Applications of AFM in Additive Manufacturing

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Additive manufacturing (AM), also commonly known as 3D printing, is a manufacturing approach wherein parts are created layer-by-layer, typically generated from a computer-designed model.[1] The term AM refers to the addition of material to create parts whereas traditional machining methods involve removal of material. Though a range of materials can be used depending on the specific AM process, various polymers are most commonly used. Polymer-based AM processes have the advantages of producing lightweight parts with much less scrap and waste compared to conventional methods. However, AM processes introduce new challenges too. The layer-by-layer nature of these processes often leads to poor mechanical properties of the final printed part compared to more traditional methods of production like injection molding.[2] Though the details vary among techniques, most AM processes can suffer from weak bonding between layers, anisotropic structure, and internal voids that compromise part performance. Characterizing the micro- and nanostructure of AM materials is therefore a crucial capability required to scale up AM processes from producing prototype parts to manufacturing parts on an industrial scale. Atomic force microscopy (AFM) is a powerful tool for this work because it can not only visualize the structure of the materials at the nanometer and micrometer scale, but it can also measure the nanoscale mechanical properties (e.g. Young's modulus and loss tangent) at these same length scales. This application note will discuss how AFM can contribute to the development of AM processes with examples taken from recent published research articles.

Understanding how the microstructure of the material is affected by the AM process can give insights into why printed parts produced by AM sometimes fail. AFM is a technique that can characterize the surface topography of materials with nanoscale resolution. AFM utilizes an ultra-sharp tip to touch and "feel" across the surface of a material, mapping the topography line by line in a raster scan pattern. Unlike electron microscopy, AFM generates true quantitative 3D topography data, it works equally well on both conductive and insulating samples, and it does not require thin sections or staining. Compared to optical microscopy or profilometry, AFM is not limited by the optical diffraction limit, so modern AFMs like the Oxford Instruments Cypher and Jupiter AFMs can readily achieve nanometer-scale lateral resolution and sub-Angstrom vertical resolution. While early AFMs were slow and difficult to use, this new generation of Asylum Research AFMs can generate images in less than one minute and ease of use improvements have made the technique readily accessible to new users and lab technicians without highly specialized training.

The example shown in Figure 1 shows AFM topography images of acrylonitrile-butadiene-styrene (ABS) samples prepared by injection molding compared to fused deposition modeling (FDM) additive manufacturing.[2] The samples were prepared by microtoming the surface of a small piece to create a flat surface and expose the butadiene particles that sit below the polymer surface. The samples were imaged on an Asylum Research Cypher AFM to visualize these particles and determine how they are affected by the production processes. The butadiene particles in the injection molded sample (Figure 1a) appear almost circular while in the AM sample they are elongated and aligned (Figure 1b).

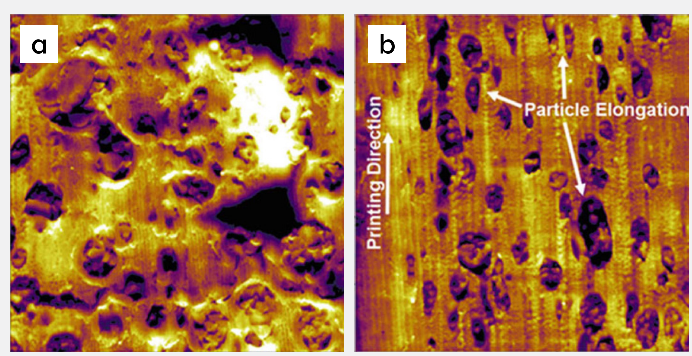


Figure 1: Topography images of ABS samples prepared by a) injection molding and b) Fused deposition modeling AM. Elongation and alignment of the butadiene particles are observed in the sample prepared by AM. Figure adapted from reference 2.

