3D printing of optical components via free-radical frontal polymerization

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3D PRINTING OF OPTICAL COMPONENTS VIA FREE- RADICAL FRONTAL POLYMERIZATION

SEAN RYAN KRUPP

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2021

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SEAN RYAN KRUPP

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Doctor of Philosophy

2021

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Abstract

Optical manufacturing is often a process dictated by high-cost machinery and long working times. In this thesis we examine the benefits and drawbacks of the different optical manufacturing technologies, and introduce 3D printing as an alternative approach. Towards this end we present a methodology towards creating freeform optical components via grayscale digital light projection (DLP) frontal polymerization. We present an instrument which can be created cheaply, offer experimental validation of its functionality, and detail the driving algorithms involved. Furthermore, as the nature of our system lends itself well to analyze the curing characteristics of various photoactive compounds, we extensively characterize several free-radical photopolymers in a deoxygenated environment in terms of their curing characteristics as a function of irradiance, cure time, and photoinitiator concentration. We find that the photoresins do not follow the Bunsen-Roscoe reciprocity law for photochemistry, and offer quasi-empirical explanations in terms of evolution of the reaction rate constants at constant degree of cure. Finally, we use the designed system to produce optical components and analyze them in terms of their surface quality and form replication, elucidating towards the limiting bounds of this technique.

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Nomenclature

Chapter 1 - Roughness, waviness, form

λ_c Cutoff wavelength for roughness/waviness

λ_s Cutoff wavelength for waviness/form

R_a Surface roughness

$S(x)$ Gaussian filter kernel

FFT Fast Fourier Transform

Chapter 1 - Scattering approach

ℓ Average surface wavelength

λ Illumination wavelength

Ω_s Solid angle for scattering

σ^2 Mean-square deviation

θ_i Incident illumination angle

θ_s Scattered illumination angle

ARS Angle resolved scattering

f Spatial frequency

$f_{min(max)}$ Minimum(maximum) spatial frequency bandwidth limit

L Profile length

m^2 Mean-square slope

N Number of profile samples

P_i Incident power

P_s Scattered power

Q Polarization reflectance

R Reflectance

$z(x)$ Profile height

PSD Power Spectral Density function

Chapter 1 - Zernike Polynomials

A_i^j	Zernike coefficient	E_c	Critical energy
$R_n^m(\rho)$	Radial component of Zernike polynomial	E_o	Incident energy on surface
$Z_n^m(\rho, \varphi)$	even Zernike polynomial	h	Plank's constant
$Z_n^{-m}(\rho, \varphi)$	odd Zernike polynomial	I_o	Incident light Intensity on surface
Chapter 1 - Zernike Polynomials		k_i	Rate constant of initiation
$[M]$	Monomer concentration	k_p	Rate constant of propagation
$[M]_o$	Initial monomer concentration	k_t	Rate constant of termination
$[PI]$	Photoinitiator concentration	N_{av}	Avagadro's number
α	Lumped photochemical properties (Eq. 2.11)	P	Power of incident light
β	Lumped processing parameters (Eq. 2.12)	R_i	Rate of initiation
ϵ	Molar extinction coefficient	R_p	Rate of propagation
λ	Illumination wavelength	R_T	Rate of termination
ϕ	quantum yield of photoinitiator	t	Exposure time
c	Speed of light	W	Top-hat beam radius
C_d	Cure depth	W_o	Gaussian width of laser beam
D_p	Penetration depth	X_n	Degree of polymerization
		z	depth measured from top of surface

Chapter 1

Introduction, Background, and Motivation

The aim of this research is to develop an alternate method of optical manufacturing which would allow for the production of sufficient quality macro optical components without severe capital investment. The medial for this however involves intense characterization of various photochemical processes, as they drive the fundamental shape of our generated optics. In this thesis we use the method of bottom-up grayscale photopolymerization to both characterize the photoactivated resins used, along with produce optics to varying degree of success. The thesis will be organized as follows: In the first chapter we will cover the various types of optical manufacturing techniques. In the second, we will discuss the various types of 3D printing and the accompanying polymer chemistry. In the third chapter we will discuss the design of the instrument which we have made, along with the software and algorithms which drive the experiments performed. The fourth chapter will show our obtained results from resin characterization, and the fifth from fabricated optics. In the final chapter, we will provide our conclusions and directions for the future.

The goal of this chapter is to provide the reader with a storyline of optical manufacturing. It will take the reader on a journey through the start of traditional optical

manufacturing and lead them through the stages of complexity which arise during optical surface generation. From the traditional methods, it will lead in to the creation of aspherical elements and freeform elements through various techniques, including variations of the traditional methods. From here, after a foundation is established in the core industry-standard methods, it will venture towards approaches in wafer-level optics, and finally it will discuss reconfigurable optics. One key idea will emerge after inspection of these processes: They often involve high cost or high time investment.

1.1 Traditional optics manufacturing methods

Before getting into the traditional methods for manufacturing, it is important to mention that during the majority of these descriptions, quality metrics for surface finish will not be used. This is because the surface quality achievable typically depends on a large number of factors, ranging from the material being studied and the accuracy of the particular machine being used to the geometry of the shape being generated and how much time is required for manufacturing. The time aspect is related to the tolerances required for a particular piece to be made in the sense that higher surface quality typically requires longer processing time, and thus a higher cost to produce. Often lower tolerances can be perfectly acceptable for a particular application, where others can leave little room for error. It comes down to finding a balance between the ideal design and its realizable counterpart.

Other considerations on the optical design side must also be taken into account in terms of the type of optic to use and the fabrication practice to seek. An aspherical element can often take place of five spherical ones, but the time and cost in creating an aspherical element is much greater. On the other hand, space restriction in a design may require an asphere element, and therefore justify the cost. To this end, the traditional methods for both spherical and aspherical manufacturing will now be discussed.

1.1.1 Spherical lenses

For the purposes of this description we will start with the method of turning considering that glasses are used, but a similar approach can be used for other materials like Aluminum and Silicon (with appropriate care). There are five basic steps to consider for spherical lenses: 1) cutting a blank from a raw slab to approximately the right shape (within a millimeter or two oversized). 2) Grinding the blank to approximately the correct radius (around 0.1 millimeter). 3) lapping the surface to remove damage from the previous step (to within a few micron of the ideal shape). 4) polishing the lapped surface to achieve the final finish, and 5) aligning the lens periphery to the optical axis by asymmetrically shaving off the edges. These steps are generally referred to as roughing, generating, lapping, polishing, and centering/edging.

One important aspect to consider during this process is the brittle nature of glass. Having a brittle surface yields a series of fractures being generated along a surface proportional to the force of a tool on that surface[53]. If the force of the tool is too great, deep fractures will be formed and the entire glass piece will break. For this reason, grinding is normally chosen, where shallow fractures will be generated, and the glass will chip away when the fracture lines intersect with one another. The grinder will typically consist of a diamond powdered metal or resin head.

Roughing. The first stage of roughing can either be carried out at the factory where the glasses were produced or, if not possible, can be carried out manually through chipping and sawing a stock piece of glass. For large scale production processes, the manufacturer will typically press heated (plasticized) glass into a metal mold slightly larger than the desired shape. The shape is specifically left oversized to allow for material removal during later processing steps.

If it is not possible to mold a blank at the factory (for reasons such as small production runs, exotic materials, or one-off customized optics), one can consider creating a rough

blank as mentioned above via sawing/chipping. While typically a manufacturer will provide a specification sheet, or "melt sheet", on the particular glass used, it can be helpful to use a polariscope to check for anisotropy within a blank caused by thermal stress. The presence of which will cause a shift in the index of refraction of the blank, and originates from poor annealing. For smaller pieces of glass, the thermal gradient will be steeper, and thereby result in higher localized stress. For larger slabs of glass however, the thermal gradient will be smaller and more uniform within the entire slab, and thus induce less stress. For this reason, blanks cut from a slab will tend to contain a more uniform index of refraction than blanks cut from smaller pieces, and should be chosen for this reason.

Generating. After a suitable blank has been created, it will be mounted on a chuck via low melting point adhesive (pitch, synthetic beeswax, etc), and spun to a particular revolution speed depending on the type of glass used. It will then undergo the process of generating, where a dimensionally true shape will be set, allowing for the remaining stages to be performed more efficiently. A spinning spherical grinding wheel will be lowered onto the spinning blank, where a grinding wheel is angled so as to set the correct radius of the soon-to-be lens. This concept can be seen in figure 1.1. The thickness of the lens will then depend on the distance which the grinding wheel is lowered onto the blank, and the lens curvature by the grinder angle with respect to the normal axis of the blank.

One other aspect that can be considered during this and the following steps is the use of *blocking*, which is the process of mounting multiple lenses on one spindle for working at the same time. This is a process often used in industry for efficiency, and for the less obvious benefit of surface improvement due to evenly distributed tool wear[89].

Lapping and Polishing. After generating, the surface of the lens will then be lapped and polished. For lapping, two surfaces which are similar in shape (in this case spherical) will be brought into contact with each other with lapping compounds of various grits sandwiched between. The grit of the lapping paste will start coarse, and progressively be

Fig 1.1: A spinning blank is ground with a spherical grinding wheel. A similar process is used for lapping and polishing, with the exception that the tool will be left to freely rotate on its mount.

swapped to a finer grit in stages. The paste itself can use emery, diamond, carborandum silica/silicon carbide, etc. as an abrasive, and typically contains an oil base. When the two surfaces are moved randomly against each other, they will erode their high spots and begin to take their ideal surface. This configuration is similar to that seen in 1.1, where it uses a concave lapping plate which is left to rotate freely on a pin, and the base of the pin is oscillated cyclically. This prevents a specific pattern from being worn into the lens, and allows for fine adjustment of the shape during processing by changing the motion of the pin.

The process of polishing will essentially follow the same procedure, with the exception that either pitch or synthetic polishing pads will be used in place of the hard lapping surface, and that instead of lapping compound a mixture of water and cerium oxide will be used. This allows for a polishing tool which will conform to the lens being polished, and results in low surface roughness (on the order of nanometers). This is of course an oversimplified description, and the field of optical polishing is still an active field of research where the mechano-chemical processes are currently being investigated[4, 5, 17, 20, 36].

Centering and edging. The final steps in the fabrication process are centering and edging. After the spherical surface is ground and polished, the optical axis will often be formed slightly off-axis with respect its mechanical axis (i.e the physical edge of the lens). In order to correct for this, the edges are shaved off asymmetrically until the centers are aligned. For this procedure, the lens will be attached flush (with pitch) against a tubular tool which is precision aligned to the rotating axis[89]. The tool is spun, and a reflection off the lens is observed. If the reflection is observed to oscillate as the tool is spun, the lens is off-axis, and it will be manually realigned on the rotating tool head. Once the reflected image no longer oscillates, it is considered centered, and the edging process can be carried out. For this final stage, the rotating lens will be lowered on to a grinding plate, which will asymmetrically shave the edges off until the correct diameter is achieved.

1.1.2 Aspherical lenses

Spherical surfaces, while easier to produce, suffer from spherical aberration, and often require multiple elements in a system to correct for such. A solution for this is to use aspherical lenses: lenses which deviate from spherical, and offer the advantage of being able to correct for spherical aberration with a single element. While more difficult to manufacture (and therefore more costly per element), taking into account less elements required in a system, less number of anti-reflective coating to create, and reduced physical constraints, aspherics can be cheaper alternatives. The most common form of an aspheric element is conic, where a conic surface can be described by:

$$z(\rho) = \frac{\frac{1}{R}\rho^2}{1 + \sqrt{1 - (1 + k)\left(\frac{\rho}{R}\right)^2}} \quad (1.1)$$

where $z(\rho)$ is the sag of the surface parallel to the optical axis, R is the radius (with $1/R$ being the curvature), and s is the radial distance with respect to the optical axis. k is the

conic constant, where a value of 0 grants a sphere; $-1 < k < 0$ grants an ellipsoid with its major axis on the optical axis; -1 a paraboloid; and $k < -1$ a hyperboloid.

Through the addition of even polynomial terms, the typical equation for aspherical elements is derived:

$$z(\rho) = \frac{\frac{1}{R}\rho^2}{1 + \sqrt{1 - (1 + k)\left(\frac{\rho}{R}\right)^2}} + A_4\rho^4 + A_6\rho^6 + A_8\rho^8 + H.O.T \quad (1.2)$$

where A_4 , A_6 , and $A_8...$ are the respective 4th, 6th, and 8th... order aspheric coefficients. The polynomial terms are used to correct for aberration and reduce the number of elements required in a system. A detailed derivation of equation 1.2 is given in Appendix A.

