# ADDITIVE MANUFACTURING OF DISSOLVABLE MANDRELS



Ahmed Arabi Hassen Vidya Kishore James Brackett Tyler Smith Kazi Md Masum Billah Subhabrata Saha Vlastimil Kunc Jeff Gerbec Brian Yarcich

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# Manufacturing Science Division

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Authors
Vidya Kishore
James Brackett
Tyler Smith
Kazi Md Masum Billah
Subhabrata Saha
Vlastimil Kunc
Ahmed Arabi Hassen

Jeff Gerbec† Brian Yarcich†

† Mitsubishi Chemical America, Inc

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#### **ABSTRACT**

ORNL collaborated with Mitsubishi Chemical America, Inc (MCA) to investigate different grades of vinyl alcohol co-polymers as a potential feedstock material for large-scale material extrusion additive manufacturing (AM). Dissolvable polymers can find potential applications in AM tooling for complex, hollow, and trapped composite structures without the need for specialized molds and tools. This CRADA work involved analysis of several developmental grades of vinyl alcohol co-polymers for thermal and rheological properties, followed by print trials on the Big Area Additive Manufacturing (BAAM) system using these materials. Finally, printed part properties, including mechanical and thermal performance, as well as dissolvability were evaluated. The properties and performance evaluated in this Phase I of the project have provided guidelines to further develop these vinyl alcohol co-polymers (six new formulations) at Phase II to enable large-scale printing at high deposition rates and obtain parts that satisfy high temperature molds and dies requirements.

#### 1. ADDITIVE MANUFACTURING OF DISSOLVABLE MANDRELS

Mitsubishi Chemical Group Corporation (MCGC) is the 9th largest chemical company in the world with 42,000 employees from 378 affiliated companies in 32 different countries. MCA. is a subsidiary of MCGC, leading one of the 5 regional divisions of Mitsubishi Chemical Group Corporation, providing products and services to customers in North and South America, and the division employs more than 2,600 people in the United States with consolidated sales of \$2.2B USD.

In this technical collaboration work, three different grades of dissolvable vinyl alcohol co-polymers were evaluated for their printability on the large-scale extrusion additive manufacturing (AM) system, followed by the evaluation of properties of printed parts, hereinafter referred to as Sample 1, Sample 2 and Sample 3. Results showed the possibility of successful extrusion of all three developmental sample grades on the Big Area Additive Manufacturing (BAAM) system. Evaluation of mechanical performance, thermal properties, and dissolvability helped identify the pros and cons of each of these grades, and outline guidelines for the development of new dissolvable polymers with properties tailored for large-scale additive manufacturing.

#### 1.1 BACKGROUND

The manufacturing of hollow composite parts usually requires a core, mandrel, or a bladder. Fabrication of such composite parts can be divided into two steps, firstly, the manufacturing of cores, mandrels, or bladders, and secondly, the process of laying the composite material and fabricating the composite hollow structure. While fabricating cores or mandrels, a mold with a specialized design is required. Once the cores or mandrels are ready, composite plies are laid on top of these structures and then placed in a mold under vacuum, followed by curing at either room temperature or at elevated temperatures in an oven. As observed here, two molds, one for the core or mandrel, and the other for composite curing, are required in this process. This leads to an increase in labor time, cost, and reduces design flexibility. In the US, the number of molds and dies establishments has decreased in the last decade alone by 36%, and employment has decreased by 45%, nearly twice the amount of other manufacturing institutions [1].

Additive manufacturing of dissolvable polymers has been of significant interest to both, AM, as well as composites community, for support structures, and molds and dies applications. The Big Area Additive Manufacturing (BAAM) system used for this project, located at the Manufacturing Demonstration Facility (MDF) at ORNL, is a dual-material single screw extrusion AM system with a build volume of 1.5 m  $\times$  3.6 m  $\times$  2.4 m (5 ft  $\times$  12 ft  $\times$  8 ft) and a deposition rate up to 45 kg/hr (100 lb/hr) [2]. This AM platform has been developed to be able to process a variety of pelletized feedstock materials such as thermoplastics (low temperature and high performance), short fiber

reinforced composites, polymer and composite blends, thermoplastics foams, bio-derived materials, etc.[3, 4] [5-10].