The FDM process, also referred to sometimes as fused filament fabrication (FFF), is a material extrusion ("MatEx") AM technology in which a thermoplastic polymer is extruded through a heated nozzle. The part is created by patterning the melted polymer layer by layer in the desired geometry. The elongation of butadiene particles observed in the FDM sample is likely due to the shear stress induced on the material during the printing process and may affect fracture toughness. In this study, carbon fibers were also added to the polymer to further strengthen the material, an approach that has been adopted from standard polymer production processes and used in other AM studies.[3-4]

As additive manufacturing processes are scaled up from prototyping to larger scale production, there is a need to reliably produce components with consistent, known mechanical properties. A key challenge in the industry is to accurately predict the mechanical properties of the parts produced by first characterizing the properties of the raw feedstock material, then understanding how the chosen AM process affects those properties in different deposition approaches and part geometries, and finally using that information to model and predict part performance in arbitrary geometries. Unfortunately, predicting final part properties produced by MatEx AM technologies (i.e. FDM or FFF) is made more challenging by phenomena including weak bonding between build layers, anisotropy created by the directionality of material extrusion, and the presence of unintentional voids in the parts.[5-6]

Toward that goal to predict part performance, polycarbonate was examined in a recent study as a model system for a MatEx process with full characterization of the bulk starting material and the final part.[7] The feedstock material was characterized with techniques including rheology, gel permeation chromatography, and dynamic mechanical analysis whilst the final product was characterized with X-ray computed tomography, scanning electron microscopy, instrumented nanoindentation, and AFM modulus mapping. For the AFM measurements, a technique known as amplitude modulation-frequency modulation (AM-FM) viscoelastic mapping was used to provide nanoscale maps of Young's modulus.[8]

The AM-FM technique provides fast nanoscale visualization of material properties at a resolution beyond that which can be achieved with instrumented nanoindentation measurements. In addition to Young's modulus (i.e. storage or elastic modulus), AM-FM can also characterize the viscoelastic response of the material by measuring its loss tangent, which is the ratio of the loss modulus and storage modulus. This capability is especially important and relevant to polymer materials because many polymer blends and composites contain both glassy components for higher strength and rubbery components to improve toughness and fracture resistance. The AM-FM technique is available exclusively on Asylum Research AFMs. In this study, the AM-FM technique was used as a complimentary technique to provide a comprehensive characterization of parts and structures produced by AM.

Examples of these AM-FM modulus maps are shown in Figure 2, where they have been overlaid on a 3D representation of topography. As in Figure 1, the sample was first microtomed to generate a flat, pristine surface for analysis. A distinct interface is observed in the modulus maps, indicating local variations in mechanical properties, which was not expected for the single component polycarbonate material. Variations were also observed in the instrumented indentation measurements, but those measurements are averaged over a much larger material volume because of the significantly larger indenter tip used. This highlights the utility of higher resolution modulus mapping with AFM, which can visualize modulus variations that might be attributed to local differences in polymer properties or the presence of additives or contaminates.

The previous example demonstrated how certain AM processes can lead to poor mechanical properties. This can be due to poor interfacial adhesion and interlayer bonding that can ultimately lead to crack propagation. There is therefore a need to be able to produce parts by AM processes that have tuned mechanical properties with a focus on improving the mechanical properties at interfaces. The addition of fillers is an approach that has been used for reinforcement of AM parts,[2-3] however there is growing interest in controlled photopolymerization methods.

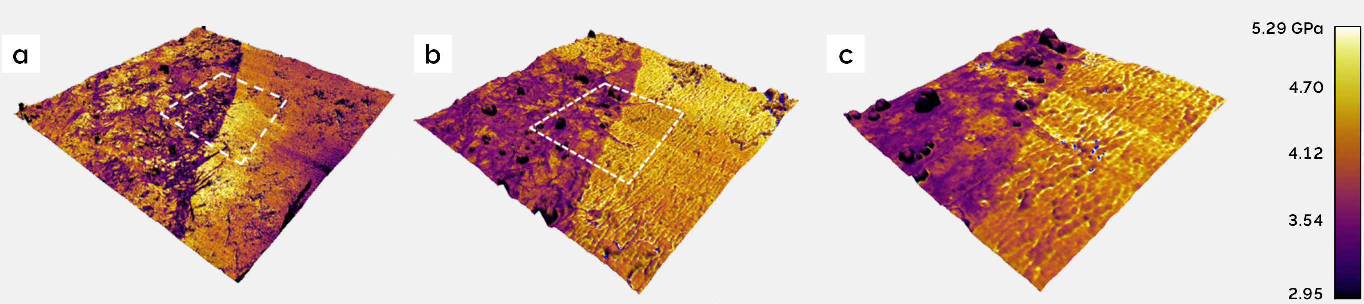


Figure 2: AM-FM Young's modulus maps overlaid on topography of a polycarbonate intralayer sample prepared by MatEx. A clear distinction in modulus is observed at a) 10 µm and then further zoomed in to b) 5 µm and c) 2 µm. Figure adapted from reference 7.

