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Nanomechanical Insights into Voxel-scale Photopolymer Cure

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Additive manufacturing (AM) is beginning to realize its potential as a transformative manufacturing technology that affords unprecedented design flexibility and customization of final parts. Numerous AM methods now exist to span the range of materials from metals to ceramics to biomaterials to plastics. Despite being one of the first material platforms for AM, plastics have lagged behind metals for deployment of AM parts in critical applications. Currently, this paradigm is shifting, with cutting edge applications in healthcare, sporting goods and transportation. These parts must exhibit high spatial resolution and robust mechanical properties to accomplish their design goals. Many parallel plastic AM methods have been developed in recent decades, including fused deposition modeling, selective laser sintering, ink jetting, and photopolymer resin-based vat polymerization methods. Of these methods, resin printing (e.g. stereolithography, digital light processing) is particularly attractive due to the potential for very high spatial resolution and parallelization of the printing process, resulting in higher throughput – a necessity for manufacturing.

In photopolymer resin printing, part formation occurs at millisecond times scales and micrometer length scales. Due to species diffusion, local depletion, and light absorption, the resultant parts exhibit inherent variation in conversion that corresponds with anisotropic chemical, thermal, and mechanical properties. This undesired heterogeneity compromises part performance compared to bulk counterparts. With high spatial and temporal resolution and local property-sensing, the atomic force microscope (AFM) is well suited to study the resin printing process in various in-situ and ex-situ modalities.[1] However, to date, integrated instruments combining 3D printing and AFM capabilities have not existed. Here, we introduce a hybrid instrument combining an AFM, an inverted optical microscope, and a spatial light modulator controlled 405 nm projection source. We show that the instrument can be operated in two core modalities. In the first, the nanomechanical properties of patterned regions are spatially mapped as a function of print conditions. Notably, these properties can be compared in the as-printed, monomer-swollen state, and the ethanol-washed, dry state. In the second modality, the SPM acts as a stationary, local, high speed probe of cure rheology. It is uniquely capable of measuring polymerization at the small length scales and fast time scales of 3D printing. By separately considering dynamic and static signals, the hybrid instrument can identify local viscosity changes as well as the onset of gelation and swelling.

Figure 1A shows a composite optical image of the hybrid instrument and a force-volume map of the photopatterned substrate. The AFM cantilever is clearly visible coincident with the 405 nm photopattern. Here, the sample is a dual cure polymer film that further crosslinks from a compliant rubber to a glassy polymer under UV illumination. The patterned substrate on right indicates the fidelity of the patterning process – the photopattern is faithfully reproduced as a stiff region in the rubbery film. Sub-micron patter resolution has been realized by varying the magnification of the projection optics. Figure 1B applies the hybrid instrument to a liquid 3D printing resin. A checker board pattern is projected into the resin, against the AFM cantilever support chip. The newly created solid is then imaged with force-volume mapping. Notably, the center square of the pattern is symmetric in structure and modulus, with some softening at the edges attributed to oxygen inhibition of the reaction. In contrast, the outer squares of the pattern exhibit geometric and modulus asymmetry. Outs outside edges appear under-polymerized based on the lower

modulus and rounding of the features. The result confirms the role of voxel-voxel interactions in affecting the printing process, as well as the intrinsic heterogeneity that arises at pattern edges.

Figure 2 shows results where the AFM tip acts as a local rheometer to detect real time cure rheology. The AFM cantilever is vibrated at its resonance frequency while the tip is immersed in a photo-curing thiol-ene resin. Upon UV exposure, increased resin viscosity results in increased drag force at the oscillating tip, detected as a decrease in resonance quality factor. The forces are detected at sub-micron spatial resolution and sub-millisecond time resolution. We show that proximity of the light source to the oscillating tip greatly affects the rate of viscosity change, directly correlating with polymer conversion. Under many print conditions, detectable reaction is observed 10s of microns outside the photopattern region, elucidating the fundamental print resolution of given process conditions.

Overall, the two modalities work together to paint a picture of the complexity of the 3D printing process when attempting to achieve precisely controlled geometry and mechanical properties with microscale resolution. Results can be used to optimize process conditions for improved printability, resolution and throughput, while further revealing spatial variations in cure that should be considered in next-generation print processes.

