Reactive Extrusion of High Temperature Resins for Additive Manufacturing

Kathy Chuang
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Thomas W. Hughes, Roger Avakian, and Ling Hu
PolyOne Corporation
Avon Lake, Ohio 44012

Summary

The objective of this project was to produce high temperature thermoplastic and thermoset polyimide resins as candidate materials for use in Additive Manufacturing (AM). Polyimides amenable to a solvent-free process were produced via reactive extrusion in forms suitable for additive manufacturing. High temperature polyimide resins were formulated to yield varied molecular weights with reactive and nonreactive endcaps; such as phenylethynylphthalic group (PEPA) and phthalic anhydride (PA), to promote and prevent cross linking, respectively. This effort successfully demonstrated the viability of using reactive extrusion to produce high temperature polyimides directly both as filaments amenable to Fused Deposition Modeling (FDM) and as resin powders suitable for Selective Laser Sintering (SLS) in additive manufacturing.

Introduction

Additive manufacturing (AM) has gained considerable attention recently, because of the promise of being able to produce 3D component structures directly by robotic machines. The technology is ideal for complex plastic, metal or composite parts or low production volume components. Two AM technologies are being considered for use in polymer for aerospace applications—Fused Deposition Modeling (FDM) and Selective Laser Sintering (SLS). However, many commercial polymers used for additive manufacturing perform below 200 °C, which is too low for high temperature applications; e.g., aircraft engine components—bearings, farings, housings and ducts.

The objective of this Phase I project was to produce high temperature, low-melt viscosity thermoset and thermoplastic polyimide resins as candidate materials for use in Additive Manufacturing (AM), such as the RTM370 oligomer shown in Figure 1. Polymers amenable to production via reactive extrusion were evaluated and produced in forms suitable for additive manufacturing. The high temperature resins were formulated to yield varied molecular weights with reactive and nonreactive endcaps such as phenylethynylphthalic group (PEPA) and phthalic anhydride (PA), respectively, to promote and forestall cross linking, respectively. Ideally, a long chain thermoplastic, such as a resin sparingly terminated with PA, could provide adequate viscosity and filament forming characteristics suitable for additive manufacturing, while maintaining the desired higher temperature performance upon exposure to heat. Dianhydride and diamines monomers supplied by NASA and were used to produce a variety of polyimides.

The conventional polyimides technology required the use of hazardous and expensive solvents, such as N-methyl-2-pyrrodidinone (NMP, bp = 202 °C). These solvents are difficult to remove from the polymer matrix without inadvertently pre-curing the thermoset resins. NASA Glenn's patented technology (Refs. 1 and 2) for making polyimides in a solvent-free manner was evaluated as a base platform. The RTM370 oligomer made by NASA is a highly viscous material which is difficult to remove

from low shear, atmospheric pressure production vessels. PolyOne's reactive extrusion process improves upon the existing NASA patents and removes the difficulties associated with transporting high temperature, highly viscous materials using extruders designed for transport and mixing of highly viscous polymer systems with short term exposures to high temperatures.

Figure 2 shows alternative approaches to the production of polyimides—typical solvent based process and PolyOne's reactive extrusion approach. Reactive extrusion is sustainable, solvent-free, well controlled, scalable and agile for production of specialty resin formulations.
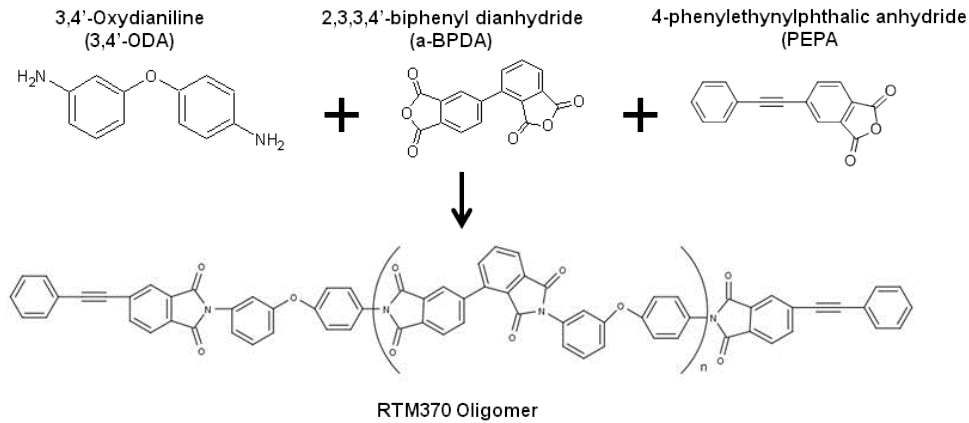

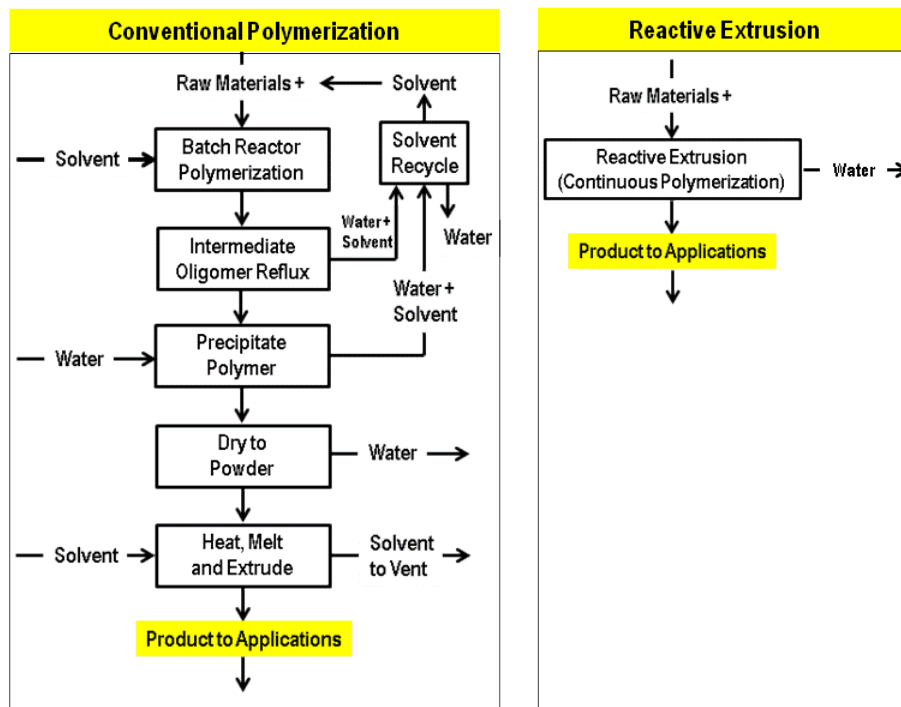Figure 1.—Solvent-Free Chemistry for making imidized oligomers.

Figure 2.—Solvent-based and reactive extrusion based production of polyimides.

2

Currently, there is no commercial scale technology available for the production of high temperature thermoplastic or thermoset polyimide resins in a solvent-free manner. PolyOne's reactive extrusion technology was adapted to produce polyimides in a solvent-free manner, particularly in a condition in which the asymmetric anhydride and the endcap competed concurrently for the diamine reactions sites. Also, the state of the art in additive manufacturing (3D printing) of plastic parts is limited to the production of prototypes and some production parts using low temperature, low mechanical strength polymers. If this project is successful, it would demonstrate both the ability to produce high temperature polyimides via reactive extrusion and their use in 3D printing for aerospace, aeronautical, and automotive parts where mass customization of engineering resins is needed. Applications include the printing of replacement or new parts in space using resin filaments and CAD artwork, production of parts to secure cables, fuel lines, signal lines, etc. on jet engines and rocket engines, rapid prototyping of extraterrestrial vehicles, and production of parts and tooling for use in some automotive applications where mass customization is required.

