APPLICATION NOTE

Hyphenated Technology

AUTHOR

Hua Cheng
PerkinElmer,
Shanghai, China

TG-GC/MS: *In-situ* Evolved Gas Analysis During the 3D Printing Procedure

Introduction

Three-dimensional (3D) printing technology has received tremendous interests due to its capability of generating complex-shaped structures, unparalleled high efficiency and zero residual feedstock[1,2,3]. The invention and development of low-cost desktop printers has made this technology widely acceptable for applications both in industry and home[4]. Normally, thermoplastic materials are utilized as the raw material of 3D printers, while more advanced and sophisticated prototype uses the precursor of thermoset materials (or a prepreg) as the feedstock sources. Due to the reaction nature of the precursor, various toxic gases could be emitted during the printing procedure, including regulation prohibited chemicals.

GC/MS is normally used for the identification of potentially harmful chemicals, though it does not necessarily provide the rough distribution of the evolved mixing gas debris. Moreover, extensive sample preparation is required.

With Hyphenated techniques coupling TG and GC/MS, labs can benefit from minimized sample preparation while qualitatively study the gas evolved and the degradation components that can be identified to discern the polymer engineering.

This application note reports the results of TG-GC/MS Analysis for the in-situ study of the chemical nature of evolved gases during the 3D printing performed with the PerkinElmer Hyphenation System with TG-GC/MS configuration.

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Experimental

The PerkinElmer Hyphenation System with the TG-GC/MS configuration was used to obtain accurate thermal decomposition data with subsequent identification of the evolved breakdown products.

The PerkinElmer TGA 8000™ System was programmed for a linear temperature range from room temperature to 800 °C with a sweep rate of 20 °C/min. High purity helium (45 mL/min) was used to purge the whole system and to transfer the breakdown products to the PerkinElmer GCMS 2400 System.

The online mode and the separation mode are both applied to monitor the molecule debris, Total Ion Chromatogram (TIC) 15~500 amu with SIR at 44 amu and 94 amu.

The temperature of lines and adaptors was maintained at 280 °C, with a pumping rate of 30 mL/min.

Table 1. Gas Chromatograph method parameters.

Gas Chromatograph	**GC 2400 System**	
GC Column	Elite-5 MS 30 m × 0.25 mm × 0.25 µm	
Injector Type	TL-9000	
Injector Temperature	280 °C	
Carrier Gas	Helium	
Split Flow	None	
Transfer Line Program		
	Online Mode GC Oven Program	
GC Oven Program	**Set Point**	**Hold Time**
Isothermal	280 °C	40 min
	Separation Mode GC Oven Program	
GC Oven Program	**Set Point**	**Hold Time**
Initial	35 °C	3 min
10 °C/min	290 °C	3 min

Table 2. Mass Spectrometer method parameters.

Mass Spectrometer:	**MS 2400 SQ System**
Inlet Line Temperature	280 °C
Source Temperature	280 °C
Scan Conditions	
Mass Range	15 – 500 m/z
Scan Duration	0.10 sec
Run Time	30 min

PerkinElmer Hyphenation System.

Results

A sample of (26.264 mg) printing stock was heated as shown in Figure 1.

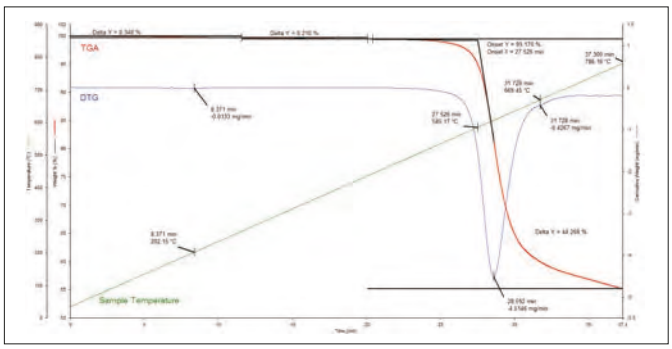

Figure 1. Initial polymer pyrolysis.

Three weight loss steps can be observed from the obtained curve. The polymer system starts to pyrolysis at 585.17 °C with a total weight loss of around 44.268%. There are two small steps existing within the low temperature range which might be the origin of the gas during the 3D printing procedure.

