

# Investigating Marine Environmental Degradation of Additive Manufacturing Materials for Renewable Energy Applications

## Preprint

Paul Murdy,<sup>1</sup> Joshua O'Dell,<sup>1</sup> David Barnes,<sup>1</sup> James R. McVey,<sup>2</sup> and Christopher Rumple<sup>2</sup>

1 National Renewable Energy Laboratory 2 Pacific Northwest National Laboratory

Presented at the Composites and Advanced Materials Expo (CAMX) Atlanta, Georgia October 30–November 2, 2023

NREL is a national laboratory of the U.S. Department of Energy Office of Energy Efficiency & Renewable Energy Operated by the Alliance for Sustainable Energy, LLC **Conference Paper** NREL/CP-5700-86315 August 2023

This report is available at no cost from the National Renewable Energy Laboratory (NREL) at www.nrel.gov/publications.

Contract No. DE-AC36-08GO28308



# Investigating Marine Environmental Degradation of Additive Manufacturing Materials for Renewable Energy Applications

## Preprint

Paul Murdy,<sup>1</sup> Joshua O'Dell,<sup>1</sup> David Barnes,<sup>1</sup> James R. McVey,<sup>2</sup> and Christopher Rumple<sup>2</sup>

1 National Renewable Energy Laboratory 2 Pacific Northwest National Laboratory

## **Suggested Citation**

Murdy, Paul, Joshua O'Dell, David Barnes, James R. McVey, and Christopher Rumple. 2023. *Investigating Marine Environmental Degradation of Additive Manufacturing Materials for Renewable Energy Applications: Preprint*. Golden, CO: National Renewable Energy Laboratory. NREL/CP-5700-86315. <u>https://www.nrel.gov/docs/fy23osti/86315.pdf</u>.

NREL is a national laboratory of the U.S. Department of Energy Office of Energy Efficiency & Renewable Energy Operated by the Alliance for Sustainable Energy, LLC

This report is available at no cost from the National Renewable Energy Laboratory (NREL) at www.nrel.gov/publications.

Contract No. DE-AC36-08GO28308

Conference Paper NREL/CP-5700-86315 August 2023

National Renewable Energy Laboratory 15013 Denver West Parkway Golden, CO 80401 303-275-3000 • www.nrel.gov

#### NOTICE

This work was authored in part by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Water Power Technologies Office. The views expressed herein do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

This report is available at no cost from the National Renewable Energy Laboratory (NREL) at <u>www.nrel.gov/publications</u>.

U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free via <u>www.OSTI.gov</u>.

Cover Photos by Dennis Schroeder: (clockwise, left to right) NREL 51934, NREL 45897, NREL 42160, NREL 45891, NREL 48097, NREL 46526.

NREL prints on paper that contains recycled content.

## INVESTIGATING MARINE ENVIRONMENTAL DEGRADATION OF ADDITIVE MANUFACTURING MATERIALS FOR RENEWABLE ENERGY APPLICATIONS

Paul Murdy<sup>1</sup>, Joshua O'Dell<sup>1</sup>, David Barnes<sup>1</sup>, James R. McVey<sup>2</sup>, Christopher Rumple<sup>2</sup>

<sup>1</sup> National Renewable Energy Laboratory, Golden, Colorado

<sup>2</sup> Pacific Northwest National Laboratory, Sequim, Washington

## ABSTRACT

Marine renewable energy is a relatively young industry where there is a great need for rapid prototyping in design-build-test campaigns to quickly mature groundbreaking technologies. Additive manufacturing has an important role to play in the industry; however, little information is available to marine energy developers to help inform them on which additive manufacturing materials are appropriate for highly loaded structures in harsh marine environments. This paper presents an initial study on the mechanical characterization of polymeric additive manufacturing materials and the degradation effects due to the marine environment. Ultem 9085, acrylonitrile styrene acrylate, and chopped carbon-filled nylon, as well as continuous carbon and glass fiberreinforced nylon were chosen for this study. Samples were manufactured to perform a variety of tension, shear, and compression mechanical characterization tests on the materials. Half of the samples were conditioned in Pacific Ocean water for approximately 6 months at the Pacific Northwest National Laboratory's Marine and Coastal Research Laboratory before being returned for mechanical characterization. The mechanical testing results showed that the Ultem 9085 and acrylonitrile styrene acrylate materials experienced little to no degradation in stiffness or strength after exposure to the marine environment. On the other hand, the nylon-based materials suffered significant stiffness and strength degradation (over 50% in some cases) after environmental conditioning. Ultimately, these data sets should serve as starting points to allow marine renewable energy developers to make informed additive manufacturing material choices for their prototype deployments.