Experimental

Reactive Extrusion of Thermoplastic and Thermoset Polyimides

Thermoplastic and thermoset polyimides based on 2,3,3′,4′-biphenyl dianhydride (a-BPDA), one or more than one aromatic diamines, and terminated with either the non-reactive phthalic anhydride (PA) or the reactive 4-phenylethynylphthalic anhydride (4-PEPA) were feed as solid powders into a laboratory scale, 16 mm diameter twin screw extruder (breadboard scale) mixed and melted at 280 to 400 °C (Fig. 3). The thermoplastic polyimides were extruded as filaments and the thermoset polyimides were grounded into powders (Fig. 4).
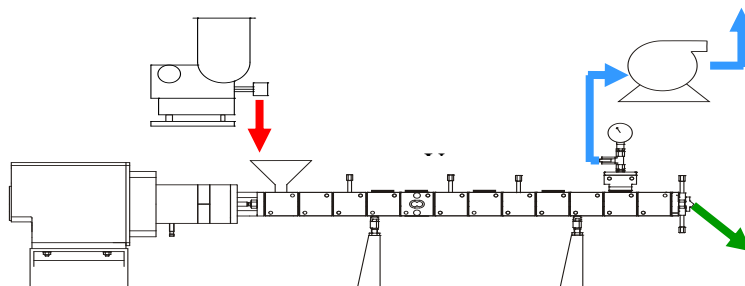

Figure 3.—Schematic diagram of a twin extruder used for reactive extrusion.

Figure 4.—Thermoset resin powder for use in Selective Laser Sintering (SLS) and thermoplastic filaments for Fused Deposition Modeling (FDM) types of 3D printers.

Fused Deposition Modeling (FDM) of Novel Polyimide Filaments

A total of 1.3 kg of five different thermoplastic polyimide co-polymers (Co-PI) were produced via reactive extrusion on a 16 mm twin screw extruder, four of which were suitable for forming into filaments. The most flexible polyimide copolymer with glass transition temperature (T_g) of 265 °C (Co-PI-265) was converted to 400 linear feet of filaments. The Co-PI-265 filament was loaded into an open-source Stratasys' Fortis 400 mc FDM machine at Thogus' RP+M subsidiary to print flex bar specimens and coins, using the upper limit of liquefying temperature of 400 °C. However, attempts to make filaments out of thermoset polyimides were unsuccessful due to premature curing of the PEPA endcap; instead, resin powder was produced that is amenable for Selective Laser Sintering (SLS).

Results and Discussions

Characterization of Thermoplastic and Thermoset Polyimides Made by Reactive Extrusion

Thermoplastic and thermoset polyimides based on 2,3,3′, 4′ -biphenyl dianhydride and 3,4′ -oxydianiline (3,4′ -ODA) with phthalic anhydride (PA) and 4-phenylethynyl phthalic anhydride (PEPA) endcaps were produced by reactive extrusion with varied chain length. Thermoset polyimide resins were subjected to a cross-linking study whereby the uncured polyimides, having glass transition temperatures (T_g) of 290 °C or lower were cross-linked to produce thermoset resins (not composites) with T_g's of up to 340 °C for the resins (RTM370 resin system), as measured by Differential Scanning Calorimetry (DSC). The results were shown in Figure 5. Figure 6 shows the rheology for several of the formulations developed as compared to Ultem® species.
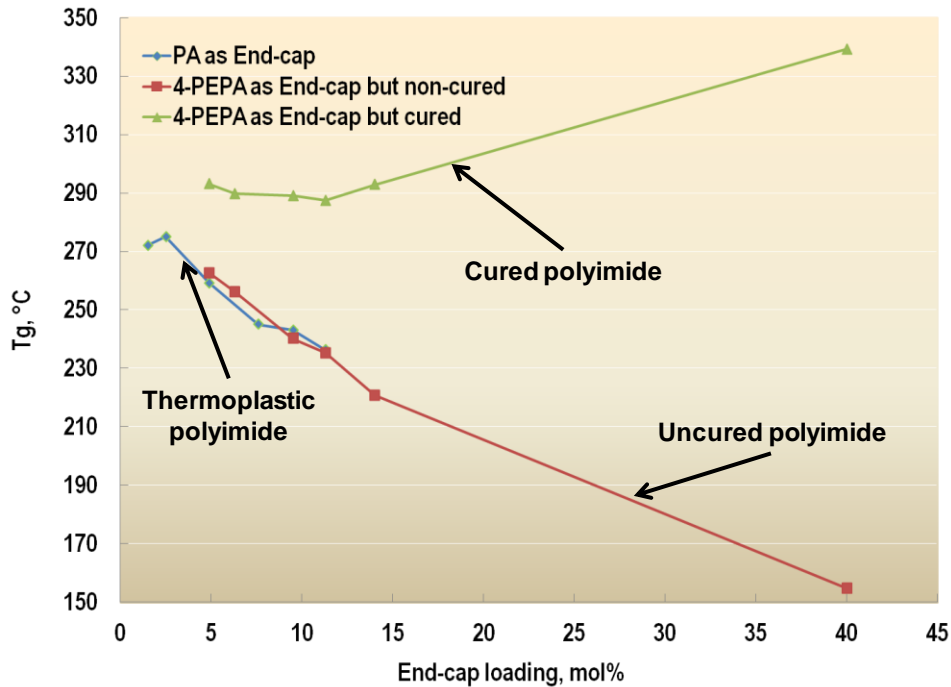

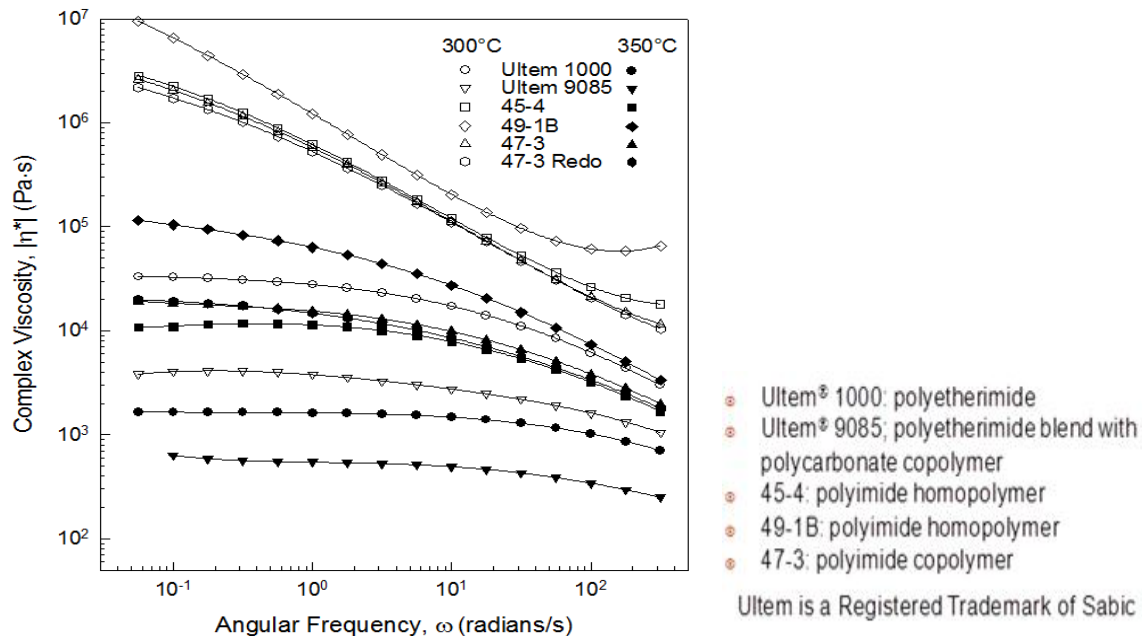Figure 5.—Effect of 4-PEPA and Phthalic Anhydride end cap stoichiometry on T_g of polyimides.