Aspherics can serve a wide range of applications, from military to consumer and ophthalmic, but are not without their limitations. Aspheric lenses still experience field curvature aberration, limiting their off-axis performance. In this sense, while a multi-element spherical lens system may be replaced with a single aspheric lens to achieve the same degree of on-axis performance, the system will still require further corrective optics to correct for aberrations which are off-axis. Nonetheless, the discussion of the manufacturing methods for aspherical lenses is of merit.

The traditional manufacturing of glass aspherical components is more difficult than the manufacturing of spherical components in that it can not take advantage of the natural sphericity of the previous grinding process (Section 1.1.1), and for this reason often involves higher costs and complexity. In order to produce an asphere of glass, several techniques may be adopted depending on the specification of the lens desired, including traditional grinding and polishing, Single Point Diamond Turning (SPDT)[2, 8, 89], or Precision Glass Molding(PGM)[52, 93, 109]. SPDT and PGM will be discussed in the following sections, and the traditional method of grinding and polishing is discussed

here.

For aspheres which only slightly deviate from spherical, they can be processed similar to the method described in the previous section, but when the desired shape deviates largely, special care is required. One common technique is to use a lathe converted into a grinder, where the basic shape will be ground into the lens. It will then be lapped with a flexible plate which can contour to the changing curvature. It is necessary to frequently test the contour of the lens to ensure that it is not deviating from the desired shape, as the natural tendency of the shape is to return to spherical. High spots on the surface can be controlled by dwelling on a respective location longer. Selective polishing/shaping can also be performed by removing sections of polishing pads (for instance using a ring polishing pad instead of a circular polishing pad)[89].

There are several other techniques which can be used to polish aspheres, one being magnetorheologic polishing[31, 76, 89]. This is a technique where the polishing compound used is magnetic (with additives such as iron). The compound is moved over the surface of the lens, where a localized magnetic field is used to cause sections of the compound to become stiff, and therefore causes localized polishing. Through computer control of the positioning of the lens, the shape can be crafted as desired.

1.2 Freeform optics manufacturing methods

At some point in designing an optical system, a need for surfaces which deviate from aspherical or spherical may occur, i.e. surfaces which have no axis of symmetry. These surfaces are classified as freeform, and offer their own unique set of challenges to manufacture, the primary being that axial rotation of the lens can not be used to craft the surface without specialized equipment. There are several solutions which have been developed, each offering their own advantages and disadvantages.

1.2.1 Plastic molded optics

Plastic molded optics have the advantage of being easily scalable, low-cost for large quantity, and having high reproducibility. The production method can be broken down into three subcategories: Injection molding, casting, and compression / embossing [93]. Injection molding is a process where a molten plastic is injected into a pressurized mold, and then subsequently cooled. Casting is different in that a liquid plastic is used and then allowed to solidify, not being a process which depends on a plastic being melted beforehand. It is primarily used in the ophthalmic sector. The final subsection compression / embossing is self explanatory in that a plastic is heated and stamped or pressed to form a lens.

The advantage that plastic molding has over traditional grinding and polishing is that it can combine most of the steps mentioned in 1.1.1 into one, where all the stages from roughing to polishing take place in a single step. It can furthermore allow for quick reproducibility of optics from the same mold/press, and the complexity of a molded component can be greater than it could be for a ground/polished optical piece. The weights of plastics are also typically less than that of glasses, and the plastics also offer greater impact resistance. There are also several disadvantages associated with using plastic optics. The selection of materials available for optics is rather limited, whereas glasses offer much more options and therefore a broader selection of abbe values / indexes. Plastics have high thermal expansion and temperature coefficients for the refractive index, and they can not be coated as easily as glasses. Plastics are also likely to suffer from stress-induced birefringence[13].

A final type of plastic molding that can be considered is Glass replication, which is a hybrid polymer-glass process. For this process, a glass spherical surface is used, and placed into a freeform mold with a liquid polymer filling the void between the glass and the mold. The polymer is then UV cured, and thus creates a freeform optical surface.

This method is normally used when the freeform surface is close to spherical. It can also be used as a wafer-level process where the freeform surface is cured on top of a silicon substrate.

1.2.2 Glass molded optics

There are two primary types of glass molding processes for optics: Glass molding (GM) and Precision Glass Molding (PGM). GM uses a non-isothermal process where a gob of glass is heated, pressed in a mold, and allowed to cool. The lens will then be post-annealed to allow for removal of stress, and have its second (typically) plano surface post-processed with a method such as grinding and polishing. This technique is generally used for optics which do not require high degrees of tolerance (such as for car headlights, etc).

Dissimilar from GM, Precision glass molding is an isothermal process which introduces finer controls of the GM process. While there are several different techniques which depend on the manufacturer, their processes will typically adhere to the following: A glass gob preform will be inserted into a machine with a specifically designed mold and tooling. The mold itself is made with a high level of precision through techniques such as diamond turning or diamond grinding. The gob preform is not as the one used for GM, where instead it is a gob with finely controlled volume and surface quality.

The system will then be heated to above the glass transition temperature, purged of oxygen using an inert gas, and the gob preform will be pressed. The process parameters will be calculated beforehand dependent on the heat transfer properties of the molding system, glasses viscosity, glass thermal properties, and surface requirements. The surface will then be rapidly cooled and metrological measurements will be conducted. This process will then be repeated for a second round after measuring how true to design the optic is, thus eliminating errors which the simulation could not account for.

While high surface quality optics can be produced with this method, its limitation

eventually lends itself to the quantity being produced and the affordability to do so. Molding processes typically offer advantage when it comes to producing a medium or large quantity of optics. For small quantities however, high cost should be anticipated as a mold and matching tooling must be created regardless of fabrication number.

1.2.3 Ultra-precision machining

When seeking to leave the realm of molding technology for freeform surface fabrication, ultra-precision machining (UPM) processes, which are today becoming industry standards, are likely to be encountered. This umbrella term encompasses several different technologies which, when considered together, often do not have a clear boundary between[32]. The one aspect which they do all share in common, however, is the use of a diamond tool to facilitate material removal. The most common techniques encountered are: UP diamond turning (UPDT), fly-cutting (UPFC), raster milling (UPRM), and grinding (UPG). These techniques may in turn be assisted through the addition of multi-axis computer numerical controlled machine (CNC) techniques, a concept discussed in the final paragraph of this section.

In ultra precision diamond turning, a diamond cutting bit is used in place of a traditional one made of High-speed stainless steel, carbide, etc. While the classic turning method would be to rotate the part on a lathe and apply a cutting bit, when generating freeform surfaces it is necessary to break the symmetry associated with this process. This can be done in several ways; the first being to offset the central axis of the part being cut to remove material asymmetrically. This method is commonly used to generate off-axis parabolic and elliptical mirrors.

The diamond turning process works as follows (regardless of axial location for symmetric/asymmetric pieces): First a blank is prepared which is similar to the blanks described in 1.1.1, and second the blank is mounted in an appropriate chuck. The proper diamond

tools are then selected for the optical component and mounted. The surface will then be machined to the correct shape and surface quality with bits of decreasing size, the final being diamond, and the part will be removed and cleaned. It is important to reiterate here that the machine used is not the same as a typical machine-shop lathe. It must have high stiffness and be vibration isolated. It has been shown that the amplitude of tool tip vibration on the order of tens of nanometer contributes to a surface roughness of the same order in cut optics [19, 103]. Furthermore, the surface structure of a diamond-turned element is periodic in nature due to the cutting blade (compared to the random surface pattern on a ground piece), and this may produce grating like effects[2] depending on final finish.

In addition to traditional UPDT with either on-axis or off-axis work pieces, adding fast-tool servo (FTS)[113] or slow slide servo (SSS)[96] processes can allow for more complex geometries to be created, such as the fabrication of microlens arrays. These two techniques, along with their sub-technologies, will be discussed in the following sections. We have described these as techniques which extend diamond turning, but in reality they can also be extended to UPFC and UPRM without much difference in description with exception of the cutting style used, as they are both in their nature derivatives of UPDT.

Fast-tool servo turning

In FTS, cutting is conducted by rotating the piece being worked about the C-axis (being defined as the rotating axis of a lathe), and bringing an oscillating diamond cutting bit into contact with the surface either along the radial or axial direction with respect to the rotating part. By controlling the amplitude and frequency of tool oscillation, along with the workpiece rotation speed, material removal can be controlled. There are several different variations of FTS, where the classification of each is based on the driving mechanism behind the oscillatory tool. The three most common variations are piezoelectric (PZT)[50, 56, 90], Lorentz force (LRT)[62, 95, 108], and Maxwell normal

stress motor-driven (MNM)[69, 70, 105].

PZT-FTS systems are best suited for small, fine-detailed applications, with the systems having resolution in the nanometer range, high dynamic stiffness ($100N/\mu M$), and the ability to produce large output powers of over $10kN$ [113]. Their drawback, however, is when the stroke of the tool becomes too large (in the micron scale). The PZT materials generate heat due to hysteresis, causing a reduction in positional accuracy[113]. This can be compensated through using the piezo-actuator in combination with a less accurate higher stroke stage.

For LRT-FTS systems, voice coil motors are primarily used. This allows for a large stroke (often in the millimeter to centimeter range), but the systems themselves have a large mass which limits their ability to obtain high response times. These systems typically have damping issues, inertial recoil, and generate large amounts of heat at higher frequency. This primarily limits their use to applications with a large stroke length.

MNM-FTS systems can be seen as the middle ground between PZT and LRT systems. They operate on electromagnetic normal stress, which can be described by the Maxwell stress tensor, as the driving force. These devices offer a medium range stroke when combined with suitable mechanics, but can be driven at much higher frequencies than their counterparts. The disadvantage with this method is that high-precision position tracking is difficult to realize.

For all three of these methods, the C-axis in the diamond lathe is typically velocity controlled and has its position recorded by encoder, which is then fed to the FTS. This is an important distinction when comparing this method to slow slide servo turning mentioned in the next subsection, which is position controlled[96]. It also must be noted here that the velocity along the cutting edge of the part is dependent on the radial displacement with respect to the C-axis, a property which can be a cause of error when determining proper tool path.

Slow slide servo turning

The second and third method, FTS and SSS, are similar in nature, with the exception that in SSS there is no high-frequency actuation of the cutting bit and the rotation of the C-axis is fully position controlled as mentioned previously. C-axis control is accomplished through the inclusion of a proportional-integral-derivative (PID) controller which will form a feedback loop between the lathe's current C-axis position and the C-axis position as required by the design. The lathe will then adjust its velocity accordingly to compensate for any offset determined, therefore controlling the position. The stages on these systems are driven in a sinusoidal motion, and typically have frequencies around 100 Hz [96].

Disadvantages of diamond turning

Diamond turning as a whole is not without its drawbacks. Several issues can arise in a piece being cut due to the simple geometry involved with a lathe - the primary being that the cutting velocity changes with the radial distance from the C-axis center. This can cause cutting inconsistencies to develop as a result of the cutting velocity differing from the spindle velocity[83]. Another drawback of UPDT would be cutting linearization error of the tool path caused by the finite sampling of the turning profile[28, 67, 83]. For example, while imagining an Archimedes spiral, under sampling can be noticed by breaking the spiral into finite sections, where the profile then becomes '*polygonish*'. A normal means to compensate this would be to increase the sampling rate, but this requires higher system bandwidth, inevitably slowing down the process or inducing its own set of surface distortions[16, 110].

Ultra-precision flycutting and milling

Considering the aforementioned drawbacks of diamond turning, along with other considerations such as material choice, geometry, or cost involved for the specific piece, other

UPM methods such as Ultra-precision flycutting (UPFC)[111] or raster milling (UPRM) could be better choices.