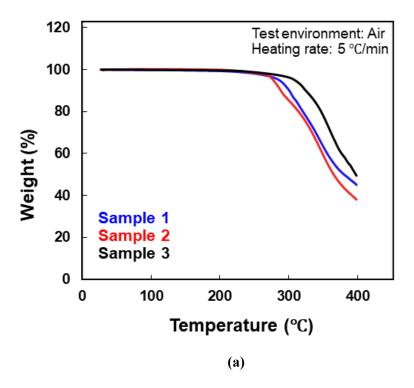
MCA is developing vinyl alcohol co-polymers, that are extrudable, moldable, water soluble, and degradable. This polymer class has found applications in packaging, oil and gas, and Additive Manufacturing. Compared to other vinyl alcohol polymers, the development grades studied here have a considerably lower melting point, thereby providing a wide processing window while exhibiting tap water solubility [11]. Other alternative products for soluble mandrels typically use epoxy resins, which require caustic solutions for dissolution, thereby making the process potentially harmful to people and the environment.

The digital nature of the AM process makes it possible to fabricate complex geometries when compared to other manufacturing processes. High design freedom leads to cost reductions and performance improvements. In this work, three different development grades, Sample 1, Sample 2 and Sample 3, were chosen. Firstly, the pellets were tested to determine their glass transition and melting temperatures to identify a suitable processing temperature range. Following this, melt rheological characterization was performed to understand the effect of temperature, shear rates or frequencies, and processing environment on the viscoelastic properties of the melt. Such tests help identify the processing parameters that could be altered while printing to achieve viscosities suitable for processing at the desired throughput, as well as with the identification of any potential material degradation or reactions that may take place during the printing process. After testing the feed pellets, print trials were conducted on the BAAM system. Infrared (IR) cameras were used for in-situ monitoring of the temperature profile of the parts being printed. Finally, mechanical properties and dissolvability of the printed parts were evaluated.

#### 1.2 TECHNICAL RESULTS

#### 1.2.1 Thermal analysis of feedstock pellets

Thermal characterization involved Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC) analysis of the three polymers to identify the upper and lower processing temperature limits, respectively. TGA testing was performed on TA Instruments Q50 TGA system by heating 1-2 mg of pellets from 25 °C to 400 °C at 5 °C/min in air. Figure 1a shows the TGA thermograms of the three polymers. Results indicated all three grades to have less than 2% weight loss at temperatures at least up to 250 °C. All successive processing was conducted at a temperature below this. To determine the glass transition temperatures (Tg) and melting temperature (Tm), DSC analysis was conducted on TA Instruments DSC Q2000 by heating 5-10 mg of pellets from 25 °C to 250 °C in nitrogen environment at 10 °C/min, holding at 250 °C for 2 min, followed by cooling the samples back to 25 °C at 10 °C/min. Figure 1b shows the thermograms for the first heating cycle and the cooling cycle. All three grades exhibited behavior of a semi-crystalline polymer, as observed by the presence of melting peaks (in the heating cycle) and crystallization peaks (cooling cycle). Among these three grades, Sample 1 showed a more amorphous behavior. Table 1 provides glass transition temperatures, peak melting temperatures, and enthalpy of fusion  $(\Delta H_f)$  obtained from these thermograms. For successive processing in extrusion-based AM process, temperatures at least about 10 °C higher than the peak melting temperatures were chosen.



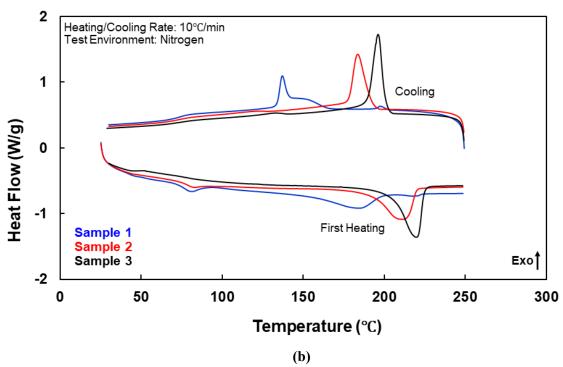


Figure 1. Thermal analysis of feedstock pellets; (a) TGA thermograms showing the degradation onset points, and (b) DSC thermograms showing melting and crystallization behavior.

