Effects of Cu and SiO_2 on Laser Sintering of Polycarbonate

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Abstract

Additives of different thermal properties, Cu and SiO_2 (amorphous and crystalline), were blended to polycarbonate (PC) powder to modify its heat transfer properties and fusion behavior during laser sintering. The blends were sintered under different energy densities of the laser beam to produce mono-layer films. The surface morphology and the thickness of the films were studied. When sintering under the same condition, the composite films which contained a high content of Cu powder exhibited a more porous surface structure. This was caused by the increased heat loss because the Cu powder has a higher thermal conductivity. Also, the solid Cu particles would hinder the flow of the molten polymer, resulting in a low degree of fusion. For a given Cu powder content, reducing its particle size gave a more porous surface structure and a smaller thickness of the sintered films. This was probably due to a more even distribution of the fine Cu particles, which increased the heat loss and reduced the effective amount of energy for fusion. On the other hand, fine SiO_2 and quartz powders caused degradation of the polymer because of the increased energy dissipation near the film surface and poor heat transfer properties of the additives comparing with Cu.

Keywords: Laser sintering; PC/Cu; PC/SiO_2; fusion behavior.

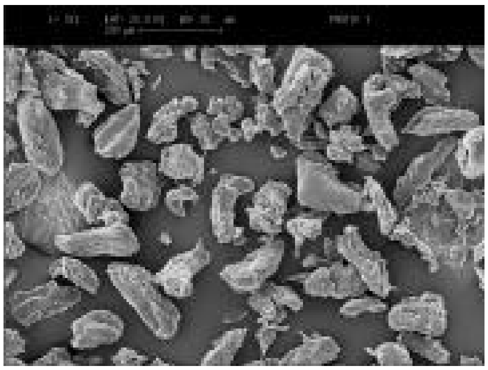
1. Introduction

In laser sintering processes, the energy source is very intense and the time for fusion is extremely short. In addition, polymer materials are poor thermal conductors. Under normal sintering conditions, the polymer particles are only slightly fused together thus the sintered components are porous and have a coarse surface finish. This not only affects their mechanical strength but also the dimensional accuracy. One possible way of improving the fusion behavior of the polymer powder is by modifying the thermal properties of the material. Polycarbonate was blended with Cu, quartz and amorphous SiO_2 and the blends were sintered using a laser-engraving machine.

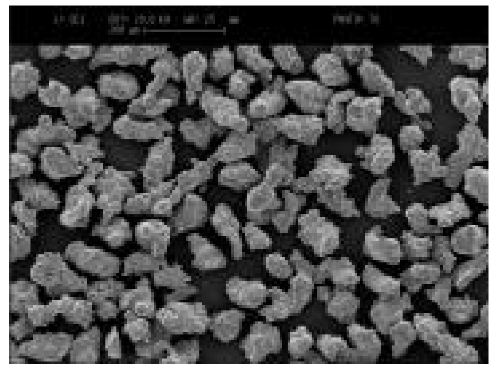
Composite materials are not rare in the SLS process, e.g. DuraForm Glass Filled, Cu with polyamide (DTM products), and Cu with PMMA[1]. The role of glass spheres in DuraForm is to increase the strength and reduce in the shrinkage of the sintered components. In the last two material systems, Cu forms the main body of the green parts and the polymers only serve as a binder. In this work, copper, SiO_2 and quartz were added to change the thermal properties of the material systems. The effects of content and particle size of the additives on surface morphology and thickness of the sintered films were studied. This paper outlines some preliminary results of the work.

2. Materials and processing

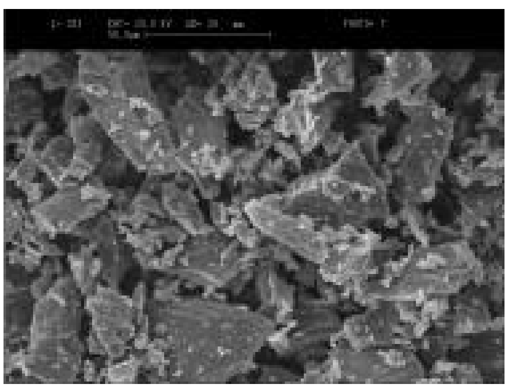
The PC powder was supplied by DTM, trade name LPC-3000. It has a glass transition temperature of 150°C. The Cu powder was ground from the Cu infiltrant by DTM. The amorphous SiO_2 and quartz powders were products of Fisher Scientific. The original size range of quartz was from 200 to 800 ↘m. After grinding, the average powder size reduced to 140 ↘m. Figure 1 shows the PC powder and the additives before sintering, and table 1 lists some of their physical and thermal properties.



