

Thermal Properties of Composite Filaments for 3D Printers

A. Naganishi

User Benefits

- ◆ DSC is effective in the selection and setting of the molding conditions of diverse 3D printer filaments.
- ◆ Differences in thermal properties, even in filaments of the same resin, can be confirmed easily by DSC.
- ◆ DSC can grasp the effects of the thermal properties of the filament on the formability and physical properties of molded products.

Introduction

3D printers, which are capable of constructing 3-dimensional molded objects, have been adopted widely not only in industrial applications but also for home use by hobbyists. The mainstream molding method in 3D printers is a technique called fused deposition modeling (FDM), in which a continuous resin filament is melted by heat and then deposited in layers. Filaments for 3D printers are made from thermoplastic resins, and various types have now been developed. Although the main filament materials are ABS resin and PLA resin, other materials include not only engineering plastics but also super engineering plastics and composites made by adding glass fiber or carbon fiber to a thermoplastic resin.

Because 3D printers utilize the characteristic that the filament material softens when heated and then hardens when cooled, the differential scanning calorimeter (DSC), which enables detailed analysis of fusion and crystallization, is extremely effective in material selection and setting of the molding conditions. This article introduces an example in which the thermal properties of several composite filaments for 3D printers were measured with Shimadzu thermal analyzers.

Measurement Samples

Table 1 shows the composite filaments for 3D printers measured here. Fig. 1 shows the external appearance of sample materials ① and ②.

Table 1 List of Measurement Samples

No.	Sample name
①	Nylon 6 + short fiber CFRP
②	Nylon 6 + continuous fiber CFRP
③	Nylon 6 + continuous fiber GFRP
④	PEEK + short fiber CFRP
⑤	PEEK + short fiber CFRP
⑥	Nylon 6 + short fiber CFRP



Fig. 1 Appearance of Sample Materials
(Left: ① Nylon 6 + Short Fiber CFRP,
Right: ② Nylon 6 + Continuous Fiber CFRP)

Sampling and Measurement Conditions

Among the sample materials shown in Table 1, the short fibers were cut into round slices and the continuous fibers were cut to a length of 3 mm, and the samples were then placed in cells, as shown in Fig. 2.

Table 2 shows the measurement conditions.



Fig. 2 Sampling Conditions (Left: Short Fiber, Right: Continuous Fiber)

Table 2 Measurement Conditions

Instrument	: DSC-60 Plus differential scanning calorimeter
Heating rate	: 10 °C/min
Temperature range	: 0 °C - 245 °C (samples ①, ②, ③, ⑥) 30 °C - 400 °C (samples ④, ⑤)
Sample weight	: 10 mg
Atmosphere	: Nitrogen

Measurement Results of Nylon 6 Filaments

Fig. 3 shows the DSC curves of samples ①, ②, ③, and ⑥. When the DSC curves were compared, differences could be seen in their respective thermal characteristics. Samples ①, ③, and ⑥ displayed large endothermic peaks due to melting at around 200 °C to 220 °C, indicating that these samples are crystalline. The melting temperature is an index of the temperature setting of a 3D printer.

On the other hand, an endothermic peak due to melting was not detected in sample ②, and a glass transition could be seen near 66 °C, showing that this material is amorphous. The fact that the melting peak of sample ③ at around 204 °C is smaller than the peaks of samples ① and ⑥ is due to the larger content of glass fiber and smaller resin content in sample ③.

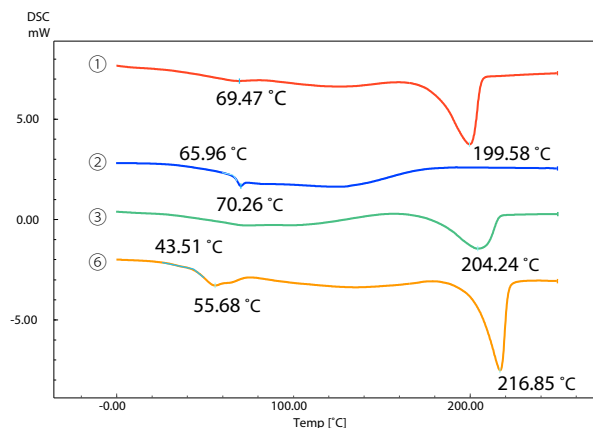


Fig. 3 DSC Curves of Samples ①, ②, ③, and ⑥

Furthermore, in addition to a glass transition or melting, all four sample materials displayed so-called gradual endothermic change over a wide temperature range from room temperature to 200 °C. Because this was expected to be due to vaporization of water, the weight change was measured with a Shimadzu DTG-60 simultaneous thermogravimetry/differential thermal analyzer.

Fig. 4 shows the TG curve of sample ②. (The DTA curve is omitted here.) A weight decrease of 2.0% was measured up to the temperature of 200 °C, and is considered to be due to vaporization of adsorbed water.

