Evaluation of Antibacterial and Mechanical Properties of 3D Shaped Metal-containing PLA resin

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Abstract:
There is a fused deposition modeling method as a three-dimensional modeling method that mainly uses a resin filament. By this method, modeling using a resin filament containing a metal is also possible. When the metal-containing PLA filament was three-dimensionally modelled under the same conditions as the pure PLA filament, defects were likely to occur in the modelled object regardless of the printing speed, melting temperature, and bed temperature, resulting in inferior strength. In addition, when a JIS standard antibacterial property test was conducted on a PLA filament model containing copper even at a few percent, antibacterial properties were confirmed against multiple bacteria.

Keywords: PLA resin, Copper alloy, Additive manufacturing, Strength, Antibacterial

1. Introduction

In 3D printing techniques, fused deposition modeling (FDM) and selective laser melting (SLM) are well known. For some kinds of resins, FDM as general-purpose device is adopted. Mechanical engineers and scientists were used FDM to clarify aerodynamic chararistics [1] and to adopt ceramics manufacturing [2]. On the other hands, SLM is mainly adopted for metal modellings [3]. In other case, design for 3D manufacturing [4] and gel manufacturing by soft and wet industrial materials - easy realizer (SWIM-ER)[5] were interested. As common task [2] to overcome for all 3D printing techniques, especially for composite (resin/powder) materials

1) For filament manufacturing
・ Selection of resin/materials
・ Optimization of material conditions
・ Confirmation of resin/powders ratio
・ Confirmation of mixing method resin and powders
・ Adjustment as composite filament
・ Control of the viscosity and yield strength of filament

2) For 3D printing
・ Control of the cooling rate of the melting filament
・ Optimization of stacking conditions
・ Optimization of 3D printer own

are listed.

In this study, 3D metal modeling by FDM is focused. Because metal modeling by SLM costs expensive and less examples of metal FDM modeling. For example, novel direct manufacturing of ABS resin on Al alloy surface by the 3D printing technique were studied [6]. However, resin and metal were not composite materials but used as jointed materials.

We found that modeling using a commercial resin filament containing a metal is also possible by FDM. This metal-containing resin filament is mainly supplied for design modeling applications such as bronze statue-like figures, but it may be industrially used as a composite material of metal and resin. Also, unlike the typical modeling method applied to metal powder such as three-dimensional modeling by the SLM, the FDM method is attractive because it can easily form metal at a relatively low temperature with a general-purpose device. Furthermore, resin filaments containing copper are attracting attention as filaments with antibacterial and antiviral properties. By applying them to everyday products such as masks and smartphone cases, they easily have antibacterial and antiviral properties. Therefore, the purpose of this study is to search for modeling conditions to obtain sufficient mechanical properties for copper-containing PLA filaments, to evaluate their strength, and to search for appropriate antibacterial properties.

2. Experimental method

2.1 Material and 3D manufacturing

Four categorized specimens were prepared for this study.
1.PLA resin (two commercial resins)
2.Metal (Cu system) containing PLA resin (two commercial resins)
3.Sueface polished bronze containing PLA resin (Only for antibacterial tests) from one of the above Cu-PLA
4.Copper plate (Only for antibacterial tests)

Two commercial PLA resins (by colarFabb as PLA-c and by Mutoh as PLA-m) were prepared. As metal containing resin filament, two commercial filaments were prepared. One was the Bronze fill by colarFabb as Cu-PLA, it was containing bronze powder. This filament was composed of 80 mass% of bronze powders and 20 mass% of PLA, so it is about 3 times heavier than pure PLA. Details of the filaments were shown in Table 1[7-8].

Other filament was called PLACTIVE by copper 3D. This filament had a nano copper concentration of 1 mass% and PLA concentration of 99 mass%. It was instructed that scientifically validated antibacterial activity eliminates over 99.99% of fungi, viruses, bacteria, and a wide range of microorganisms. And ideal for manufacturing other medical applications that have a risk of bacterial contamination such as prostheses, wound dressings, and surgical instruments. Table 2 shows the PLACTIVE technical data [9].

In this study, MUTOH Value3D MagiX MF-800 was used. Table 3 shows the specifications of 3D printer.

2.2 Antibacterial Test

The procedure was as follows with reference to JIS Z 2801-2012(Figure1(a)) for touchable housing equipment as door knob and door lever. Escherichia coli NBRC3972 and Staphylococcus aureus NBRC12732 were mixed with 5 mL of ordinary bouillon medium (Eiken Kagaku Co., Ltd.) at 27 ° C. After culturing in the evening shake, Escherichia coli was diluted with sterilized water containing a normal bouillon medium at a final concentration of 1/500, and Staphylococcus aureus was diluted with sterilized water containing a normal bouillon medium at a final concentration of 1/50. 0.4 mL of the turbid solution was placed on the sample in a plastic container, covered and left at 30 ° C. After 24 hours, this bacterial suspension was placed in 4.5 mL of SCDLP medium "Daigo" (Nippon Seiyaku Co., Ltd.). The cells were collected (operation 1), diluted 10-fold in 4 steps, and the viable cell count in 1 mL of these bacterial suspensions was measured. The viable cell count was measured by the hygiene test method and