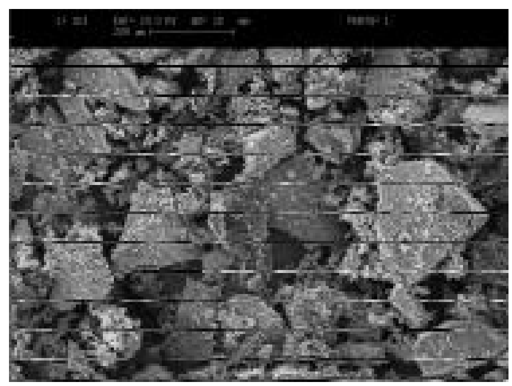
a) PC powder



b) Cu powder



c) SiO_2 powder



d) Quartz powder

Figure 1. SEM micrographs of polycarbonate, Cu, SiO_2 and quartz powders.

Table 1. Physical and thermal properties of the polycarbonate and additives [2,3].

Material	PC	Cu	amorphous SiO_2	Quartz	air (at 300K)
Thermal conductivity (W/(m.k))	0.18	400		8.14	0.0263
Specific Heat Capacity (J/Kg.K)	1206	385		795	1046
Average particle size (↘m)	90	28 & 293	32	140	
Density (g/cm^3)	0.62	6.74	2.56	2.64	

Sintering was carried out on a M25e Universal Laser Engraving Machine. According to Nelson[4], the energy density (ED) of the laser beam during selective laser sintering (SLS) can be expressed as follows:

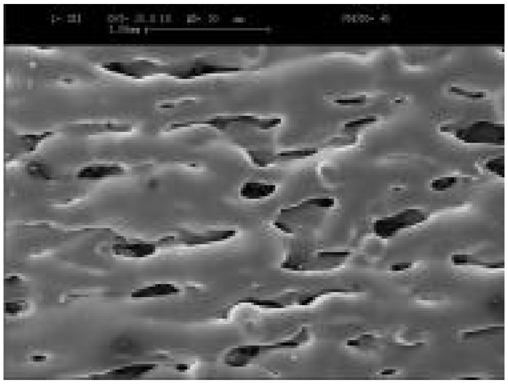
$$ED = \frac{P \dashleftarrow f}{BS \dashleftarrow SCSP}$$

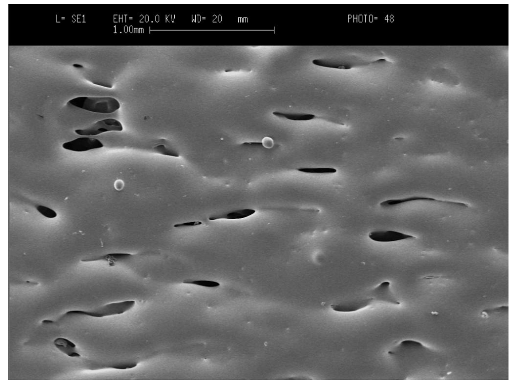
where P is fill laser power, BS is beam speed, SCSP is the scan spacing and f is a conversion factor. In this work, ED was varied by different settings of P and BS. An increase in P or decrease in BS would result in a higher ED and vice versa. The number of pulses per inch (PPI) of the laser beam along the scanning direction and the number of dots per inch (DPI) perpendicular to the scanning direction were kept constant at 500. The sintered samples were examined with a Cambridge Stereoscan 360 scanning electronic microscope (SEM) at an operating voltage = 20kV and working distance = 20mm. The thicknesses of the films were measured from SEM micrographs of the cross sections and verified by a caliper. The samples were coated with gold-palladium before SEM examination.

3. Results and discussion

Effect of Cu additive

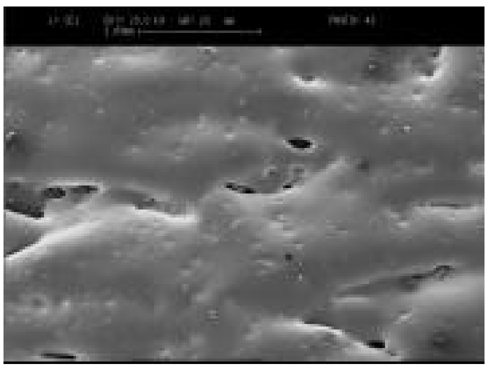
Figure 2 shows the surface morphologies of the pure PC films sintered at different scanning speeds. For BS = 100%, figure 2a, many voids are present due to incomplete fusion of the PC particles. As BS was reduced to 80 & 70%, i.e. increasing the laser energy density, the number of voids dropped and the surface became smoother. When BS was further reduced to 60%, however, there were some blemishes on the surface. These were signs of material degradation under an excessively high energy density of the laser beam.

