 151	24.2	340	45.5	140

Measurement of Sintering Rates and SLS

Samples of spray dried UCAR 430 materials including pure polymer, polymer coated alumina, and alumina mixed with spray dried polymer were prepared according to the method described by Nelson. Sintering rates were measured at 50°C for 2 hr. Samples of spray dried UCAR 430 materials were processed by the SLS process. Process operating conditions are presented in Table 4.

Table 4. Selective Layer Sintering operating parameters

Part	Roller speed	Laser	In, (")	Out, (")	Temp., (°C)	δx , (")	δy , (")	SS, (Grid units)	SP, (μs)
CIRC2	Slow	CO ₂	0.003	0.002	35.0	0.01	0.01	5	5

Results and Discussion

A typical electron micrograph of pure spray dried UCAR 430 polymer is shown in Figure 1. From the micrograph it can be seen that an extremely fine polymer particulate results. Coulter Counter measurements have shown the mean particle size diameter produced to be between 2 and 10 μm in size. Hycar 26256, UCAR 148, and UCAR 430 each produced good free flowing powders. Of the remaining latexes Geon 151 and Geon 460x49 produces highly static powders and tended to form small balls of material. UCAR

133 solidified over a short period of time due to a low T_g . Typical product yields based on fluid through-put, emulsion percent total solids, and amount of polymer collected are shown in Table 5. Amounts not recovered are explained by losses to the air flow and sticking within the system.

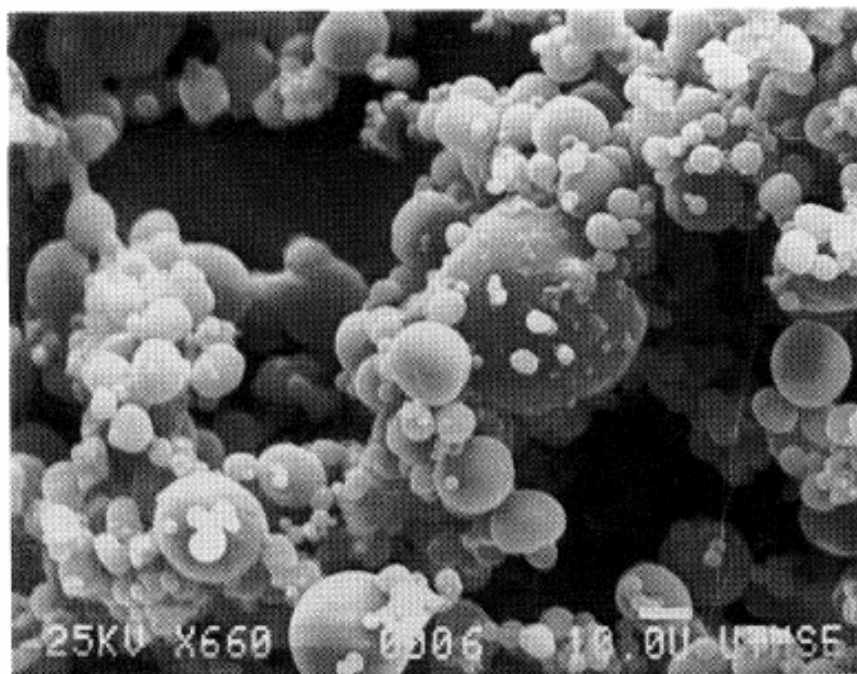


Figure 1. Spray dried UCAR 430 polymer

Table 5. Spray dried pure polymer yields

Emulsion	Percent Total Solids	Yield, % recovered
UCAR 133	60.0	46.0
UCAR 148	46.7	75.8
UCAR 430	44.0	84.0
Geon 151	54.6	82.7
Geon 460x49	52.2	63.9
Hycar 26256	50.1	69.3

An electron micrograph of an alumina particle coated with UCAR 430 is shown in Figure 2. A comparison electron micrograph of pure alumina is provided in Figure 3. It is clear the particle shown in Figure 2 is indeed an alumina particle due to the underlying feature similarities with the pure alumina shown in Figure 3. Electron micrographs of alumina coated with Hycar 26256 are similar. Of the coated samples, however, yields of solids were not much different than those obtained for the pure samples. The amount of

Figure 4 shows sintering rates obtained for pure UCAR 430, alumina coated with UCAR 430 (50% wt.), and alumina mixed with UCAR 430 (50% wt.). The coated sample clearly compacts more than the mixed sample. Repeated results are shown in Figure 5.