Keywords: Marine renewable energy, additive manufacturing, environmental degradation, mechanical characterization, fused deposition modeling Corresponding author: Paul Murdy

## **1. INTRODUCTION**

The marine renewable energy (MRE) industry is rapidly growing, and technologies such as tidal energy converters and wave energy converters are maturing to the point of producing reliable, clean energy for coastal communities. However, the industry as a whole is relatively nascent, and many MRE developers are still in the prototyping phases of developing their technologies. Additionally, understanding how polymeric materials, such as additively manufactured (or "3D-printed") materials and fiber-reinforced polymers, react to long-term exposures to harsh marine environments is critical to the success of MRE deployments. Therefore, the U.S Department of

Energy's (DOE's) Water Power Technologies Office (WPTO) has been funding the Marine Energy Advanced Materials project, which is an ongoing multilaboratory project with the main goals of addressing barriers and uncertainties facing MRE developers in adopting advanced materials for structural applications [1]. Recently, the project held a marine energy materials and manufacturing workshop, which involved the DOE, national laboratories, universities, and marine energy developers. Experts highlighted the need to use additive manufacturing (AM) to accelerate prototype manufacturing and deployment of MRE devices [2].

There are many AM processes and materials available for commercial use, but there is very little public information available to guide MRE developers' AM process and material selection. Current AM applications for MRE have generally been limited to small-scale tank testing and manufacturing demonstrations [3, 4]. AM has been more widely researched for other comparable renewable energy technologies, such as wind energy at both small and large scales [5–7]. However, wind energy structures are not subjected to the same harsh environments as wave or current energy converters [8]. Fiber-reinforced thermoplastic and thermoset polymer composites are susceptible to strength and stiffness degradation when subjected to ocean water for extended periods of time, and these effects have been well researched [9-12]. However, little research has been performed to understand the effects of water absorption and harsh marine environments on polymeric AM materials. Understanding marine environmental degradation effects on these materials is critical for informing AM process and materials selection, as well as de-risking prototype MRE technology deployments. Additionally, water absorption and the resulting mass change could have profound effects on the dynamic response and performance of laboratory-and even commercialscale current and wave energy converter models and prototypes. AM is commonly utilized for demonstration projects at this scale [13].

Therefore, the goal of this research was to characterize the marine environmental effects by measuring water absorption and resulting mechanical property degradation for polymeric materials commonly used in additive manufacturing. A variety of polymeric and fiber-reinforced polymeric materials were selected for the investigation using previous case studies for axial- and cross-flow tidal turbines. This manuscript will outline the development of appropriate test methods for evaluating environmental degradation for AM materials. The dry and conditioned specimen data sets presented in this manuscript provide vital information for MRE developers who plan to use AM for components that are to be deployed in ocean environments and for scale models for laboratory-based wave basin and tank testing.

## 2. EXPERIMENTATION

#### 2.1 Material Selection and Specimen Manufacturing

To determine appropriate polymeric materials to test, this testing campaign leveraged an AM task that is part of WPTO's Powering the Blue Economy<sup>™</sup> portfolio—a collaborative effort between the National Renewable Energy Laboratory (NREL) and Pacific Northwest National Laboratory (PNNL), where small-scale current energy converter components are being designed and structurally evaluated [14]. The most important criteria for the AM process and material selection were cost, scalability, ease of adding reinforcement, strength, stiffness, corrosion/environmental resistance, and availability. Fused deposition modeling (FDM) processes were generally favored due to their scalability and material availability [15]. Table 1 shows the materials chosen for this study and their defining characteristics that led to the selection.

Material	AM Process	Defining Characteristic
Acrylonitrile Styrene Acrylate (ASA)	FDM	Low cost, environmental
		resistance
Ultem 9085 <sup>*</sup>	FDM	High environmental
		resistance
$Onyx^{\dagger}$	FDM	Moderate stiffness and
		strength
Carbon fiber-reinforced Onyx <sup>†</sup>	Continuous fiber	High stiffness and strength
	FDM	
Glass fiber-reinforced Onyx <sup>†</sup>	Continuous fiber	Lower cost, high stiffness
	FDM	and strength

Table 1. Materials and their defining characteristics for selection in this study.