UPFC and UPRM are process which were born out of UPDT. One can imagine taking a diamond turning lathe and switching the location of the cutting bit and the piece being worked, and applying a radial offset to the cutting bit. This would give either UPFC or UPRM based on the orientation of the cutting bit - if the cutting bit faces radially outward from the spindle it would be milling, and if it faces parallel to the spindle axis it would be flycutting[111]. Both configurations can be mounted either vertically or horizontally, depending on the current configuration of the machine being used. The primary advantage with UPFC and UPRM is that the tool bit moves at a constant velocity in comparison to UPDT, where the cutting velocity in UPDT changes with the radial distance of the cutting bit from the C-axis. While avoiding this drawback of UPDT, both of these techniques tend to be less efficient than diamond turning due to intermittent contact of the diamond bit with the work piece, compared to the constant contact of UPDT. For this reason, they are choice techniques for small, complex parts. It is important to note that these systems can be combined with either FTS or SSS techniques to allow for more complex geometries to be created.

1.2.4 Material considerations and ultra-precision grinding

When choosing to fabricate an optical component through UPM methods, the material properties of a required material may not always be suitable for the techniques described above. These processes are cutting-based techniques, and are typically only suitable to materials which fall on the softer/ pliable end of the spectrum in the ductile regime (aluminum, copper, and plastics). But what does it mean for a material to be ductile, and how do we cut materials which are not in this regime? The answer to this question is not so straightforward, and in fact encompasses a fundamental question in

Fig 1.2: Schematic representation of the various ultra-precision processes. (Top-Left) shows flycutting and milling, where the workpiece is stationary and the tool rotates. In turning (top-right), the tool is stationary while the workpiece rotates. For FTS (bottom-left), the workpiece is rotates while the tool is modulated back and forward at high frequency. In SSS (bottom-right), the workpiece is rotates while the tool slowly moves back and forward at low frequency.

UPM. A material being cut in the ductile regime means that it is pliable enough so that it does not crack underneath the cutting path, and is desirable for machined surfaces. Brittle materials like glasses, however, will form micro-fractures beneath the cutting path and overall ruin the surface quality. The complexity in this process arises in that the ductility of a material is not constant, and is in fact dependent on several parameters such as the temperature, material strain rate, cutting tool geometry, and compression / tensile stresses in all directions within the work-piece[10]. Some solutions to this have been to machine brittle materials under hydrostatic compression[9, 81] or to use a negative rake angle on a diamond cutting tool[23, 24, 30]. Using a negative rake angle effectively creates a localized region under compression, and based on the cutting depth, allows for ductile cutting of brittle materials. For common optical glasses however, this depth, known as the critical depth, can range anywhere from a few micron to a few nanometers[10]. When the critical depth is exceedingly small, one option is to move towards ultra precision grinding, where other methods would be too inefficient at such low cutting depths. It is important to note however that the cutting depth is not the only factor to consider, and aspects such as cutting speed play a role as well.

Grinding can conceptually be looked at as using a large number of small cutting bits at the same time. The UPG process is one that, as most of the techniques described, is different depending on the person describing the process. One possible setup is very similar to that described in 1.1.1, with the exception that finer abrasives are used and more stringent specifications are held for the machinery. The key difference between UPG and typical grinding is that the goal is to remove the need for the polishing step, and achieve suitable surface parameters within a single run.

1.2.5 Multi-axis computer numerical controlled (CNC) machining

Ultra precision techniques can also be combined with multi-axis Computer Numerical Controlled (CNC) machining to increase the degrees of freedom workable within a system. A traditional mill would contain three degrees of freedom: the X, Y, and Z-axes. For multi-axis CNC machines, more degrees of freedom are added to the system. A typical setup consists of five axes, where both the roll and pitch are automated along with the typical Cartesian coordinates. Most industrial machines do not include yaw rotation as it does not provide enough benefit to outweigh the cost, but sometimes for specific cases a machine such as this is created. Some multi-axis CNC machines may advertise having more degrees of freedom, which could arise due to having multiple spindles or turrets which can transverse/rotate independently. Any of the aforementioned techniques (UPDT, UPFC, UPRG, or UPG), depending on component requirements, can be implemented in a multi-axis configuration given correct tolerances being held to the entire system.

1.3 Micro and nano fabricated optics

If it is desired to fabricate optics which are on a smaller length scale, there are several wafer-level techniques which may be utilized in place of the aforementioned machining practices. Techniques like binary/grayscale lithography and two-photon polymerization(TPP) are bottom-up techniques which utilize the UV curing of photopolymers to produce various optical elements on a substrate.

1.3.1 Binary and grayscale lithography

For this process, typically a substrate is coated with a photoactivated resist which under irradiation with UV light will undergo a chemical change based on the type of resist. If it is a positive resist, under development in a post-treatment bath, the areas which were exposed will be removed. If it is a negative resists, the areas which were exposed will remain. Binary optics can be fabricated by knowing the thickness of the resist which was placed on the substrate, and carefully controlling the pattern used. Grayscale optics are fabricated via use of a gradient exposure profile, and require more careful tuning. When a portion of the resist is exposed, it will cure from the top downward at a certain function of the time and intensity, otherwise known as the dose. These curing characteristics however are a related to the chemistry of the resin itself, and normally must be experimentally determined. Once these characteristics are determined, the exposure profile can be adjusted to that of the resin to achieve curing in a desired shape. With traditional photolithography, a mask is placed very close to the surface of a wafer. This mask is typically made of fused silica and has a chrome coating with the inverse of the desired pattern. Grayscale can be achieved by having a thinner coating of chrome particles such that there are undercoated regions interspersed within the pattern.

1.3.2 Two-photon polymerization

Two-photon photopolymerization(TPP) utilizes the non-linear property of some molecules to absorb two photons of lower energy (typically, but not necessarily the same frequency) and excite them to some higher energy state. For photopolymers, these particular molecules are called photoinitiators, and under excitation will decompose to start a chain polymerization reaction. A similar process is described in detail and shown schematically in section 2.6.3 for a single photon absorption process. In that section, one could imagine replacing a single photon with two of lower energy with the sum of their energies equal to

the single photon. After the absorption process, the chemical process would be identical. TPP has two key benefits over single photon polymerization: 1) as two-photon absorption is a nonlinear process, the absorption rate is dependent on the square of the illuminating intensity. 2) The wavelengths used for excitation are typically in the NIR wavelength range, where many prepolymers do not absorb strongly, allowing for higher penetration depths. The first point is an advantage as it allows for a very small, and therefore high resolution, region to be polymerized. Considering a focusing beam, only regions near to the focal point will have high enough intensity to polymerize, allowing for sub-diffraction limit feature sizes down to around $100nm$ laterally and $10nm$ longitudinally[48, 49, 112]. The primary drawback to this methods is that to achieve the high intensities required, ultrafast mode locked[48] or custom Q-switched lasers[74] are required, significantly increasing cost.

One example of optical fabrication with this technique is presented by [44], where the authors have produced compound optics directly on the surface of a camera sensor. This was performed by dipping the sensor in a polymer solution, and making the lenses in place by using the sensor as a substrate. TPP polymerization can also be used to fabricate various types of metamaterials[112], which tailored properly can facilitate materials with negative refractive indices..

A prominent example of commercial printers are those created by Nanoscribe GmbH [49], where they demonstrate microoptics printed with surface roughness below $R_a = 10nm$ with lateral resolution down $160nm$. One of the advantages to a nanoscribe system is their proprietary TPP resin, which along with the system, influences the roughness and resolution.

1.4 Surface characterization and tolerancing

While we have made mention of various manufacturing techniques, we did not make explicit mention in most cases of the level of surface quality achievable, or for that matter how industry defines a surface of sufficient quality. We will dedicate this section to such discussion, and we will also include discussion of how to quantify optical aberrations due to shape error. We rely heavily on the theory discussed herein for the results in sections 5.1-5.3.

1.4.1 Roughness, waviness and form

Broadly, when considering an optical surface (or any surface for that matter), the surface itself can be represented as a sum of waves of various wavelength. In this scheme, the longer wavelengths determine the general shape or *form* of the overall surface, the medium wavelengths are slight undulations to this shape (known as *waviness*), and the shorter wavelengths make up the texture of the surface, known as *surface roughness*. When considering a surface which has been created to have a specific form, due to imperfect manufacturing one can expect deviation from ideal in the form of waviness and surface roughness. Furthermore, a surface may also have irregularities such as scratches or pits. The interplay between these various aspects thus determines the quality of an optical component, and the determination of each will be discussed in the following paragraphs. For convenience we consider the wavelength components in terms of their frequencies. The surface roughness of a particular piece is determined by the root-mean-squared (RMS) deviation of a surface after undergoing low/medium frequency (high-pass) filtering to remove waviness and form. Along this same line of logic, the waviness is derived from removing the low and high frequencies, and the form from removing the medium and high frequencies. While conceptualization is one aspect, definition of the two boundaries between the three regimes then becomes a matter of subjectivity, and industry standards

have then been put in place to encompass this aspect. There are several approaches determine these values, and the naming scheme is different depending on the filter type used. The proper choice of filter itself is also a matter of ongoing research, and there are several options available. The historic choice of filter was the $2RC$ filter (industry standards ASME B46, deprecated in ISO 11562), but it has since been replaced as it can succumb to phase errors while fitting, and therefore will not be discussed. The most prominent replacement is the Gaussian filter (ASME B46 / ISO 11562, ISO 16610-21) and its modified variant the robust Gaussian filter (ISO 13565/ISO 11562, ISO 16610-31)[77]. Both the Gaussian and robust Gaussian are currently used in industry, with the robust variant being a modification to the Gaussian filter to remove the effects of a sudden, deep, valley on the mean line determined by a Gaussian filter. These features are typically presented as a sudden step in the part height, or as an erroneous data point. For the cases of optical components with continuous surfaces measured by a stylus profilometer (as in this research), the standard Gaussian filter will suffice as the aforementioned features are not present. The filter is defined by its constituent weighting function (also known as a kernel):

$$S(x) = \frac{1}{\alpha\lambda_{c/s}} \exp \left(-\pi \left(\frac{x}{\alpha\lambda_{c/s}} \right)^2 \right) \quad (1.3)$$

where $\alpha = \sqrt{\ln 2\pi}$, λ is the wavelength components in the profiles, $\lambda_{c/s}$ is the cutoff wavelength for filtering, and x is position, with the 0 being defined at the center of the weighting profile. The c/s subscript denotes the cutoff between the roughness/waviness (c) or waviness/form (s), and recommended values for these can be found in ISO 16610. A filtered profile for a given measurement is determined by the convolution of equation 1.3 with the measured profile, which can then be taken at face value for the longer wavelength component, or subtracted from the original measurement to obtain the shorter wavelength portion. Instead of direct convolution however, an alternative fast Fourier transform

(FFT) approach[78] can be used, where the FFT of the profile is multiplied (element wise) by the FFT of the weighting function, and an inverse FFT is then performed to yield the convoluted profile. Some other notable filters to consider are the cubic spline, recursive cubic spline, spline wavelets, and morphological filters, which are all defined in ISO 16610. Often alternate terminology for the cutoff is used, called the nesting index, which expands the definition of cutoffs to nonlinear filters[40]. Other techniques must be considered to apply nonlinear filters to data, dependent on the specific filter, as the convolution/FFT method mentioned above is only suitable for linear filters. The FFT of an image can also directly be edited to remove selective frequency components without using a weighting function.

Another aspect to consider when working with surface data is the type of instrument used to do the collection. Each style of equipment, whether it be a stylus profilometer, confocal microscope, white light interferometer, or atomic force microscope, will be sensitive to a certain bandwidth range and have its own inherent digitization of data caused by sampling and physical limitations. For this reason, the surface profile is often referred to as the extracted profile, meaning the profile after correction has been applied by the device to take into account its own noise and known measurement errors. Care should be taken to ensure that the measurement desired is able to be performed on the selected device.

1.4.2 Scattering approach

When considering light incident on a surface, we must first realize that any surface will be rough to some extent due to processing parameters, and that it then becomes a matter of determining the implications on the optical performance of the surface. For high power laser systems, the primary implication is damage to the lens due to localized hot-spot formation at a surface defect site[15, 25], noting that surface roughness can be considered

as a collection of individual defects. These defects, along with the surface roughness itself, will cause scattering, thereby decreasing image quality[98]. These effects can compound each other as well, where the laser damage creates even more scattering centers[25].