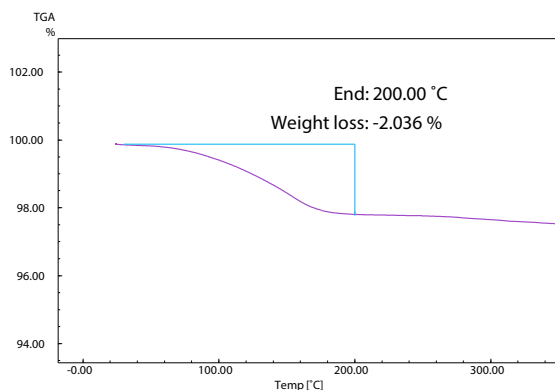


Fig. 4 TG Curve of Sample ②

Because Nylon 6 readily adsorbs water in this manner, it is normally dried before use as a 3D printer filament. Fig. 5 shows the results of DSC measurements of sample ② after drying at 80 °C for 0 h (start), 1.5 h, and 18 h. It can be observed that the glass transition temperatures of the respective samples increase from 65.8 °C to 103.1 °C and then 108.7 °C as drying proceeds. Since water acts as a plasticizer, this corresponds to the occurrence of the glass transition at a lower temperature as the water content increases.

Moreover, because formability also changes depending on the water content,⁽¹⁾ it can be understood that pretreatment to dry the filament material is important.

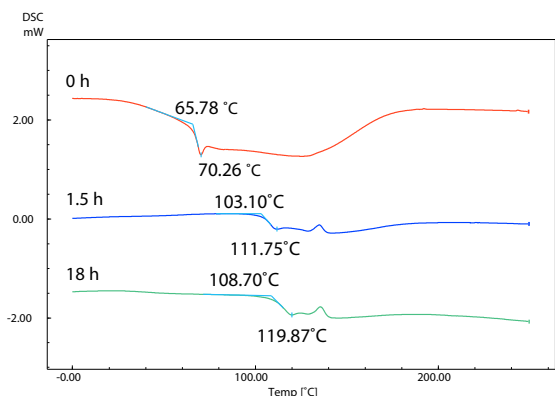


Fig. 5 DSC Curves of Sample ② with Different Drying Times

■ Measurement Results of PEEK Filaments

Fig. 6 shows the DSC curves of samples ④ and ⑤. In the case of sample ④, the glass transition can be seen at 143.1 °C and melting occurs at 340.2 °C. In sample ⑤, the glass transition occurs at 146.8 °C, an exothermic peak due to crystallization can be seen at 189.5 °C, and an endothermic peak due to melting can be observed at 336.6 °C. Thus, a difference of approximately 4 °C can be seen in the melting temperatures of these two samples.

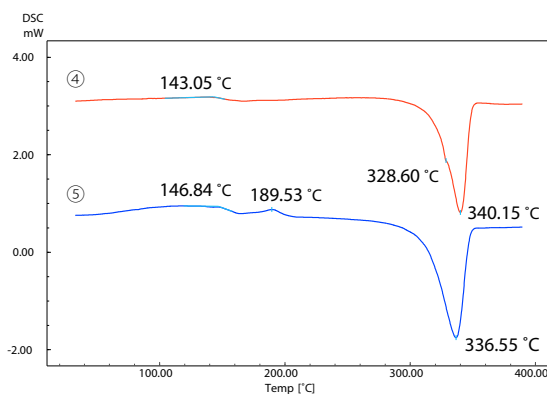


Fig. 6 DSC Curves of Samples ④ and ⑤

Next, Fig. 7 shows the results of a 2nd run, in which these two samples were first heated to 400 °C and then cooled to room temperature and heated again. Here, the relative crystallinity was estimated by comparing the heat of fusion of the two sample materials. Heat of fusion was calculated by dividing the amount of heat required for melting by the resin weight obtained with the DTG-60.

In molding with a 3D printer, the filament is heated and melted, extruded from the nozzle hole and deposited, and then cooled and solidified. If the 2nd run of the DSC is considered to be equivalent to measurement of the molded product after cooling and solidification, the molded product of sample ④ is estimated to have a higher crystallinity than the product of sample ⑤ because the heat of fusion of sample ④ was larger. Differences in the crystallinity may possibly affect the physical properties of molded products, and particularly their mechanical strength.

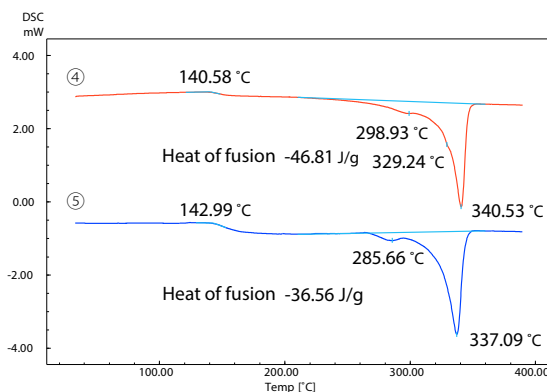


Fig. 7 DSC Curves of Samples ④ and ⑤ in 2nd Run

■ Conclusion

Various types of composite filaments for 3D printers were measured with a DSC. Even in filaments made from the same resin, differences were found in thermal properties such as the melting temperature, glass transition temperature, and heat of fusion. Because these differences affect the formability and physical properties of the molded product, a thermal analysis which can grasp the thermal properties of the filament material is extremely important.

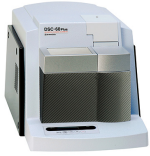
<Reference>

- (1) N. Jia and H. A. Fraenkel, Journal of Reinforced Plastics and Composites, 23 (7), 729, (2004)

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