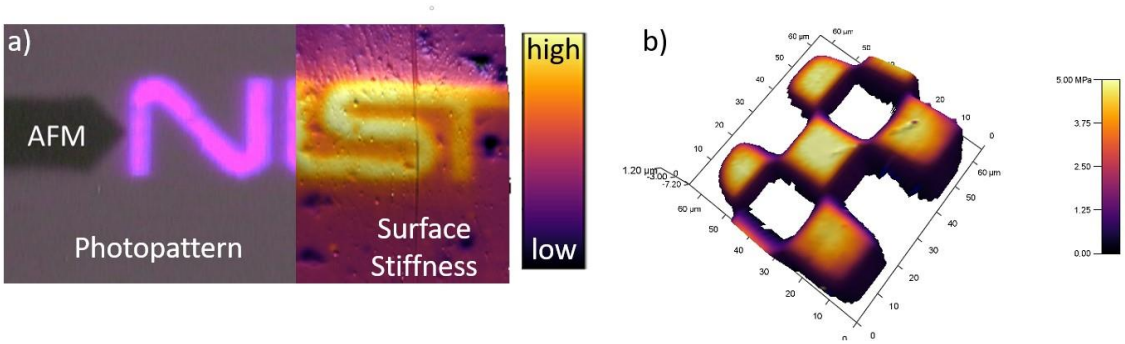

Figure 1. In-situ photopolymerization in the hybrid SLA/AFM. a) Optical view of AFM cantilever and projected 405 nm pattern, with composite map of resultant surface stiffness on right. b) Checkerboard 3D print nanomechanically mapped in monomer-swollen environment. Significant effects of inter and intra voxel interaction are observed as stiffness variations.

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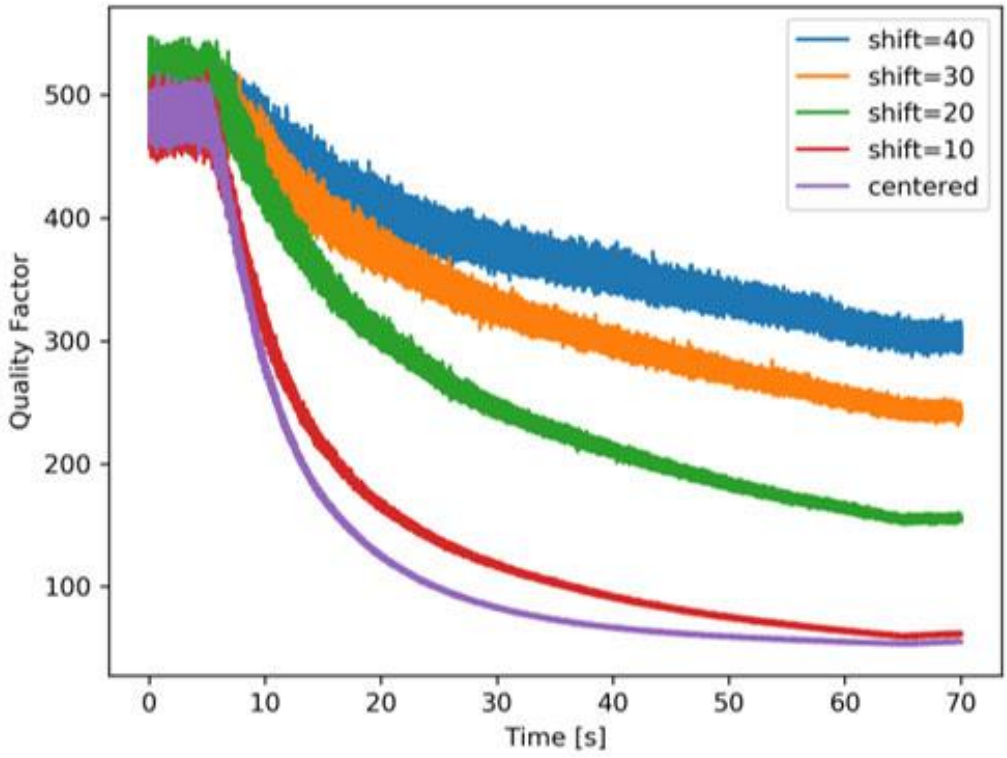

Figure 2. In-situ AFM rheometry of curing resin. A photopattern of varying Gaussian intensity is applied to resin at different offset distances (indicated as number of pixels offset) between photopattern-center and oscillating AFM tip. Upon illumination, increases in resin viscosity are revealed as decreases in resonance quality factor Q. The rate of reaction, inferred by rate of Q change, is dependent on local pattern intensity.

References

1) Fiedler-Higgins, C. I., Cox, L. M., DelRio, F. W., Killgore, J. P., *Small Methods*2019, 3, 1800275. https://doi.org/10.1002/smtd.201800275

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