Resin materials known as two-stage reactive polymer networks (TSRPs) offer the ability to create structures with mechanical heterogeneity.[15] These materials can go through two stages of reactions that can give spatial control over the cross-linking density within the polymer material. The first stage sets the liquid polymer into a rubbery network whilst the second stage transforms the material into a higher modulus glassy polymer. These polymerization steps have been shown to be triggered by light of different wavelengths.[9] To understand how the mechanical properties can be tuned on a spatially resolved basis, films composed of TSRPs were produced with a patterned photomask applied. After exposure to light, the mask was removed, and AFM was used to characterize the mechanical properties.

A technique known as fast force mapping (FFM) was employed, which provides high resolution maps of topography whilst simultaneously acquiring maps of Young's modulus and adhesion.[10] AM-FM modulus mapping and FFM can provide similar types of information, except that FFM can only measure the elastic response while AM-FM characterizes the full viscoelastic response. However, on soft sticky samples like the partially polymerized rubbery component in this study, tapping mode techniques like AM-FM can fail because of very high tip-sample adhesion. In these cases, FFM works well because the AFM tip is fully retracted from the sample after each indentation. FFM measurements are also more readily comparable to instrumented nanoindentation measurements since they are based on similar indentation and contact mechanics theory and are measured at relatively low loading rates. The FFM option on Asylum Research Cypher and Jupiter AFMs offers advantages relative to other FFM-related techniques in the AFM market. Both the indenter force (cantilever deflection) and the indentation depth (Z axis sensor) are measured, unlike some implementations that use a calculated Z axis. Furthermore, the full force-distance data is collected and saved for every image pixel. This allows it to be reanalyzed later using more advanced contact mechanics models like JKR or Oliver Pharr models. This is not possible on implementations that calculate the modulus in real-time but then discard the force-distance data.

Figure 3 shows the modulus maps from FFM measurements of samples with different photomasks applied. These masks consisted of stripes of different widths, 5, 10 and 100 µm. Clear and distinct regions of Young's modulus can be observed with the unmasked region showing a considerably stiffer response. The two regions show a modulus of ~10 MPa for the masked area and ~ 1 GPa for the unmasked area, highlighting the ability of FFM to investigate materials with a wide range of properties. As well as mapping