\*Polyetherimide blend from Stratasys

†Chopped carbon fiber-reinforced nylon from Markforged

Several standard test geometries were chosen for mechanical characterization (more details on the geometries are provided in Section 2.2). Ideally, specimens were to be cut from larger panels with the goal of producing homogeneous specimens with continuous tool paths and filament lines. The ASA and Ultem 9085 were CNC cut from 3 mm thick panels that were printed on a Stratasys Fortus 450MC machine. The neat Onyx and carbon and glass fiber-reinforced Onyx (Onyx/CF and Onyx/GF) specimens were printed on a Markforged Mark 2 printer (see Figure 1). Unfortunately, the panels that were printed with this material could not be machined or waterjet cut without introducing delaminations. Therefore, the specimens were printed individually, so their material properties determined in this study should only be used for comparative purposes rather than as absolute data. The continuous fiber-reinforced specimens were printed with [0/90]<sub>nS</sub> layups and a continuous fiber volume fraction of approximately 10%. Purely unidirectional layups and/or high continuous fiber volume fractions would have led to excessive warping of the specimens during printing and removal from the build plate. Figure 2 shows some of the specimens that were printed prior to environmental conditioning and mechanical characterization.



Figure 1. The Markforged Mark 2 printer printing a renewable energy component prototype (photo by Paul Murdy, NREL).



Figure 2. A photo of some of the test specimens that were prepared for environmental conditioning (photo by Paul Murdy, NREL).

#### 2.2 Degradation and Mechanical Characterization

To compare as-manufactured to environmentally degraded mechanical properties, half of the specimens were subjected to ocean water conditioning. Specimens were sent to PNNL to be conditioned in their ocean water conditioning tanks at the Marine and Coastal Research Laboratory (MCRL) in Sequim, Washington, (see Figure 3), where untreated seawater from Sequim Bay is regularly circulated, and marine organisms are able to grow and interact with test specimens for a variety of different biofouling, corrosion, and degradation type studies. The temperatures in the tanks typically average around 12°C. Water temperatures were not elevated in this study, which is common practice to accelerate the degradation of polymer composites [12]. Since this study was aimed at short-term and laboratory-scale deployments, the minimal thickness of the specimens was assumed to be sufficient to make long-term comparisons for larger components. The specimens were conditioned in the tanks for a total of 155 days. Masses of the specimens were measured before and after the conditioning periods to a precision of  $\pm 0.0001$  g as a means of quantifying water absorbed by the specimens, as well as biofouling that may have accumulated within the porous materials. Samples were wiped clean of any surface biofouling and dried of any surface water before weighing final mass measurements were taken.



Figure 3. The specimens suspended in PNNL's seawater water conditioning tanks (photo by Christopher Rumple, PNNL).

Several American Society of Testing and Materials (ASTM) standard test methods were used to characterize a variety of mechanical properties for the chosen materials. The ASA, Ultem 9085, and neat Onyx materials were tested in tension (ASTM D638), compression (ASTM D6641), and shear (ASTM D7078). It should be noted that fiber-reinforced polymer test methods were used for determining compression and shear properties of the materials, due to a lack of consensus on acceptable standard test methods to be used for materials manufacturing using FDM-type AM processes. The continuous fiber-reinforced specimens were only tested in tension using the ASTM D3039 standard test method. Garolite end tabs approximately 2 mm thick were bonded prior to tensile testing to minimize stress concentrations at the gripping surfaces. Table 2 provides a summary of the overall specimen dimensions for each test type. Figure 4 shows photos of each specimen type being tested in NREL's 100 kN servo-hydraulic load frame.

Test Method	Geometry	Length (mm)	Outer Width (mm)	Gauge Width (mm)	Thickness (mm)
D638	Type I dog bone	150	19	13	3
D6641	Rectangular	140	13	13	3
D7078	V-notched	76	56	32	3
D3039	Rectangular	200	25	25	2

Table 2. A summary of specimen geometries and dimensions for each ASTM test type conducted.



Figure 4. Specimens being tested in the various configurations: (a) ASTM D638 tension, (b) ASTM D6641 compression, (c) ASTM D7078 V-notched rail in-plane shear, and (d) ASTM D3039 tension (photos by Joshua O'Dell, NREL).

