

Hyphenated Technology

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In-situ Evolved Gas Analysis During the 3D Printing Procedure

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 home⁴. 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 unpleasant gases would emit during the printing procedure which may include regulation prohibited chemicals from time to time.

PerkinElmer can provide effective hyphenated solutions to in-situ study the chemical nature of evolved gases during the 3D printing. At the same time, since the TGA 8000™ can cover the temperature range up to 1200 °C, we may also count on the TG-GC/MS platform to reverse-engineer target products regardless of a fully cured product or an additive included prepreg.

Introduction

Three-dimensional (3D) printing technology has received tremendous interests due to its capability of generating complex-shaped structures, unparalleled high efficiency and

Experimental

The study utilized the TG-GC/MS hyphenated module to obtain accurate thermal decomposition data with subsequent identification of the evolved breakdown products.

The TGA 8000 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 GC/MS.

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.

Maintain the temperature of lines and adaptors at 280 °C, with a pumping rate of 30 mL/min the TL9000 sampling split ratio is 1.:1.5.

Table 1. Gas Chromatograph method parameters.

Gas Chromatograph	Clarus 680 GC	
GC Column	Elite-5 MS 30 m × 0.25 mm × 0.25 μm	
Injector Type	TL-9000	
Injector Temperature	280 °C	
Injector Liner	TL-9000	
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:	Clarus 680 GC
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

Results

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

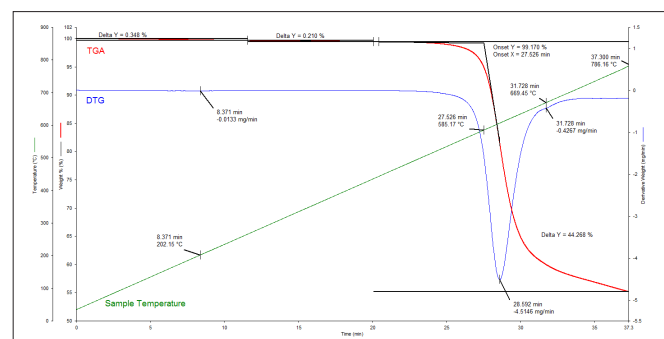


Figure 1. Initial polymer pyrolysis.

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 unpleasant 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.

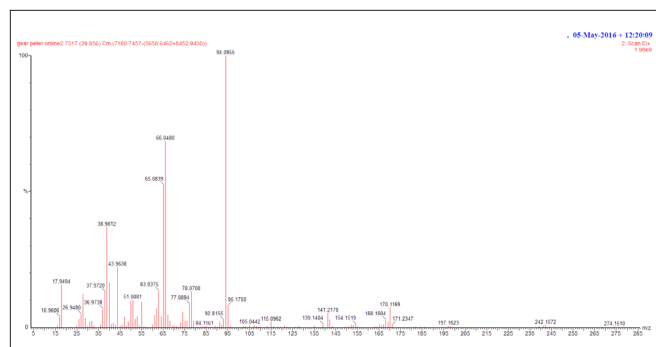


Figure 2. Total spectra at 29.856 minutes.

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.

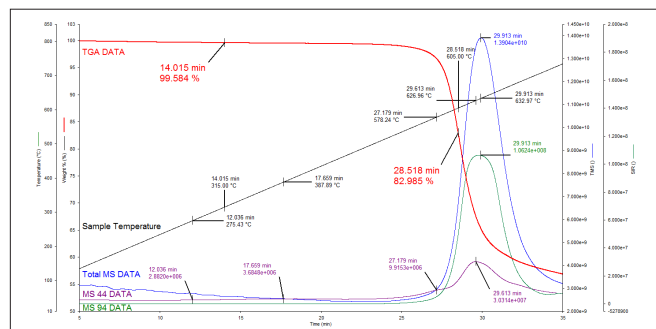


Figure 3. MS data in relation to the thermal program demonstrating the evolved components.

In order to qualitatively study the unpleasant gas evolved during the 3D printing procedure, we've collected 80~100 μL of evolved gas 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.

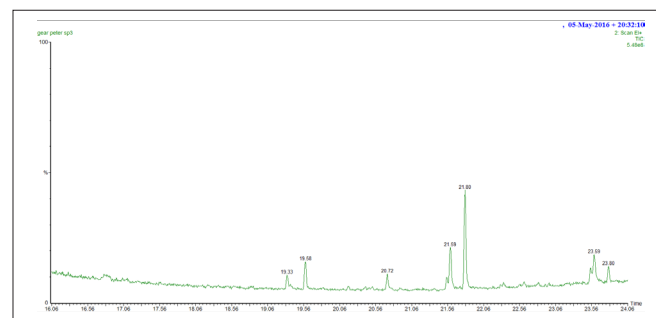


Figure 4. Separated breakdown products at 315 °C for analysis.