Unlike the previous section which considers a separation between the wavelength and roughness, for scattering considerations it is useful to look at the entire range of wavelengths as a whole (or at least that within the bandwidth of the measurement instrument). We will first discuss how to characterize the surface through the use of the power spectral density function (PSD), and then later combine it with scattering theory. The PSD is defined as the squared modulus of the Fourier transform of the profile, and is represented in one dimension by[86, 91]:

$$PSD(f_x) = S_1(f_x) = \lim_{L \rightarrow \infty} \frac{1}{L} \left| \int_{-L/2}^{L/2} z(x) e^{-2\pi i(f_x x)} dx \right|^2, \quad (1.4)$$

where L is the total length of the profile, and $z(x)$ is the height of the profile assumed to have a mean value of 0. The units of PSD in 1 dimension are length cubed. From equation 1.4 we can then determine a mean-square value by:

$$\sigma^2 = 2 \int_{f_{min}}^{f_{max}} (2\pi f_x) S_1(f_x) df_x \quad (1.5)$$

where f_{min} and f_{max} are the spatial frequency bandwidth limits for the measurement. It is important to note the distinction that the PSD is defined over all space, and that only a portion of this data will be captured by a specific instrument. For this reason, equation 1.5 defines a *relative* roughness, taking into account the instrumental bandwidth. For the case of a surface profilier, the minimum frequency can be defined by $f_{min} = 1/Nd$, where N is the number of points in the profile, and d is the spacing in the spatial domain. The bandwidth maximum is defined by $f_{max} = 1/2d$. f_{min} also acts as the frequency spacing

Δf . Additionally, the 2 in equation 1.5 and 1.6 come from the symmetry associated with equation 1.4, where only the positive values are used for integration, and the value simply doubled at the end. Observing equation 1.5, it can be seen that only the amplitude of a particular feature is utilized, and it does not consider the spatial frequency of said parameters. For example, a surface could consist of several high frequency features with the same amplitude, or few low frequency ones, and still yield the same mean-square value. For this reason another useful parameter for surface characterization can be introduced, which is the mean-square slope, where its definition is given by:

$$m^2 = 2 \int_{f_{min}}^{f_{max}} (2\pi f_x)^2 S_1(f_x) df_x. \quad (1.6)$$

Combining equation 1.5 and 1.6 we can then determine an average surface wavelength by

$$\ell = 2\pi\sigma/m \quad (1.7)$$

with the approximation that our surface features are sinusoidal in nature.

Now that the parameters of the PSD function have been defined, we can relate it to scattering through the use of Rayleigh-Rice (RR) vector perturbation theory. We define what is known as the angle resolved scatter (ARS)[91], meaning the scattered power (P_s) from a solid angle component (Ω_s) divided by the incident power (P_i), from the PSD function in one dimension by:

$$ARS(\theta_s) = \frac{P_s/\Omega_s}{P_i} = \frac{16\pi^2}{\lambda^3} Q \cos(\theta_i) \cos^2(\theta_s) S_1(f_x) \quad (1.8)$$

where λ is the illumination wavelength, θ_i and θ_s are the incident and scatter angle, f is the spatial frequency at a given scattering angle determined by the grating equation $f = |\sin \theta_s - \sin \theta_i|/\lambda$, and Q is the so called polarization reflectance, which is angle

dependent and contains information about how the material affects the reflected light. Q is also dependent on the complex dielectric constant and the scatter angle, along with the polarization state of both the incident and scattered light. A discussion of evaluating Q for different material cases, incidence angles, and polarization is discussed in [91], but for $\theta_i = 0^\circ$, Q is simply the reflectance:

$$R = \left(\frac{n - 1}{n + 1} \right)^2, \quad (1.9)$$

with n being the index of refraction. ARS is also known as the cosine-corrected bidirectional scatter distribution function (CCBSDF) in some literature, with the difference between BSDF and ARS being an extra $\cos(\theta_s)$ term in ARS, hence the cosine-corrected addition. It should be noted that equation 1.8 is only valid in the so-called smooth surface regime, being a loosely defined ratio of $\sigma/\lambda \ll 1$. Authors have reported acceptable ranges to span from 0.01 to 0.05[86, 91, 102], although higher values can be used with the understanding that low scatter angle will overestimated the ARS.

When it comes to dealing with scattering from the surface/bulk defects, the theory becomes more complicated, and can often be a moot point to calculate for manufacturing purposes. Typically scratches or bubbles in a lens are large enough that they can be spotted quickly under operator inspection under a microscope, and for this reason the scratch/dig standard set by the United States military for fire control optics, MIL-PRF-13830B, is often used[64]. It sets a maximum allowable number of defects per surface area of an optical component, and also takes into consideration bubbles within a part. For high-powered laser optics this might not be sufficient, however, and individual scattering experiments may need to be performed in an integrating sphere type experiment. To summarize briefly MIL-PRF-13830B, the document offers how to quantify the severity of a scratches based on their total length and number on the optic, and offers limits per surface area of the component. It also notes how to classify digs,pits, and bubbles (a

bubble is treated as a dig) in terms of their diameter and quantity per surface area of the component. Details for anti-reflective coatings can also be found.

1.4.3 Zernike Polynomials

Zernike polynomials can be described as a set of polynomials which are all orthogonal on the unit disk. They are frequently used in the analysis of optical components to determine the different types of wavefront aberration present within a system, where the different ordered polynomials represent different aberrations. They can be calculated via the following equation for the even and odd polynomials:

$$Z_n^m(\rho, \varphi) = R_n^m(\rho) \cos(m, \varphi) \quad (1.10)$$

$$Z_n^{-m}(\rho, \varphi) = R_n^m(\rho) \sin(m, \varphi) \quad (1.11)$$

where φ is the azimuthal angle between 0 and 2π , ρ is the radial distance between 0 and 1, and R_n^m are radial polynomials given by, when $n - m$ is even,

$$R_n^m(\rho) = \sum_{l=0}^{(n-m)/2} \frac{(-1)^l (n-l)!}{l! \left(\frac{n+m}{2} - l\right)! \left(\frac{n-m}{2} - l\right)!} \rho^{n-2l} \quad (1.12)$$

and zero for the case of $n - m$ being odd. n and m are integers with $n \geq m \geq 0$, and n is positive. Considering a plano-convex lens incident with collimated light, the wavefront distortion is proportional to the shape of the convex surface, and we can make use of this to analyze our surface profiles. A surface can be fit by a summation of the various ordered polynomials, along with an accompanying order coefficient (known as the Zernike coefficients), where the value for the coefficient determines the strength of that particular aberration (e.g. $Z_{surf}(x) \approx A_1 Z_0^0 + A_2 Z_1^1 + A_3 Z_1^{-1} \dots A_i Z_n^m$, where A_i are the coefficients). Care must be taken when working with Zernike polynomials, as there are several ordering

Fig 1.3: The first 16 Zernike polynomials plotted over the unit disk. Polynomials are given in both n, m notation (Z_n^m), and Noll index notation[71].

schemes which are used to determine a linear index scheme from the n, m indices. We use the Noll index scheme for measurements[71], which can be found in table 1.1 for the first 16 coefficients. In table 1.1 we also show the name of the corresponding optical aberration which the n, m pair represents in column 3. Similarly, the first 16 Zernike polynomials have been shown plotted over the unit disk in figure 1.3.

1.5 Reconfigurable optics

A discussion on the manufacturing of optics would not be complete without mention of reconfigurable optics. These are nontraditional in the sense that they are no longer bound to the strict shape requirements of traditional manufacturing, as their entire purpose is to be adjustable. Some of the most common ones are spatial light modulators, liquid lenses,

n , m	Noll index	Aberration
0, 0	1	Piston
1, 1	2	Tip (Horizontal tilt)
1,-1	3	Tilt (Vertical tilt)
2, 0	4	Defocus
2,-2	5	Oblique astigmatism
2, 2	6	Vertical astigmatism
3,-1	7	Vertical coma
3, 1	8	Horizontal coma
3,-3	9	Vertical trefoil
3, 3	10	Oblique trefoil
4, 0	11	Primary spherical
4, 2	12	Vertical secondary astigmatism
4,-2	13	Oblique secondary astigmatism
4, 4	14	Vertical quadrafoil
4,-4	15	Oblique quadrafoil
5, 1	16	Horizontal secondary coma

Table 1.1: Names of the first 16 aberrations represented by the Zernike Polynomials.

and electronically actuated lenses.

1.5.1 Spatial light modulators

Spatial light modulators are a unique type of reconfigurable optic that makes use of arrays of individually adjustable components. These individual components can either be miniature mirrors, or liquid crystals such as those in a computer monitor.

Digital micromirror devices

Micromirror arrays, or Digital Micromirror Devices (DMDs) were first patented by [18] in 1973, and later commercialized by Texas Instruments for large scale production. These devices consist of millions of individually addressable mirrors which are tilted to either an *on* or *off* position based on an applied voltage to a piezoelectric actuator. They will typically tilt to around $\pm 12^\circ$ in either direction, and can switch at frequencies up to tens of kilohertz. While these are inherently binary devices, grayscale can be rendered on

them by using time averaging and pulse-width modulation, where over a given time frame, the mirror will be set to the *on* state for a fraction of the time, where the length of time that it is in the *on* state reflects the gray value which it represents. For example, if a system with 8-bit modulation (256 possible values) was considered, and it was desired to have two pixels, P_1 and P_2 , at values of 128 and 256, this could be accomplished by, over a fixed time frame, having P_1 be in the *on* state for half the time of P_2 .

The manufacturing of these type of devices follows a standard series of wafer level processes where a base substrate can be made with either subtracted or additive processes, such as focused ion beam or by lithographic patterning. For a focused ion beam approach, a substrate is bombarded by heavy ions which have been tightly focused and scanned across the surface, eroding the underlying substrate. In a lithographic process, photoresist is exposed to create a pattern, where the pattern is then developed. From here, the substrate can either be acid etched to remove material, or have others deposited on top. After this step, the excess resist is removed, leaving behind the intended shape.

Liquid crystal on silicon

The other type of spatial light modulators are known as Liquid Crystal on Silicon (LCoS) devices, or simply Liquid Crystal Displays (LCD). These devices are arrays of individually addressable birefringent crystals, and the particular difference between them is whether they are transmission or reflective, LCoS being reflective. These displays use twisted nematic liquid crystals, which reorient themselves under application of an electric field. This provides them with electrically tunable birefringence, allowing the polarization to be modulated via applied voltage. Depending on configuration, these can be used for amplitude modulation, phase modulation, or a combination thereof.

These liquid crystal modulators will often be composed of a layer of liquid crystals sandwiched between glass/silicon. They will have two electrodes on either side, with one common to all. They will also contain two layers on each side known as alignment layers,

which will set the initial alignment of the crystals by maintaining some passive charge. In the past, this layer has typically been composed of a polymer coating which has been rubbed with a felt cloth[38]. The individual pixel electrodes on the other side of the common electrode will generate a local electric field in the region of the pixel, aligning only those pixels in the path between the pixel and common electrode.

1.5.2 Tunable lenses

Mechanically/electromechanically actuated elastomer lenses

Both mechanical and electronically actuated lenses will typically consist of some flexible polymer which has been molded to an approximate shape, and then use an applied force around the edges to distort the lens. A common choice of material for this process is polydimethylsiloxane (PDMS). One approach to produce a lens which is mechanically actuated can be seen in [3], where the authors use an injection molding type of process to set a basic lens shape in PDMS, and by placing the formed lens in a lens tube with a retaining ring are able to adjust the focal length via compressive force.

Lenses which are electromechanically modulated can be created via a similar casting technique, but with replacement of the purely mechanical components with electronically actuated ones. One example of this is given in [29], where they use a dielectric elastomer actuator (DEA) to compress a premolded PDMS layer to correct for optical aberration. They have made use of a 4-sectioned DEA, allowing for control of both horizontal and vertical astigmatism by activation of two electrodes, or defocus by activation of all four. Another example is given by [58], where the authors use a molded PDMS lens with metal anchors attached on four sides. These anchors are then pulled normal to the lens wall via electromagnets, creating strain/deformation in the lens and change in lens curvature.

Liquid / semiliquid lenses

Purely liquid lenses are closed cell devices which contain two immiscible liquids inside: one which is conductive and one which is nonconductive. They work on the principle of electrowetting, where the wetting ability of one of the liquids will be determined by a voltage applied across electrodes at the edge of the cell. As the cells are without air and the liquids used are typically of the same density, these are also isolated from vibration. One of the key producers of these lenses is Corning Inc. under the trade name Varioptic[39].