#### 2.2.1 Instrumentation

For tensile testing, the specimens were instrumented with an extensioneter with a 12.7 mm gauge length (see Figure 4. (a) and (d)) to measure strain and calculate tensile moduli and elongation-atbreak. The compression and shear specimens were instrumented with back-to-back resistive foil strain gauges to determine compressive and shear strains. Back-to-back uniaxial gauges were used for the compression specimens and measured strains from stacked  $\pm 45^{\circ}$  gauges ( $\epsilon_{-}(+45)$ ) and  $\epsilon_{-}(-45)$ ) were used to calculate shear strains ( $\gamma$ ) for the shear specimens where:

$$\gamma = |\varepsilon_{+45}| + |\varepsilon_{-45}| \tag{1}$$

The majority of the strain gauges were adhered to the specimens with Micro Measurements M-Bond 200 alkyl cyanoacrylate adhesive, following their recommended procedure. It was difficult to get good adhesion with the 3D-printed substrates, particularly the Ultem 9085. Instead, Micro Measurements M-Bond AE-10 two-part epoxy adhesive was used for the Ultem 9085 specimens, which has a considerably longer cure time: 6 hours compared to 5 minutes for the M-Bond 200. Nonetheless, all specimens that had been conditioned at PNNL were instrumented and tested in batches to minimize their time out of water prior to testing. Due to time and budget constraints, only three specimens of each material for the D6641 and D7078 tests were strain gauged.

## **3. RESULTS**

#### 3.1 Water Absorption and Biofouling

Mass measurements of the specimens returned from PNNL were taken when the specimens were completely dry of any surface water. Figure 5 shows a comparison of the percentage mass changes of the specimens arranged by materials and specimen geometries. The error bars represent standard deviation and indicate a lot of variation between data sets. This is typically expected when conditioning specimens in unfiltered ocean water, due to salt buildup and unpredictable biofouling on the specimen surfaces [1]. On average, it appears that the mass changes of the Ultem 9085 and ASA specimens were fairly comparable (on the order of 4.5%). The Onyx D638 and D6641 specimens appear to have taken up less water mass during the conditioning period at PNNL. It is unknown why the Onyx D7078 specimens' mass changed so much more than the other Onyx specimens. Generally, nylons are considered to be very hygroscopic compared to other polymers [16], so it is surprising that the mass changes of the other Onyx specimens are less on average than their Ultem 9085 and ASA counterparts.



Figure 5. A comparison of percentage mass changes of the specimens conditioned at PNNL arranged by materials and specimen geometries (error bars represent standard deviation).

The continuous fiber-reinforced Onyx specimens appear to have absorbed more water than the majority of the unreinforced Onyx specimens. This is counterintuitive because carbon and glass do not absorb water and account for approximately 15%–20% of the total specimen weight. It is possible that the continuous fiber reinforcements produced pathways for water to be drawn into the specimens more quickly by capillary actions.

Overall, the amount of water absorbed and possible internal biofouling by all the specimens was quite considerable. However, aside from the mass changes, visual changes were fairly minimal. Many of the specimens, especially the slender ones (D638, D3039, and D6641), were bowed. Throughout the conditioning period, bubbles formed on the surface of the ASA and Ultem 9085 specimens, which were removed on a weekly basis to prevent them from floating. The cause is unknown, but it could be an indication of chemical reactions. Total mass changes ranged from 3% to 8% over a relatively short conditioning period. From a laboratory-scale wave or flume tank

testing perspective, these mass changes are certainly sufficient to affect the static and dynamic response of reduced-scale current and wave energy converter test pieces. Additionally, water diffusivity rates in polymers increase exponentially with temperature [17]. Therefore, testing at higher ambient temperatures (up to 25°C) could have even more pronounced effects.

## 3.2 Modulus Results

Figure 6 and Figure 7 show dry and environmentally conditioned comparisons of tensile and shear moduli, respectively, for all the materials tested. Compressive moduli for the D6641 specimens were not calculated due to excessive specimen buckling during the tests. Further details on this are provided in Section 3.3. Of the D638 specimens, the Ultem 9085 had consistently higher moduli than the ASA and Onyx materials. It is unknown why the average tensile modulus of the conditioned Ultem 9085 specimens apparently increased after environmental conditioning, although it may be due to random material and testing variations. The average tensile modulus of the ASA material appears to be unchanged by the environmental conditioning period at PNNL. However, the average tensile modulus of the Onyx material did degrade significantly (~37%). The D3039 tensile moduli of the continuous fiber-reinforced Onyx specimens (Onyx/CF and Onyx/GF) also appear to have degraded measurably. The dry tensile moduli were close to what one would expect based on classical laminate plate theory for glass and carbon fiber [0/90] layups with volume fractions of ~10% [18]. They also exhibited a measurable amount of degradation, which was surprising when considering the large differences in moduli between the fiber reinforcements and the Onyx matrix. It is well known that carbon and glass fibers themselves do not degrade in marine environments; however, the fiber/matrix interface can. Therefore, this may be an indication of degraded adhesion between the Onyx material and the fiber reinforcements and ultimately their ability to transfer stresses between the continuous fibers.