Table 1. DSC analysis results for the three developmental polymers.

Developmental Polymer	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	$\Delta H_f (J/g)$
Sample 1	~ 77	183	30.37
Sample 2	~ 79	212	57.74
Sample 3	N/A	220	62.6

# 1.2.2 Rheological analysis

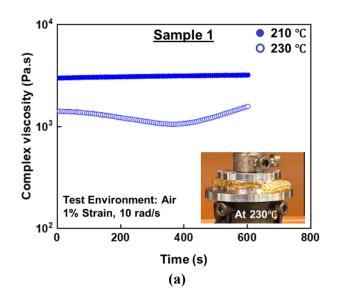
Rheological analysis was then conducted to determine the melt rheological properties of asobtained pellets to understand the effect of processing parameters such as temperature and shear rates on the viscoelastic properties of these materials. Such data obtained from thermal and rheological analysis help with the understanding of the printability of new materials on large-scale platforms like the BAAM, wherein trial and error test can be time consuming, add to the material and operating costs, as well as risk potential equipment downtime [7].

Melt rheological analysis (small angle oscillatory shear or SAOS tests) was conducted on TA Instruments DHR-2 (Discovery Hybrid Rheometer) system fitted with 25 mm parallel plates fixture. Samples (pellets) were melted directly on the plates, holding them in place using melt rings. Initially, time sweep tests were conducted for 10 min in air, starting with Sample 1 at 210 °C and 230 °C, using an oscillatory frequency of 1 rad/s and a strain of 1% (within the linear viscoelastic regime). These tests help with determining the thermal stability of materials with time, observed as changes to viscoelastic properties such as complex viscosity (n\*). As the temperature increased from 210 °C to 230 °C, viscosity reduced, as expected for several low temperature thermoplastics (Figure 2a), At 210 °C, viscosity was stable almost during the entire test duration. However, at 230 °C, viscosity showed a slightly different trend, where it dropped and then increased during the test duration. Upon observing the plates after the test, severe bubbling effect was observed (Image in Figure 2a), which could have led to the changes in viscosity observed. Note that this data at 230 °C is not a true measure since the material was not stable during the test and is shown here only to discuss the effects observed. Hence, for subsequent testing, higher temperatures were avoided, and the tests were conducted in a nitrogen environment to minimize degradation. The maximum test temperatures were chosen to be 10 °C or above the peak melting temperatures for all the three grades and did not exceed 210 °C, 225 °C, and 230 °C, for Sample 1, Sample 2, and Sample 3, respectively. This maximum processing temperature limit was based on the bubbling effect observed, as well as processing recommendations from MCA.

Following this, frequency sweep tests were conducted using 1% strain in a nitrogen environment from 100 rad/s to 0.1 rad/s at different temperatures and the variation in complex viscosity with frequency is as shown in Figure 2b. As observed, Sample 1, having the lowest maximum processing temperature among these three polymers, showed the highest complex viscosity. Samples 2 and 3 had  $\sim 68\%$  and  $\sim 80\%$  lower viscosities respectively (measured at 100 rad/s) than Sample 1 at the candidate processing temperatures. Among the three grades, Sample 1 exhibited a higher degree of shear thinning at frequencies greater than 10 rad/s.

Initial thermal and rheological analysis indicate these materials to have a narrow processing temperature window, as well as less significant variations in viscoelastic properties as a function of frequency (or shear rates), especially in the shear rate region of interest to BAAM ( $\sim$  10 to 100 s<sup>-1</sup>) [7]. Although Sample 1 exhibits greater shear thinning than the other two grades, its viscosity is much

higher at the suitable processing temperature. From extrusion AM standpoint, modifying the processing temperatures or shear rates (typically by varying screw speed) are the primary ways to modify the flow properties of materials by the operator during printing. Since both these modifications for extruding and depositing beads (or layers) on the BAAM are limited for all as-received developmental polymers, this could limit the range of deposition rates attainable on the current BAAM configuration.



