Effect of mixing time of coupling agent on properties of 3D printing prototype of fly ash filled ABS

YE Xuan, TU Huajin, QIU Zhiwen
Mechanical and Electrical Engineering College, Heyuan Polytechnic, Heyuan 517000, China
yexuan 1216@sina.com

Abstract. Fly ash was modified by being mixed with silane coupling agent for 10min, 20min, 30min, 40min and 50min. Pure ABS, compounded materials consisting of unmodified and modified fly ash and ABS were extruded into filaments. 3D printed specimens were manufactured with extruded filaments. Results show, ABS filaments have good 3D printing process and product performance and unmodified fly ash is harmful to ABS filaments. To improve interface bonding between ABS and fly ash, silane coupling agent can be introduced, and mixing it with fly ash for 30min may be a better choice, which has better dimension stability, impact strength and tensile strength.

1. Introduction
Fly ash is a by-product of coal-fired power plants and other coal-burning industry. With the steady growth of power demand of China, coal-fired power plants, which generate 76% of China’s electricity, are constantly making more and more fly ash. The large amount of fly ash have caused tremendous pressure on the environment, because the accumulation of fly ash can take up a lot of land and the dust of fly ash can cause PM2.5 air pollution[1]. In order to reduce the environmental pollution of fly ash and turn it into treasure, the recycling of fly ash is an important way. A large number of scholars have conducted widespread thorough research to the comprehensive recycling and utilization of fly ash, and using the modified fly ash as a filler for plastic materials is one of the methods to reuse fly ash. Filling fly ash can reduce the cost of plastic and the waste of fly ash, which kills two birds with one stone[2].

Meanwhile, 3D printing is a kind of advanced manufacturing technology in recent years, and it is said that it would cause the third industrial revolution[3], thoroughly change the existing manufacturing, vigorously promote the development of intelligent manufacturing. Different from traditional subtractive manufacturing technology, 3D printing is an additive manufacturing technology, which can realize rapid prototyping of complex structure products of different kinds of material. With advantages of fast response and material saving, 3D printing has been widely used in different fields such as industry, archaeology, health, culture, and so on[4-7]. Fused deposition molding (FDM) is a kind of important molding technology of 3D printing, which is relatively simple and easy to use with low threshold. FDM has effectively promoted the popularization of 3D printing technology[8]. And ABS is one of the commonly used material for 3D printing, after years of research, performance of ABS 3D printing products can reach 80% or more of injection molding products, but when using ABS material for FDM molding, there are still problems such as warping deformation, deformation and insufficient accuracy. Therefore, domestic and foreign scholars have been using a variety of materials and techniques to modify ABS to try to improve its 3D printing process and product performance, in order to broaden its application scope.
2. Experiment method

2.1. Experiment materials

ABS particles (CHIME, PA-763A), fly ash powder (collected from Heyuan Thermal Power Station, Heyuan Guangdong, China), silane coupling agent (KH-550) were adopted.

Fly ash powders were processed by drying and sieving through 100 meshes sieve. Silane coupling agent was used to modify the fly ash powders, a quantity of 50g of fly ash was first introduced into a mixture of 50ml water/ethanol (20:80wt%), and the temperature was kept at 60℃. Then, 4g silane coupling agent was added into the abovementioned solution and continuously mixed for different time at 200r/min and 60℃. The resultant product was dried, grinded and sieved through 100 meshes sieve, and continually dried till completely dry. Fly ash processing parameter was shown at table 1. Except specimen 1#-5#, pure ABS and unmodified fly ash were used and coded as specimen ABS and 0#.

ABS particles were dried in woven to remove moisture. Then, ABS was mixed with modified fly ash at the ratio of 9:1(wt%) in a mechanical stirrer for 30min, and the temperature was kept at 60℃. Compounded materials stirring parameter was shown at table 2.

Compounded materials were used to feed a single screw extruder (Guangzhou Baiyun Tiancheng Machinery Factory, SJ-45). The processing temperature of the extruder were 180℃ (barrel zone 1), 190℃ (barrel zone 2), 200℃ (barrel zone 3), 210℃ (rod die zone1), 220℃ (rod die zone2). Filament was extruded with the diameter of 1.75 ± 0.10 mm. Extruder processing temperature was shown at table3.

Extruded filaments were used to feed the 3D printer (Flashforge, Finder) to manufacture 3D printed specimens with printing parameters: object infill 15%; layer height 0.18 mm; nozzle temperature 240℃; bed temperature 30℃; deposition rate 30mm/s, as shown at table 4.

| Specimen | Fly ash | Water/ethanol mixture | Silane coupling agent | Mixing speed | Mixing temperature | Mixing time |
|----------|---------|-----------------------|-----------------------|--------------|--------------------|-------------|
| 1#       | 50g     | 50ml                  | 4g                    | 200 r/min    | 60℃                | 10min       |
| 2#       | 50g     | 50ml                  | 4g                    | 200 r/min    | 60℃                | 20min       |
| 3#       | 50g     | 50ml                  | 4g                    | 200 r/min    | 60℃                | 30min       |
| 4#       | 50g     | 50ml                  | 4g                    | 200 r/min    | 60℃                | 40min       |
| 5#       | 50g     | 50ml                  | 4g                    | 200 r/min    | 60℃                | 50min       |

| Specimen | Fly ash | Temperature | Time |
|----------|---------|-------------|------|
| 9:1(wt%) | 60℃    | 30 min      |

| barrel zone 1 | barrel zone 2 | barrel zone 3 | rod die zone 1 | rod die zone 2 |
|---------------|---------------|---------------|----------------|----------------|
| 180℃          | 190℃          | 200℃          | 210℃           | 220℃           |

| object infill | layer height | nozzle temperature | bed temperature | deposition rate |
|---------------|--------------|---------------------|-----------------|-----------------|
| 15%           | 0.18mm       | 240℃                | 30℃             | 30mm/s          |