Figure 6.—Rheology data for polyimides produced via reactive extrusion.

3D-Printed Specimens Produced by FDM Using Co-Polyimide Filament (Co-PI-265)

Five thermoplastic polyimide copolymers made by reactive extrusion exhibited glass transition temperatures (T_g) of 265 to 270 °C. One preferred formulation (Co-PI-265) was chosen based on its flexibility for filament winding and processability amenable to Fused Deposition Modeling.

Co-PI-265 filament was used in a Fortis 400 mc Fused Deposition Printing machine, with open architecture that enabled manipulation of parameters, to print 3D flex bars and coins for mechanical and thermal oxidative stability testing, respectively. Ultem® 9085 coins were printed and used as a standard for isothermal aging studies. Figure 7 shows the picture of 3D printed parts prior to testing.
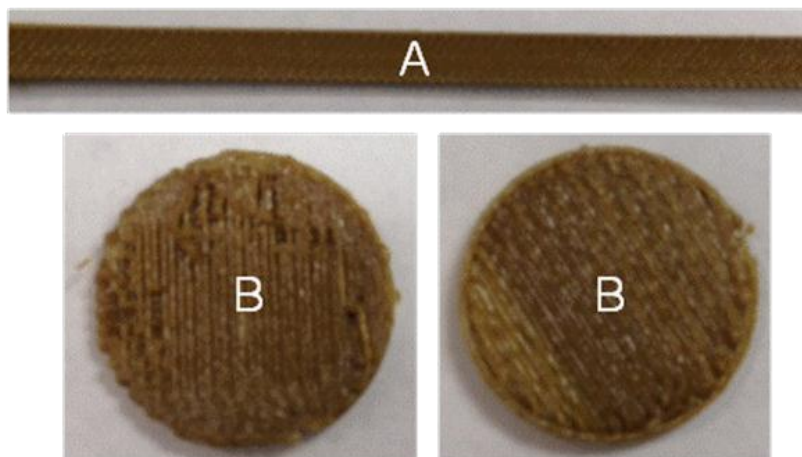

Figure 7.—3D-printed flex bar (A) and coins (B) by FDM using thermoplastic Co-PI-265 filaments produced by reactive extrusion.

Mechanical Testing Results of Ultem® 1000, Ultem® 9085 and Co-PI-265

Tensile tests (ASTM 638) were conducted on polymer filaments made from Ultem® 1000, Ultem® 9085 and the Co-PI-265 polymerized by reactive extrusion. A summary of the test results is presented below in Table 1.

TABLE 1.—TENSILE STRENGTH TEST FOR FILAMENTS MADE FROM POLYETHERIMIDES AND Co-PI-265

	Ultem® 1000	Ultem® 9085	Co-PI-265
Tensile strength, MPa	77	66	79
Tensile modulus, MPa	3,064	2,817	1,174
Elongation at break, %	25.2%	4.7%	4.1%

Flammability Testing Results of Ultem® 1000, Ultem® 9085 and Co-PI-265

Ultem® 1000, Ultem® 9085 and the Co-PI-265 were evaluated for their inherent flame retardant characteristics. Published data for limiting oxygen index values were collected for the Ultem® 1000 and Ultem® 9085 resin systems. PolyOne conducted limited oxygen index texting (ASTM 2863) on the Co-PI-265 filament and compared it to Ultem® 1000 and Ultem® 9085 as shown in Table 2. These data indicate that Co-PI-265 (LOI = 47.5) is inherently flame retardant with performance similar to Ultem® 1000 (LOI = 45) and Ultem® 9085 (LOI = 47.5).

TABLE 2.—LIMITED OXYGEN TEST FOR FILAMENTS MADE FROM POLYETHERIMIDES AND Co-PI-265

	Ultem® 1000	Ultem® 9085	Co-PI-265
Limiting oxygen index, % O_2	45	49	47.5

TG-GC-MS Measurements on Ultem® 1000, Ultem® 9085 and Co-PI-265 (Ref. 3)

The samples of PCMB (standard Polycarbonate), Ultem® 1000 (Sabic's neat polyetherimide resin), Ultem® 9085 (Sabic's blend of Ultem® 1000 and polycarbonate), and a Co-PI-265 filament were subjected to thermogravimetric (TG) analysis of the temperature-dependent mass changes, including gas analysis employing the NETZSCH TG 209 *F1 Libra*® simultaneously coupled to the Agilent 7890A gas chromatograph and the Agilent 5975 MSD (mass selective detector).

Ultem® 1000 GT-DTG Results

The TG (mass loss) and DTG (mass loss rate) curves for Ultem® 1000 are shown in Figure 8. Superimposed on these curves is the total ion chromatogram (TIC) from the quasi-continuous analysis of the evolved gases by GC-MS. As can be seen from the TG curve, mass loss from the sample did not commence until approximately 460 °C and had not leveled off by 600 °C, where the total mass loss was 41.3 percent. The DTG curve shows a peak in the mass loss rate at 548 °C.

Ultem® 9085 TG-DTG Results

The TG and DTG curves and TIC from a quasi-continuous sampling of gases evolved during the thermal decomposition of Ultem® 9085 are shown in Figure 9. The mass loss, which peaked in rate at 515 °C, was not complete by 600 °C, as it had not yet leveled off. At this point the total mass loss reached 53.4 percent.
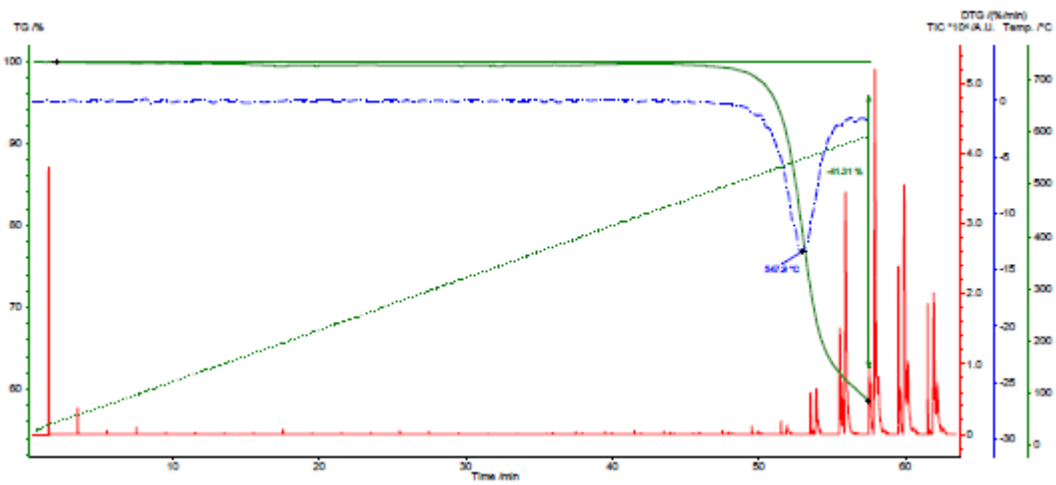
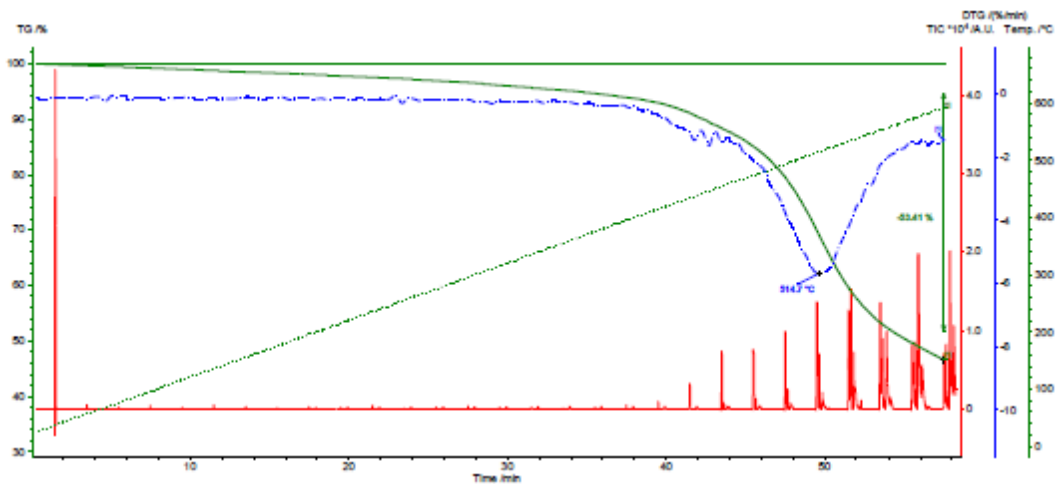Figure 8.—Overlay of TG and DTB curves and TIC for Ultem® 1000.