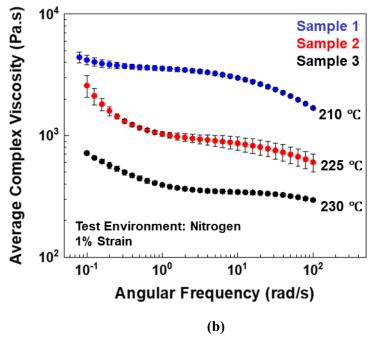


Figure 2. Variation of complex viscosity with (a) Time for Sample 1, and (b) Frequency for all the three grades at the candidate test temperature.

#### 1.2.3 Print trials on the BAAM system

Following the feed pellets analysis, print trials were conducted on the BAAM system with all the three developmental polymers. The temperatures set in the different zones of the extruder are shown in Table 2. The nozzle tip temperature was at least 10 °C higher than the peak melting temperature for all the three materials and as discussed in the rheological analysis, the maximum set temperature did not exceed 210 °C, 225 °C, and 230 °C, for Sample 1, Sample 2, and Sample 3. With these temperature settings, two beads wide hexagons with each side measuring 250 mm (10 in) and a height of  $\sim$  380 mm ( $\sim$  15 in) were successfully printed on the BAAM platform using a nozzle with a diameter of 7.62 mm (0.3 in) as shown in Figure 3. The layer times for these prints varied between 1.5 min to 2.5 min, depending up on the maximum achievable throughput for each polymer.

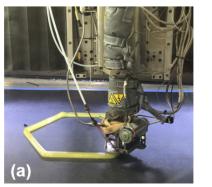
Although the three polymers were printable, producing thin-walled parts with smooth beads, the deposition rates were still low. The maximum screw speed that could be set for continuous extrusion was only 30-40 RPM (at  $\sim$  100-120% torque) for Sample 1 ,60-80 RPM (at  $\sim$  85% torque) for Sample 2 and Sample 3. These torque percentages indicate torque on the motor, and as this value gets higher, the more difficult it gets to deposit the material at higher rates (or screw speeds). Such high torques observed for all the three grades indicate their viscosities to be relatively high when compared to other low temperature polymers and composites processed on the BAAM. For example, the complex viscosity of unreinforced ABS that can be processed on BAAM at screw speeds as high as 400 RPM (60-80% torque), evaluated from an SAOS test (at 100 rad/s) is in the range of 400-700 Pa.s (depending upon the temperature), and that of 20 wt.% carbon fiber (CF)/ABS processable at 400 RPM (80-100%) torque) lies between 1000-2500 Pa.s [6]. As observed from rheological analysis, the viscosities of these dissolvable polymers are high (approximately over 1000 Pa.s at 100 rad/s), in addition to having low shear thinning. Typically, temperature and shear rates are the two parameters that can be easily varied while processing to obtain optimal printing conditions. In this case, firstly, the possibility of increasing the processing temperature was limited due to the formation of bubbles at higher temperatures. Next, since the materials were not highly shear thinning, increasing the screw speed (or shear rate) did not have a very significant effect either. Although the maximum torque observed for Sample 2 and Sample 3 with the settings used here was about 85% and there might have been a small room for increasing the deposition rate, tests trials done at higher screw speeds (torque reaching ~ 100%) produced beads with several small bubbles. Hence hexagons were processed at lower speeds to avoid this effect. Over torqueing also can be overcome by using a bigger extruder and a more powerful motor. The rheological properties and processing conditions on the BAAM for some of the other materials such as unreinforced acrylonitrile butadiene styrene (ABS), short CF reinforced ABS, CF reinforced polyphenylsulfone (PPSU), that have been successfully used can be found in [6].

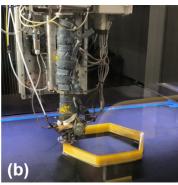
Table 2. Extruder temperature settings on the BAAM for printing the three developmental polymers.

