

Effect of Polymer Coatings as Intermediate Binders on Sintering of Ceramic Parts

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Abstract

It has been proposed that a thin polymer layer applied to the surfaces of finely divided ceramic powders would serve as a suitable intermediate binder for Selective Layer Sintering of ceramic parts. In this study, the effects of completeness and fraction of coating and particle size distribution on sintering rates and strengths of coated spheridized glass are examined. The effect of the coating as a binder during Selective Layer Sintering as well as the binder's burnout capability during post processing steps are also investigated.

(Key Words: Microencapsulation, Glass, Sintering, Polymer, Spray Drying)

Introduction

Selective Layer Sintering (SLS) is an innovative process for producing three-dimensional objects directly from a CAD database. SLS has found use in the rapid prototyping of commercial parts using polymer and wax materials. However, parts made of these materials have limited uses, such as models and patterns for investment casting. Methods to extend the capabilities of SLS to the manufacture of ceramic and metal parts is the focus of several research projects.

In a previous study (Vail and Barlow, 1990), spray drying was shown to be an effective and efficient method to encapsulate alumina with a polymer binder. In this ongoing study, spray drying is used to encapsulate spheridized glass particles. Green parts were made from coated glass materials using SLS. These green parts were post-processed in a furnace to observe the effects of binder burnout and to observe dimensional and density changes in the sintered part.

Materials and Methods

Samples of UCAR 430 Acrylic Polymer Latex were obtained from Union Carbide Corporation. UCAR 430 is a styrene-methylmethacrylate-butylacrylate-methacrylic acid copolymer with a glass transition of approximately 45°C. Spheridized soda-lime glass was obtained from Potters Industries, Inc. The spheridized soda-lime glass, obtained in two different particle size distributions, are designated A-5000 and A-3000 glass. These two size distributions have mean particle sizes of $5.0 \pm 2.5 \mu\text{m}$ and $24.0 \pm 15 \mu\text{m}$, respectively, as measured by a Coulter Multisizer.

Glass powder was coated with polymer by first mixing the glass powder with the polymer latex to produce a slurry. This slurry was then spray dried using an Anhydro Laboratory Spray Drier #1. This drier has a cylindrical drying chamber with conical base. The drier is equipped with a 1hp air blower which provides positive pressure drying air to the chamber. Drying air can be heated from 125°C to 300°C via a 9kW electrical heater. Feed to the drier can be atomized either by centrifugal or by pressurized nozzle means.

Centrifugal atomization was used for the purposes of this paper. The centrifugal atomizer contains a four veined atomizing wheel which is driven by a motor to speeds of 50000 revolutions per minute. The atomizer wheel speed was verified by an optical tachometer. Dried product powder is separated from the drying air by a cyclone.

Characterization of Spray Drier

Several experiments were conducted to determine the effects of inlet drying temperature, solids content through the drier, and polymer content of the product on the product particle size. Ten samples each were run at two inlet drying temperatures, 130°C and 160°C. At each temperature, samples contained 25% and 50% total solids by weight. Each total solids concentration was further divided into 1%, 2.5%, 5%, 10%, and 15% polymer weight of total solids for a total of twenty samples. Each sample contained a fixed amount of A-5000 glass spheres. Other than water being added to the mixture of materials to attain desired concentrations the materials were used as supplied. Typical sample compositions are listed in Table 1. Spray drier operating conditions for selected materials are shown in Table 2.

Table 1. Spray drier sample compositions

| Glass, (g) | Total Solids, (wt %) | Polymer Content, (wt. % total solids) | UCAR 430 Emulsion, (g) | Water, (g) |
|------------|----------------------|---------------------------------------|------------------------|------------|
| 250 | 25.0 | 1.0 | 5.7 | 754.4 |
| | | 2.5 | 14.6 | 761.4 |
| | | 5.0 | 29.2 | 773.4 |
| | | 10.0 | 61.7 | 799.4 |
| | | 15.0 | 100.3 | 826.2 |
| | 50.0 | 1.0 | 5.7 | 249.3 |
| | | 2.5 | 14.6 | 248.6 |
| | | 5.0 | 29.2 | 247.1 |
| | | 10.0 | 61.7 | 243.8 |
| | | 15.0 | 100.3 | 238.0 |