Figure 9.—Overlay of TG and DTB curves and TIC for Ultem® 9085.

Co-PI Filament TG-DTG Results

An overlay of the TG and DTG curves and the TIC from a quasi-continuous sampling of gases evolved during the thermal decomposition of a Co-PI filament sample are shown in Figure 10. Since significant mass loss did not really commence until around 500 °C, the sample was heated to 800 °C. Two distinct mass loss steps were apparent that peaked at 573 and 621 °C in the DTG curve. The first mass loss step accounted for 16 percent of the initial sample mass. The second mass loss step, which was not yet complete by 800 °C, accounted for more than 23 percent of the initial sample mass. When the TG curves for Co-PI-265,Ultem[®] 1000 and Ultem[®] 9085 were plotted on the same scale (Fig. 11), the data clearly indicate that Co-PI-265 is thermally more stable than Ultem[®] 1000, Ultem[®] 9085, based on the onset of decomposition of 550, 538, and 420 °C, respectively.
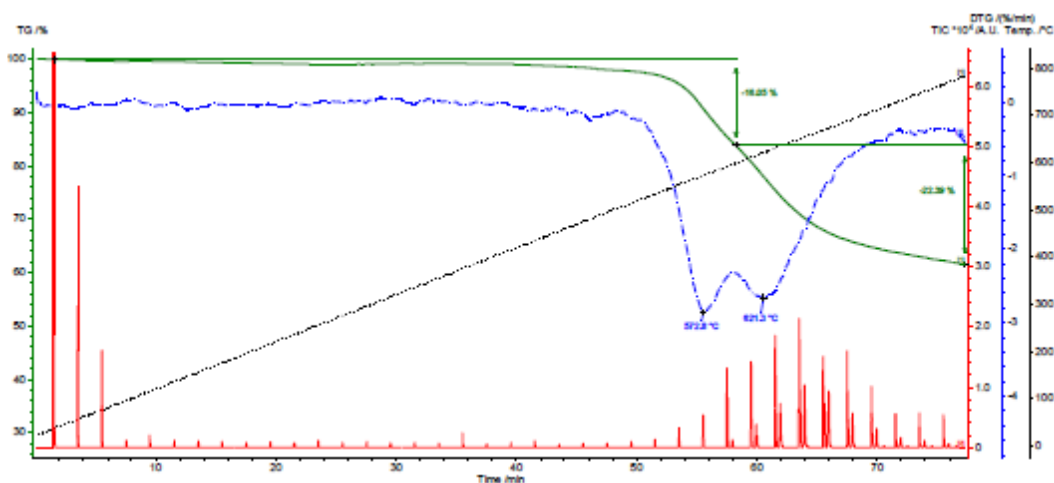

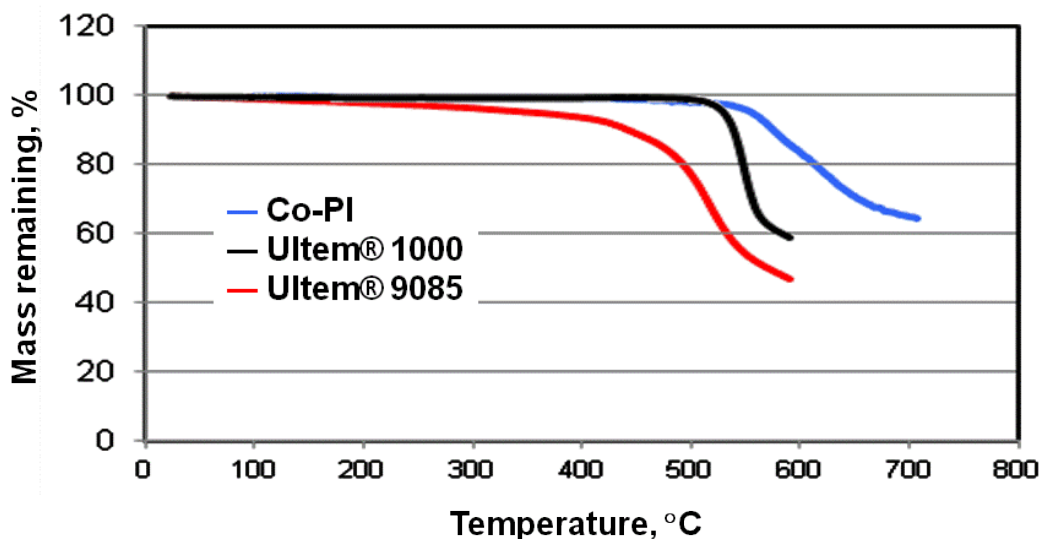Figure 10.—Overlay of TIC from quasi-continuous measurement with TG and DTG curves for Co-PI-265.

Figure 11.—Novel polyimide copolymer (Co-PI-265) out performs Ultem[®] 1000 and Ultem[®] 9085 on TGA testing.

Ultem® 1000 GC-MS Results

The Total Ion Chromatograph (TIC) analysis identified carbon dioxideand phenol early in the decomposition. Toluene, Xylene, and benzene appeared shortly thereafter, followed by cresol. Cresol and phenol were the predominant species as the decomposition progressed. TG-GC-MS data results are shown below in Figure 12.

