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Perspective: Controlling Anisotropy in Stereolithographically Printed Polymers

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The ability to print three dimensional objects was first developed in the 1980s and was originally strictly limited to polymeric materials. Through most of the intervening years the approach has been thought of as a rapid prototyping method. This allowed low volume, high fidelity structures to be quickly fabricated to test things like fit and finish. However, more recently the term additive manufacturing has entered usage to represent the same methods, and implies that the field is transitioning to creating finished parts. When we begin to think about these techniques as a real manufacturing approach, then the materials properties achieved during manufacture become much more important. This is true for all materials, as additive manufacturing has grown to encompass structures formed from metals and ceramics, but the bulk of work remains centered on polymers.

Polymeric additive manufacturing is dominated by two general approaches: fused deposition and stereolithography. In forming a part using fused deposition, a molten polymer is extruded through a narrow opening while the extruder is translated relative to the printed part. Layers of extruded polymer solidify and build up to form the structure. A well-known weakness of this method of forming parts is the mechanical anisotropy that results from lowered strength transverse to the printing direction that is caused by imperfect adhesion between the individual layers of printed polymer[1].

On the other hand, sterolithography is performed in a liquid polymer resin containing polymerizable functionalities, where thin layers are subjected to UV light to solidify the resin through chemical reaction. Since the polymerization reactions allow strong chemical bonds to form between layers, structures formed using stereolithography have long been known to have no significant mechanical anisotropy[1,2].

Recently, Chung et al have been studying the anisotropy that does exist in stereolithographicallly formed polymer structures. For example, they have shown that stereolithography leads to acrylate polymers that have enhanced electrical permittivity in one specific direction[3]. Even more surprisingly, they have discovered piezoelectric behavior in acrylates in the same direction, even though bulk acrylic polymers are not known to be piezoelectric[4]. These surprising results can be explained rather simply as a result of the molecular alignment of the polymer molecules. Acrylate polymers have carbonyl groups that are aligned approximately perpendicular to the direction of the main polymer chain, and alignment of the chains would be expected to direct the strong dipoles of these carbonyl groups in a uniform manner. Preferential alignment of these dipoles explains both the enhanced permeability and the piezoelectricity. The simple explanation also leads to the surprising conclusion that while the mechanical properties may be uniform, it does not mean that the polymers are in fact isotropic. This body of work shows clear evidence for molecular alignment.

To understand the reasons for this molecular alignment, we must understand the specific steps in the forming of these structures. Here we will discuss the process of stereolithography, in the most

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common arrangement where structures are formed by curing thin films of resin formed between a platform holding the growing structure and the transparent bottom of the resin tank. The fundamental processes involved shown graphically in Figure 1. In a typical sequence for stereolithography, each application of UV light leads to the newly cured parts in physical contact with the resin tank bottom (Figure 1a). The platform supporting the part being constructed is raised to allow fresh resin to fill in below (Figure 1b), then is lowered to restrict the resin to the thickness of an individual layer in preparation for the application of UV light in the regions to be solidified (Figure 1c).

This final motion of the stage, sets the layer thickness of the print by squeezing the excess fluid out of the gap. The squeezed flow that results from this final motion has long been known to induce molecular alignment in polymer systems[5]. This molecular alignment, where the polymer chains are extended laterally during the sheering flow, is what leads to the unexpected dielectric properties across the thin deposition layers.

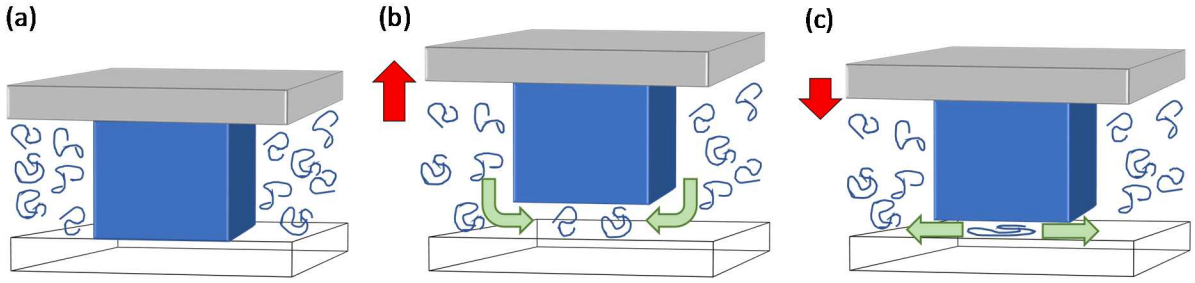

Figure 1. Schematic of the stage movements in stereolithography. a. Each layer of polymer is polymerized to form a structure that is in contact with the clear base of the resin tank. b. The stage lifts from the tank bottom and resin rushes into the newly formed gap. c. The stage moves lower to form the microscale gap between the partially formed structure and the tank bottom. During this last motion, resin between the part and the tank bottom experiences high sheer during squeeze flow leading to the extension of the polymer molecules. Polymer molecules are not drawn to scale.

In the current issue, Chung et al take this work one step farther and demonstrate a method to control the degree of molecular alignment[6]. describe an approach to relieve the stress that results from squeezed flow in a stereolithography print. They achieve this by introducing a pause between the final motion of the print stage toward the tank bottom and the beginning of the photolithography. This pause allows time for the polymer molecules to relax, thereby decreasing the molecular alignment. While the amount of time required will naturally depend upon the specifics of the experiment, including the resin viscosity, molecular weights of polymers, thickness of layers, among others, the work here shows the parameters for some typical systems. For a 25 µm thickness layer with a relatively low viscosity resin (98 cP), a delay time of 10 seconds lowers the permittivity by 39%, nearly returning it to the bulk value. On the other hand, for the same layer thickness, a high viscosity resin (2950 cP), the change was much less dramatic at only 14%.

This new work provides a roadmap to the intentional control of of molecular alignment of polymers in stereolithographically printed structures. While the work to date has focused on the dielectric and piezoelectric properties of acrylates, the polymer behavior that gives rise to these properties is universal. With this new knowledge, one could envision a conscious effort to create polymeric structures with strongly enhanced properties in one or more directions. This could include designing for higher piezoelectric effects akin to what has already been demonstrated, or could be as far afield as highly oriented polymer parts with an enhanced modulus in the plane of elongation.

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