Table 2. Spray drier operating conditions

| Material | Fluid Flow, (ml/min) | Atomizer Speed, rpm | Inlet Temp., (°C) | Outlet Temp., (°C) |
|---|----------------------|---------------------|-------------------|--------------------|
| UCAR 430 Emulsion | 90 | 37500 | 130 | 60 |
| Geon 151 Emulsion | 120 | 37500 | 160 | 63 |
| Glass/UCAR 430 Mixture (25%/50% Solids) | 80/90 | 37500 | 130 | 60 |
| Glass/UCAR 430 Mixture (25%/50% Solids) | 100/110 | 37500 | 160 | 65 |

Particle Size and Polymer Coating Analysis

Particle size distributions of glass materials and of all spray dried materials were determined by Coulter Multisizer measurements. Polymer coatings were observed by scanning electron microscopy and polymer content of the spray dried powders were determined by Thermal Gravimetric Analysis (TGA).

Selective Layer Sintering

Three samples of A-5000 glass were processed via spray drying to produce coated particles with polymer contents of 5%, 10%, and 15% by weight. Pure UCAR 430 polymer was spray dried for the purposes of mixing with the same spherical glass to produce samples with comparable polymer compositions to the coated samples. The prepared samples were processed by SLS using a CO₂ laser operating at three different scan speeds. All part processing was conducted at ambient bed temperatures and in an open atmosphere. Twelve parts, one inch square by one-quarter inch thick, were made from each coated glass sample. SLS processing conditions are presented in Table 3.

Table 3. Selective Layer Sintering operating conditions

| Power, (W) | Layer Thickness, (") | Scan Speed, (ips) | Roller Speeds | |
|---------------|----------------------------|----------------------|------------------|----------------------|
| | | | Linear, (ips) | Rotational, (rpm) |
| 25 | 0.003 | 32.0, 40.0, 64.0 | 4.0 | 82.0 |

Post-Processing of Selective Layer Sintered Parts

To examine effects of post-processing on SLS parts, the samples previously prepared were heat treated using a high temperature box furnace. Samples were removed from the SLS machine, brushed to remove loose powder, weighed and measured, and packed in fine alumina in a porcelain crucible. Samples were placed in the center of the furnace and brought to temperature at a heating rate of 10°C/min. As the sample came to sintering temperature, the polymer was burned off. Furnace temperature was monitored by a K-type thermocouple placed directly above the sample crucible. The thermocouple was connected to a digital thermometer. All samples were processed at 637°C.

Results and Discussion

Scanning electron micrographs of Potters A-5000 soda-lime spherical glass and a typical spray dried coated sample of the same glass are shown in Figures 1 and 2, respectively. The pure glass micrograph shows the material to be nearly spherical and of almost uniform size. The coated glass micrograph shows the spray dried particles to be agglomerates of the spherical glass coated with a thin layer of polymer.

The Thermal Gravimetric Analysis of a spray dried sample is presented in Figure 3. From these data it is clear UCAR 430 decomposes at about 400°C, in nitrogen, and is completely decomposed within a few minutes. TGA analysis of the pure glass and the pure polymer show the mass loss to be due entirely to polymer burn-off and the residue of polymer burn-off to be negligible. A summary of the polymer contents of samples used in these studies is provided in Table 4.