Ultem® 9085 GC-MS Results

An expanded view of the TIC is shown in Figure 13. Besides CO_2 and the same aromatic species that were identified for Ultem® 1000, 4-ethylphenol was evolved. This species was probably also present in the evolved gases from Ultem® 1000 but not identified. Several cyclic polymethylsiloxanes were also identified. The regular appearance of the hexamethylcyclotrisiloxane, in particular, in multiple injections indicates that it originated from the polymer sample rather than from the GC column.
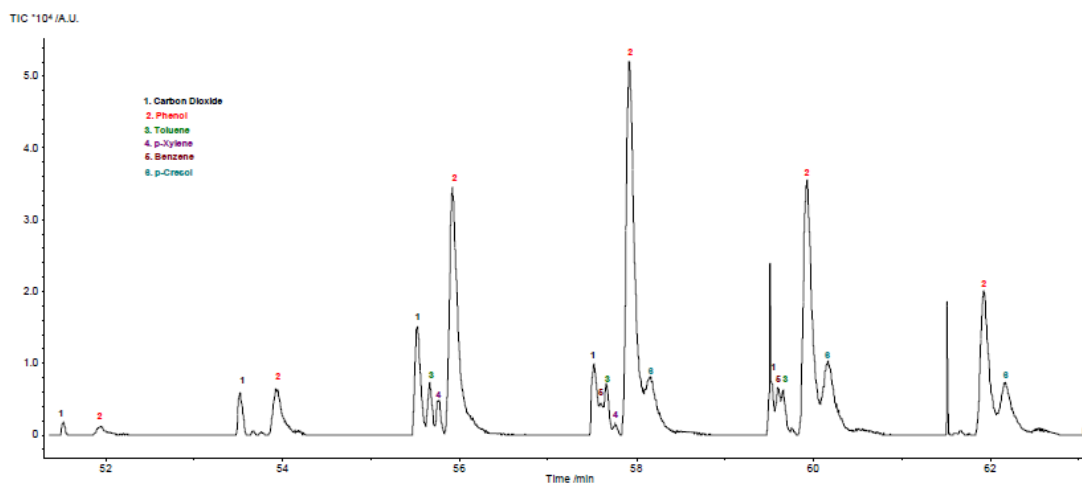

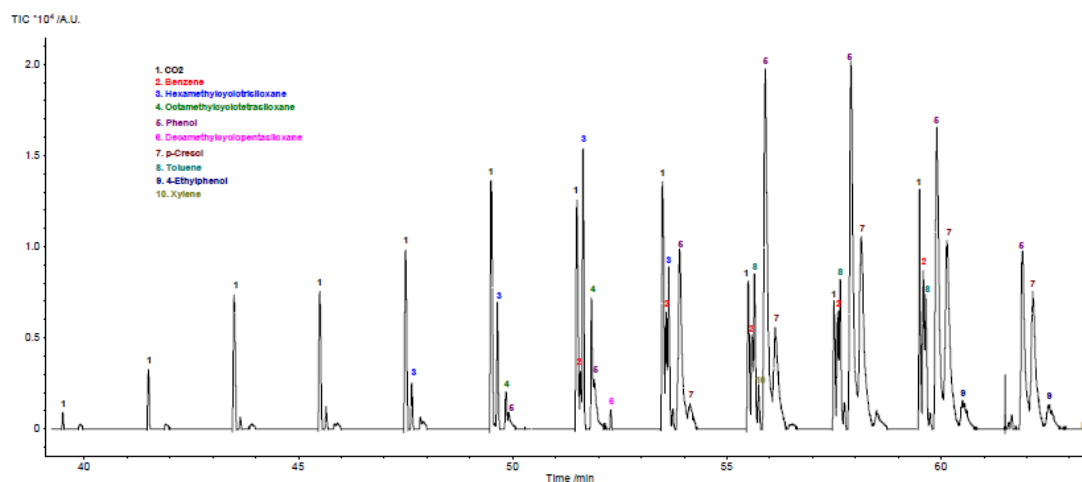Figure 12.—Expanded view of the TIC of evolved gases from Ultem® 1000 sample with peak identification.

Figure 13.—Expanded view of TIC of evolved gases from Ultem® 9085 sample with peak identification.

An additional TG-GC-MS analysis of Ultem® 9085 was performed using a cryotrap cooled to –50 °C in order to concentrate any species that may have not been identified in the quasi-continuous analysis, because of either weak or overlapping signals. The TIC of the species that were collected in the cryotrap is shown in Figure 14. A number of additional species were identified besides the ones found during the quasi-continuous measurement. Significantly, the nitrogen-containing species N-hydroxy methyl-2-phenylacetamide, 3-methyl-3-phenylazetidine, and 2-isopropylphenol methyl carbamate were identified as possible degradation products, consistent with the polymer's identification as a PC/PEI blend.

Co-PI-265 Filament GC-MS Results

An expanded view of the TIC for the evolved gases acquired in quasi-continuous mode is shown in Figure 15. Besides water, CO_2, benzene, and phenol, a number of nitrogen-containing heterocyclic species were identified. A second measurement on the sample was performed using the cryotrap in order to better resolve the organic species generated during the sample pyrolysis. An expanded view of the TIC from this measurement is shown in Figure 16. Additional organic species were identified in this measurement along with some large polycyclic methylsiloxanes, which may have been residual contaminants from the Ultem® 9085 sample measurement.
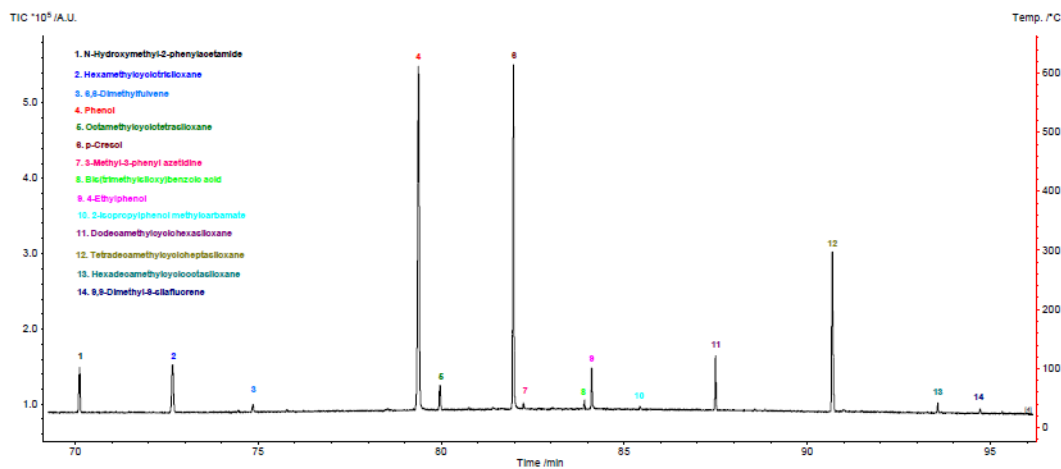

Figure 14.—Expanded view of TIC of evolved gas species form Ultem® 9085 condensed in cryogenic trap.
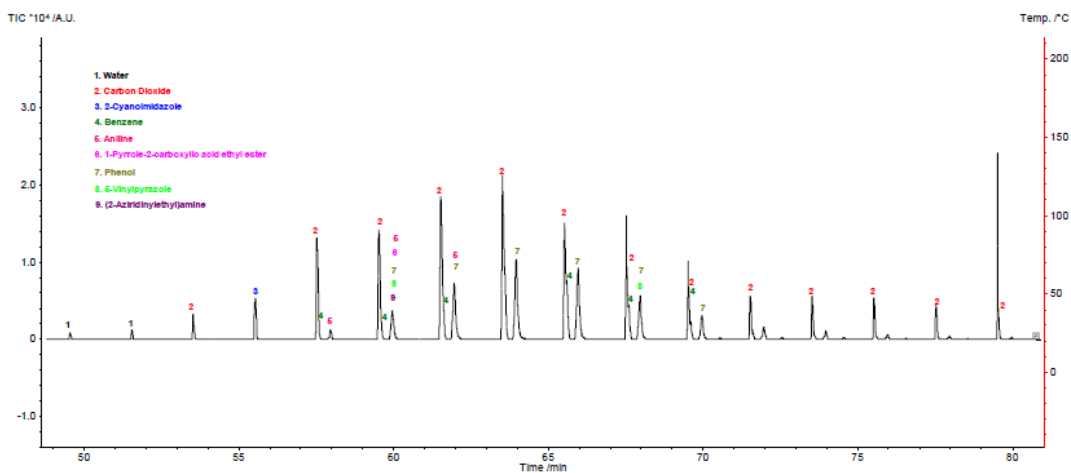