Figure 6. A comparison of calculated average tensile moduli for the dry and conditioned ASTM D638 and D3039 tensile specimens tested (error bars are standard deviation).



Figure 7. A comparison of calculated average shear moduli for the dry and conditioned ASTM D7078 shear specimens tested (error bars are standard deviation).

The calculated shear moduli for the Ultem 9085, ASA, and Onyx specimens showed similar results (see Figure 7). The Ultem 9085 and ASA materials possessed comparable shear moduli under dry conditions, but again, the shear modulus of the conditioned Ultem 9085 materials appeared higher than that of the pristine, dry material. The statistical scatter of the dry ASA specimens was high due to a very limited number of replicant tests with bonded strain gauges.

Interestingly, the shear modulus of the dry Onyx material was considerably higher than its tensile modulus. This may be due to the filament orientation in the specimens. Typically, toolpaths cannot be easily controlled with the Stratasys and Markforged FDM printers, so the bulk of the filaments within the specimens are oriented at  $\pm 45^{\circ}$ , or the in-plane shear directions in this case. Additionally, the chopped carbon fiber within the Onyx filament may be well oriented in the filament direction. However, after environmental conditioning at PNNL, the shear modulus of the Onyx material degraded significantly (~65% on average). This may be a further indication of the loss of the nylon material's ability to transfer stresses between the fiber reinforcements, no matter how small.

Overall, these results imply that the stiffness responses of components 3D-printed from Ultem 9085 or ASA are unlikely to change after moderate exposure to marine environments. This would certainly be sufficient for short-term deployments or wave basin and flume tank testing campaigns. On the other hand, the stiffness of the Onyx (nylon-based) material degraded significantly, even though the conditioning period was relatively short. This type of degradation would certainly have pronounced effects on the dynamic response of components used for short-term deployments and tank testing and would subsequently affect the validation of computational models for predicting MRE device performance.

## 3.3 Strength Degradation and Failure Modes

Figure 8 shows a comparison of the tensile strength results for the ASTM D638 specimens, as well as comparisons of representative stress-strain curves for each dry material. Table 3 also shows a comparison of all dry and conditioned strength properties derived from the Ultem 9085, ASA, and

Onyx test data. Yield strengths and strains were calculated using the 0.2% offset method. The tensile yield and ultimate strength properties of the Ultem 9085 and ASA were relatively unchanged after the conditioning period. Again, the properties of the Ultem 9085 appear to have been enhanced by the environmental conditioning. Further investigation is necessary to properly verify this and rule out any possible sources of systematic error. Like the degradation in elastic moduli, the tensile strength of the Onyx materials was also reduced significantly (~50%) by the environmental conditioning at PNNL. Again, this demonstrates the unsuitability of the nylon-based material for aqueous environments. The Onyx material exhibited very large strains to failure and necked considerably under both dry and conditioned test cases. The Ultem 9085 and ASA both failed more abruptly, as shown in Figure 9(a).



Figure 8. Comparisons of dry and conditioned ultimate tensile strength data for the ASTM D638 specimens (left) and representative stress-strain curves of the dry ASTM D638 specimens tested (right).