The initial mass spectrometry (Figure 2) of the evolved gas at 29.856 min (approximately 630 °C) shows the presence of aromatic compounds with further separation by chromatography required to correctly identify which aromatic compounds and to separate the aromatics from other thermal breakdown compounds that are evolved at the same temperature.

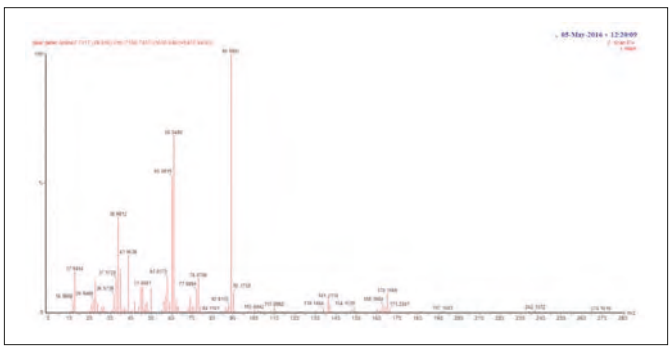

Figure 2. Total spectra at 29.856 minutes.

In order to understand the rough distribution of the evolved mixing gas debris, the online TGA-MS mode is applied firstly. As shown in Figure 3, the primary MS signals reach peaks at 315 °C and 605 °C respectively. Based on this fact, we will focus our attention on these two points using the separation mode.

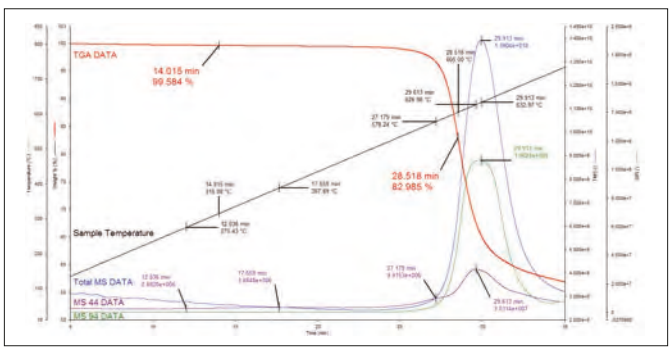

Figure 3. MS data in relation to the thermal program demonstrating the evolved components.

In order to qualitatively study the gas evolved during the 3D printing procedure, 80~100 µL of evolved gas were collected at 315 °C and injected it into the GC column to fully study its components using the method described in Table 1. As can be seen in the obtained chromatogram (Figure 4), there are many degradation components that can be identified to discern the polymer engineering.

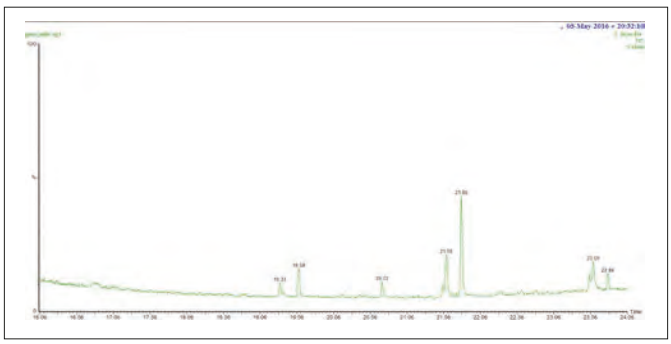

Figure 4. Separated breakdown products at 315 °C for analysis.

Analysis of the peaks evolved at 315 °C tentatively identified the peaks to consist of linear hydrocarbons terminated with a triple bonded nitrogen atom such as Figure 5.

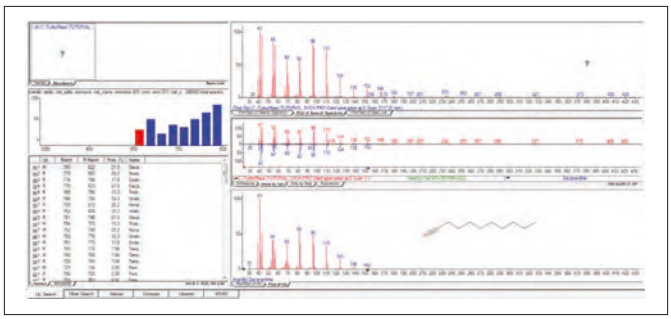

Figure 5. Linear hydrocarbon breakdown product generated at 315 °C.