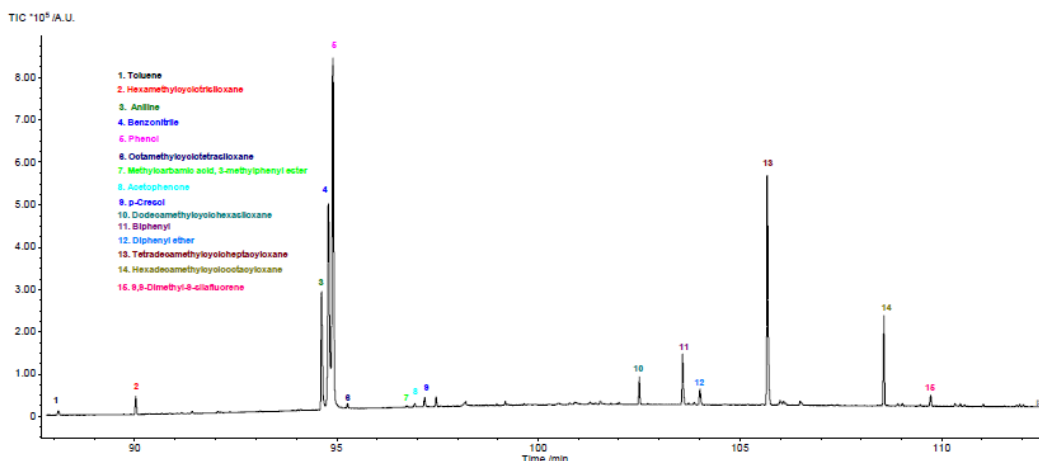Figure 15.—Expanded view of TIC from quasi-continuous measurement mode for Co-PI-265 filament.

Figure 16.—Expanded view of the TIC from TG-GC-MS analysis of Co-PI-265 filament with the cryotrap.

Co-PI-265 and Ultem®9085, Ultem®1000 Isothermal Aging at 232 °C (450 °F)

Coin specimens of the co-polyimide (Co-PI-265, T_g = 265 °C) and Ultem® 9085 (T_g = 186 °C) printed by FDM were aged at 232 °C (450 °F) along with Ultem® 1000 (T_g = 217 °C) pellets in an air circulating oven for 1000 hr. Figure 17 shows that FDM printed Co-PI-265 sample (a) remained intact after 1000 hours whereas Ultem® 9085 coin (b) totally melted within 95 hr, and Ultem® 1000 (c) pellets were darkened from champagne color to brown, partially melted and glued to the glass vial after 400 hr. Separately, after 204 °C (400 °F) isothermal aging for 100 hr, Ultem® 9085 coin adhered to the glass vial and damaged the glass by implosion, but Co-PI-265 coin remained intact.

Isothermal aging tests were conducted on both Co-PI-265 and Ultem® 9085 at 232 °C (450 °F) for 1,000 hr. Periodically, samples were removed from the oven and weighed to determine the percent weight loss as a function of time of exposure. Figure 18 shows the plot of weight loss data from isothermal aging of FDM printed Co-PI-265 and Ultem® 9085 coins, which indicated that the Co-PI-265 lost weight slower than Ultem® 9085 at the 232 °C. The data are consistent with the TG data shown above for these materials after about 20 to 22 min of testing via TG. The results as shown in Figures 17 and 18 along with previous Figure 11 clearly indicate that 3D-printed Co-PI-265 object is thermally more stable than the corresponding state-of-art Ultem® 9085 parts printed by FDM for long-term application at 232 °C (450 °F).
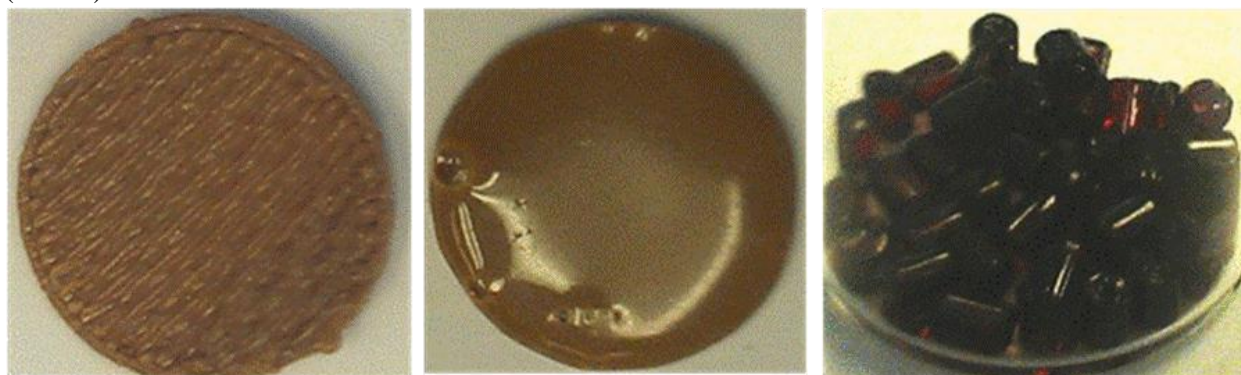
a) Co-PI /1000hours @450°F   b) Ultem 9085/95 hours @450°F   c) Ultem 1000/400hours @450°F

Figure 17.—Pictures of Co-PI-265, Ultem® 9085 and Ultem® 1000 after aging at 232 °C (450 °F).
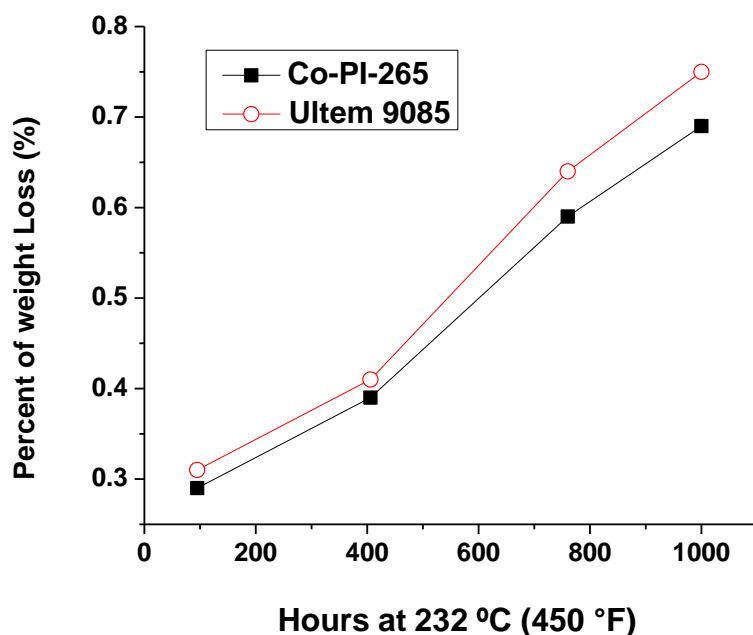
Figure 18.—Isothermal aging of Co-PI-265 and Ultem[®] 9085 coins printed by fused deposition modeling.

RTM370 Composites and Nanocomposites

RTM370 composites and nanocomposites were made using chopped carbon fiber (Fortafil 201CF) and vapor grown carbon nanofiber (VGCNF: Pyrograf III product = PR-24-XT-LHT) produced by Applied Sciences. The composites and nanocomposites were produced using both melt processing of the carbon fiber and VGCNF into RTM370 oligomer produced via reactive extrusion. Also, the carbon fiber and VGCNF based composites and nanocomposites were produced via the in-situ polymerization of the RTM370 monomers and with carbon fiber and VGCNF during the reactive extrusion/polymerization to produced composites and nanocomposites during polymerization. The preparation methods, filler loading, curing process and characterization techniques were summarized as follows:

- The preparation methods:
  - Two-step process to make the following RTM 370 composites.
  - In-situ polymerization of RTM370 monomers with carbon fiber
- Filler loading:
  - 5, 10, 20, 50 wt% vapor grown carbon nanofiber (VGCNF = Pyrograf III, PR-24-LHT) carbon nanofiber
  - 10, 50 wt% chopped carbon fiber
- The RTM370 oligomers and in-situ polymerized composites were cured at 350 °C for 5 hr
- Characterization of the neat resin, melt processes and in-situ polymerized composites and nanocomposites was performed using:
  - SEM to check dispersion and adhesion of both un-cured and cured-composites
  - DSC to determine T_g's of both un-cured and cured composites we determined for all samples.