	Extruder Temperature Settings on BAAM (°C)		
	Sample 1	Sample 2	Sample 3
Barrel Zone 1	182	210	210
Barrel Zone 2	188	210	215
Barrel Zone 3	196	215	220
Barrel Zone 4	204	220	225
Nozzle Tip	210	225	230

One of the advantages of large-scale printing with these developmental polymers would be their low thermal diffusivity. As observed from the in-situ IR imaging data shown in Figure 4 for Sample 1, the

surface temperature of the printed beads (or layers) remained above the materials' glass transition temperature ( $T_g$ ) of  $\sim 77$  °C for over 50 min. This behavior is helpful for obtaining good bonding between the printed layers and reducing the mechanical anisotropy (mechanical properties in the transverse direction being lower than the properties in the in-plane direction), which is often intrinsic to additively manufactured components using the material extrusion process. Therefore, this indicates the possibility of obtaining parts with almost isotropic properties, as well as using these developmental polymers for very large prints of thin-walled structures with long layer times, without compromising too much on the interlayer bond strength.





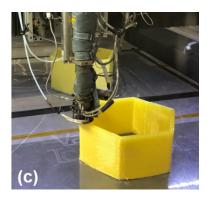


Figure 3. Test parts being printed on the BAAM using; (a) Sample 1, (b) Sample 2, and (c) Sample 3.

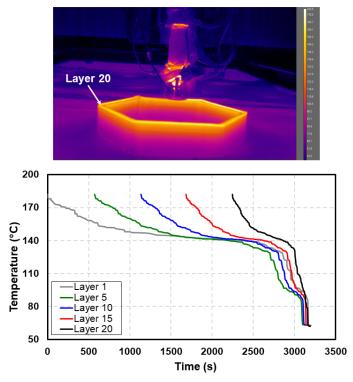


Figure 4. In-situ IR imaging during the print for Sample 1 print trial showing the ability of the material to retain heat that enable printing with long layer times.

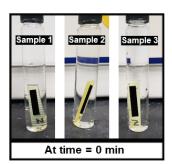
#### 1.2.4 Properties of printed parts

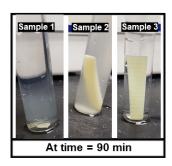
#### **Dissolvability**

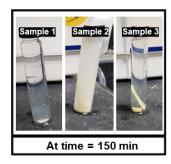
Dissolvability testing was conducted on samples (60 mm X 12 mm X 3 mm) machined from the printed hexagons. The samples were placed in vials with water and subjected to sonication at 60 °C in a water-filled Fisher CPX3800 Ultrasonic Bath. The samples were checked for disintegration every 30 min. As observed in Figure 5, Sample 1 dissolved completely after approximately 150 min, leaving behind a clear solution. On the other hand, Sample 2 disintegrated completely after approximately 300 min, leaving behind a yellowish-white cloudy solution and some paste-like residue at the bottom. Sample 3 had only disintegrated into smaller pieces in 300 min.

# **Tensile testing**

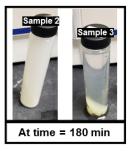
Tensile testing was conducted on dog-bone samples machined from the printed hexagons along the x-direction or the print direction, with dimensions as per ASTM D638 (Type I) and sample thickness of 3 mm. The testing speed used was 1.5 mm/min. 5-10 samples were tested for each grade and the tensile modulus and ultimate tensile strength (UTS) data is shown in Figure 6. The mean values of the modulus indicated all the three grades to have a similar performance. On the other hand, the ultimate tensile strength of Sample 1 was more than double that of the other two grades. Modulus is a crucial material property for molds and dies application. It's worth noting that the modulus of these polymers (without any fillers) is higher than neat ABS when printed on BAAM (~2.5GPa) and is just about ~26% less when compared to CF/ABS that is printed on the BAAM system.



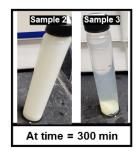




Sample 1 completely dissolved here. It was revealed by shaking the vial



Increased cloudiness in Sample 2.



Sample 2 disintegrated but the solution was cloudy, along with pastelike residue at the bottom.

Figure 5. Dissolvability testing for different grades of developmental polymers.