Table 1 Details of PLA-c and Cu-PLA[7-8]

Properties	PLA-c	Cu-PLA
Density (g/cm^3)	1.24	3.9
Humidity absorption (23℃, 50%RH) (%)	-	0.3
Tensile strength (MPa)	61.5	30
Flexural strength (MPa)	40	40
Flexural modulus (MPa)	3295	9000
Tensile elongation (%)	10	5-10
Impact strength (kJ/m^2)	30.8	10

Table 2 Details of PLACTIVE[9]

Properties	PLACTIVE
Density (g/cm^3)	1.24
Melt Temperature (℃)	145-160
Glass Transition Temperature (℃)	55-60
Tensile Yield Strength (MPa)	60
Tensile Strength (MPa)	53
Tensile Elongation (%)	6
Notched Izod Impact (J/m)	16
Flexural Strength (MPa)	83
Flexural Modulus (MPa)	3800

Table 3 3D printer specification

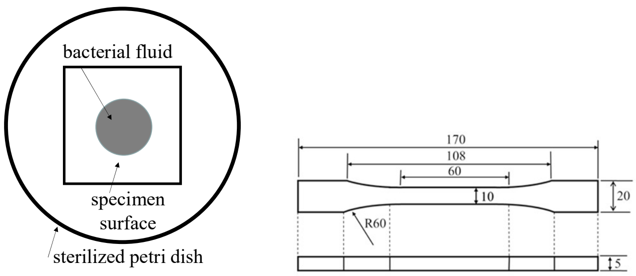
Modeling metohd	FDM
Maximum modeling size (mm)	200×200×170
Minimum stacking pitch (mm)	0.1
Melting temperature (˚C)	RT-250
Heat table temperature (˚C)	RT-100

commentary (2005) /1.2.1.1. Bacterial general test method /3) Bacterial count measurement/ (1) Escherichia coli plate culture method, was used as a reference. SCDLP agar medium "Daigo" (Nippon Pharmaceutical Co., Ltd.) was used for culturing microorganisms. It was used and cultured at 37 ° C for 48 hours.

The above tests were conducted on four types specimen which size of 50 mm ×50 mm ×10 mm of copper plate, PLA, Cu-PLA, and Cu-PLA-P (surface-polished Cu-PLA). Two each for Escherichia coli and Staphylococcus aureus were prepared. Here, Cu-PLA and Cu-PLA-P were prepared for comparing the states of surface copper matrix. By #60 sandpaper polishing for five minutes on Cu-PLA surface, Cu-PLA-P specimen was prepared.

2.3 Tensile test

The tensile strength tester was Shimadzu Corporation; precision universal tester Autograph AG-X plus (load capacity: 50 kN). The test pieces for the tensile test are shown in Figure1(b). It was based on JIS K 7161 1B. Tables 4 shows the manufacturing conditions for each test piece.



(a) Antibacterial (b)Tensile

Figure 1: Specimen

Table 4: Printing conditions (Tensile Test)

Filament	Print speed (mm/s)	Fill density (%)
PLA-c	60	100
PLA-m	60	100
Cu-PLA	30, 60, 90	100
PLACTIVE	30, 60, 90	100

Nozzle Head temperature 220 (℃)

Heating bed temperature 60 (℃)

3. Results and Discussion

3.1 Antibacterial Test

Table 5-1 and 5-2 show the results of the antibacterial test in a JIS standard antibacterial property test. PLACTIVE was said to have an antibacterial property [9]. So, the JIS antibacterial evaluation did not conduct. It was conducted on a PLA filament model containing copper even at a few percent, antibacterial properties were confirmed against multiple bacteria. On the other hand, the pure PLA model did not have antibacterial properties, resulting in the growth of bacteria. Furthermore, it was clarified that the copper containing PLA filament has antibacterial properties even on the surface of the as-shaped material that has not been subjected to the post-processing polishing treatment. From these results and antibacterial property of the PLACTVE, only a few coppers was sufficient effective for bacteria. It was possible for 3D manufacturing to ease modeling because post process could reduce to expose copper on the surface.

3.2 Tensile Test

When the metal containing PLA filament was three-dimensionally modeled under the same conditions as the pure PLA filament in table 4, defects were likely to occur in the modeled object regardless of the printing speed, melting temperature, and bed temperature, resulting in inferior strength.

Figure 2 shows the appearance of the specimen made of bronze containing PLA. Right specimen (print speed is 90 m/s) had observed gaps between the filament path (bead width). This is more remarkable as the amount of metal contained in the resin increases, and it is considered that the metal having a high melting point does not contribute to the modeling under the modeling method and the modeling conditions mainly using the resin PLA.

