Chapter 1
Effect of Coatings and Additives on the Water Absorption and Mechanical Characteristics of Additive Manufactured Nylon Polymers

James LeBlanc, Irine Chenwi, Julianna Martinez, Olivia Dube, Dillon Fontaine, Eric Warner, Tyler Chu, Arun Shukla, and Lewis Shattuck

Abstract The use of baseline material data taken in controlled laboratory conditions on dry, unaged specimens is largely insufficient for the design of critical structures to be deployed in deep-water, wetted applications. Recent studies have shown that Nylon based materials absorb a substantial amount of water when exposed to marine environments. This effort conducted an experimental investigation of the effectiveness of surface coatings and material additives on the reduction of water absorption into nylon based AM polymers and the corresponding effects on the mechanical properties of the materials. The study is divided into two unique parts: (1) effects of post print surface coatings on 3D printed specimens, and (2) effects of nanoclay additives on nylon base material. The study's findings highlight that the use of surface coatings and nanoclay additives can reduce the amount of salt water absorbed by the respective materials. However, the coatings and nanoclays also have a degrading effect on the mechanical properties of the materials themselves, even in the absence of salt water exposure. Therefore, significant consideration must be given to material selection when choosing surface coatings and material additives. Similarly, the use of nanoclay additives are shown to change the material behavior from highly ductile to highly brittle. These changes can potentially cause premature failures when utilized with AM polymers without detailed material characterization data obtained before and after salt water exposure.

Keywords Additive Manufacturing · Mechanical characterization · Water absorption · Material Additives · Surface Coatings

Introduction

Additive Manufacturing (AM) is one of the largest growing areas of novel manufacturing approaches, with applications ranging from home hobbyists up to full scale commercial production of parts. The technology lends itself to ready access to parts on demand, ease of manufacture for complex designs not otherwise possible, shorter design to manufacturing cycle times (rapid prototyping), lightweight designs, and cost savings. These manufacturing techniques provide the ability to achieve part geometries not possible with "subtractive" manufacturing methods (e.g. CNC milling), and eliminate the need for complex and expensive tooling/molds when small part quantities are needed, for example ad-hoc spare parts in an on-demand setting. Despite these advantages, there are also associated disadvantages with these technologies such as potential part variability based on print parameters, print post-processing, and increased part porosity.

The effects of moisture and water absorption on the performance of additively printed materials has become a recent topic of research interests. Research findings have shown moisture and water absorption can result in decreases in modulus,

James LeBlanc · Irine Chenwi · Julianna Martinez · Olivia Dube · Dillon Fontaine · Eric Warner · Lewis Shattuck
Naval Undersea Warfare Center (Division Newport), Newport, RI 02841
e-mail: james.m.leblanc.civ@us.navy.mil; irine.n.chenwi.civ@us.navy.mil; julianna.a.martinez3.civ@us.navy.mil; olivia.m.dube.civ@us.navy.mil; dillon.t.fontaine.civ@us.navy.mil; eric.a.warner8.civ@us.navy.mil; lewis.b.shattuck.civ@us.navy.mil

Tyler Chu · Arun Shukla
Dynamic Photo Mechanics Laboratory, Department of Mechanical, Industrial and Systems Engineering, University of Rhode Island, Kingston, RI 02881
e-mail: tylerchu@uri.edu; shuklaa@uri.edu

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ultimate tensile strength, decreased energy release rate (GIC), and stress intensity factor (KIC). These studies have investigated common AM polymers such as ABS, PLA, and PETG. In addition to the specific materials themselves, the effect of layer thickness and associated print parameters can affect water absorption levels and material swelling. Furthermore, the effectiveness of post print surface treatments and coatings to reduce water absorption for FDM printed materials have been the subject of recent publications. Recently, the effects of salt water exposure have been investigated and highlighted the base material composition is a key contributor to the level of material degradation due to saline fluid exposure.