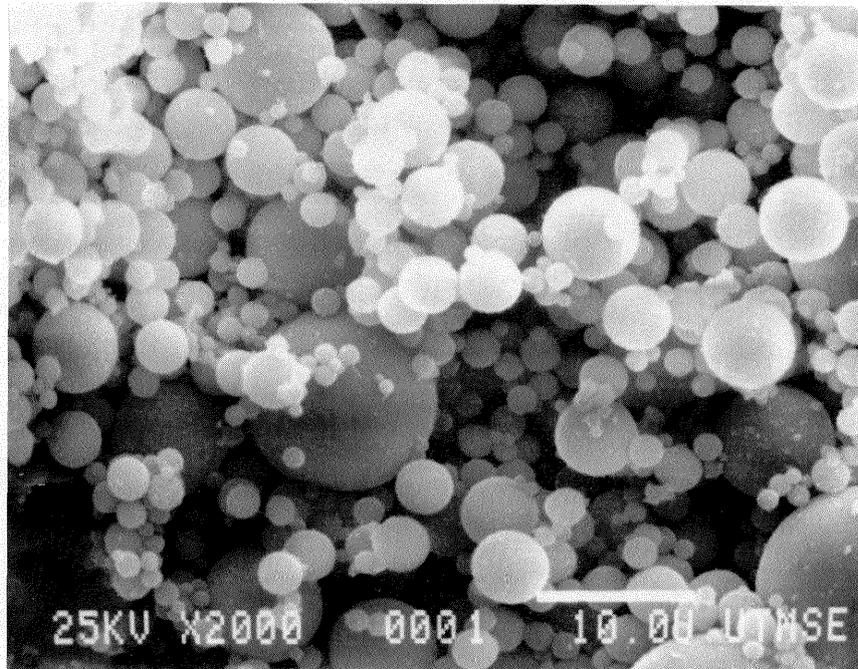


Figure 1. Potters A-5000 Soda-lime Glass

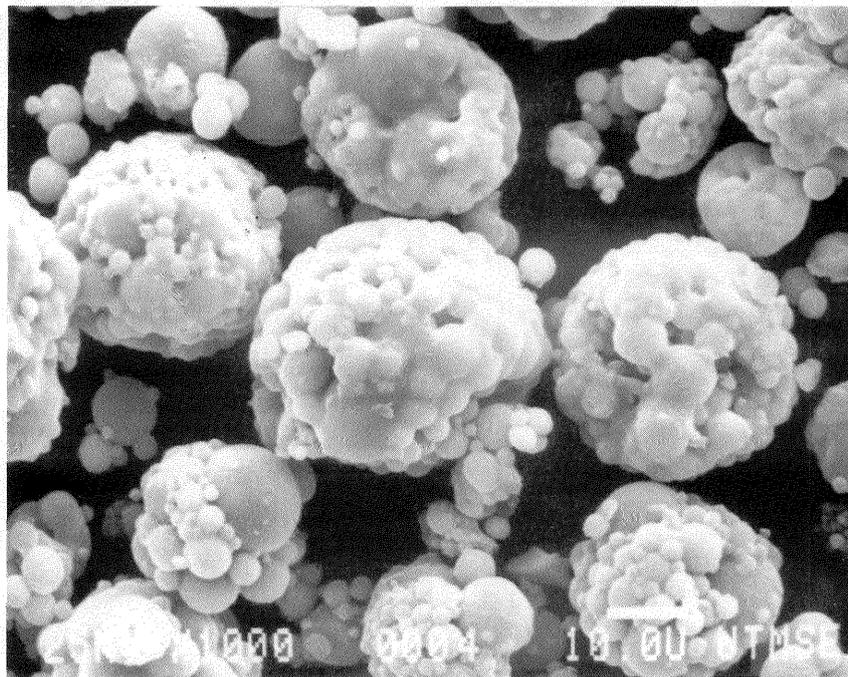


Figure 2. Polymer coated glass particles.
15% weight polymer content.

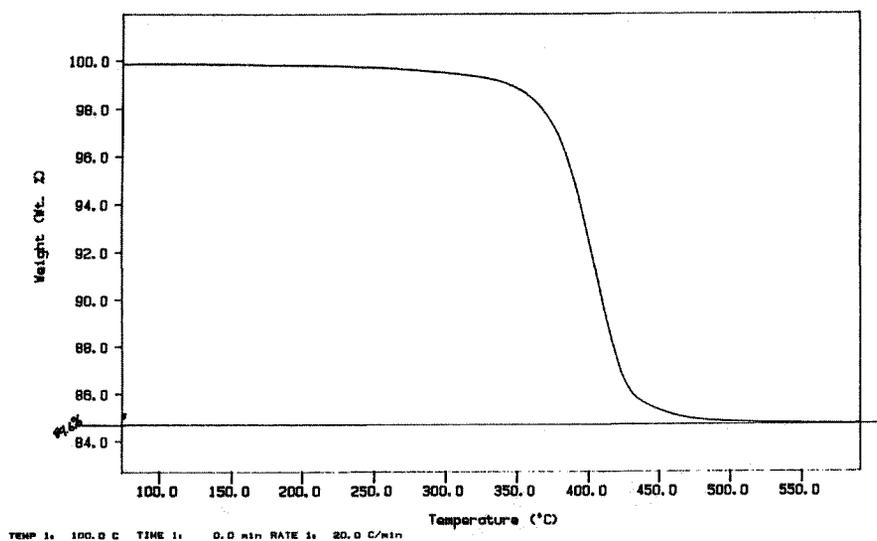


Figure 3. TGA curve for A-5000 glass coated with UCAR 430 polymer 15% by weight.