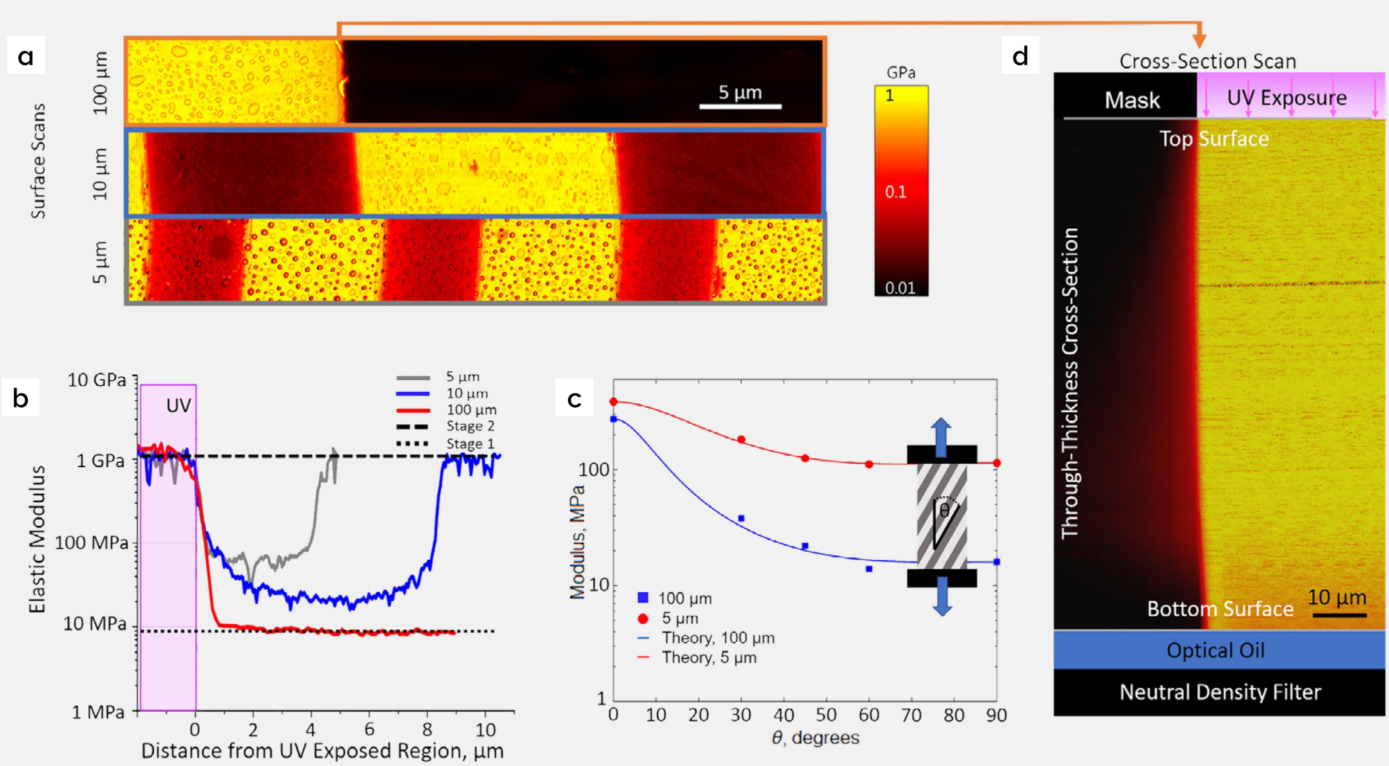


Figure 3: a) FFM Young's modulus maps of TSRPs with different sized photomasks applied. b) Line section profiles across interfaces of masked and unmasked areas. c) Modulus measurements at different loading angles from dynamic mechanical analysis (DMA), showing anisotropy d) FFM Young's modulus map of a cross section of a TSRP layer showing good uniformity. Figure adapted from reference 11.

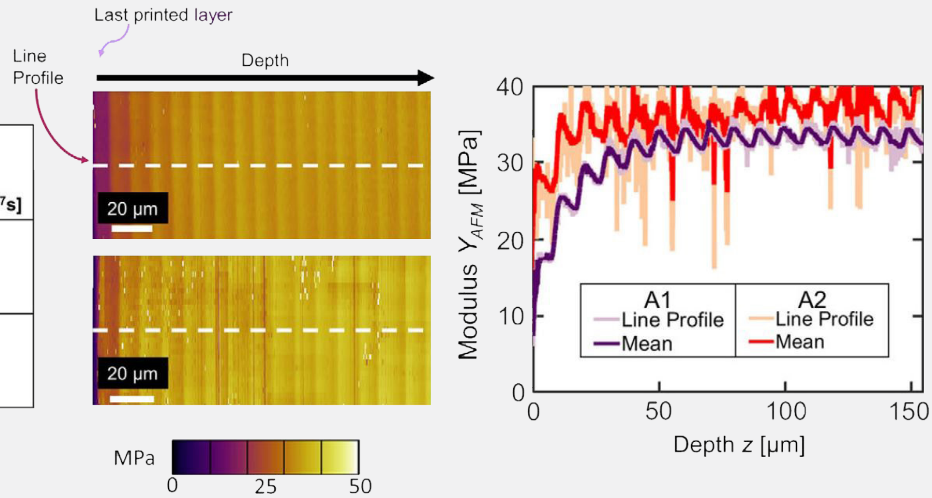
out distinct regions, FFM was used to investigate how the size of the photomask pattern affected masked regions. It was found that the modulus of masked regions increased with decreasing mask size, indicating partial polymerization in these regions. Further to this, the film was sectioned to investigate the extent of polymerization on the vertical axis and showed good uniformity across the entire thickness. With the ability to locally fine tune mechanical properties at the micron scale, interfaces within AM parts can be stabilized leading to an overall improvement in the mechanical performance.