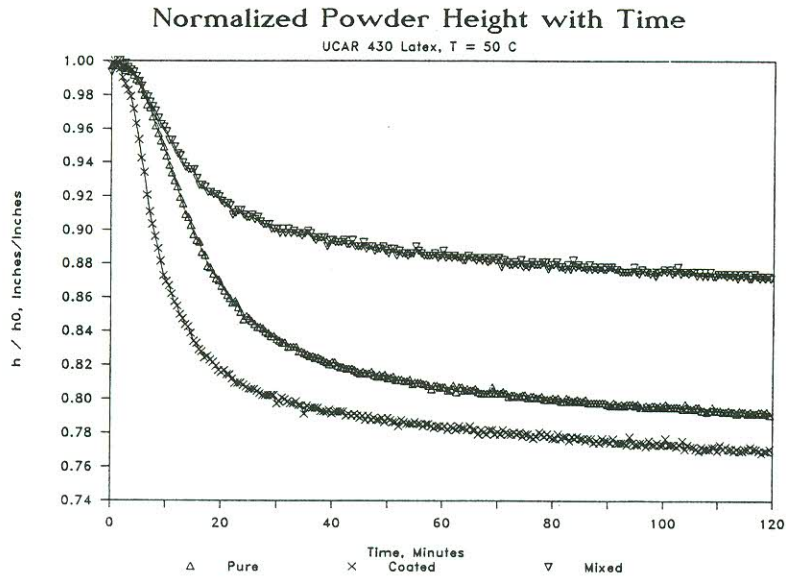


Figure 4. Sintering rates of UCAR 430 samples

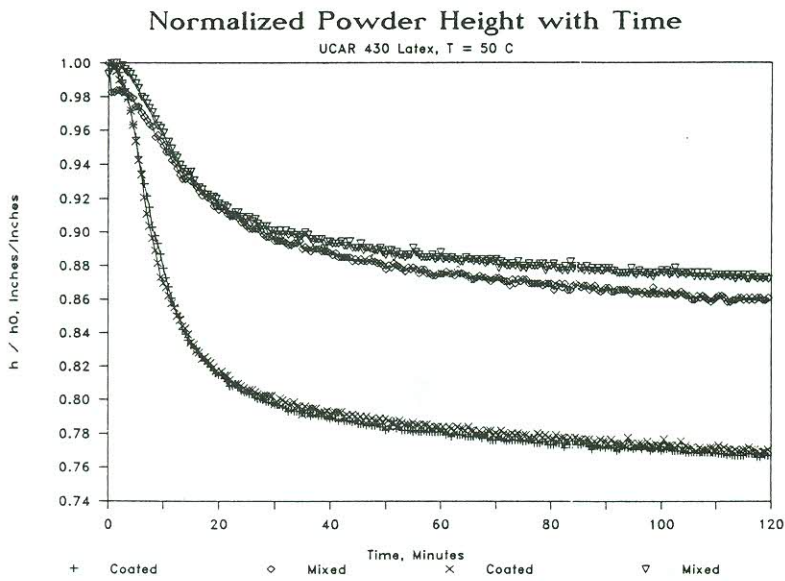


Figure 5. Sintering rates of mixed and coated alumina

It is unclear at this time why these results are obtained. It has been suggested that what is observed can be explained by probability. For the case of alumina mixed with polymer the probability of two adjacent particles being polymer decreases with increasing alumina content. It then follows that as the alumina content of the mixture is increased fewer and fewer polymer particles are adjacent to affect sintering. As a result a less structurally sound part would be expected. The converse is true for the alumina coated with polymer. Since each alumina particle is coated the probability of two adjacent particles being polymer is one. Therefore, increasing the alumina content would not effect the ability of the material to sinter.