The composites and nanocomposites were evaluated via Differential Scanning Calorimetry (DSC) to determine the T_g for the RTM370 oligomer and the corresponding composites and nanocomposites. Neat RTM370 oligomers, composites and nanocomposites were cured at 360°C for 5 h and T_g data are presented in Table 3.

TABLE 3.—DSC CHARACTERIZATION OF RTM370 OLIGOMERS, COMPOSITES AND NANOCOMPOSITES IN THE UNCURED AND CURED STATES

[Crosslinking condition: 360 °C for 5 hr.]

Sample ID	Sample information	T_g, °C	
		Uncured	Cured
156-002-019#1	Neat RTM370 resin made via REX on the 16 mm TSE	138.5	338.7
156-002-019#2	10 wt% LHT VGCNF, made via melting on the 16 mm TSE	144.2	335.9
156-002-019#3	20 wt% LHT VGCNF, made via melting on the 16 mm TSE	143.9	Not detected below 400 °C, $T_g > 400$ °C
156-002-019#4	50 wt% chopped CF, made via melting on the 16 mm TSE	142.6	337.6 but not very clear
156-002-019#5	50 wt% LHT VGCNF, made via melting on the 16 mm TSE	146.4	336.7 but not very clear
156-002-021-1	Neat RTM370 resin made via REX on the 16 mm TSE	Not tested	344.4
156-002-021-2	5 wt% LHT VGCNF, made via melting on the 16 mm TSE	Not tested	338.0
156-002-021-3	50 wt% LHT VGCNF, made via melting on the 16 mm TSE	Not tested	340.6
156-002-014#1	Neat RTM 370 resin made via REX	138.6	334.3
156-002-014#2	10 wt% chopped CF, made via in-situ REX on the 16 mm TSE	138.3	334.3
156-002-014#3	10 wt% chopped CF, made via melting on the 16 mm TSE	142.2	337.3

Images of Scanning Electron Micrographs (SEM) in Figures 19 to 22 show that there is good dispersion and distribution of the chopped carbon fibers and vapor grown carbon nanofibers in all of the samples in cured and uncured states. The images also show that there is good adhesion between the resin and the filler—both RTM370 oligomer and cured RTM370 with the carbon fiber and carbon nanofibers.

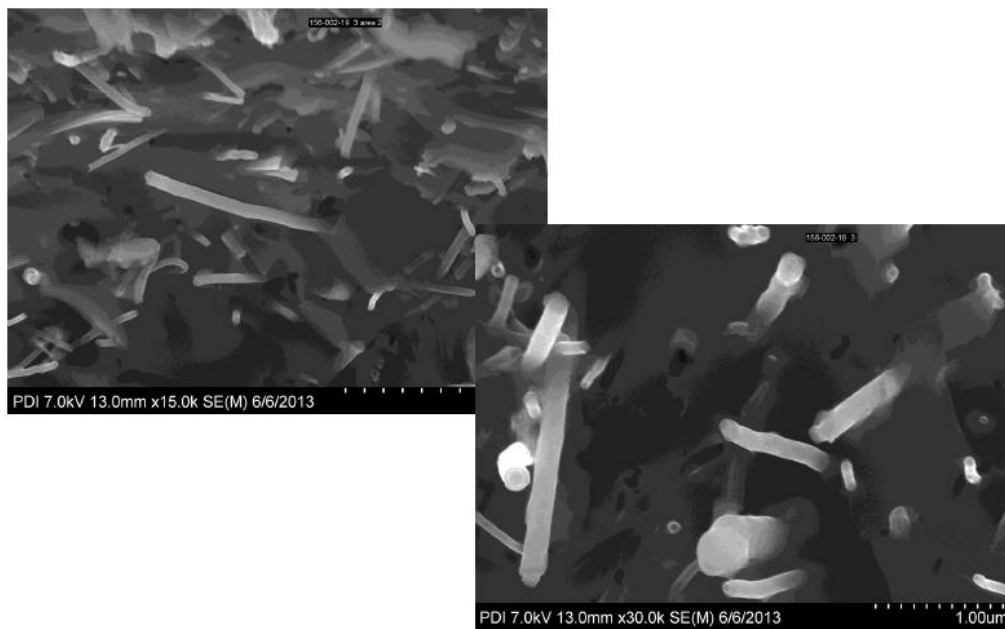Figure 19.—SEM Characterization of uncured RTM370 with 10 wt% VGCNF.

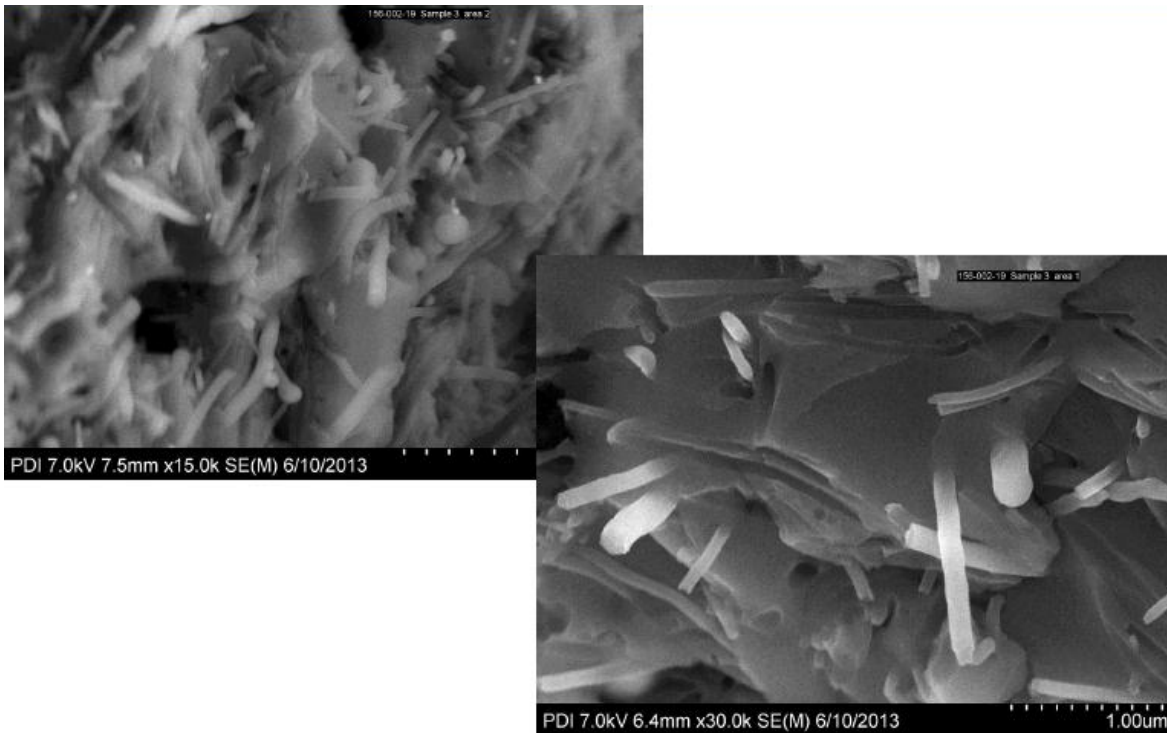Figure 20.—SEM Characterization of uncured RTM370 with 20 wt% VGCNF.