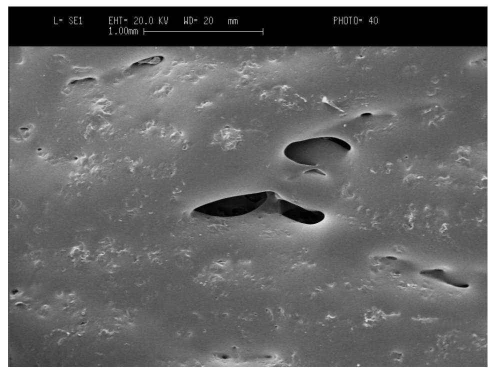




a) 50% P, 100% BS

b) 50% P, 80% BS





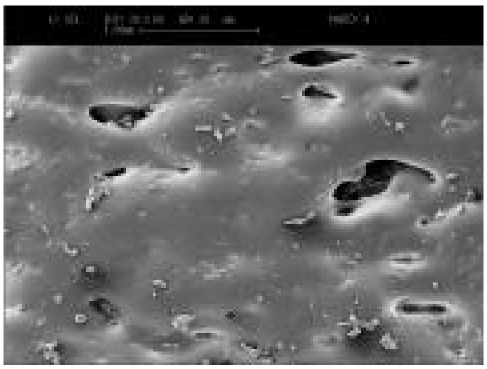
c) 50% P, 70% BS

d) 50% P, 60% BS

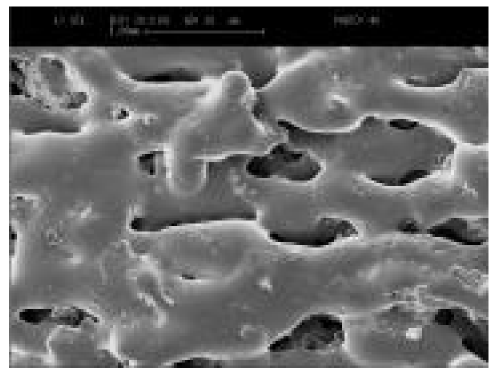
Figure 2 SEM micrographs showing the surface views of PC films sintered at 50% of P and different values of BS.

Figure 3 shows the surface morphologies of the PC/Cu films. A higher Cu content led to a more porous surface structure, as if the films had been sintered at a lower energy density of the laser beam. For blends of PC/Cu (1/1), figures 3b&d, finer Cu powder gave more voids than the coarser Cu powder did. Perhaps, the larger amount of smaller Cu particles had adversely affected the flow of molten polymer during the sintering process. In comparison, blends of PC/Cu (10/1), figures 3a&c, showed a very similar surface morphology despite the difference in particle size of the Cu additive. This was probably due to the fact that the Cu content was low and the effect of particle size was not apparent.

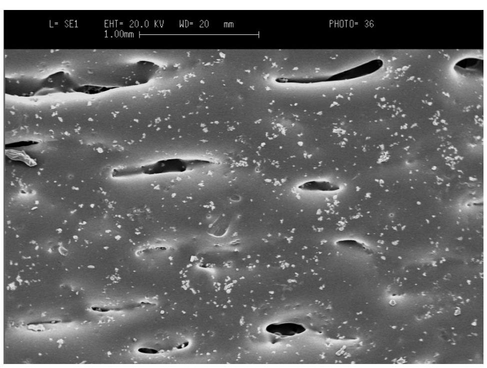
Besides, the thickness of the films with a high Cu content was smaller than that of the films with a low Cu content, figure 4. The phenomenon was probably due to increase in heat loss after addition of Cu. In order to prove that increasing the heat loss (particularly through the powder bed), would reduce the film thickness, sintering was carried out on powder beds of different thicknesses. When the thickness of the powder bed, supported on a stainless steel base, was reduced from 4.9mm to 1.6mm, there was a corresponding drop in thickness of the sintered PC films, figure 5. It is also noteworthy that when sintering at P/BS ratios below 1 (the lower the P/BS ratio, the lower the ED), reducing the powder thickness from 4.9 to 3 mm did not cause any major change in the thickness of the sintered films. However, when P/BS ratio was above 1, the sintered films became significantly different in thickness. One possible explanation is that at a low P/BS ratio, i.e. the rate of energy input is relatively low, a 3mm thick powder bed is sufficient to provide good insulation against heat loss through the stainless steel base. Further increase in the powder bed thickness only improves the insulation properties marginally. For a high P/BS ratio, however, the temperature gradient through the powder bed thickness might change significantly when it was reduced from 4.9mm to 3mm. Figure 6 shows the surface morphologies of the PC film and the PC/Cu (1/1) film. There is a sign of degradation on the PC film but not on the PC/Cu film. This again is an indication of the improved heat transfer properties of the composite system.