Another notable type of liquid lens is the tunable acoustic gradient (TAG) lens created by the Craig Arnold group[63], which used acoustic actuation to variably adjust the index of refraction of a liquid. A piezoelectric actuator is operated to create standing waves within a closed liquid medium, and the resulting differences in fluid density modify the index of refraction. Unlike electrowetting liquid lenses, TAG lenses contain a single fluid.

Aside from these two category of lenses, semiliquid lenses can also be considered. These lenses will typically consist of a liquid reservoir which is enclosed by a rigid backing and a flexible cover. By adjusting the amount of liquid in the reservoir, the curvature of the flexible membrane can be adjusted. The most prominent current method is to compress the liquid reservoir using piezoelectric actuators[35, 72, 85], although this can also be done with electric motors, electrostatic actuators, etc.

1.6 Motivation to use 3D printing for optical manufacturing

After reviewing the techniques in this chapter, some general trends can be observed for non-adaptive optical components. For refractive optics made in glass, the machinery involved can be very costly, and depending on the complexity of the optic can be very time consuming to produce. For plastic molded optics, a similar trend follows for the

cost of small quantities, as a suitable mold must be machined with appropriate surface quality. For grayscale lithography and TPP, the machinery required is similarly expensive for commercial options.

One emerging technology that may be able to close the cost/time gap is 3D printing, otherwise known as rapid prototyping, and offers design flexibility such that the created shape is independent of surface type (i.e. freeform, aspheric, or spherical). Different printer methods are thoroughly discussed in the next chapter with the context of optical components in mind, along with their limitations. A subsection of these printing methods (similar in principle to that discussed in 1.3.1) is also used as the foundation of our research, and the remaining chapters are used to describe the necessary knowledge and processes. We should note that while TPP discussed in this chapter is a type of 3D printing, the femtosecond lasers required to produce sufficient two-photon absorption are very costly, and UV based single-photon alternatives can instead be considered which do not require such specialized light sources.

Chapter 2

Printers and Polymers

**note: The theory discussed in the latter half of this chapter is used extensively in chapter 4 to analyze obtained experimental data. Chapter 3, however, discusses design of the experimental apparatus necessary to obtain said data, and primarily relies on the former half of this chapter drawing from the discussed printing techniques.*

2.1 3D Printing for optical fabrication

While the previous chapter introduced the more traditional methods to fabricate optical components, these all share a common feature that they require extremely specialized equipment which often comes at a very high cost. It could also take a substantial amount of time to have one component created. One alternative to this would be to take a 3D printing approach. While still in its infancy in many ways, and depending on the technology can rival the cost of the traditional methods, we will now discuss the application of 3D printers to optical fabrication and cover recent work in the field, but will first begin by explaining the different types of technology available. The type of fabrication can broadly be separated into three areas: thermoplastics, photoactivated resins, and metals.

2.1.1 Thermoplastic printers

One of the most common printing technologies is that which is called fused deposition modelling (FDM). These are the type typically owned by hobbyist and used in classrooms due to their inexpensive nature. In general, they operate by heating various thermoplastics just above their melting point, and depositing the chosen plastic in a layer-by-layer fashion according to a CAD drawing. Typically, a motor will feed the plastic, or filament, into a heated nozzle at a user-defined rate, where it is subsequently forced out through a smaller diameter hole at the tip. As the filament cools below its melting point, it re-hardens, leaving behind a solid strand of plastic. The entire nozzle is placed on a 3-dimensional XYZ stage operated by stepper motors and pulleys/lead screws, allowing for controlled placement of the heated plastic.

In terms of optical components, this method is mostly limited to that of light guides and parts which do not require a precise shape, as these printers can not provide the accuracy necessary for high-precision optical fabrication. Some good examples of light guides being used are given in [27] and [104]. Both of these show use of printing with multi-color printers, where a frame is printed with an opaque thermoplastic while the light carrying component is printed in a clear thermoplastic. While there are a large variety of plastics which are currently being used for printing, the most common two are polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS).

2.1.2 Photoactivated resin printers

Resin based printers are the predominant method for printing optical components as of the time of writing, and the focus of the research in this thesis. All of these printers work by using a photoactivated resin and under irradiation in a particular pattern, form a part layer-by-layer. A detailed discussion of the resins themselves will be given in section 2.5. The primary methods for resin printing are stereolithography (SLA), digital

light processing (DLP) and poly-jet modeling(PJM). There is also the use of two-photon photopolymerization, which provides the most true-to-shape parts, but is limited to small features.

Sterolithography

SLA based printing is the oldest form of resin printing, and in this process resin is cured via scanning a UV laser over a resin, curing as it goes. A steering mirror will typically be used to direct a focused laser in a raster-like motion, with the velocity and laser power governing the exposure of the resin. Printing of this sort is carried out in a top-down fashion, where a stage is placed inside a deep vat of liquid resin just below the surface. The laser is scanned, and after each successive layer, the stage is lowered deeper. Normally this method will require that a part be recoated with fresh resin after each exposure via a mechanical recoater moving across the surface. The primary drawback with this technique is that your resin vat must be deep enough to encompass the entire part which is being printed, making it costly for large parts. This drawback can be negated however by using a modified version of this technique where the illumination is inverted, and the resin cured from the bottom of the vat. In this configuration the stage is placed just above a bottom window (with a distance of the layer height). The unique aspect of this method is that the bottom window is made of an oxygen permeable membrane, which prevents polymerization close to the window due to the oxygen inhibition effect[99] (See section 2.6.1 for discussion). This allows the printed part to cure entirely on the stage without sticking to the window, and the stage can be raised to repeat the layers. The window is typically made of Teflon.

Digital Light Processing

DLP type printers work in a similar method to that of SLA printers in regard to their mechanical configuration, but differ in the illumination system used. A DLP printer will

expose an entire layer at once by projecting an image of the surface of a spatial light modulator, making this a form of maskless lithography.

Poly-jet Modeling

Poly-jet type printing makes use of a printer head like that found in a traditional 2D printer. The print head will be placed on a movable stage, and as a liquid resin is dispensed from the nozzle, UV lights attached to the head will cure the dispensed ink. One of the advantages of this technique is that it does not require a resin vat, and that multiple colors can be used in the printing process if the head is configured in such a way.

2.2 Metal Printing

Aside from thermoplastics and resins, there is also the possibility to print in metal. The printing techniques involved with this are selective laser sintering(SLS), selective laser melting(SLM) and laser power bed infusion(LPBF). In these processes, CO₂ or Nd:YAG lasers are used to sinter/melt powdered material within a build chamber. They will operate with the same mechanical principle as sterolithography via the top-down approach, and after each successive layer require recoating of powder on top of the newly created layer. Typically the powders used in these systems have particle sizes in the 50 μm range, and must be sintered under an inert gas environment. After part creation, the part will need to be cleaned and polished to improve the surface quality.

2.3 Challenges for printing optics

One of the key challenges for printing optics, or any smooth surfaces for that matter, is to overcome what is known as the stair-stepping effect. This can be described as the waviness generated on the surface as a result of the finite layer height, where lines between the

Fig 2.1: (Left) pictorial representation of the stair-stepping effect, where deviation from an ideal shape is generated by the finite layer size on a printer. a) Shows a sample plano-convex lens printed on a commercial SLA printer after cleaning, where b) shows this same part after recoating with fresh resin and curing.

successive layers can be seen on the printed component. A pictorial representation can be seen in figure 2.1, where the left most image depicts the rough ridges that can be formed due to the discrete nature of the layers. The right images depict plano-convex lenses printed on a commercial SLA printer in our lab, where a) shows the lenses *as is* after cleaning away excess resin. b) shows the same lenses after they have been re-dipped in the original resin and cured. The dipping/recoating process has been thoroughly explained in the work of [73] and [100], where for surfaces which are facing upwards, by properly controlling the layer height and allowing gravity to pull the resin down the surface of a part, the piece can be smoothed by the meniscus formed along the edges of the layers. This method, while reducing the stair step effect, does not entirely remove it, although the work for [100] has shown very promising results for high resolution prints. For downward facing surfaces (such as the bottom three layers seen in figure 2.1), a gradient exposure can be used on the region between the layers to create a smoothed surface[79, 92].

2.4 Current work in the field

While challenging, there are several notable projects which have produced medium to large scale optical components. The work of [14] uses a combination of [73] and [79] applied to top-down type printing, where the authors use a DLP style system which projects on to a resins surface. They then create a mask which utilized a grayscale exposure pattern between the layers. Theoretically, this would create freestanding "spikes" from the edges of the part because, as the exposure is decreased, the cure depth into the resin will also decrease. If the cure depth is below that of the layer height, partial cure will create a freestanding ledge between each layer. As the part is raised above the surface of the liquid, the spikes would be pushed down by the weight of the liquid, forming a smooth surface between layers. The authors claim a surface roughness under $S_a < 7nm$ from a plano-aspheric lens with deviation less than $2\mu m$ near the edges of a lens of diameter $D = 2mm$. The same author later improved on this technique by using an inverted configuration with an oxygen inhibition window[88], where the window is described in [99]. Instead of using discrete layer heights, however, the author used a continuous exposure with a stage moving at a constant velocity (as done in [99], but not for optical applications). This method is traditionally called continuous liquid interface production (CLIP), and improves the throughput of a system. They claim a roughness of $S_a = 15nm$, but were able to print a $3mm$ high aspheric lens in under 2 minutes. The created asphere had an imaging resolution of $3.1\mu m$.

Another notable printing techniques comes from [45], where they use a similar optical/mechanical configuration to [14] described above. The authors of [45] however, make use of a resin system which consists of both free radical initiators and cationic initiators (see section 2.6.1 and 2.6.2 for discussion), which is based on a mix of acrylates and vinyl ethers to tailor the properties of the reaction[61]. The authors were able to achieve a surface roughness of $S_a = 25nm$ and deviation from desired shape under $200nm$ near the

edges of a plano-convex lens with diameter $D = 2mm$. By using a hybrid mixture, the authors were able to control the direction of cure of the photoresin, allowing for either bottom-up or top-down curing per layer, regardless of the fixed top-down configuration of the system.

A simplistic approach has been performed by [6, 100] where after printing a component on a commercial SLA printer, they recoat the component with fresh polymer and spin coat the piece to spread the resin over the surface. They are both able to achieve surface roughness on the order of $S_a = 20nm$, but the optical components created are larger in nature (1" Diameter in [6], several inches in [100]). In [100], they then proceed to deposit aluminum films on the surfaces to create reflective optics.

In terms of PGM printing, the prominent application of this technology towards optics comes from the company Luxexcel[1]. In their process, a traditional 2D printer head is used to disperse micro droplets of liquid resin, which are then cured using UV irradiation from the print head. They report achieving surface roughness values of less than $12nm$ for some large scale freeform surfaces. They have also created ophthalmic lenses with air gaps in the center, allowing for bespoke on-eye displays to be created.

2.5 Radiation curing of polymers

While the technology behind the various types of 3D printers is one major aspect to consider when attempting to print optics via the polymerization route, the other is which polymer system to choose and how it will behave. While some systems which use a top-down type scenario (described in section 2.4) are less sensitive to the resin used, other methods such as that attempted in this thesis require precise knowledge of how the resin will respond under different conditions. We will now cover the theory which is necessary to understand the results and methodology behind the later chapters.

We start with a description of the most commonly used equation for polymer based

Fig 2.2: A simplified illustration of the photopolymer system under consideration. A monochromatic light source (typically UV) passes through the window, resulting in polymerization of the underlying resin, curing from the glass surface down into the pool.

printing, and then delve deeper into the chemistry involved and more developed models. All models shown here will consider a system with a large pool of photoinitiated resin which is illuminated by a monochromatic source of either a scanning laser, or by a fixed LED. Differentiation will be given when each is used, but for the most part the equations are interchangeable. The illumination will pass through a window and polymerize the resin closest to the window first. Figure 2.2 provides an illustration of this simplified system.

In 1992, Paul F. Jacobs described photopolymerization from the standpoint of a laser beam scanning across a resin surface[22], as used in many stereolithographic 3D printers, and developed what has since become the standard working curve equation. As it is fundamental to the field, we will show its derivation in this section for our specific experimental configuration, and then later in the chapter discuss the limitations of this model and further discuss how this model has evolved over time.