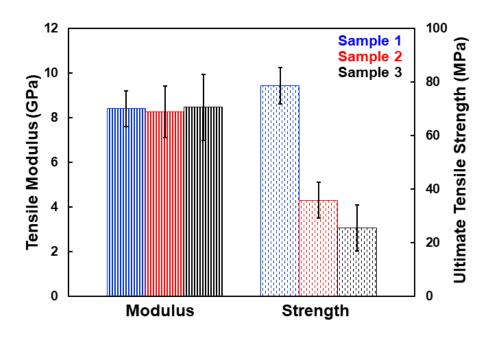


Figure 6. Tensile modulus and strength of the three polymers (along the x-direction or print direction).

# **Coefficient of Thermal Expansion (CTE)**

The coefficient of linear thermal expansion (CTE) is an important property, especially for high temperature tooling applications. Here, a thermomechanical analyzer (TMA) was used to measure the CTE of all the three grades. Rectangular samples measuring  $\sim 8$  mm x 8 mm x 8 mm were machined from the printed hexagons along the x-direction. The test procedure involved heating the sample from room temperature to 70 °C (close to  $T_g$ ) first at a rate of 5 °C /min, followed by cooling it back to room temperature and equilibrating. This helps eliminate any residual stress existing from prior processing steps. Then the sample length was measured again, followed by heating up to 180 °C at the rate of 5 °C/min. At least 3 samples were tested for each grade. The CTE data shown in Table 3 was obtained for analysis in the temperature range below the  $T_g$  of the three materials. Although CTE measurements were conducted at temperatures above  $T_g$ , the CTE data and the trends in the variation of dimension with temperature were inconsistent and inconclusive for some of these grades and hence have not been reported here. Results below  $T_g$  indicated the Sample 3 grade to have the highest CTE among the three polymers tested.

Table 3. CTE analysis of printed samples along the x-direction.

Developmental Polymer	Temperature Range	X-direction CTE (μm/m.°C)
Sample 1	30°C - 75°C	$55.21 \pm 3.15$
Sample 2	30°C - 80°C	$54.71 \pm 1.70$
Sample 3	30°C - 80°C	$62.34 \pm 2.93$

# 1.2.5 New feedstock optimization and development

Once the initial round of material evaluation trials was conducted, the optimal base polymer was

selected which maximized both the level of printability and the overall material properties. Although this base material worked well, it was determined that specific physical and thermal properties could be improved to maximize the stability and functionality of the end parts produced. A second round of trials with four new formulations were conducted in which modifications to the formulation were made to improve CTE and printability. This round resulted in improved CTE, but some layer adhesion and warping issues were also noted with these formulations. MCA determined that incorporating their KyronMax technology into their formulations was the best method for optimizing physical and thermal properties such as CTE, strength, and modulus that would be required for the end product. Modifications were also made to the formulation to allow for slower layer cooling and improved material flow which ensures proper layer adhesion and a reduction of warpage during printing.

A final round of six formulations (KyronMax Test samples 1-6), were created utilizing a synergy of KyronMax technology and the ecologically friendly base polymer, see Figure 7. These formulations were created to find the correct balance between physical properties and printability. A standardized printing protocol was utilized which was designed to be a worst-case scenario and maximized the warping and cracking of the material to ensure the formulation would achieve acceptable results with any design the end user would attempt.

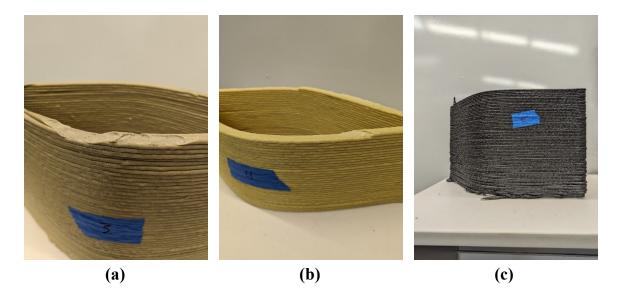


Figure 7. Example for sample printed using the new developed material formulations, (a) KyronMax Test Sample 3, (b) KyronMax Test Sample 4, and (c) KyronMax Test Sample 6.