ASTM Test Method	Material	Property	State	Average Result	Change (%)
D638	Ultem 9085	Yield strength	Dry	20.3 ± 3.4 MPa	
tension			Wet	25.8 ± 4.4 MPa	+27.0
		Yield strain	Dry	$13,900 \pm 2,300 \ \mu\epsilon$	
			Wet	$15,900 \pm 4,300 \ \mu\epsilon$	+14.5
		Ultimate strength	Dry	39.6 ± 0.6 MPa	
			Wet	44.9 ± 1.0 MPa	+13.3
		Ultimate strain	Dry	$53,700 \pm 8,300 \ \mu\epsilon$	
			Wet	$50,900 \pm 4,200 \ \mu\epsilon$	-5.2
	ASA	Yield strength	Dry	15.5 ± 4.8 MPa	
			Wet	17.3 ± 1.3 MPa	+11.6
		Yield strain	Dry	$11,400 \pm 2,900 \ \mu\epsilon$	
			Wet	$12,700 \pm 800 \ \mu\epsilon$	+11.5
		Ultimate strength	Dry	25.8 ± 0.5 MPa	
			Wet	24.8 ± 1.2 MPa	-3.9
		Ultimate strain	Dry	$43,900 \pm 5300 \ \mu\epsilon$	
			Wet	$46,400 \pm 1,400 \ \mu\epsilon$	+5.8
	Onyx	Yield strength	Dry	12.5 ± 1.7 MPa	
			Wet	5.8 ± 1.3 MPa	-53.2
		Yield strain	Dry	$18,800 \pm 2,800 \ \mu\epsilon$	
			Wet	$16,400 \pm 7,900$ με	-12.9
		Ultimate strength	Dry	$41.2 \pm 6.3$ MPa	
			Wet	$20.9 \pm 0.2$ MPa	-49.4
		Ultimate strain	Dry	$409,700 \pm 165,800 \ \mu\epsilon$	
			Wet	$469,000 \pm 41,000 \ \mu\epsilon$	+14.5
D3039	Onyx/CF	Ultimate strength	Dry	173.0 ± 7.8 MPa	
tension		Ultimate strain	Dry	$13,400 \pm 500 \ \mu\epsilon$	
	Onyx/GF	Ultimate strength	Dry	124.3 ± 7.6 MPa	
		Ultimate strain	Dry	36,000 ± 1,600 με	
D7078	Ultem 9085	Ultimate strength	Dry	34.4 ± 2.0 MPa	
shear			Wet	37.7 ± 2.3 MPa	+9.7
	ASA	Ultimate strength	Dry	19.2 ± 3.5 MPa	
			Wet	19.7 ± 0.8 MPa	+2.2
	Onyx	Ultimate strength	Dry	26.4 ± 1.4 MPa	
			Wet	13.7 ± 0.7 MPa	-48.2
D6641 <sup>†</sup>	Ultem 9085	Ultimate strength	Dry	74.3 ± 5.1 MPa	
compression			Wet	62.7 ± 5.4 MPa	-15.6
	ASA	Ultimate strength	Dry	53.9 ± 8.8 MPa	1
			Wet	41.1 ± 2.3 MPa	-23.0
	Onyx	Ultimate strength	Dry	41.6 ± 0.9 MPa	
			Wet	$14.3 \pm 0.4$ MPa	-65.7

Table 3. A comparison of all dry and conditioned strength properties for the Ultem 9085, ASA, and Onyx materials tested.

<sup>†</sup>Not true compressive strengths due to specimen buckling.

This report is available at no cost from the National Renewable Energy Laboratory at www.nrel.gov/publications.



Figure 9. Comparisons of failure modes for the various ASTM test methods: (a) D638, (b) D7078, (c) D6641, and (d) D3039 (photos by Paul Murdy, NREL).

The conditioned Onyx/CF and Onyx/GF D3039 specimens could not be tested to produce representative tensile failure modes. The through-thickness properties of the specimens had been degraded so much that they could not be clamped sufficiently without crushing them in the wedge grips before the tests were even started. Therefore, dry and conditioned strength comparisons could not be made, despite being able to acquire sufficient stress-strain data to compare tensile moduli between the batches of specimens.

As mentioned in Section 3.2, the ASTM D6641 compression specimens failed due to buckling rather than pure compression. The thickness of the specimens were insufficient to produce pure compression failures without buckling over the short gauge length. Therefore the results presented in Table 3 should not be taken as true compression strengths, but only as further comparison between the dry and conditioned materials. In this case, all three materials appear to exhibit some degree of degradation after their conditioning period in seawater. Again, the Onyx material was considerably worse off than the ASA and Ultem 9085 materials.

Finally, the ASTM D7078 shear tests showed similar changes in strengths. Overall, the Ultem 9085 exhibited the highest shear strength under dry conditions, followed by the Onyx. This is most

likely due to the same reasons as its higher shear modulus outlined in Section 3.2, where the alignment of filaments and chopped fibers appears to have enhanced this property. The shear strength of the Ultem 9085 and ASA were unchanged by the environmental conditioning and consistently failed by sudden shear cracking at the V-notches of the specimens. Again, the Onyx material degraded significantly, with a loss of over 60%. Rather than abrupt shear cracking, the specimens tended to buckle and slowly tear in the shear direction during failure (see Figure 9(b)).