Figure 6 shows green parts of alumina and UCAR 430 produced by the SLS process. Each part consists of 100 layers. No part was made from pure UCAR 430 since this powder could not be spread due to static charge build up during leveling. In fact, static charge build up was experienced by all spray dried polymers. This stems from the nature of polymers and the size of particles being spread. The sample of mixed alumina and UCAR 430 spread easily, not unlike pure alumina, producing a very smooth surface. Evidence of this smooth surface can be seen on the final part. The sample of alumina coated with UCAR 430 spread only marginally better than pure UCAR 430. A further indication the alumina is coated with polymer since it behaves as the pure polymer. Evidence of clumping produced by static charge build up is seen as a rough surface on the resulting part.

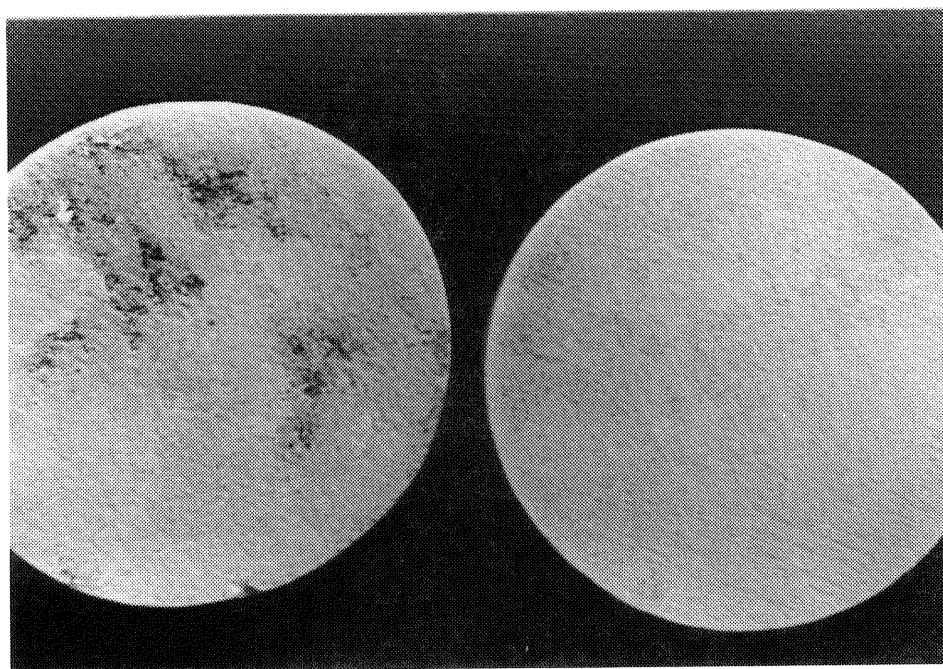


Figure 6. Alumina/UCAR 430 sintered parts.
(l-r) Mixed, coated material

Both parts experienced significant heat conduction in the radial and axial directions. This resulted in the parts being distorted in shape upon removal from the powder bed. However, build up in the radial direction was more easily removed by simple tapping and scraping than was build up in the axial direction.

Aside from the surface differences both parts are similar and exhibit excellent resistance to scratching and breakage.

Conclusion

Spray drying is sufficient to produce microcapsules with marginal solids content. However, as reported by the literature (Masters, 1985) and is evident from the results the solids content is limited to about 50% wt. This is inadequate to produce full density ceramic parts. To effect an increase in solids content of coated material other methods of microencapsulation are being investigated. Of considerable interest are methods used to produce electrostatographic toner material. Toner materials show properties which are desirable for the SLS process. Namely, good flow characteristics, good static properties, high T_g , good binding capacity, and good storage capabilities.

Methods of encapsulation under investigation utilize either emulsion polymerization or coacervation. Methods involving emulsion polymerization (Sole 1986, Martin 1988) produce materials not unlike those studied here. The emulsions produced however, incorporate the solid material into the polymer micelle. Effectively performing the polymerization around the solid material. These emulsions can then be spray dried to produce powder. Alternatively, coacervation takes advantage of certain polymer solubilities under acidic or basic conditions. In one example (Yuda *et al.* 1987) ter-polymers are solubilized in acidic media. Solid toner particles are then added and the suspension subjected to agitation. Encapsulation of the toner material is affected by raising the pH of the aqueous media.

By using these methods to produce coated materials with high solids content it is hoped further experiments will show microencapsulation to be the preferred method for producing ceramic materials from the SLS process.

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