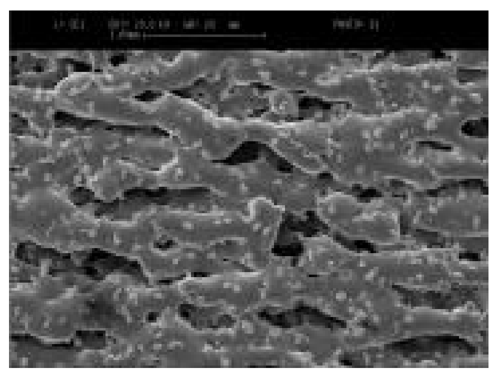
a) PC/Cu (10/1) Cu powders 180-500 ↘m



b) PC/Cu (1/1) Cu powders 180-500 ↘m



c) PC/Cu (10/1) Cu powders <45 ↘m



d) PC/Cu (1/1) Cu powders <45 ↘m

Figure 3 Surface views of sintered PC/Cu films, sintering parameters: P = 50%, BS = 70%, DPI = 500 and PPI = 500, the numbers in brackets are weight ratios.

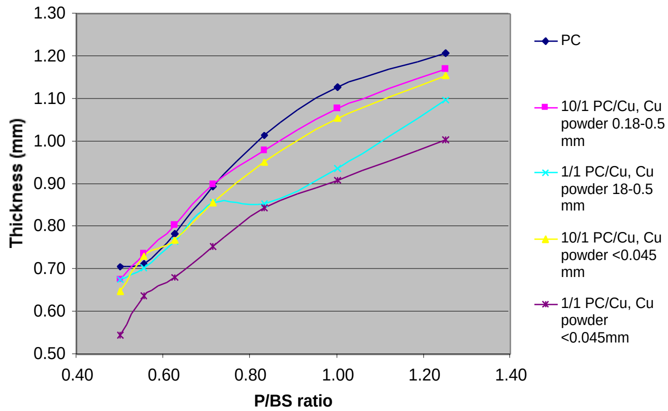


Figure 4. Plots of thickness against P/BS ratio for sintered films with different Cu contents and powder sizes.

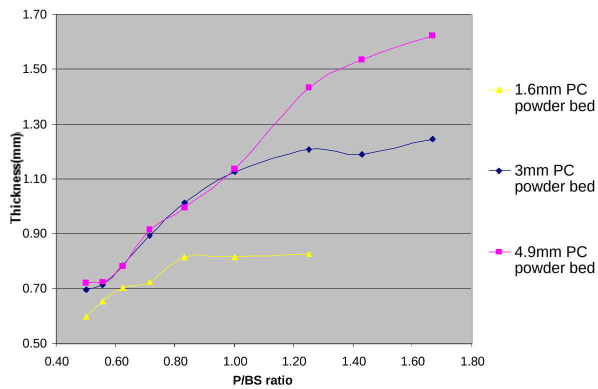
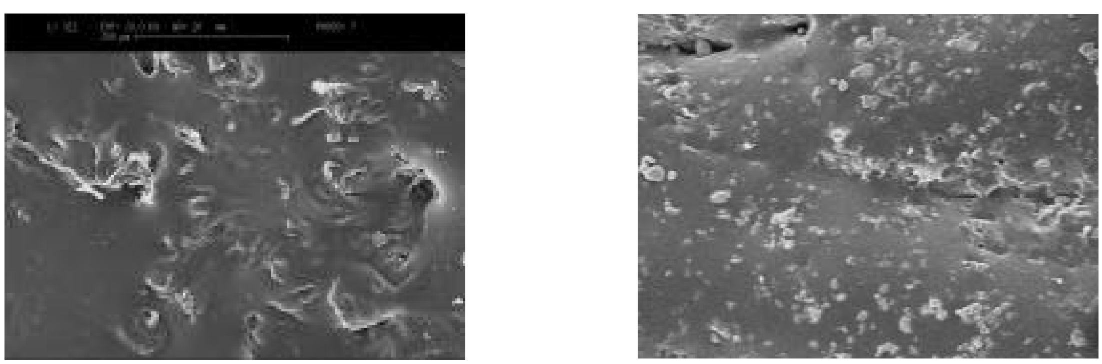


Figure 5. Plots of thickness against P/BS ratio for sintered films with different powder bed thicknesses.