The process of photopolymerization within a resin obeys the Beer-Lambert law of absorption, where given a system with the normal of the resin surface defined in the Z-direction, the absorption of a photon decays exponentially with the penetration depth

into the resin. This process, when applied to a system with a uniform exposure across a given surface area, can be derived using simple calculus. Starting with the Beer-Lambert law:

$$I(x, y, z) = I(x, y, 0) \exp(-z/D_p) \quad (2.1)$$

where $I(x, y, z)$ is the irradiance at some given point, $I(x, y, 0)$ is the irradiance on the surface of the resin at this same point, and D_p is the penetration depth into the resin which is dependent on the wavelength. As mentioned, this process was described for a scanning laser over a resins surface. We have instead adapted his methodology to describe uniform illumination by a perfectly homogenized top-hat beam of radius W imaged on to a resin's surface, as in our own configuration. We start by defining the illumination as

$$I(x, y, 0) = I(r, \theta, 0) = \begin{cases} I_o, & \text{for } r \leq W_o \\ 0, & \text{for } r > W \end{cases} \quad (2.2)$$

Given the irradiance distribution and considering only the region inside the beam, we can integrate over the area of exposure to determine our source power, P , as a function of the irradiance. Starting with the power our of top-hat source as:

$$P = 2\pi \int_0^W I_o r dr = \pi I_o W_o^2, \quad (2.3)$$

we can then rearrange to determine I_o as

$$I_o = \frac{P}{\pi W^2} \quad (2.4)$$

giving us the final solution for our irradiance as

$$I(r, \theta, z) = \frac{P}{\pi W^2} \exp(-z/D_p), \quad \text{for } r \leq W_o \quad (2.5)$$

Next, in order to determine the exposure of our sample, we integrate this over the exposure time to get the total energy, or dose, of the exposure

$$E(r, \theta, z) = \frac{Pt}{\pi W^2} \exp(-z/D_p) = E_o \exp(-z/D_p). \quad (2.6)$$

Under irradiation, a photopolymer will begin to polymerize once it reaches a particular threshold of energy, called the gel point. Any energy above this will begin to see some degree of crosslinking of the polymer, where anything under will be too loosely crosslinked to form a solid. Setting equation 2.6 to E_c and solving for $z = C_d$ (The cure depth of the resin at this critical point), we can derive the commonly seen Jacobs working curve equation:

$$C_d = D_p \ln(E_o/E_c). \quad (2.7)$$

For a specified exposure time, the Jacobs working curve equation holds quite true. In fact, we use it to analyze some of the data in this thesis as well due to its ease of use. However, this equation does not consider the underlying chemistry involved in the process, and will fail when the exposure time is changed if the photoinitiator used to start the reaction undergoes photobleaching. When this occurs, a nonlinear dependence of the cure depth on E_o arises. Experimental evidence for this can be seen in Chapter 4 figure 4.3. One could also expect slight deviation in the penetration depth (and therefore the absorption) as photoinitiator is consumed locally, but as the percentage of initiator is typically quite small in a resin (2%w or less), this effect is predicted to be small. It would also be less pronounced in slower curing reactions which allow for fresh initiator from the rest of the

bath to diffuse into the sample. There are however different adaptations/approaches to fill the shortcomings of equation 2.7, which will be discussed later in the chapter in detail. As these methods take into account the the underlying chemistry of a resin system, we will first discuss the basics of polymers.

2.6 Polymer Chemistry

A typically resin for photopolymerization will often contain a mixture of prepolymers, initiators, and other additional types of additives to control the desired physical properties. A prepolymer is just as its name would suggest - it contains the building blocks necessary which act as the base for the polymer. They are often either monomers or oligomers, where an oligomer is a larger, more complex, version of a monomer in simplified terms. A typical polymerization reaction will occur via the following route: *Initiation* of the reaction will start when the initiator will decompose into a reactive species via some mechanism (discussed later). One of the prepolymer bases will then link with the reactive species, which will in turn create another reactive species to link with another prepolymer, leading to a chain reaction called *propagation*. The reaction will end when two chains connect end-to-end, or another activated initiator caps off the chain, thus leading to a process known as *termination*. As the chains begin to form a dense, solidified network, the process is described as *crosslinking*.

In general, for photopolymerization there are two primary methods to consider, free radical and ionic polymerization, with the former being the most popular for 3D printing. These will be discussed individually in the following subsections.

2.6.1 Free radical polymerization

A radical is a molecule (or ion / atom) which is missing a valence electron, and for this reason is highly reactive. Falling in line with this, a free radical photoinitiator is one

that, under absorption of a photon, will decompose to form highly reactive radicals. High reactivity yields a high reaction rate, and as a result free radical initiators are often chosen for 3D printing because they allow for localized control over initiation and termination of the polymer chains. In other words, if a radical is created within a bath of resin, it will not travel very far from the initiation site before reacting with a prepolymer molecule and therefore diffusion will be limited. Similarly, a quick reaction rate prevents a process known as *dark initiation*, where polymerization will continue after light exposure has ceased (as the radicals will be consumed within a very short time after being generated). Free radical initiators are normally used to polymerize acrylates.

One drawback to free radical initiation, however, is that because the radicals are so reactive, they can react with other atoms or molecules foreign to the polymer bath, and in particular with oxygen. This leads to what is called the oxygen inhibition effect, where free radicals are scavenged so extensively by oxygen that the reaction with the prepolymer is limited, or even fully quenched. In terms of 3D printing, this can have dire consequences. For this reason, the printing community has found ways around this by either exposing resins in an inert gas / vacuum environment (as done in this thesis), or has made use of the effect in a positive way. That is, by placing an oxygen permeable membrane at the bottom of a resin bath, and placing a stage within the resin bath just above the window, a thin layer can be cured onto the stage through the window without sticking, as the resin closest to the window will experience a polymerization “dead zone” with a strong oxygen inhibition effect, while the region near the stage will be oxygen depleted[99]. This allows a solidified layer to form only on the stage, where it can be mechanically moved back and the process can be repeated.

It is our experience, and also noted by [80], that for bulk systems the oxygen diffused within the resin is non-negligible, but the effect is more severe near an oxygen/resin interface. For the case of a permeable window described above, the phenomenon still makes sense however because the local oxygen between the stage and window is fully

consumed due to the small volume between the stage and interface, leaving an oxygen depleted space for polymerization closer to the surface of the stage.

2.6.2 Ionic polymerization

Ionic polymerization, on the other hand, initiates through disassociation of an initiator to form an acid or base (photo-acid generation or photo-base generation). These will then proceed to start the polymerization reaction. The primary draw for ionic polymerization is that it negates the effect of oxygen inhibition as the initiation mechanism differs. However, this can also be difficult to use with 3D printing because once started, the reactions tend to continue regardless of if they are being irradiated in a process known as dark polymerization. These often tend to be vinyls or epoxides. For this thesis we choose to stick to free radical initiators and acrylates, so we will direct discussions to these going onward.

2.6.3 Photoinitiation

Photoinitiators can be classified into three different types, based on the reaction types discussed in the previous subsection: free-radical, photo-acid generators(cationic), or photo-base generators(anionic). While different in their mechanism, they all follow the general formula that they absorb a photon, undergo a chemical change, and in turn trigger a chain reaction within the polymer.

For free radical initiators, they are divided into two categories- Norrish type I and Norrish type II- based on whether they can function with or without a co-initiator present. For both types of initiator, the process begins when a photon is absorbed by the initiator, adding energy to the system, and therefore causing an electron to be excited to an elevated energy state. This electron can then either relax to the ground state via a radiative or non-radiative process, or undergo an intersystem crossing into a triplet state. The electron

transferring to a triplet state means it is no longer coupled to its ground state electron, as its spin has reversed and they are now of the same sign. At this point, the electron may relax to the ground state via phosphorescence, or depending on the type of the initiator, homolytic cleavage / energy transfer (hydrogen/electron donation) will occur. Figure 2.3 shows a simplified Jablonksi state diagram of this process, where the first singlet excited and ground state are represented by S_1 and S_0 , and the first triplet state is represented by T_1 . Type I initiators undergo homolytic cleavage of their covalent bonds to form two free radicals on their own, and therefore do not require a co-initiator. Type II initiators on the other hand function as either hydrogen(electron) abstractors or hydrogen(electron) donors, where they must be paired together in order to operate. In a type II process, under absorption of a photon, the initiator will take a hydrogen(electron) from the co-initiator, making the co-initiator reactive towards the prepolymer base as it is left with a dangling unpaired electron. We note that *electron* is in parenthesis because, depending on the composition of the initiator, either a hydrogen atom or an electron can be transferred.

Figure 2.4 shows four common free radical initiators, where the initiator used extensively in this thesis is phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide (BAPO), and has strong absorbance peaks at 290nm and 370nm[11]. It is often sold under the trade-name Irgacure 819. Under irradiation with UV light, it cleaves between the phosphine and carbon bonds in a series of two reaction (one cleavage for each bond). This would provide a total of 3 radicals per molecule. b) cleaves between the carbon-carbon bond to form two radicals. c) and d) are type II initiators and would need to be used together in a co-initiator system, as one acts as a hydrogen donor and the other and an abstractor. After c) abstracts a hydrogen from d)'s double bonded oxygen, d) would act as the radical.

Fig 2.3: Diagram depicting the possible states under absorption of a photon by a Type I free radical photoinitiator. The route for polymerization is as follows: An electron will be excited to state S_1 , whereby it will undergo an intersystem crossing to state T_1 . As the spins will then be decoupled, the covalent bond will undergo homolytic cleavage, creating two radical species.

Fig 2.4: Chemical structure of four common free radical initiators. The structure shown in a) is the initiator used extensively throughout this thesis.

2.6.4 Prepolymers

Once a radical has been generated, it will now carry on to interact with the prepolymer base in a mixture to form long chains which eventually terminate to form a crosslinked matrix. To control the final properties of this matrix, a cocktail of oligomers or monomers is typically chosen where each component will have characteristics which are desired, and a compromise can be met by mixing them. For example: does the final matrix need to be rigid, flexible, or have strong chemical resistance? Perhaps it needs to be able to withstand high temperature and have high abrasive resistance instead. By choosing base polymers that are both compatible with each other, and display the desired properties, a resist can be fine tuned. This being said, a mixture is not necessary and often a single monomer can be used.

The prepolymers most frequently chosen for 3D printing fall within the acrylate family. This is due to their quick ability to react, preventing the effects of dark polymerization. One aspect to consider when choosing a prepolymer is its functionality - that is how many reaction sites it has available. Typically the more reaction sites, the more dense of a crosslinked network which can be formed. This can be beneficial, but at the same time typically higher functionality leads to an increase in the molecular weight of the liquid, and therefore its viscosity. Whether this is ideal or not would depend on the application. If it is desired for the prepolymer to be deoxygenated, we have found that higher viscosity requires longer times in an inert environment to fully remove oxygen from the system.

2.6.5 Additives

Besides the prepolymers and initiators, often in a particular mixture other additives are included such as UV absorbers, optical whiteners, fillers, or inhibitors. UV absorbers work by absorbing some of the incoming light and transferring it to energy in the form of vibration or rotation. They can be beneficial to control the reaction rate of a polymer,

and also the depth at which light can penetrate into the resin. In terms of additive manufacturing, these are very commonly used to adjust the curing depth of a resin for a set exposure to tailor a resin to a particular system. This prevents over-curing of the part and allows finer control of the curing process. As many resins have a yellow hue (as they absorb in the blue/UV), optical brighteners are sometimes added to improve the final look of the cured part. These work by absorbing some of the incoming UV radiation, and re-emitting it in the blue range, therefore compensating the lack of blue light within the reflected spectrum. For practical purposes, this is simply for aesthetics. For most prepolymers ordered, they will also include some parts per million quantity of inhibitor added. These are used to scavenge free radicals which may be present within the mixture, so as to not trigger unexpected polymerization during transportation. It is important to note that aside from these additives, another source of strong radical scavenging comes from oxygen, and it can drastically change the characteristics of a polymerization reaction. One final source of additive is the filler, which can range anywhere from quantum dots and other nanoparticles to silicon dioxide to tailor the properties of the polymer. For example, resin dental filling are often packed with silica and other additives to thicken them and provide strength. Another application of this can be seen in the work of [51], where they have added silica nanoparticles into their printed components, and further placed them in a furnace to remove the polymer matrix, leaving behind a sintered glass printed part.