2.2. Performance test

Printing warping deformation was measured by vernier caliper, as shown in figure 1. Charpy impact strength, tensile strength were tested by impact tester (Jinan Weipin Tester, XJF-5.5) and universal tester (Jinan Weipin Tester, WDW-10).
3. Results and discussion

3.1. Effect of mixing time of coupling agent on printing warping deformation

Printing warping deformation of specimens with different mixing time of coupling agent is shown in figure 2. As shown in figure 1, the printing warping deformation of specimens printed from pure ABS, namely specimens ABS, is 7.5mm, which is quite obvious. Adding 10wt% unmodified fly ash into ABS results in greater printing warping deformation, namely specimens 0#, which is 11.6mm. Adding 10wt% fly ash modified by silane coupling agent into ABS can reduce printing warping deformation of specimens, which is further reduced by raising the mixing time. Printing warping deformation of specimens 1#-5# are 8.0mm, 8.1mm, 7.9mm, 4.2mm and 4.5mm respectively.

![Figure 1: Test method of printing warping deformation](image)

![Figure 2: Printing warping deformation of specimens with different mixing time of coupling agent](image)

3.2. Effect of mixing time of coupling agent on impact strength

Impact strength of specimens with different mixing time of coupling agent is shown in figure 2. As shown in figure 3, the impact strength of specimens printed from pure ABS, namely specimens ABS, is 12.5KJ/m². Adding 10wt% unmodified fly ash into ABS results in poor impact strength, namely specimens 0#, which is 7.5KJ/m². Adding 10wt% fly ash modified by silane coupling agent into ABS can improve impact strength of specimens, which is further elevated by raising the mixing time to 40min. Impact strength of specimens 1#-5# are 8.5KJ/m², 8.4KJ/m², 10.2KJ/m², 10.3KJ/m² and 8.3KJ/m² respectively.
3.3. Effect of mixing time of coupling agent on tensile strength

Tensile strength of specimens with different mixing time of coupling agent is shown in figure 3. As shown in figure 4, the tensile strength of specimens printed from pure ABS, namely specimens ABS, is 28.2MPa. Adding 10wt% unmodified fly ash into ABS results in poor tensile strength, namely specimens 0#, which is 24.7MPa. Mixing the fly ash with silane coupling agent for 10min even further reduces the tensile strength of specimens, namely specimens 1#, which is 24.0MPa. Mixing the fly ash with silane coupling agent for 20min and 30min may be helpful to tensile strength of specimens, which are 30.3MPa and 31.1MPa respectively. When raising the mixing time to 40min and 50min, tensile strength of specimens decreases to 25.9MPa and 23.9MPa respectively.

4. Conclusion

In order to make full use of the fly ash and improve ABS materials’ 3D printing process and product performance, fly ash was introduced to prepare ABS filaments. Results show, (1)ABS filaments have good 3D printing process and product performance, which make it a proper 3D printing material. Unmodified fly ash is harmful to ABS filaments, which results in greater printing warping deformation, poor impact strength and tensile strength. This may be due to the weak interface bonding between ABS and fly ash. (2)To improve interface bonding between ABS and fly ash, silane coupling agent can be introduced, and mixing it with fly ash for 30min may be a better choice, which has a better integration properties, including better dimension stability, impact strength and tensile strength.

Acknowledgments

Fund project: 2017 youth innovative talent project of education department of Guangdong province (natural science) (2017GkQNCX075, 2017GkQNCX076).

References

[1] Ma Zhuang, Tao Ying1, Yang Juan, et al. Research Progress on Fly Ash Composite Materials[J].
Bulletin of the Chinese Ceramic Society, 2016, 33(4): 826.

[2] Asokan P. Recent advances on coal ash particulates’ fortified glossy finish polymer composites[C]/2015 World of Coal Ash (WOCA) Conference. Nashville, American coal ash association (ACAA) and university of Kentucky center for applied energy research (CAER), 2015: 1.

[3] The third industrial revolution. The Economist, 2012-4-21.

[4] McMenamin P G, Quayle M R, McHenry C R, et al. The production of anatomical teaching resources using three-dimensional(3D) printing technology[J]. Anatomical Sci Education, 2014, 7(6): 479.

[5] Goyanes A, Wang J, Buanz A, et al. 3D printing of medicines: engineering novel oral devices with unique design and drug release characteristics[J]. Molecular Pharmaceutics, 2015, 12(11): 4077.

[6] Gunther D, Heymel B, Gunther J F, et al. Continuous 3D-printing for additive manufacturing[J]. Rapid Prototyping J, 2014, 20(4): 320.

[7] Paulsen S J, Miller J S. Tissue vascularization through 3D printing: Will technology bring us flow?[J]. Developmental Dynamics, 2015, 244(5): 629.

[8] Chen Shuoping, Yi Heping, Luo Zhihong, et al. The 3D Printing Polymers and Their Printing Technologies[J]. Materials Reports, 2016, 30(4): 54.