A similar 80~100 µL evolved gas at 605 °C was injected and analysed in the same manner with the chromatogram shown in Figure 6.

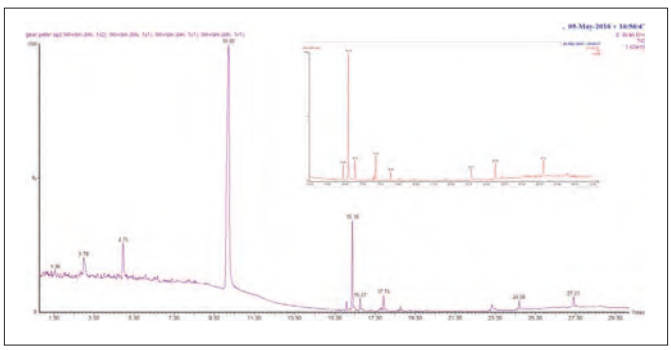

Figure 6. Separation of evolved components at 605 °C.

Analysis of the evolved gases at 605 °C identified many aromatic structures such as shown in Figures 7 and 8.

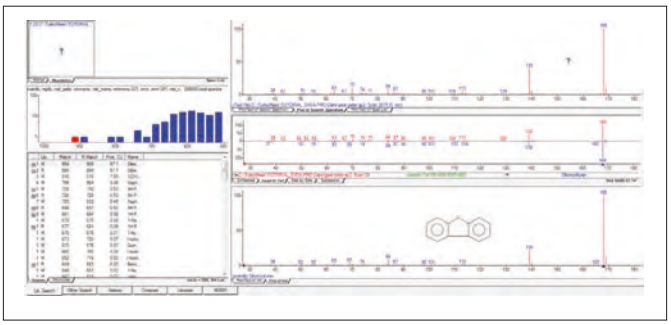

Figure 7. Evolved product of thermal degradation at a retention time of 17.74 minutes.

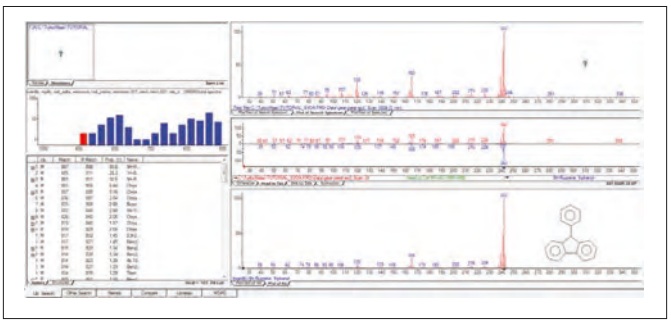

Figure 8. Evolved product of thermal degradation at a retention time of 24.50 minutes.

The 3D-printed polymer starts to degrade at 585.17 °C under helium atmosphere. It gives us a hint that this polymer should belong to the high performance engineering polymer category;

The primary pyrolytic products are phenol, biphenyl derivative and other aromatic derivatives, this is the characteristic fingerprints of aramid group polymers (such as Kevlar or Nomex);

The TG-GC/MS analysis detected that the evolved gas during the 3D printing procedure are mostly azoic compounds and they are most likely used as the initiator of the chain extension reaction.

Conclusion

For the in-situ evolved gas analysis during the 3D printing procedure, the PerkinElmer Hyphenation System with TG-GC/MS configuration enabled the qualitatively study of the gas evolved and of the degradation components that can be identified to discern the polymer engineering.

The analysis was performed with the TG-GC/MS configuration of the PerkinElmer Hyphenation System that enables to obtain crucial insights not available with a single technique, while requiring a minimized sample prepation process.

This study shows that with the PerkinElmer Hyphenation System, labs can reverse-engineer target products regardless of a fully cured product or an additive included prepreg.

References

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PerkinElmer, U.S. LLC.
710 Bridgeport Ave.
Shelton, CT 06484-4794 USA
(+1) 855-726-9377
www.perkinelmer.com

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