2.6.6 Kinetic analysis approach

As mentioned at the end of section 2.5, the approach of using a Jacobs working curve only applies for a specific set of dose conditions. This has been noted by several studies ([7, 12]) without comprehensive analysis. We will now provide an overview of current work in the field which approaches the issue from a kinetic analysis standpoint. Before

doing so, however, it is important to note that the kinetic analysis approach typically looks at the different components of the polymerization process as taking place at a given rate. That is, initiation, propagation, and termination all proceed at rates given by terms R_i , R_p , and R_T , and are naturally related to one another. They are also related to the concentration of prepolymer (or monomer) $[M]$ and concentration of photoinitiator $[PI]$. The reaction rates themselves also typically have some characteristic constants which are given by k_i , k_p , and k_t , which can themselves be initial condition dependent.

In section 2.5 we also spoke of a critical gel point which defines a cure depth in a photocuring system. This can be defined in more appropriate terms by considering the degree of polymerization of a system, X_n . The degree of polymerization can be defined as the ratio between the concentration of unreacted monomer at some point in the polymerization to the initial starting concentration:

$$X_n = \frac{[M]}{[M]_o} \quad (2.8)$$

where $[M]_o$ is the initial concentration of monomer, and $[M]$ is the concentration remaining after reaction. As the value of X_n ranges from 1 to 0, we can make it an increasing scale by subtracting from one[60]:

$$C_{eff} = 1 - \frac{[M]}{[M]_o} \quad (2.9)$$

which we define as the extent of polymerization, C_{eff} . We next consider a critical threshold value C_T , where when the extent of polymerization of a particular system reaches $C_{eff} > C_T$, the polymer matrix is considered dense enough to form a gel, and results in a solidified part with a particular cure depth (such as from equation 2.7 and 2.10).

One of the early works which tries a kinetic analysis approach is from Lee et al.[55], who uses kinetic equations for radical polymerization and an assumption that the concentration

of initiator in the system remains constant over time. Their equation for the cure depth, which is fully derived in Appendix B, can be described by

$$C_d = \frac{2}{2.303\epsilon[PI]} \ln \left(\frac{E_o[PI]^{0.5}}{\alpha\beta} \right) \quad (2.10)$$

where C_d is the cure depth, $[PI]$ is the initiator concentration, E_o is the dose, ϵ is the Molar extinction coefficient, and α and β are lumped photochemical properties and process parameters, respectively. The constants α and β are defined by the following equations:

$$\alpha^2 = \frac{k_t [\ln \left(\frac{1}{1-C_T} \right)]^2}{k_p^2 \phi \epsilon} \quad (2.11)$$

and

$$\beta^2 = \frac{chN_{av}P}{\lambda W_o^2 (2\pi)^{1/2}} \quad (2.12)$$

where in equation 2.11, k_p and k_t are the rate constants for propagation and termination, ϕ is the quantum yield of the initiator, and C_T is the critical extent of polymerization. In equation 2.12, c is the speed of light, N_{av} is Avagadro's number, h is Plank's constant, λ is the wavelength of the illumination, W_o is the Gaussian width of a scanned laser beam, and P is the power of the illuminating laser.

Drawing analog between equation 2.10 and 2.7, they predict that the penetration depth depends on $1/[PI]$ and the critical energy on $1/[PI]^{0.5}$. One of the unique features of equation 2.10 is that it predicts that there is an initiator concentration which will provide a maximum cure depth, given by the equation

$$[PI]_{critical} = \frac{2.718\alpha^2\beta^2}{E_o^2} \quad (2.13)$$

This allows for tailoring of a particular resin to achieve an optimal photoinitiator concentration. While this may be the case, during the derivation of equation 2.10, the authors make the assumption that the concentration of the photoinitiator remains constant over the duration of the reaction and is not consumed, and that the initiator does not photobleach. This leaves us with a similar issue which persisted for the Jacobs cure depth equation, which is that it will remain accurate for a specific set of dose conditions, but will fail if these conditions were to change. It also does not consider the effects of oxygen inhibition.

This work is particularly included because, to the best of our knowledge, it was the first to draw parallels between the concept of having a critical degree of polymerization for a polymer, which is typically measured via bulk processes like Fourier transform infrared spectroscopy (FTIR)[34, 84] or via differential photocalorimetry[33, 54], and between a tangible cure depth in a polymerizing system. In other words, it was the first attempt to crossover between the polymer world and printing world.

Around this same time, there was also a series of work published in parallel by [41, 65, 94], where in the study of thick polymer systems they consider the effects of photobleaching on the concentration of photoinitiator, and as a result, on the intensity within the sample. At the time this work was not considered in the context of 3D printing, and no attempt was made to carry this over to an equation for cure depth (this would be done later by [60]), but it did provide a foundation for understanding of these systems.

The key result from this series was that, due to the fact that as an initiator is irradiated, over time it will begin to photobleach at a certain rate proportional to the irradiance, and will also be consumed as a function of the same. The irradiance however, decreases as a function of the absorbance and depth penetrated within the sample. The photobleaching and the consumption of initiator will also result in a change in the absorbance of the resin. As a result of this complex relationship, the system can be explained by a set of

three coupled partial differential equations. They are as follows:

$$\frac{\partial C_i(z, t)}{\partial t} = -\epsilon_i \phi_i \left(\frac{I(z, t)}{N_A h \nu} \right) C_i(z, t) + D_i \frac{\partial^2 C_i(z, t)}{\partial z^2} \quad (2.14)$$

$$\frac{\partial C_{pb}(z, t)}{\partial t} = \epsilon_i \phi_i \left(\frac{I(z, t)}{N_A h \nu} \right) C_i(z, t) + D_{pb} \frac{\partial^2 C_{pb}(z, t)}{\partial z^2} \quad (2.15)$$

$$\frac{\partial I(z, t)}{\partial z} = -[\epsilon_i C_i(z, t) + A_m + \epsilon_{pb} C_{pb}(z, t)] I(z, t) \quad (2.16)$$

where $C_i(z, t)$, $C_{pb}(z, t)$, and $I(z, t)$ represent the molar concentration of the initiator, the molar concentration of photobleached initiator, and the irradiance, all as a function of depth z and time t . The constant ϵ_i and ϵ_{pb} are the molar absorptivity of the initiator and of the photobleached species, and the constant ϕ_i is the quantum yield of the initiator. The quantum yield is defined by the ratio of absorbed photons which lead to cleavage of the initiator. D_i and D_{pb} are the diffusion coefficients for the initiator and photobleached species, and A_m is the absorption coefficient of the monomer. N_{av} is Avagadro's number, h is Plank's constant, and finally ν is the frequency of the illumination. If diffusion is ignored,

While these equations shed light on how these systems behave, they are also cumbersome to solve and require numerical simulation. The works of [59, 60] offer some valid analytic solutions, while also showing the behavior under variation of each of the components. They start by considering each part of a photoinitiating system by component in a single monomer and single initiator system. That is, they consider a system such as that described in figure 2.3, where they will take into account the population of the triplet state and radical concentration. They also consider how this relates to the concentration of monomer, and how oxygen will effect the reaction. To re-summarize the process, under absorption of a photon by the initiator, an electron will be excited to an excited state(S_1), where it can either undergo an intersystem crossing to a triplet state(T^*), or relax back down to the ground state(S_0). Once in the triplet state, it will then result in scission of

the carbon bond to form two radicals (R and R'), or react with oxygen in the system to quench the process. These radicals would react with the monomer (M) to form chains which could propagate further, or crosslink with each other resulting in termination. Using the analytic formulas derived in [59] for the intensity of light and concentration of initiator,

$$I(z, t) = I_o \exp(-A'z) \quad (2.17)$$

$$C(z, t) = C_o \exp(-B't) \quad (2.18)$$

$$A'(z, t) = 2.3(a'C_o + Q) - A_1t \quad (2.19)$$

where I_o is the initial intensity, C_o the initial initiator concentration, a' the extinction coefficient of the initiator, Q the absorption coefficient of the monomer at the exposure wavelength λ . The term A' represents an attenuation coefficient which decreases with time by the $-A_1t$ term, where the A_1t terms describes the increase in intensity due to initiator being consumed. $-A_1$, along with the other coefficients, can be given by:

$$A_1(z) = 2.3(a' - b')C_oI_o z(83.6a'\phi\lambda) \quad (2.20)$$

$$B'(z) = (83.6a'\phi\lambda)I_o \exp(A''z) \quad (2.21)$$

$$A'' = 2.3\left(\frac{a' + b'}{2} + Q\right) \quad (2.22)$$

where ϕ is the quantum yield of the initiator, and b' is the extinction coefficient for photobleaching (otherwise known as the photolysis product). The term A'' represents the average absorption coefficient of the resin, and B' is a term to describe the consumption of initiator with light intensity. The additional numeric multiplication factors in these

equations are from the multiplication of physical constants. All units of length are in *cm* and all concentrations are in *mM*, where the rest are in their international standard unit.

Now taking equation 2.8 for the degree of polymerization and realizing that it is related to the concentration of radicals in the system by

$$X_n = \frac{[M]}{[M]_o} = \exp(-S) \quad (2.23)$$

where S is given by the time integral of $k_p[R]$. k_p represents the rate constant for radical to monomer linkage, where $[R]$ is the concentration of radicals. Rearranging equation 2.23 and dropping the brackets yields

$$[M] = [M]_o \exp(-S) \quad (2.24)$$

with the deoxygenated version of S given by

$$S = k_p \int_0^t \sqrt{0.5(83.6a'\phi\lambda)C(z,t)I(z,t)/k_t} \quad (2.25)$$

where k_t is the rate constant of termination. Equations 2.17–2.22 can now be used to create an analytical solution for S , yielding the function

$$\boxed{S_{analytic} = G(z,t) \sqrt{\left(\frac{83.6a'\phi\lambda C_o I_o(k_p)^2}{2k_t}\right) \exp(-2.3z(a'C_o + Q))}} \quad (2.26)$$

with

$$G(z,t) = \frac{1 - \exp[-0.5t(B'(z) - 0.5A_1(z)t)]}{0.5(B'(z) - 0.5A_1(z)t)} \quad (2.27)$$

where $A_1(z)$ and $B'(z)$ are given by equations 2.20 and 2.21.

As discussed earlier, when the polymer system reaches a certain extent of polymer-

ization, that is when $C_{Eff} = 1 - \exp(-S_{analytic}) > C_T$, a gel will be formed. For a part cured to a certain height, C_d , exactly at that height (the max height of the sample), the S -function would be constant for the set of parameters used to create that particular C_d . a' , b' , ϕ , and λ are all constants within these equations, but the behavior of k_p and k_t remains unknown and would need to be determined experimentally via other means. The experimental variables will be C_o , I_o , and t . The drawback of this equation is that it requires that the value of either C_T or K be determined beforehand, with K being defined as $k_p/k_t^{0.5}$. The value of C_T is characteristic of a polymer system, but depending on the mixture can fall anywhere within the range of 0 to 100% [26, 97].

Chapter 3

Projection Printer Design and Testing

3.1 Motivation

When deciding to pursue 3D printing techniques for optical components, we first considered existing technology in the market, and if an existing system could be modified to meet the need. We ultimately decided to assemble a new system for several reasons, with the primary being that most companies do not provide optical data for their systems, direct software access to the display hardware within their printers, or access to the controllers for the light units. Without the latter two, grayscale polymerization becomes prohibitively challenging. Furthermore, most low-end commercial systems within the same budgetary range in terms of DLP-style technology utilize a LCD display which acts as a dynamic mask, aimed at larger scale production. This is not suitable for a higher magnification system, where the pixel pitch is typically in the range of 35 μ m. To adapt a system such as this, one would need prohibitively large lenses or a longer optical path. There are also currently no grayscale-based commercial printing systems with exception of direct laser write and two-photon polymerization printers. In this aspect, there more

suitable option is to build a new system from scratch, as to modify other exiting technology would involve higher complexity, higher cost, and would hinder wider accessibility than an openly available design with off-the-shelf components.

3.2 First iteration - Top-down printing

**note: We have included this section in its entirety (methods and results together), as it is not relevant to the remaining thesis. It is used solely as a justification for the design route chosen, and is best left as a whole.*

As seen in section 2.1, there are several different printing techniques which can be used for the fabrication of optical components. We decided to pursue a route of bottom-up polymerization, but before doing so we attempted to replicate a top-down approach as described in [14, 92]. The mentioned technique makes use of the same physical mechanism as described by section 2.1-Digital Light Processing, where a stage is used to lower a sample further into a resin bath after each successive layer is cured, and each layer is cured in a single pass (rather than by scanning laser). The approach mentioned by [14, 92] is unique in that they add a grayscale gradient along the edges between projected images (for successive layers), which creates a smooth transition and reduces the severity of the stair-stepping effect. They also allow the part to retain a thin film of excess resin after creation, which is cured at the end. They claim to generate optical components with several millimeter height and surface roughness below $7nm$. If setup properly, the aforementioned technique would allow for optical components to be made which are not limited by the curing depth of a particular resin, and for this reason reproduction of experiments was performed.