With the control of mechanical heterogeneity to stabilize AM parts, functionally graded materials (FGMs) offer an opportunity to produce parts with enhanced mechanical properties.[12] Typically, AM parts produced from FGMs would require the printing of multiple materials, each with its own printing nozzle. A process known as digital light processing (DLP) vat polymerization offers the ability to print a single

a

Z_L = 10 µm

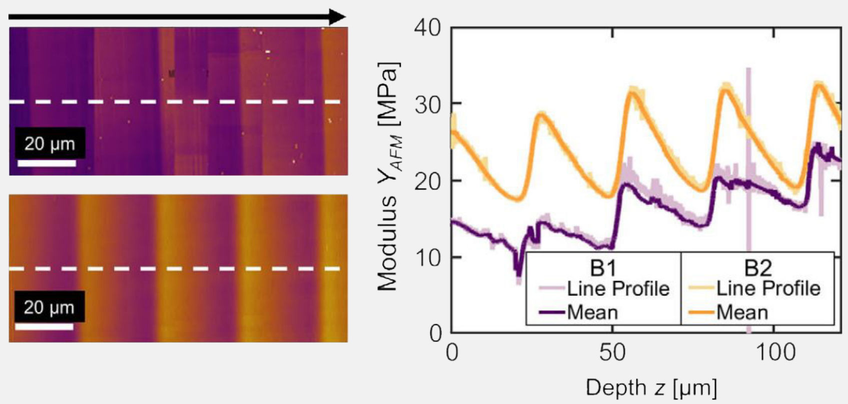
	I_0 [mW/cm²]	t_{exp} [s]	E [mJ/cm²]	E^* [(mW/cm²)$^{0.77}$s]
A1	30	6	180	82
A2	15	12	180	97



b

Z_L = 30 µm

	I_0 [mW/cm²]	t_{exp} [s]	E [mJ/cm²]	E^* [(mW/cm²)$^{0.77}$s]
B1	30	6	180	82
B2	3	60	180	140



c

Z_L = 100 µm

	I_0 [mW/cm²]	t_{exp} [s]	E [mJ/cm²]	E^* [(mW/cm²)$^{0.77}$s]
C1	30	6	180	82
C2	3	60	180	140

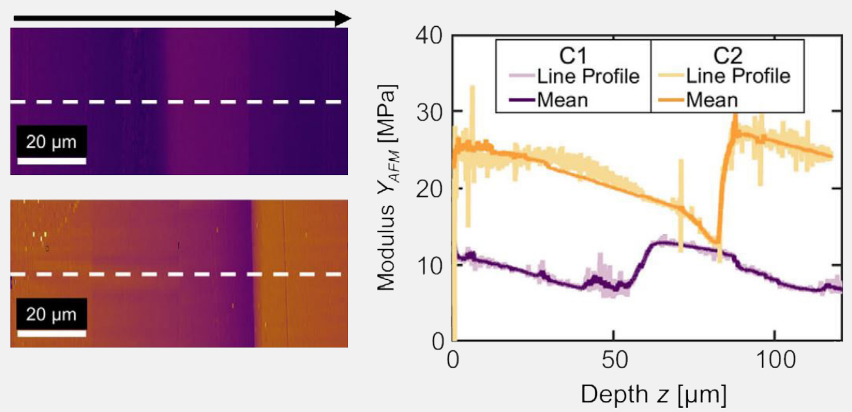


Figure 4: FFM Young's modulus maps of through-thickness 3D-printed structures, different exposure intensities (I_o) and time (t_{exp}) for layer thicknesses (Z_L) of a) 10 µm, b) 30 µm and c) 100 µm. Thin layer thicknesses produced layers of material with step changes in modulus whereas thicker layers produce a gradient. A lower I_o and longer t_{exp} leads to an overall higher modulus. Figure adapted from reference 14.