Once initial printing trials were completed, a generic duct part was printed, see Figure 8, to optimize the printing speeds, temperatures as well as layer height and width. Multiple materials were tested during the same print. Initial printing parameters resulted in some minor warping/cracking but were eliminated when the printing parameters were optimized. it should be noticed that the bottom crack seen in the Figure 8, were the result of the part unintentionally rolling off a 2 ft. tall table during handling.



Figure 8. Test duct printing using multiple material formulations during the same print, KyronMax Test Sample 3,4, and 6. The bottom crack were the result of the part unintentionally rolling off a 2 ft. tall table during handling.

# Thermogravimetric analysis of new feedstock pellets

TGA is required to investigate the thermal stability of the new KyronMax based formulations during processing as well as to determine the service temperature range. TGA was conducted from 30 to 800 °C under Argon atmosphere at a heating rate of 10 °C/min. The initial degradation temperature, i.e. the temperature at which 5 wt.% weight loss occurred, ranging between 273 to 293 °C for all the compositions (Figure 9a). The derivative of TGA indicates two-step degradation. Tmax, i.e. the peak temperature, appeared at around 350 °C for all the composites as shown by the dotted line, Figure 9b. TGA results indicated that all compounds were thermally stable at 220 °C which was used to process the compounds.

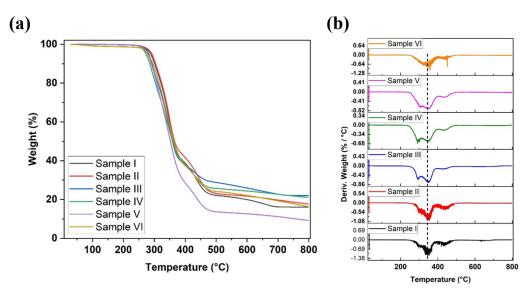


Figure 9. (a) TGA thermograms and (b) derivative of TGA of all six KyronMax Test Sample under Argon atmosphere.

# Rheological analysis

Rheological analysis was carried out to understand the flow behavior of the new different KyronMax based compositions which is crucial to optimize the processing condition. Oscillatory shear rheological analysis was conducted in a parallel plate rheometer at 220 °C at 1% strain (which is within the linear viscoelastic range). The angular frequency varied from 0.1 to 100 rad/s. All the compositions exhibited a reduction in complex viscosity with the increase in frequency implying the shear thinning behavior (Figure 10a). The highest complex viscosity was noted for the composition KyronMax VI and in this case maximum shear thinning behavior was also observed. Unlike complex viscosity, the storage modulus (G') increased with frequency as sufficient time is not available at higher frequencies to orient the polymer chain along the shearing direction replicating solid-like behavior. Like the complex viscosity results, sample KyronMax VI exhibited maximum storage modulus.

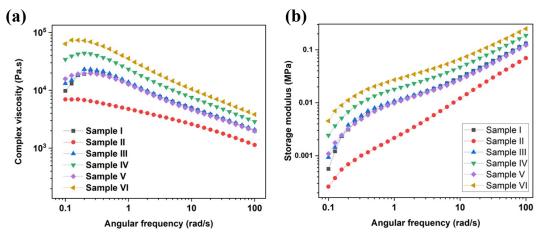


Figure 10. Rheological analysis for all six KyronMax Test Sample; (a) Complex viscosity versus angular frequency (representative of shear rate), and (b) Storage modulus (G') versus angular frequency plot of all the six compositions at 220 °C.

## **Dissolvability**

Dissolution testing of the six KyronMax formulation samples was also conducted to ensure modifications to the formulation did not impact the overall time required to remove the mold from the part, see Figure 11. Only minor variations in time or parameters were seen and the waste produced was still as environmentally friendly as the original formulation. Additional trials were conducted varying the solution temperature and movement rates to determine the optimal parameters for the quick elimination of the mold from the molded composite part. Varying these parameters from the parameters originally used resulted in a reduction of the mandrel material dissolution time by more than 50%.



Figure 11. Dissolution testing for all six KyronMax Test Sample conducted at MCA.

