Study on optimization of PES/CaCO₃ composite powder for selective laser sintering (SLS) 3D printing technology

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Abstract. In this study, a new type of friendly environment material including polyether sulphone resin powder (PES), and limestone flour (CaCO₃) (referred to as CO-PES-CaC) has been developed for selective laser sintering (SLS) additive manufacturing that is low cost, environmentally friendly and energy efficient. The aims of this study were to optimization of PES/CaCO₃ composite powder for SLS printing technology. The mechanical properties and microstructure of CO-PES-CaC affected by different the ratio of PES powder and CaCO₃ powder has been studied. The experimental results indicate that the CO-PES-CaC quality was optimum when the ratio of PES powder and CaCO₃ powder was 75/25. The mechanical properties peak at 8.09 MPa for tensile strength and 15.28 MPa for flexural strength, and 3.91 kJ/m² for impact strength.

1. Introduction

Laser sintering (LS) is a laser based rapid manufacturing technique that builds objects layer by layer from powders through computer-aided design (CAD) technology. There are various laser fabrication processes such as directed-light fabrication (DLF) [1], laser engineered net shaping (LENS) [2], direct metal deposition (DMD) [3, 4], selective laser sintering (SLS) [5, 6], etc. These techniques incorporate features from stereolithography and laser surface engineering, using a CAD model to control the sequentially thin-layered forming process. SLS technology is a 3D printing technology. Unlike other 3D printing technologies, in the SLS process there is a wide material selection, no support is needed during manufacturing, and unsintered material could be recycled and reused [7]. Therefore, SLS has been widely applied in industries [8].

Currently, creating environmentally friendly materials for 3D printing technology is essential. CaCO₃ is an environmentally friendly material, combining CaCO₃ with PES is a new research direction to create environmentally friendly, low-cost materials for 3D printing technology. However, how to combine the PES / CaCO₃ ratio appropriately is a problem that needs to be addressed, so this study we conducted with five ratios of PES / CaCO₃ is 80/20, 75/25, 70/30, 65/35, 60/40, then based on micro observation, and evaluate the mechanical properties of each ratio to choose the best ratio.
2. Materials and Methods

2.1. Material
In this study using Polyether sulphone resin powder (PES), and limestone flour (CaCO₃) supplied by the company Shanghai Tian Nian Materials Technology Ltd (Figure 1a). Before the limestone flour powder was mixed with PES it was dried at 55°С for 8 h. The particle diameter of most of the PES and CaCO₃ particles is between 43 and 55 mm.

The polymer mixture composed of PES and CaCO₃ powders is referred to as CO-PES-CaC mixture in this research. Both polymers were placed in a thermostat and dried for 8 h at 55°C. Then, PES and CaCO₃ powders were mechanically mixed in a high-speed paddlemixer for 30 min to obtain a homogeneous mixture (Figure 1b). The mixing temperature was held under 50°C to prevent powder agglomeration caused by local overheating. The combination of PES/CaCO₃ powder has a composition ratio (80/20, 75/25, 70/30, 65/35, and 60/40) used as input material for SLS technology.

![Polyether Sulphone Resin(PES) and Limestone Flour(CaCO₃)](image)

**Figure 1.** (a) Polyether sulphone resin and limestone flour powder; (b) High-speed paddle mixer

2.2. Selective laser sintering
The experiment was performed on the Selective laser sintering (SLS) 3D printer: AFS-360 rapid prototyping instrument (Long yuan Technology Ltd., Beijing, China) equipped with a CO2 laser generator (wavelength of 10.6 μm and laser power of 55 W). The dimensions of the forming box were 360x360 x500 mm with a forming speed of 60 cm³/h to 100 cm³/h, a layer thickness range of 0.08 mm to 0.3 mm, and without any N2 protection.

CO-PES-CaC powders are delivered in a gas stream or spread from the feed beds across the part bed using a roller into the focus of a high power laser beam to create a molten pool. After solidification, a thin solid layer is formed and fused to the previous sintered layer. By repeating the process, a nearly fully dense structure can be made. Schematic of two laser sintering techniques is shown in (Figure 2).

![Schematic of two laser sintering techniques](image)

**Figure 2.** The selective laser sintering (SLS) system.
2.3. Mechanical analysis

Mechanical testing was performed on a CMT5504 testing machine from TMS System Company and a TCJ-4 impact touching screen testing machine with simply a supported beam produced by the Tai He Testing Machine Limited, Jilin Province. The test standards are as follows:

Tensile strength test: Dog bone-shaped tensile specimens with typical dimension of 166x13x3.2 mm were fabricated. The crosshead speed was 5 mm/min according to ASTM D638-10.

Flexural strength test: For flexural strength, thin specimens of 127x12.7x3.2 mm were tested according to the three-point bending method of ASTMD790-10. The support span was 52 mm, crosshead speed was 2 mm/min and maximum midspan deflection was 15mm.

Impact strength test: A digital Charpy impact tester was used to measure normal impact strength of unnotched specimens (80x10 x4 mm) based on ISO179-1.

The morphology of samples for mechanical testing showed in (Figure 3)

2.4. Scanning Electron Microscopy (SEM)

The surface structure of the CO-PES-CaC samples was analyzed with Scanning Electron Microscopy (SEM). The extrusion surfaces of the SEM images were taken in a QUANTA200 Scanning Electron Microscope provided by FEI Co., Ltd. All specimens were sputtered with a thin layer of gold to eliminate electrical charging prior to SEM observation.