Table 4. Polymer contents of processed samples

| Material | Theoretical | Measured |
|--------------|-------------|----------|
| Coated Glass | 5 | 5.2 |
| Coated Glass | 10 | 9.9 |
| Coated Glass | 15 | 15.3 |
| Mixed | 15 | 15.0 |

Effect of Spray Drying Conditions on Powder Particle Size
A-5000 Glass Spray Dried with UCAR 430

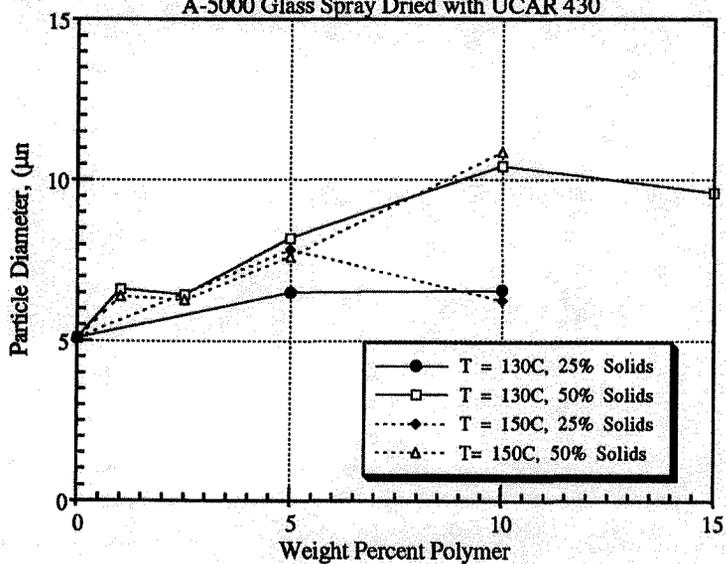


Figure 4. Spray dried particle size results

Results of particle size measurements are shown in Figure 4. Particle size is influenced both by the amount of solids in the spray drier feed and by the amount of polymer in the product. Temperature did not appear to play a role in product particle size. As expected, particle size increases with increasing polymer content in the product and, particle size decreases with decreasing solids in the spray drier feed. These results were discussed by Masters (1972) who stated that there are two reasons why larger particle sizes result at larger solids loading. First, lower moisture content of the atomized droplets facilitate higher drying rates resulting in hollow particles and overall higher bulk densities. This effect is most prevalent in feeds containing dissolved solids. Second, the initial atomized droplet size is reduced in proportion to the amount of moisture evaporation from the droplet. Therefore, assuming equal initial droplet sizes, feeds with high solid concentrations will produce particles of larger size than will feeds with low solids concentrations. SEM photos of spray dried materials show no evidence of hollow particles but do, however, show evidence of smaller particles collapsed about larger particles producing what appear as agglomerates. Measured particle sizes are in agreement with theoretical particle sizes assuming uniform glass particles with uniform polymer coatings. At 10% wt. polymer content, theoretical particle size is $5.95\mu\text{m}$ while the observed particle size is $6.56\mu\text{m}$.