#### **Down selection**

Once all testing was completed, a side-by-side evaluation of all formulations was conducted. They were ranked based on their flow, printability, layer bonding, warpage, CTE, as well as other physical properties. Several performed well, Sample III offered the highest physical and thermal properties while still being printable. Basic printing parameters have been determined that will allow the printing of parts; however, additional printing trials will occur with this formulation to fine tune the process and allow for a more robust process that will allow the printing of a wide variety of geometries and sizes successfully.

### 1.3 IMPACTS

The impact of a successful BAAM-produced polymeric dissolvable structure is the ability to rapidly manufacture customized parts in a short period of time, and at a lower cost relative to current manufacturing techniques that use high-cost metal alloys. Conventional manufacturing process for hollow and trapped composite parts lead to increase in labor time, cost, and reduction in the design flexibility. MCA will be able to develop an AM dissolvable feedstock material that is optimized for the BAAM system. The nature of the AM process makes it possible to fabricate complex geometries when compared to other manufacturing processes. High design freedom leads to cost reductions and performance improvements. The new material accompanied with the BAAM technology will allow the fabrication of a dissolvable complex cores and mandrels that eliminate the need for tooling and associated warehousing/inventory of large volume tools (can be fabricated on demand), reduce processing time (compression of mold development time and manufacturing) and reduce the labor for manufacturing hollow composite component. The utilization of tap water soluble polymeric tooling enables additional cost savings compared with caustic material handling associated with incumbent process and further benefits worker safety. In summary, AM dissolvable mandrels will save on cost of manufacturing, energy required to extrude polymer shapes is significantly lower than forging a metal tool. Furthermore, such AM dissolvable mandrels reduce risk in tooling cost (to better accommodate design changes) and enable more flexibility in the design phase. Finally, they offer unique flexibility

in composite repair, along with the ability to print specific temporary shapes to layup the damaged section.

#### 1.4 CONCLUSIONS AND RECOMMENDATIONS

In this work, several grades of water soluble vinyl alcohol copolymers were evaluated for their printability on a large-scale print platform, the Big Area Additive Manufacturing (BAAM) system. The primary objective of Phase I of this work was to evaluate the printability of these materials, and if successfully printed, evaluate selected part properties relevant to tooling.

Using the analysis from thermal and rheological testing of the as-received pellets, processing conditions were set for printing with these materials on the BAAM. Initial print trials conducted in this work showed successful printing of structures using all the three grades of polymers. In-situ infrared analysis also indicated the potential of observing lesser anisotropy in these materials owing to the surface temperature of the deposited layers being well above the glass transition temperature for sufficiently long times. Dissolvability testing, tensile testing and coefficient of thermal expansion analysis were also conducted on samples harvested from the printed parts to obtain some initial understanding of printed part performance of these materials.

This phase of the work proved that the current materials can be printed on BAAM systems and can be used for mandrels and molds used in room temperature applications. Phase I of this work provided a good understanding of the gaps that need to be bridged. We have found that the viscosities of these polymers have been observed to be relatively high at the optimal processing temperatures, thereby limiting the deposition rates. This led to development and evaluation of better materials (six new formulations) at Phase II to enable large-scale printing at high deposition rates and obtain parts that satisfy high deposition rates with reduced motor over torquing and better printability.

The following recommendations have been made for practical application (focused on oven/autoclave tooling) of parts fabricated using these materials on large-scale material extrusion AM platforms.

#### Recommendations

- Adding fillers such as carbon fibers or platelets, would have three primary benefits: increasing shear thinning (which is highly preferred for BAAM processing), lowering CTE of the printed parts, and further improving the mechanical properties. In addition, fillers would also improve the heat deflection temperature of the part, enabling its use in autoclave processing.
- Measuring heat deflection temperatures (HDT), mechanical properties at elevated temperatures
  used in oven/autoclave tooling, creep testing, are some of the other recommended tests to evaluate
  properties relevant to autoclave tooling applications.

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#### 2. PARTNER BACKGROUND

Mitsubishi Chemical Group Corporation is the 9th largest chemical company in the world with 42,000 employees from 378 affiliated companies in 32 different countries. Mitsubishi Chemical America, Inc. is one of the 5 regional divisions of Mitsubishi Chemical Group Corporation providing products and services to customers in North and South America, employing 2,650 people in the United States with consolidated sales of \$2.2B USD.