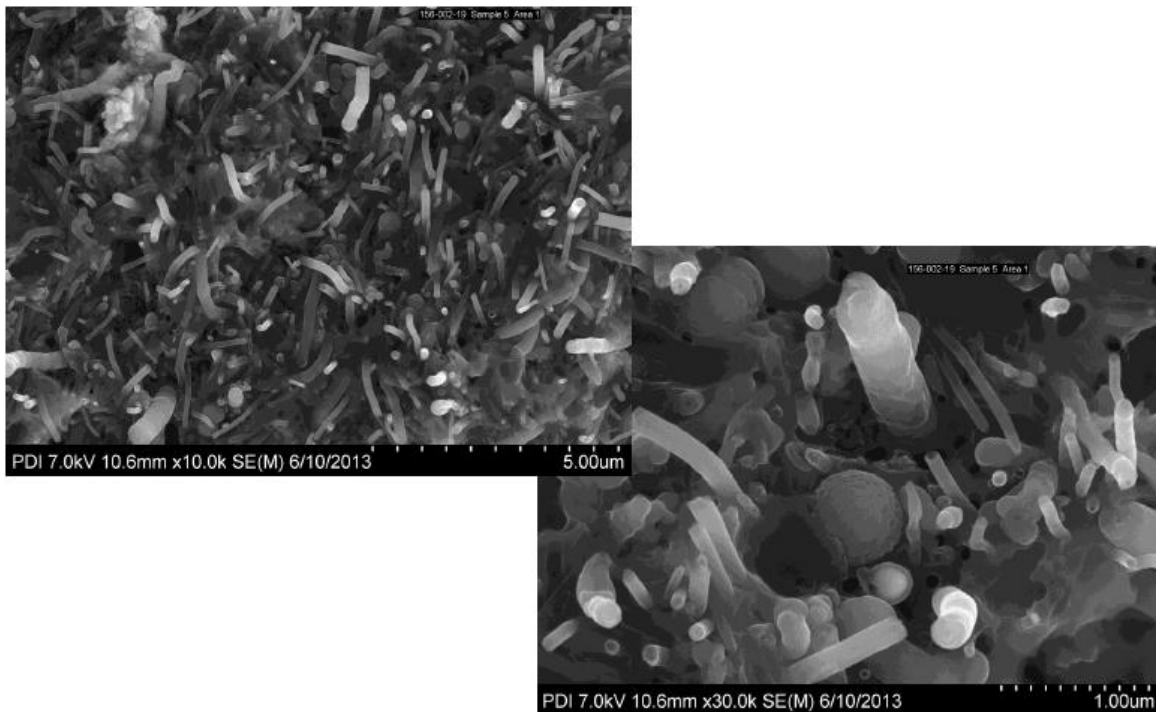Figure 21.—SEM Characterization of uncured RTM370 with 50 wt% VGCNF.

Figure 22.—SEM Characterization of cured RTM370 with 50 wt% VGCNF.

PolyOne consulted with GE Aviation to obtain CAD files to print engine components for aeronautic application in subsonic aircrafts. FDM also has potential to perform in a space environment. Example applications are for aeronautical applications are shown below in Figure 23. Parts in blue would be produced via fused deposition modeling and the parts in red would be produced via selective laser sintering.
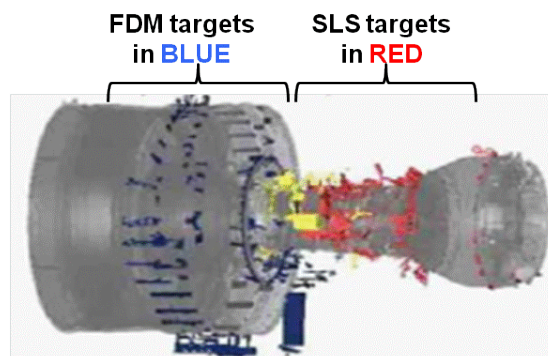

Figure 23.—Potential use of polyimides produced via reactive extrusion for aircraft engines.

ARMD Seedling Phase I Accomplishments

- Demonstrated reactive extrusion to produce both thermoset and thermoplastic polyimide resins via reactive extrusion in a solvent-less, efficient and continuous manner, instead of using conventional solvent-based reactor.
- Produced 4 new polyimides into filaments amenable for Fused Deposition Modeling (FDM) and polyimide resin powder suitable for Selective Laser Sintering (SLS).
- Produced 3D printed tensile specimens via FDM for mechanical testing at RP+M and round coins for thermal oxidative stability evaluation at NASA Glenn.
- Demonstrated the feasibility of adding carbon fibers into the thermoset polyimide as nanocomposites. However, addition of nanofillers into thermoplastic polyimide increased viscosity many fold that hindered the extrusion of filaments.
- Raised TRL from the 1 to 2 level at the start of the project to TRL 3 at Phase 1 completion.
- Concurrent reactive extrusion RTM370 patent application has been filed at the U.S. Patent and Trademark Office.
- Four newly identified, high temperature aromatic polyimides have been conceived and reduced to practice via continuous reactive extrusion to make filaments potentially suitable for Additive Manufacturing (3D Printing), and a patent application has been filed at the U.S. Patent and Trademark Office.

Conclusions

PolyOne and NASA have produced novel co-polyimide filaments in this Phase I project that displayed softening temperature (T_g) in the range of 265 to 270 °C, exceeding the state-of-art FDM polyimide Ultem® 9085 ($T_g = 186$ °C) by 80 °C. The team also demonstrated that the novel polyimide filament can be melted and deposited layer by layer into tensile bar specimens. The higher temperature capability would allow the use of FDM-produced polymeric parts to be used in higher temperature environments in the airframes or aircraft engine components. There are hundreds of odd-shaped polymeric components could be produced via AM, instead of injection or compression molding which requires the use of molds that can be costly to build for low volume production.

Additionally, PolyOne was able to produce the Glenn Research Center patented thermoset polyimide (RTM370) by concurrent reactive extrusion in lieu of reactors, via an improved method which is the subject of a patent application also filed. Preliminary tests have shown that RTM370 (T_g = 370 °C) can be heated and fused by laser; therefore, it should be amenable to the SLS process to produce net-shape components or composites for use in the hotter section of aircraft engines in place of metals to reduce the weight and machining cost. The advancement of AM for aircraft components is beneficial to NASA ARMD Fixed Wing program and the national manufacturing initiative. Several lessons were learned from the work conducted to date as shown below.

- Learned that current closed architecture FDM machines are not suitable for handling high temperature polyimides, and that collaboration with the machine vendors with an open source FDM machine is needed to print parts, using newly-developed polyimide filaments.
- Developed new FDM protocol and software parameters at RP+M, a small 3D printing company in Avon Lake, OH with an open source FDM machine, to print specimens using high temperature polyimide with 80 °C higher capability than the state-of-art FDM resin Ultem® 9085.

Acknowledgements

References

1. US Patents #7,015,304 and RE43, 880 E, "Solvent Free Low-melt Viscosity Imide Oligomers and Thermosetting Polyimide Composites".
2. K.C. Chuang, D.M. Revilock, J.M. Pereira, J.M. Criss, Jr., E.A. Mintz: "High Temperature RTM370 Polyimide Composites Fabricated by RTM: Characterization and Impact Testing," SAMPE Journal, 40(5), 48–57 (2013).
3. TG-GC-MS Measurements on Four Polymer Samples, Report Number 620000510, submitted by: Pamela J. Shapiro, Thermal Applications Scientist of PolyOne, July 2, 2013.