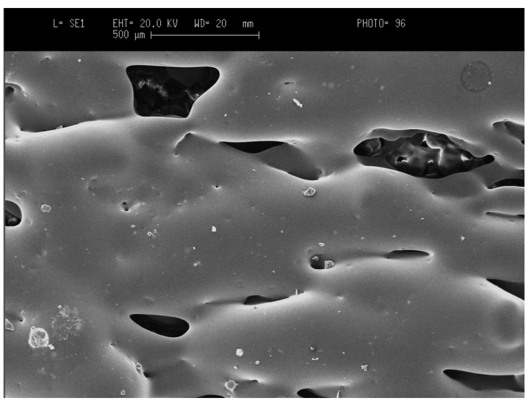
a) PC

b) 1:1 PC/Cu composite with Cu powders < 45↘m

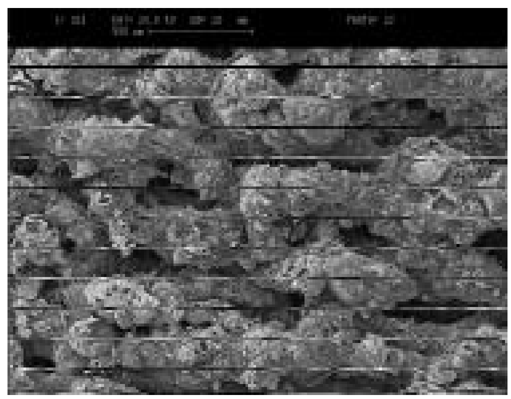
Figure 6. SEM micrographs of sintered films, sintering parameters: P = 50%, BS = 50%, DPI = 500 and PPI = 500, white spots in (a) are signs of material degradation and those in (b) are Cu particles.

Effect of SiO_2 and Quartz

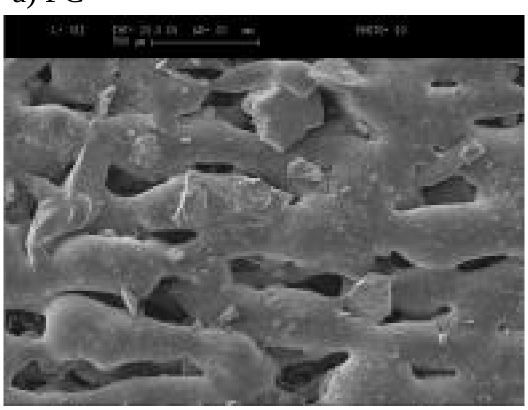
Figure 7 shows the surface views of three different films, i.e. PC, PC/SiO_2 and PC/quartz, sintered under the same condition. The additives seem to have an adverse effect on the fusion of the polymer. In particular, the SiO_2 powder led to severe degradation of the polymer on the film surface. Polymers degrade under exposure to high temperature, oxygen and ozone, ultraviolet light, moisture, radiation and chemical agents[5]. In this case, degradation is likely due to high temperature generated on the film surface. The chemical composition of SiO_2 and quartz are basically the same and their thermal properties are extremely similar. The different morphologies of the two films, figures 7b&c, were probably caused by the different amounts of energy dissipated on the surface during the sintering process. According to Karapatis[6], with a suitable size ratio between coarse and fine particles (over 10:1) and adequate composition (30%) of fine particles, the powder bed density can increase by 15%. Adding fine SiO_2 powder will partially fill up the voids of the powder bed, hence reducing the penetration depth of the laser beam, and more energy was dissipated near the surface. Table 2 shows a decrease in porosity after adding additives. More importantly, the fine SiO_2 powder (32↘m) had a larger total surface area than the coarse quartz powder (140↘m). This would enhance interaction with the laser beam.