Overall, these results indicate that the Ultem 9085 and ASA would be suitable materials for shortterm deployments of 3D-printed components in marine environments as well as for scaled wave basin and flume testing. Further investigation for longer conditioning periods or accelerated aging at elevated temperatures would be required to determine whether they are suitable for more prolonged exposure to marine environments. The nylon-based, chopped carbon fiber-filled Onyx material showed significant degradation by almost every stiffness and strength measure. This demonstrates that it is unsuitable for use in marine environments and should be used with caution for any such application.

## 4. CONCLUSIONS

This paper presented a baselining study investigating the effects of marine environments on commonly used polymeric AM materials for MRE applications. The main goals of this study were to get an initial understanding of how AM materials perform in marine environments and demonstrate the characterization and testing process for such materials. In this case, Ultem 9085, ASA, and Onyx (chopped carbon fiber-filled nylon), as well as continuous carbon and glass fiber-reinforced Onyx were chosen due to their marketed environmental resistance and attractive mechanical properties. The materials were submerged in raw seawater from Sequim Bay at PNNL-Sequim. Specimens were then mechanically characterized in various standard test configurations and the results compared to pristine, dry specimen data sets. Strength and modulus results indicated that the Ultem 9085 and ASA specimens were relatively unchanged by the environmental conditioning. In fact, the conditioned Ultem 9085 specimens apparently had increased strength and stiffness properties in some cases, although further testing is required to properly verify this.

On the other hand, the Onyx, Onyx/CF, and Onyx/GF specimens suffered significantly from their relatively short time exposed to the marine environment. In some instances, they lost over 50% of their elastic modulus and strength properties. In fact, the continuous fiber-reinforced specimens' through-thickness properties had degraded so much that they could not be clamped sufficiently to even quantify their conditioned tensile strengths to compare.

Overall, we can conclude that Ultem 9085 and ASA are good candidates for polymeric AM components to be used for short-term MRE deployments or laboratory-scale wave basin and tank testing. The Onyx material, or any nylon-based AM material should be used with caution, due to nylon's hygroscopic properties. While the Onyx material has attractive mechanical properties, those samples suffered significantly in the aqueous environment that they were subjected to.

This study only evaluated materials in a marine environment under ambient conditions for a relatively short period of time (~6 months). Additionally, these 6 months spanned the winter months where biological life is least active. Therefore, the results are only limited to this time period. Future work will focus on accelerating the water diffusion and environmental degradation

process with elevated temperature conditioning, so that resulting data sets can be extrapolated to understand degradation over much longer time periods. Additionally, this study was fairly limited in its AM process and AM material choices. There are many other AM processes and polymeric materials available to MRE developers that may also be good candidates for marine environments.

Finally, another aspect that has not been explored in this research is the porosity and sparse infill that is commonly applied to AM processes to minimize material usage and print times. In particular, wave basin or flume tank components may fill with water over time, leading to dramatic changes in mass and therefore dynamic response. It may be prudent to apply protective coatings to AM scale models and components to prevent such effects. Understanding the best choice of coatings for specific AM materials, how they degrade and delaminate in marine environments, and how they affect the degradation mechanisms of AM materials will also be important for future research.

Ultimately, this project aims to continue to build knowledge bases and understanding of marine environmental degradation effects on advanced materials to help MRE developers make informed material choices for their mission-critical components and structures.

## 5. ACKNOWLEDGEMENTS

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308, and by Pacific Northwest National Laboratory, operated by Battelle Memorial Institute for the U.S. DOE Office of Science under Contract No. DE-AC05-75RL01830. Funding provided by U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Water Power Technologies Office. The views expressed herein do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