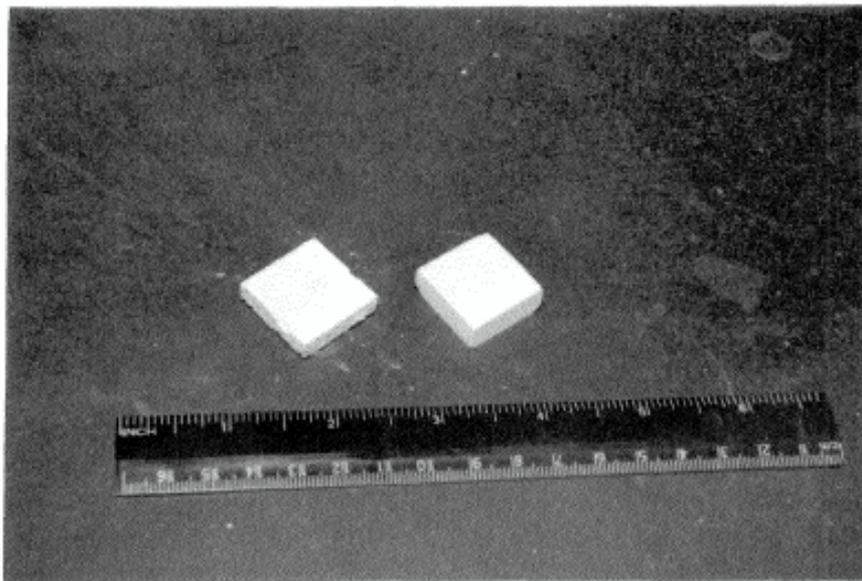


Figure 5. Soda-lime glass/UCAR 430 SLS parts.
(l-r) Mixed, coated glass.

All green parts made from coated glass materials by SLS showed sufficient strength to permit handling. This was not true for the green parts made from the single sample of mixed glass and polymer. Figure 5 shows one green part each made from coated and mixed samples with polymer compositions of 15% wt. Clearly the green part made from the mixture of glass and polymer is of poorer quality than the part made from polymer coated

glass. In fact, the green part made of mixed glass and polymer is too delicate to handle. It is for these reasons that only one sample of glass and polymer mixture was processed. In addition to producing poor quality parts with low green strength the mixed sample could only be processed at the fastest laser scan speed since significant part curling occurred at the slower scan speeds.

Figures 6 and 7 show sintering results of green parts fired for times of ½, 1, 2, 4, and 8 hours. Green parts made from 15% wt. polymer coated glass SLS processed at three laser scan speeds were sintered. Figure 6 shows the final relative densities of these parts to be independent, within experimental measurements, of the laser scan speed. Figure 7 shows the axial shrinkages of parts at all sintering times to be very consistent in all directions. The z-direction does show a slightly higher shrinkage at all sintering times, but it is not drastically different. This indicates the porosity in the z-direction to be equal to the porosity in the xy-plane.

Figure 8 shows densities of green parts made from the three different coated glass materials. To determine the significance of these green part densities, the density of the bulk coated glass powder was measured. The powder density was measured first by allowing a fixed amount of powder to settle freely in a graduated cylinder. The cylinder was then tapped vigorously to settle the powder and the density again determined. Each measurement was repeated four times. It is interesting to note that green densities lie between the densities observed for untapped powders and tapped powders. In fact, densities of all green parts produced from the three coated samples varied only 1.04% from the mean relative density of 36.0%.

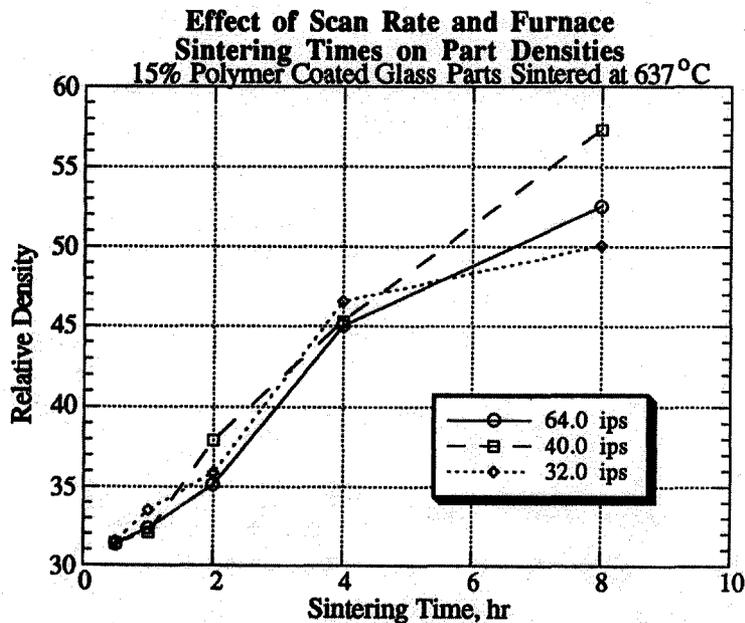


Figure 6. Densities of glass parts at different sintering times.