a) PC



b) 20% SiO_2



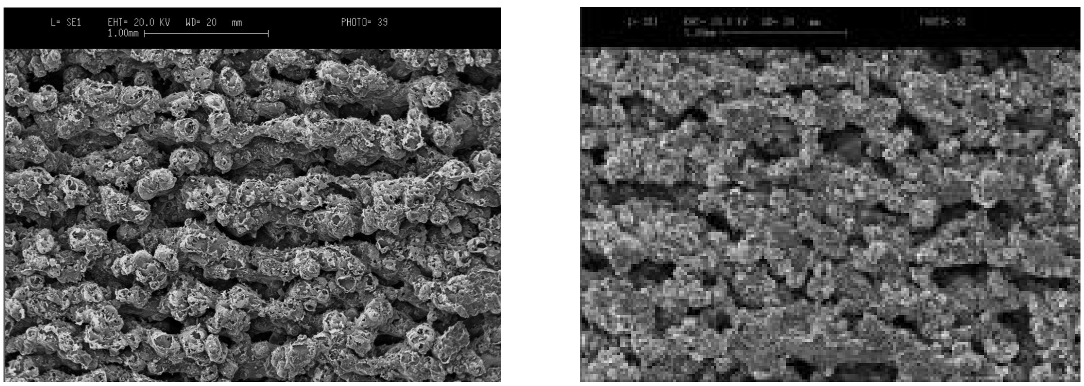
c) 20% Quartz

Figure 7. Effect of quartz and SiO_2 on surface morphology of sintered PC films, sintering parameters: P = 30%, BS = 50%, DPI = 500 and PPI = 500.

Table 2 Bulk density and porosity of PC, PC/SiO_2 and PC/quartz.

Materials	PC	PC/SiO_2	PC/quartz
Bulk density (g/cm^3)	3.77	4.602	4.984
Volume occupied by PC (%)	60.81	59.38	64.31
Volume occupied by additive (%)		3.60	3.78
Porosity (%)	39.19	37.02	31.91

Some finer quartz powder (<45↘m) was used to blend with PC and sintered under similar conditions. The result is shown in figure 8. It is now obvious that the finer additives indeed caused heavier degradation of the polymer near the surface of the sintered films. A thickness measurement, figure 9, shows that the PC/SiO_2 and PC/quartz films are thinner than the pure PC film. The phenomenon is in agreement with the argument that most of the laser energy was dissipated near the surface of the composite films.



a) 20% SiO_2 b) 20% Quartz

Figure 8. Effect of quartz (<45↘m) and SiO_2 (32 ↘m) on surface morphology of sintered PC films, sintering parameters: P = 35%, BS = 50%, DPI = 500 and PPI = 500.

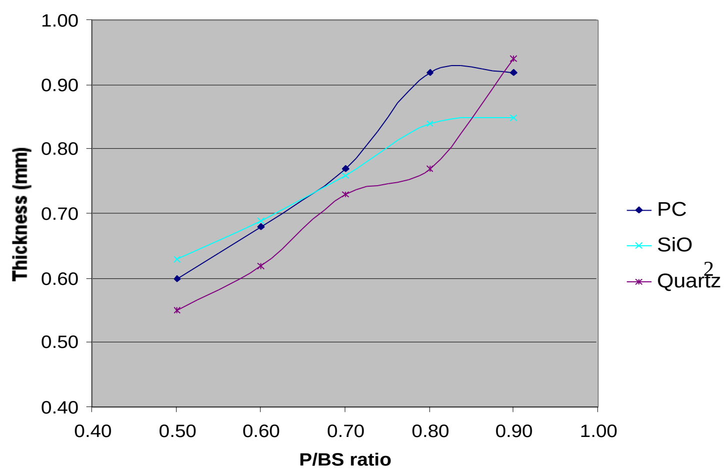


Figure 9 Thickness change of sintered films with SiO_2 and quartz.

4. Conclusions

All three additives had an adverse effect on the fusion behavior of PC and resulted in a more porous surface structure of the sintered films. This can be attributed to increase in viscosity of the polymer melt because the additives remained solid during the laser sintering process. For a given additive content, a smaller particle size would increase energy dissipation near the surface of the powder bed because of the enhanced area of contact with the laser beam. However a smaller particle size of the additives would hinder fusion of molten polymer more significantly, probably due to the increased area of the polymer/additive interface. The Cu powder has a considerably higher thermal conductivity than the PC powder, which helps to improve the overall heat transfer properties and hence alleviates the phenomenon of polymer degradation on the film surface. However, the increased rate of heat loss resulted in a reduction in the thickness of the sintered films. In contrast, SiO_2 and quartz caused degradation of the polymer. The phenomenon was likely caused by the increased energy dissipation near the film surface and poor heat transfer properties of these two additives.

References

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