3. Results and discussion

3.1. Mechanical property analysis

(Figure 4) shows the mechanical properties of the mixture CO-PES-CaC with the PES/CaCO₃ ratio 80/20, 75/25, 70/30, 65/35, and 60/40. Through (Figure 4), we can see that the value of tensile strength, bending strength, impact strength decreased with increased CaCO₃ powder content, or reduced PES powder content. Specifically, the tensile strength value of CO-PES-CaC materials is 13.08, 8.09, 7.58, 4.45, and 3.09 MPa with the ratio PES/CaCO₃ is 80/20, 75/25, 70/30, 65/35, and 60/40, respectively. The bending strength value of CO-PES-CaC materials is 32.78, 15.28, 12.58, 11.88, and 10.62 MPa with the ratio PES/CaCO₃ is 80/20, 75/25, 70/30, 65/35, and 60/40, respectively. The impact strength value of CO-PES-CaC materials is 4.13, 3.91, 3.88, 2.21, and 1.78 kJ/m², with the ratio PES/CaCO₃ is 80/20, 75/25, 70/30, 65/35, and 60/40, respectively.
The results show that the increase in the content of CaCO₃ powder will lead to the mechanical properties of the CO-PES-CaC mixture is reduced. The cause of the decreased mechanical properties of CO-PES-CaC mixture when the increased CaCO₃ powder content is due to the possibility of linking CaCO₃ - PES, and PES - PES is reduced. In particular, when the connection between PES - PES is reduced, the mechanical properties of the CO-PES-CaC mixture is reduced. The cause of the decreased mechanical properties of CO-PES-CaC mixture are also reduced. This is also confirmed in the scanning electron microscopy analysis below.

Comparing the ratios of CO-PES-CaC materials shows that with the ratio PES/CaCO₃ is 80/20, the mechanical properties have the highest value. With the ratio PES/CaCO₃ is 60/40, the mechanical properties have the lowest value. However, with the aim to create environmentally friendly materials, the PES content in the material is the lowest, and the highest content of CaCO₃ while can still ensure the mechanical properties of the material, thus 75/25 ratio is the optimal ratio of CO-PES-CaC material mixture.

### 3.2. Scanning electron microscopy analysis

(Figure 5) shows the microstructure (magnification is 1000x) of CO-PES-CaC materials with different the PES/CaCO₃ component ratios.

From (Figure 5a) shows that, with the 80/20 ratio, the PES content is very large, so the link is mainly PES-PES, the PES-CaCO₃ bond is low, the surface of PES plastic blocks is smooth, there are not many CaCO₃ powder particles on the surface. Therefore, in the 5 ratios that we studied, the 80/20 ratio has the highest mechanical value.

(Figure 5b, 5c, 5d) show the microstructure of CO-PES-CaC composite materials with PES / CaCO₃ ratios of 75/25, 70/30, 65/35, respectively. From the 3 figures, we can see that, PES plastic blocks are getting smaller, CaCO₃ powder particles increase gradually, which means that the PES-PES bond gradually decreased, and the PES-CaCO₃ bond gradually increased. This explains the reduced mechanical properties of the material with the increased CaCO₃ powder content in CO-PES-CaC materials.
Figure 5. SEM images of CO-PES-CaC materials with the ratio PES/\( \text{CaCO}_3 \): (a) 80/20, (b) 75/25, (c) 70/30, (d) 65/35, (e) 60/40. (Figure 5e) show the microstructure of CO-PES-CaC composite materials with PES / \( \text{CaCO}_3 \) ratios of 60/40. As can be seen from the (Figure 5e), the number of \( \text{CaCO}_3 \) powder particles on the surface CO-PES-CaC is very large, it covers most of the surface of PES plastic blocks, so the PES-CaCO3 bond is the main link. This explains the mechanical properties of the CO-PES-CaC material with the smallest value.

In summary, CO-PES-CaC composite materials with a ratio of 75/25 (Figure 5b) shows that the PES-PES, and PES-CaCO3 bonds are the most reasonable. At this ratio, materials both ensure mechanical properties and ensure environmentally friendly materials. Therefore the 75/25 ratio is the optimal ratio in the 5 studied rates.

4. Conclusion
This study has successfully used PES / \( \text{CaCO}_3 \) powder mixture for SLS 3D printing technology. The results indicated:

1. Materials created with high mechanical properties. With 5 ratios that the study has chosen, the ratio of 75/25 is optimal. The mechanical properties of CO-PES-CaC materials are 8.09 MPa, 15.28 MPa, 3.91 kJ/m² with tensile strength, bending strength, impact strength, respectively.

2. SEM analysis showed that the PES-PES bond was the primary link in the 75/25 ratio, so at this rate the mechanical properties were the most reasonable.

3. Research has succeeded in creating a new type of friendly environment material including polyether sulphone resin powder (PES), and limestone flour (\( \text{CaCO}_3 \)) (referred to as CO-PES-CaC) has been developed for selective laser sintering (SLS) additive manufacturing that is low cost, environmentally friendly and energy efficient.
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