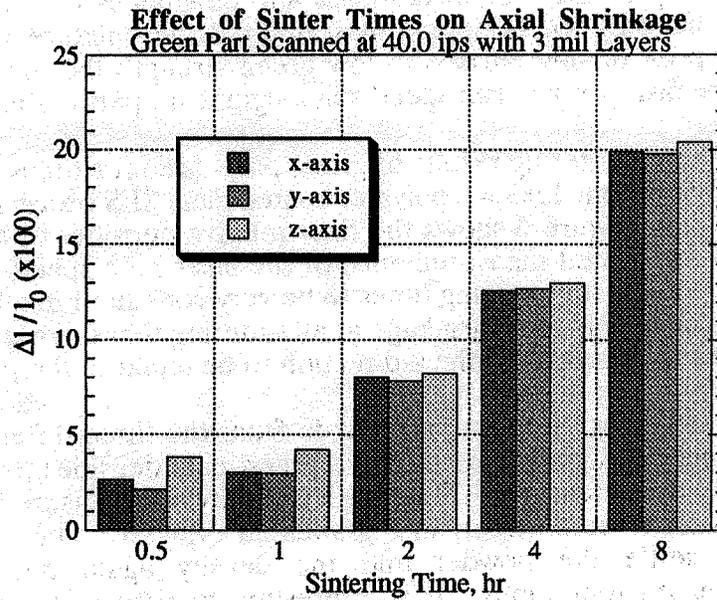


Figure 7. Axial shrinkages of sintered glass parts.

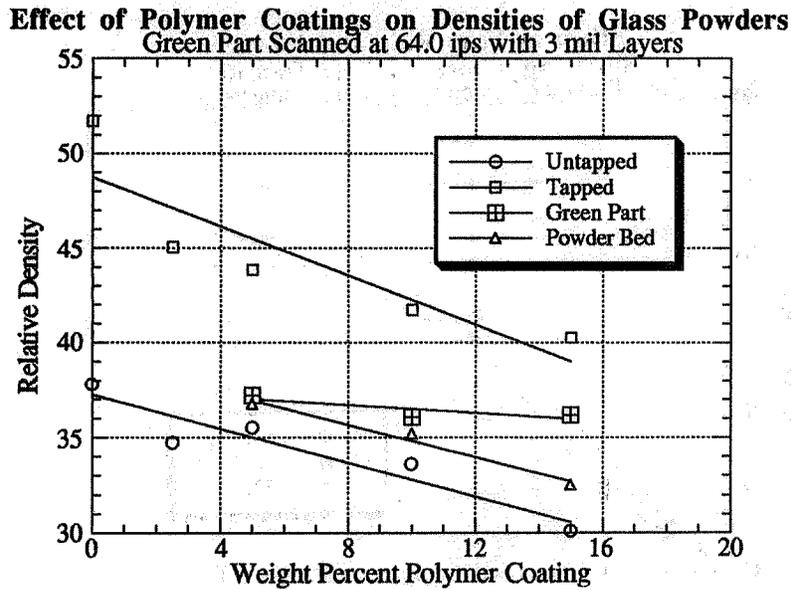


Figure 8. Densities of polymer coated glass powders.

To further investigate these results, two supplementary sets of experiments were conducted. In the first set of experiments powder bed densities of pure A-5000 glass and the polymer coated A-5000 glass were measured by determining the depth of a fixed number

of powder layers deposited by the SLS machine and then weighing the powder. Powder leveling conditions for these experiments were the same as those listed previously in Table 3. A second set of experiments was conducted to observe the effect of adding a larger size spherical glass to a sample of 15% wt. polymer coated glass on powder bed densities. Two samples were prepared by adding A-3000 glass to the coated glass to reduce the polymer content of the entire sample to 10% and 5% wt.

Figure 8 also shows the results of bed density measurements of the coated glass powders. The powder bed densities are only slightly higher than the untapped powder density and are considerably lower the tapped powder densities. Part densities lie slightly above the bed densities and green part density increases are related to the amount of polymer present. Further, powder bed density is also related to the amount of polymer present. Indeed, the presence of polymer causes a drastic change in bed density when the data are compared to the observed relative bed density of about 60% for pure A-5000 glass.