Materials

There are several distinct materials utilized in the study, which are categorized into baseline filaments, filament additives, and post print coatings. The Markforged Onyx material is utilized to manufacture mechanical specimens that were subsequently coated with one of two surface treatments. The Nylon filament was used as a base material to which the nanoclay additive was added to through a secondary filament extrusion process. Markforged Onyx is a nylon-based material, which contains micro carbon fibers, with a nominal material density of 1.2 g/cm^3. The first post-print surface treatment applied to the Markforged Onyx specimens was an epoxy hardpot coating, Henkel Loctite Stycast 2651 Epoxy Encapsulant which was mixed with Henkel Loctite Catalyst 9. The second post-print surface treatment applied to the Markforged Onyx specimens was an epoxy based paint system, Sherwin Williams E2A933 Epoxy Primer and Sherwin Williams Genesis GC 3.5 Automotive Top Coat. Markforged Nylon is a pure nylon-based material with a nominal material density of 1.1 g/cm^3. The nanoclay powder that was used as an additive for the Markforged Nylon was Sigma-Aldrich Montmorillonite Clay (MMT) with surface modification, particle size of <= 20 microns, and a density of 200-500 kg/m^3. The nylon material was pelletized and subsequently combined with the nanoclay additives at weight percentages of 2% and 5%. Two extrusion cycles were carried out for each nylon composite to ensure that the nanoclay was sufficiently dispersed in the nylon.

Water Absorption and Mechanical Characterization

The water immersion of the epoxy hardpot and painted Markforged Onyx specimens was carried out in a novel test facility specifically designed for high-pressure water immersion experiments. The material specimens were placed in a 3.5% NaCl solution, pressurized to 5000 psi, and were left untouched for 60 days. The water immersion study for the nylon specimens with nanoclay additives was performed at ambient pressure and at room temperature. Both the neat nylon and nylon composites were immersed in a 3.5% NaCl solution for 30 days. The coated Markforged Onyx specimens were characterized for the following properties before and after the 60-day immersion: Tension, Compression and Flexure per ASTM standards. The Nylon with nanoclay additives underwent the following characterization: thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA), and Tension.

Results

This effort conducted an experimental investigation of the effectiveness of surface coatings and material additives on the reduction of water absorption into nylon based AM polymers and the corresponding effects on the mechanical properties of the materials. The study is divided into two unique parts: (1) effects of post print surface coatings on 3D printed specimens, and (2) effects of nanoclay additives on nylon base material. The study's findings highlight that the use of surface coatings and nanoclay additives can reduce the amount of salt water absorbed by the respective materials. The surface coatings that were applied to the AM printed specimens were found to be effective in reducing both the rate of water absorption and the overall mass change due to water absorption from 6% to 3%. The incorporation of nanoclay additive into the baseline nylon material was shown to reduce the amount of mass absorbed during salt water immersion from 1.7% to 1.6%. The thermogravimetric analysis was performed to quantify the thermal decomposition of the baseline nylon and nanoclay modified nylon. The baseline nylon experienced the onset of decomposition at a temperature of 416 °C and the nanoclay modified material showed the onset of decomposition at 406 °C and 397 °C for the 2% and 5% material respectively. DSC quantified the changes in the thermal properties of the nylon and modified nylon materials. The quantities of interest included glass transition temperature (Tg) and melting temperature (Tm). The glass transition temperature for the pure nylon, 2% nanoclay, and 5% nanoclay materials were 45°C, 44°C and 43 °C, respectively. The melting temperatures were found to be 200 °C for the pure nylon, 203 °C and 204 °C for the 2% and 5% nanoclay materials. Therefore, the inclusion of the nanoclays into the nylon lower the T_g and increase the T_m temperatures. The tension, compression, and flexure testing of the surface coated material indicate that both the coatings and salt water exposure affect the mechanical behavior of the Markforged Onyx material. When coated with both the epoxy hardpot and paint there is a reduction in modulus and strength as compared to the dry uncoated material. For each coating configuration there is a further drop in both stiffness and tensile strength after 60-day salt water exposure. The incorporation of the nanoclay additive into the pure nylon baseline material had two adverse effects on the tensile behavior of the material. The first is that the tensile strength of the nylon was reduced by the nanoclays, with the 2% nanoclay specimens having a lower strength than the 5% specimens. More significantly, the inclusion of the nanoclays changed the behavior of the nylon from a highly ductile material to one of high brittleness. The tensile strain at failure was reduced from above 100% for the nylon itself to 2% when nanoclay was incorporated. DMA results show that adding nanoclay increases the stresses and storage and loss moduli of the composite materials. The presence of the clay also reduced the overall loss in stiffness associated to water ingression. There was a remarkable increase in stiffness when the wet samples were tested at -2°C indicating that the water had changed to solid. The nanoclays led to an overall brittleness in the nylon composites for both dry and wet samples.

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