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.

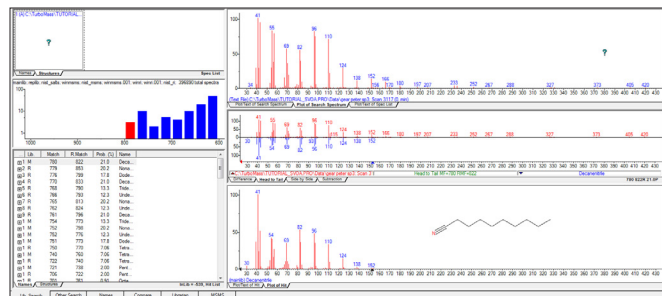


Figure 5. Linear hydrocarbon breakdown product generated at 315 °C.

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.

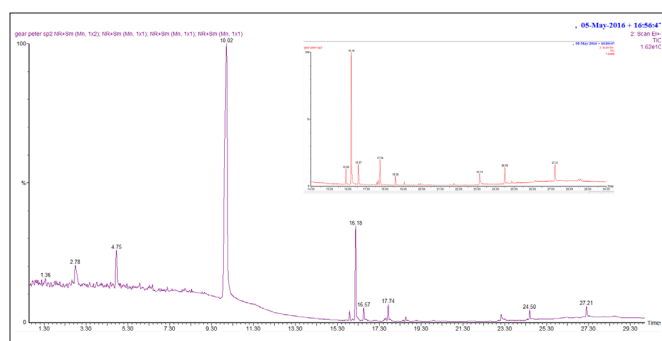


Figure 6. Separation of evolved components at 605 °C.

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

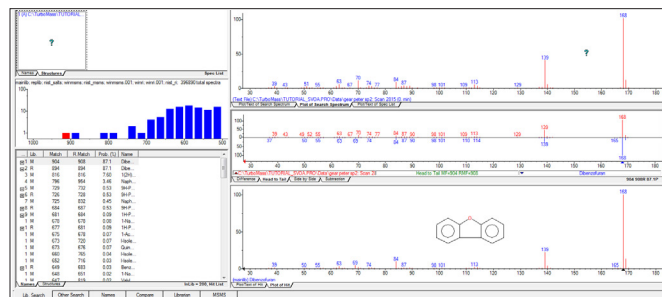


Figure 7. Evolved product of thermal degradation at a retention time of 17.74 minutes.

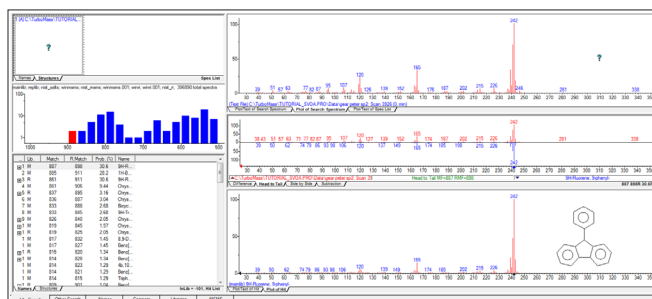


Figure 8. Evolved product of thermal degradation at a retention time of 24.50 minutes.

Conclusion

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 evolved “unpleasant gas” during the 3D printing procedure are mostly azoic compounds as revealed by the TG-GC/MS data, and they are most likely used as the initiator of the chain extension reaction.

References

1. Mohammad Vaezi, Hermann Seitz, Shoufeng Yang, A review on 3D micro-additive manufacturing technologies, *Int. J. Adv. Manuf. Technol.*, 2013, 67: 1721.
2. Brent Stephens, Parham Azimi, Zeineb El Orch, Tiffanie Ramos, Ultrafine particle emissions from desktop 3D printers, *Atmos. Environ.*, 2013, 79: 334.
3. J.M. Taboas, R.D. Maddox, P.H. Krebsbach, S.J. Hollister, Indirect solid free form fabrication of local and global porous, biomimetic and composite 3D polymer-ceramic scaffolds, *Biomater.*, 2003, 24: 181.
4. Matt Zarek, Michael Layani, Ido Cooperstein, Ela Sachyani, Daniel Cohn, Shlomo Magdassi, 3D printing of shape memory polymers for flexible electronic devices, *Adv. Mater.*, 2015, 28: 4449.