## 6. REFERENCES

- 1. Murdy P, Hughes S, Miller D, Presuel-Moreno F, Bonheyo G, Hernandez-Sanchez B, et al. "Subcomponent Validation of Composite Joints for the Marine Energy Advanced Materials Project." Golden, CO, 2023. DOI: https://doi.org/10.2172/1909582
- 2. "Summary Report: October 5, 2021 Workshop on Materials & Manufacturing for Marine Energy Technologies." United States, 2022.
- 3. Rouway M, Tarfaoui M, Chakhchaoui N, Omari LEH, Fraija F, Cherkaoui O. "Additive Manufacturing and Composite Materials for Marine Energy: Case of Tidal Turbine." *3D Printing and Additive Manufacturing* (2021). DOI: https://doi.org/10.1089/3dp.2021.0194
- 4. Murdy P, Dolson J, Miller D, Hughes S, Beach R. "Leveraging the Advantages of Additive Manufacturing to Produce Advanced Hybrid Composite Structures for Marine Energy Systems." *Applied Sciences* 11 (2021). DOI: https://doi.org/10.3390/app11031336

- 5. Bassett K, Carriveau R, Ting DSK. "3D printed wind turbines part 1: Design considerations and rapid manufacture potential." *Sustainable Energy Technologies and Assessments* 11 (2015):186-193. DOI: https://doi.org/10.1016/j.seta.2015.01.002
- Post BK, Chesser PC, Roschli AC, Love LJ, Gaul KT. "Large-Scale Additive Manufacturing for Low Cost Small-Scale Wind Turbine Manufacturing." Oak Ridge, TN, 2018. DOI: https://doi.org/10.2172/1493993
- 7. Post BK, Richardson B, Lind R, Love LJ, Lloyd P, Kunc V, et al. "Big Area Additive Manufacturing Application in Wind Turbine Molds." Austin, TX, 2017.
- 8. Hernandez-Sanchez BA, Gunawan B, Nicholas J, Miller D, Bonheyo G, Murdy P, et al. "Developing Materials for Marine Renewable Energy Technologies." Albuquerque, NM, 2019.
- Alam P, Robert C, Ó Brádaigh CM. "Tidal turbine blade composites A review on the effects of hygrothermal aging on the properties of CFRP." *Composites Part B: Engineering* 149 (2018):248-259. DOI: https://doi.org/10.1016/j.compositesb.2018.05.003
- Nunemaker JD, Voth MM, Miller DA, Samborsky DD, Murdy P, Cairns DS. "Effects of moisture absorption on damage progression and strength of unidirectional and cross-ply fiberglass-epoxy laminates." *Wind Energy Science* 3 (2018):427-438. DOI: https://doi.org/10.5194/wes-3-427-2018
- 11. Davies P, Arhant M. "Fatigue Behaviour of Acrylic Matrix Composites: Influence of Seawater." *Applied Composite Materials* 26 (2019):507-518. DOI: https://doi.org/10.1007/s10443-018-9713-1
- 12. Miller DA, Samborsky DD, Stoffels MT, Voth MM, Nunemaker JD, Newhouse KJ, et al. "Summary of Marine and Hydrokinetic (MHK) Composites Testing at Montana State University." Albuquerque, NM, 2020. DOI: https://doi.org/10.2172/1668132
- Jiang B, Li X, Chen S, Xiong Q, Chen B-f, Parker RG, et al. "Performance analysis and tank test validation of a hybrid ocean wave-current energy converter with a single power takeoff." *Energy Conversion and Management* 224 (2020):113268. DOI: https://doi.org/10.1016/j.enconman.2020.113268
- 14. Gonzalez-Montijo M, Murdy P, Candon C, Beach R, Nichols C, Barden P. "Additive manufacturing for Powering the Blue Economy applications: A tidal turbine blade case study." *European Wave and Tidal Energy Conference*. Bilbao, Spain, 2023.
- 15. Post B, Richardson B, Lloyd P, Love L, Nolet S, Hannan J. "Additive Manufacturing of Wind Turbine Molds." Oak Ridge, TN, 2017. DOI: https://doi.org/10.2172/1376487
- Celestine A-DN, Agrawal V, Runnels B. "Experimental and numerical investigation into mechanical degradation of polymers." *Composites Part B: Engineering* 201 (2020):108369. DOI: https://doi.org/10.1016/j.compositesb.2020.108369
- 17. Grace LR, Altan MC. "Characterization of anisotropic moisture absorption in polymeric composites using hindered diffusion model." *Composites Part A: Applied Science and Manufacturing* 43 (2012):1187-96. DOI: https://doi.org/10.1016/j.compositesa.2012.03.016
- 18. Barbero EJ. Introduction to Composite Materials Design. Boca Raton, FL: CRC Press, 2017.

This report is available at no cost from the National Renewable Energy Laboratory at www.nrel.gov/publications.