Then the strength evaluation of each material and the strength evaluation due to the change in printing speed was reported. The tensile strength comparison of each material

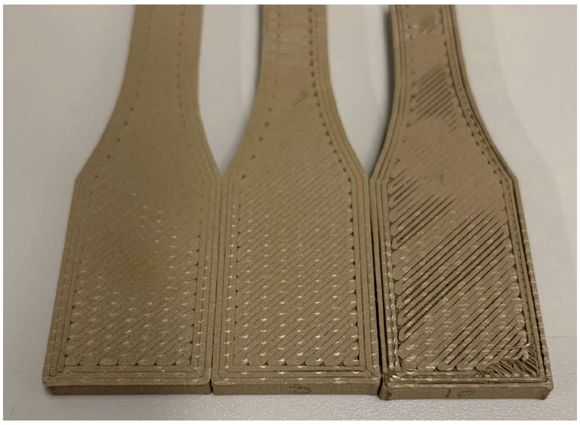


Figure 2: Manufactured specimen of tensile, each print speed is 30(left), 60(center) and 90(right) mm/s

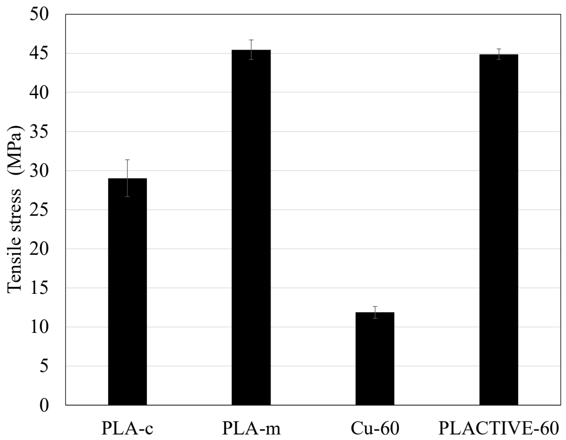
Table 5-1: Results of the antibacterial test for Escherichia coli

Test bacteria	Specimen	measurement	Viable cell count (cfu/mL)	Detected Number of colonies
E. coli	Copper plate	24 hours after inoculation	Below the detection limit	0
	PLA		2.6×10^{7}	Over 300
	Cu-PLA		Below the detection limit	0
	Cu-PLA-P		Below the detection limit	0
	-	(Control) At the time of inoculation	2.0×10^{6}	Over 300

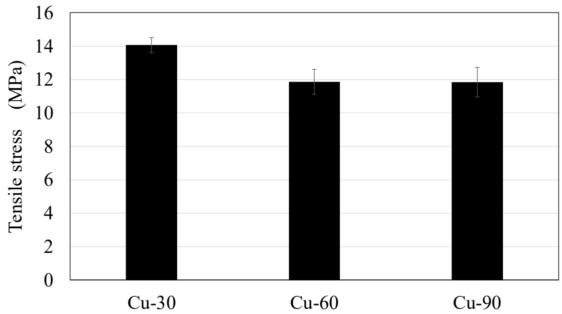
Table 5-2: Results of the antibacterial test for Staphylococcus aureus

Test bacteria	Specimen	measurement	Viable cell count (cfu/mL)	Detected Number of colonies
S. aureus	Copper plate	24 hours after inoculation	Below the detection limit	0
	PLA		9.3×10^{6}	Over 300
	Cu-PLA		Below the detection limit	0
	Cu-PLA-P		Below the detection limit	0
	-	(Control) At the time of inoculation	4.3×10^{6}	Over 300

is shown in figure 3(a). From the figure, the average strength of PLA-m is the largest. Then PLACTIVE shows almost same strength as PLA-m. Specimen strength were inferior to that of the filament strength shown in table1, 2. Defects as pore and bead gaps might be affect the strength. On the other hand, PLA-c and Cu-PLA showed inferior strength than that of filaments. PLACTIVE had a nano-copper concentration of 1 mass%, and it is confirmed that it is almost the same as PLA as can be seen from the aspect of strength despite its antibacterial properties. Difference of the strength on PLA-m and PLA-c might be because of D/L ratio of PLA. From figure 3(b), Cu-PLA tended to decrease in strength as the printing speed increased. By macro fracture surface observed shown in figure 4, it was found that pore caused week strength.



(a) comparison of each categories (Cu-60 is Cu-PLA and print speed, 60 mm/s)



(b) comparison of print speed for Cu-PLA (30, 60, 90 means print speed (mm/s))

Figure 3: Results of the tensile test

Figure 4: Results of the tensile teste, each print speed is 30(left), 60(center) and 90(right) mm/s

4. Conclusion

FDM modeling by using copper alloy containing PLA filament had revealed the below results.

・By containing copper in the filament, products had antibacterial properties, nevertheless surface states of specimens.

・Because printing temperature of FDM was lower for copper alloy, tensile strength of copper alloy containing PLA was inferior than pure PLA.

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