material and fine tune the materials properties on a 3D basis.[13-14] Recent developments in the DLP process have meant that the degree of polymerization, and therefore mechanical properties, can be accurately controlled by adjusting irradiance intensity (I_0), exposure time (t_{exp}), and layer thickness (Z_L) during the AM production process. By modeling the effect that each of these parameters has on the degree of curing, mechanical step functions and gradients can be created within the final part. To verify these models, AFM with nanomechanical mapping can be employed to characterize samples produced by these DLP methods. Figure 4 shows an example where varying the exposure time, intensity and layer thickness was investigated. Samples were created with layer thicknesses of 10, 30 and 100 µm and then sectioned with a microtome to expose the layer structure. To determine the variations in Young's modulus, FFM was again employed this time using a model to account for adhesion between the tip and sample to provide a more accurate measurement of Young's modulus. From a qualitative perspective, smaller thicknesses led to step changes in modulus whereas larger thicknesses produced gradients. For all layer thicknesses, a lower intensity and longer exposure time lead to an overall higher modulus.

Additive manufacturing (AM) processes have attracted growing interest due to the benefits of creating highly customized parts that are often lighter in weight and with minimal waste. These processes have been typically used for producing prototype parts but there is increasing demand for these to be used in larger scale production. One of the challenges with AM is that the layer-by-layer nature of production often results in poor mechanical performance, often due to poor bonding between layers. It is therefore critical to characterize these parts on a spatially resolved basis to develop processes to mitigate these issues. Asylum Research Jupiter and Cypher AFMs can go beyond topography and measure nanoscale mechanical properties, making them ideal tools for AM part characterization.

References

1. S.D. Nath and S. Nilufar, *Polymers* **12**, 2719 (2020).
2. T. Wu, K. Brand, D. Hewitt, and A. Tovar, in *Advances in Structural and Multidisciplinary Optimization*, edited by A. Schumacher, T. Vietor, S. Fiebig, K.-U. Bletzinger, and K. Maute (Springer International Publishing, Cham, 2018), pp. 1783–1797.
3. R. Han, F. Buchanan, L. Ford, M. Julius, and P.J. Walsh *Mat. Sci. and Eng.*: C **120**, 111755 (2021).
4. Z. Khalkhali, K.S. Rajan, and J.P. Rothstein, J. *Therm. Spray Tech*. **29**, 657 (2020).
5. O.S. Es-Said, J. Foyos, R. Noorani, M. Mendelson, R. Marloth, and B.A. Pregger, *Materials and Manufacturing Processes*, **15**(1), 107-122 (2000).
6. A.K. Sood, R.K. Ohdar, S.S. Mahapatra, *Materials & Design* **31**(1) 287-295 (2010).
7. D.P. Cole, F. Gardea, T.C. Henry, J.E. Seppala, E.J. Garboczi, K.D. Migler, C.M. Shumeyko, J.R. Westrich, S.V. Orski, and J.L. Gair, *Integrating Materials and Manufacturing Innovation* **9**(4), 358-375 (2020).
8. M. Kocun, A. Labuda, W. Meinhold, I. Revenko, R. Proksch, *ACS Nano* **11**(10) 10097 (2017).
9. X. Zhang, W. Xi, S. Huang, K. Long, and C.N. Bowman, *Macromolecules* **50**, 5652 (2017).
10. Fast Force Mapping on Asylum Research AFMs (https://afm.oxinst.com/assets/uploads/products/asylum/documents/FFM_22APRIL2021.pdf)
11. L.M. Cox, A.K. Blevins, J.A. Drisko, Y. Qi, Y. Ding, C.I. Fiedler Higgins, R. Long, C.N. Bowman, and J.P. Killgore, *Adv. Eng. Mater*. **21**, 1900578 (2019).
12. H. Gao, B. Ji, I.L. Jäger, E. Arzt, and P. Fratzl, *Proc. Natl. Acad. Sci. USA* **100**, 5597 (2003).
13. X. Kuang, J. Wu, K. Chen, Z. Zhao, Z. Ding, F. Hu, D. Fang, and H.J. Qi. *Science Advances* **5**(5), eaav5790 (2019).
14. A.C. Uzcategui, C.I. Higgins, J.E. Hergert, A.E. Tomaschke, V. Crespo-Cuevas, V.L. Ferguson, S.J. Bryant, R.R. McLeod, and J.P. Killgore, *Small Science* 2000017 (2021).