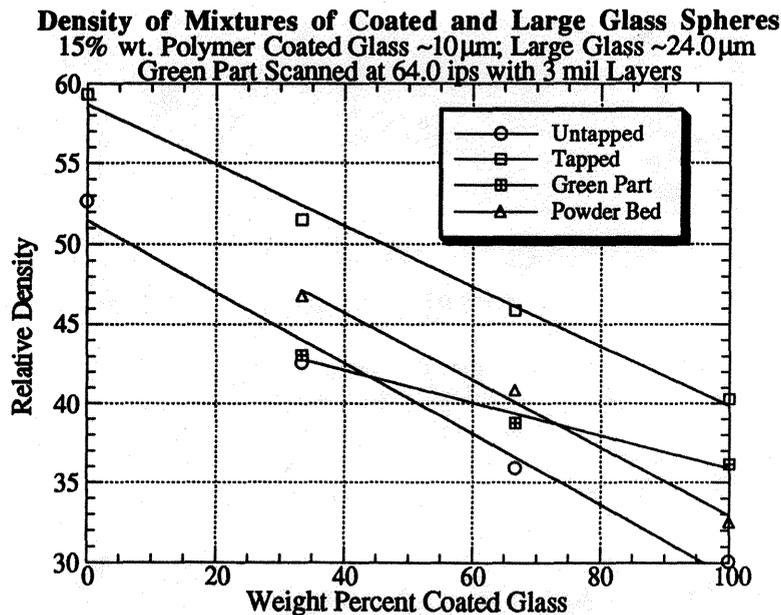


Figure 9. Densities of coated glass spheres mixed with large size glass spheres.

Figure 9 shows the results of mixing 15% wt. polymer coated A-5000 glass with two different proportions of larger sized A-3000 glass. The bimodal powder densities are significantly higher than the densities of plain coated glass powders. Reed (1988) states these results are as expected since the smaller coated glass particles fill the interstices of the large glass compact. Why the green densities are lower than the bed densities and, in the case of 33% coated glass, lower even than the untapped density is unclear. Still, it is interesting to note that green parts from these mixtures showed sufficient green strength to permit handling.

Finally, post processing was performed on these green parts. Two parts from each of the two bimodal samples were fired at 637°C for two hours. These results are compared

to results of similar post processed 15% wt. coated glass green parts in Figure 10. For the same conditions the bimodal parts show smaller density changes and therefore smaller axial shrinkages.

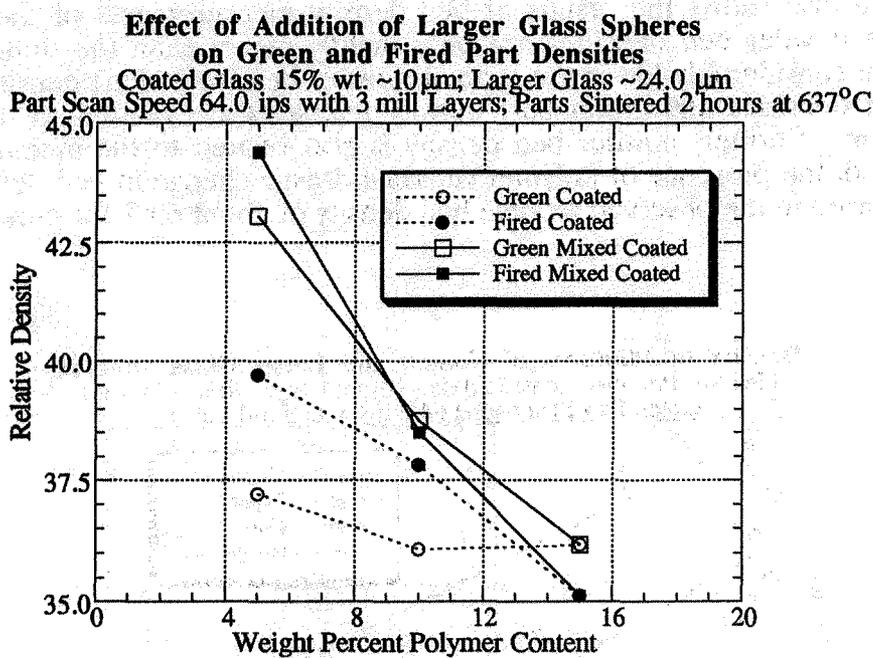


Figure 10. Fired densities of coated glass green parts and coated glass mixed with larger glass green parts.

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