Shown without accompanying imaging / illumination system, our device can be seen in figure 3.1, and consists of a removable resin pool, a sample holder, and a manual translation stage for vertical movement. Illumination is provided through the hole on the

Fig 3.1: Top-down small scale printer. A stage is manually lowered into a pool of resin under flowing nitrogen manually. Each consecutive layer is re-coated via dipping.

top of the container, and nitrogen is pumped into the bottom of the container. A hole around the micrometer handle serves as an outlet for the nitrogen gas. With sufficient gas flow, enough oxygen is purged to prevent the oxygen inhibition effect (See section 2.6.1). Conceptually, a printed part is produced by placing a substrate below the surface of the resin by a displacement equal to the desired layer thickness. After exposure, the cured resin is dipped further into the bath to re-coat the top, and returned to a position equal to the initial position plus the thickness of the new desired layer. The goal of this technique in regard to printed optics is to reduce the step height to a small range (approximately $5\mu m$), and use grayscale photopolymerization to smooth the transition between layers (see section 2.4). This creates a balance between printing time and surface degradation as a result of the stair step effect (see figure 2.1 for description/visualization of the stair step effect).

After several months of experimentation, this method was abandoned due to the inability of the resin to disperse over the top of a newly re-coated layer after dipping.

Fig 3.2: Temperature dependence of HDDA with 1% Irgacure 819 and 2% UV absorber BDO. Dotted line is for reference only.

It was found that for a desired layer height, after exposing, dipping, and returning to the next step height, surface tension caused an overly thick layer to form on the surface of the newly coated part, exceeding the step height. In order to quantify our observations, we calculated the expected film thickness following the work of Morey[66]. Based on his observations, it was found that at a given temperature, the thickness of a film on a plate lifted from a pool of liquid could be calculated by the relationship

$$t = k(vs)^n, \quad (3.1)$$

where t is the thickness, v is the viscosity, s is the speed of withdraw from a liquid, and both k and n are characteristics constants of the liquid. They observed that liquids typically have k and n values close to 0.015 and 0.63, respectively. We also follow suit and use these as estimation parameters, as the speed in our experiment was controlled by hand rotation of the micrometer, making it infeasible to determine these values through fitting. As the goal at this point was to establish if the method was “in the ball park”, these approximations were accepted. The viscosity vs temperature results are shown in

Fig 3.3: Viscosity versus stage speed at temperatures of 23, 40, 50, and 90C. Values were typically observed in the range of the gray box with step height set to 50 μm . Inset shows a zoomed-in scale at lower stage speeds closer to the desired range of 5 μm .

figure 3.2 for the photopolymer HDDA with 1% photoinitiator Irgacure 819 and 2% UV absorber BDO. The experiment was performed on a Brookfield DV-II+ Pro viscometer. A mostly-linear trend can be observed at higher temperatures. Once we determine the viscosity trend, we can extrapolate values at various temperatures to use with equation 3.1.

We then plot theoretical thickness versus withdraw speed for several different temperatures in figure 3.3. We typically observe thickness values within the range of the dotted gray box, from 70 – 100 μm , with a step size smaller than these values and velocity within this range. It is believed that our speed was too high, therefore resulting in a thicker layer. In order to reduce this to the desired range of under 5 μm , we would need to use a platform speed of around 2 $\mu\text{m/s}$. Considering that this would *significantly* increase the printing time required (even with a motorized / automated system), it was decided to pursue other methods of fabrication.

It should be noted, however, that after abandonment of this method, it became ap-

parent that others[46] had successfully applied this configuration as well through making use of the oxygen inhibition effect to simply create a layer below the surface of the resin. It is suspected that this effect likely plays a role in the work of [14, 92] as well, but is not mentioned. Therefore this method is still viable but careful choice of exposure parameters must be made in order to prevent the top surface from fully curing, therefore preventing the meniscus effect.

3.3 Bottom-up Projection Printer - Methods

In the previous section we described our first attempt at designing a projection based printer, and the reasons for using a different approach. In this section we will cover the system which was developed in the aftermath, starting with an overview, and in the following subsections dive into deeper detail on each aspect of the design.

A rendering of the full system can be seen in Figure 3.4, where the associated components are compiled in table 3.1. In the system, a collimated LED is reflected from a 45° steering mirror and directed on to a digital multi-mirror device (see section 1.5.1). When the DMD is in the “on” state, the light will be reflected in the normal direction from the DMD surface and sent through the imaging lenses. Subsequently, when it is in the “off” state, the light will be directed towards the DMD guard which acts as a light stop. The system is focused on the bottom surface of a coverslip placed on the exposition platform, which is situated on a vertical translation stage. The DMD is connected to its controller via a fairly rigid ribbon cable, and therefore the controller must be appropriately attached to the back of the printer in nearby proximity to the DMD. When it is desired to view the pattern being exposed, the exposure platform can be easily removed and replaced with a CCD. This is frequently done for loading of resins/substrates and for calibration before each exposure. The exposition platform contains a removable lid for sample loading, and a pair of inlet/outlet nitrogen flush valves to remove oxygen (see section 2.6.1).

3.3.1 Optical configuration

For the imaging system we choose a simple two lens design consisting of two $f = 150mm$ Edmund optics achromatic lenses (Stock No. 49-362) placed at $L = 140mm$ separation distance. Through the use of this compound lens, we are able to reduce spherical aberration in the system. The DMD is placed at object distance $O_1 = 190mm$ with respect to

Fig 3.4: Projection based printer rendering with parts as follows: 1) High Power LED. 2) Steering mirror. 3) Angled DMD / LED adapter. 4) Mounted LCR 6500 DMD. 5) Imaging lenses. 6) Oxygen purging exposition platform. 7) Newport Z-stage. 8) DMD guard / light stop (Displaced in leftmost image, proper placement in right). 9) DMD Controller and mounting bracket.

#	Component	Manufacturer/Model
1	450mW, 405nm collimated LED	ThorLabs M405LP1-C2
2	45° Mirror	ThorLabs
3	DMD to LED mounting bracket	Bespoke
4	DMD	Texas Inst. DLP6500EVM
5	Achromatic 150mm Imaging Lenses	Edmund Optics
6	Exposure Platform and mounts	Bespoke
7	Z-Stage	Newport M-462-Z-M
8	DMD Guard / Light stop	Bespoke
9	DMD Controller and housing	Texas Inst. DLPC900 /Bespoke

Table 3.1: Components and manufacturer/model number for reference with Figure 3.4

Fig 3.5: Completed system as described by the rendering in figure 3.4

Fig 3.6: a) Optical configuration for our system, consisting of two $f=150\text{mm}$ achromatic lenses, allowing for reduced spherical aberration from a typical one lens system. We use an object and image distance of 190mm and 115mm , along with lens separation of 140mm . b) on-axis Huygens point spread function of our system, consisting of a Strehl ratio of 0.968 and symmetric FWHM of $2.5\mu\text{m}$. c) shows a simulated image of a star target using the on-axis PSF with a wavelength of $\lambda = 405\text{nm}$.

the first lens, where the first lens would form an image at $I_1 = 712\text{mm}$. The second lens then uses the image of the first as an object at $O_2 = -572\text{mm}$ (the difference between the lens spacing of $L = 140\text{mm}$ and I_1), and forms a final image at $I_2 = 115\text{mm}$ with respect to the second lens. The total system then has a magnification of $M = 0. - 0.76$, providing a real inverted image at the sample plane. The optical system schematic can be seen in figure 3.6a, where the ray paths for the marginal and chief ray are plotted. We also simulate the point-spread function (PSF) of the optical system in figure 3.6b, where we can see a Strehl ratio of 0.968 and a centrally symmetric full-width-half-maximum

(FWHM) of $2.5\mu m$. The PSF can be described as how the system would image an ideal point source through the system, or as the system's impulse response. This can then be extrapolated to how a system will perform when imaging an object by convolution of this object with the PSF. To this end, by fitting the PSF with either Seidel or Zernike polynomials, the type and extent of optical aberration can be determined. A detailed discussion of Zernike polynomials can be found in section 5.3, along with visual representation of several aberrations in figure 1.3. Pairing the visual depiction with the PSF, it is also possible to determine the type of aberration by inspection.

In the realm of determining performance, the Strehl ratio, proposed by Karl Strehl in 1895, is the ratio of the peak intensity of the aberrated PSF to that of a non-aberrated ideal diffraction-limited system and spans the range of 0 to 1. For our system with a simulated Strehl ratio of 0.968, it does not suffer from severe aberration on-axis and meets the criteria for being diffraction limited (Strehl ratio > 0.8 , known as the Marechal criterion). Similarly, comparing the PSF FWHM of $2.5\mu m$ to the pixel pitch of our DMD of $7.1\mu m$, we can see that the system has sufficient resolution to image an individual pixel on the DMD. In figure 3.6c a simulated single wavelength star image is shown using an object height of $3mm$, which is half of the height of the DMD display. Note that as the spatial frequency decreases (represented by the spacing between the lines), the line pairs can still be resolved. All simulations were performed using a single wavelength of $\lambda = 405nm$, the same as that of our LED used for photopolymerization. While diffraction limited on-axis, we naturally must use the system off-axis as well. In figure 3.7 we show the result of Zernike polynomial fitting for both on-axis and off-axis PSFs, where it can be seen that towards the edges there is an increase in tilt and coma (Z_3 and Z_7). The tilt term can be misleading in this data, as the PSF was calculated at a particular point in space on the y -axis. This effect can better be represented by the Seidel aberration concepts of field curvature (FC), where the focal point shifts with increasing height from the optical axis. Along this line we can also consider distortion, being the shift in magnification with

Fig 3.7: First 37 Zernike coefficients calculated from the PSF both on-axis and at 1.5mm off-axis, along with accompanying peak-to-valley(PV), root-mean-square(RMS), and Strehl ratio.

Fig 3.8: Field curvature and distortion as a function of axial displacement. We typically utilize a radius of 1.5mm for patterning, corresponding to a maximum field curvature of 20 μ m and distortion of 0.008%.

increasing height. In figure 3.8 we show the FC and distortion aberrations plotted versus the radius of our DMD. These become apparent with our samples because as the focal point shifts, so does the intensity distribution in the sample. To minimize the effects, we limit our samples to a radial distance of $1.5mm$, which corresponds to less than $20\mu m$ shift in focal point, and a magnification change of 0.008% .

3.3.2 Fabricated hardware

During the development of our projection printer, it was often necessary to create custom hardware to facilitate design. We used both a combination of 3D printing techniques and CNC machining, depending on the tolerance required for the parts. In order to fabricate the 3D printed components, a commercial Fused Deposition Modeling (FDM) 3D printer was used to create models in the thermoplastic polylactide (PLA), while others requiring higher tolerances were machined via third party in stainless steel or aluminum.

Our projection based resin printer consists of three components which were 3D printed on an Artillery Sidewinder X1 FDM printer, allowing the setup to be mounted vertically and allowing the LED, DMD, and optics to be aligned. It also consists of a resin exposition platform which was CNC machined from stainless steel and accompanying mounting brackets from aluminum. The design of these components will be discussed in the following subsections.

High-power LED to DMD Mount

While DMDs in general have been described in section 1.5.1, a key design feature of the TI LCR-6500 DMD is that its mirrors tilt at a maximum angle of $\pm 12^\circ$ along a 45° axis within the x-y plane of the micromirror array. This translates to the requirement that a collimated source would need to illuminate the DMD at both a 45° azimuth angle and a 24° zenith angle in order to reflect along the normal of the DMD, as well as to reject

the reflections from the mirrors switched to the off position. To satisfy this condition, a mount has been created which will fit on a standard metric optical table and connect to a 60mm cage system, while still allowing for the odd angles associated with the use of this DMD. We have chosen a source which uses a Leica DMI dovetail, and have designed a separate mating ring to mount it on a 60mm cage plate. The LED will be attached to a steering mirror which is attached via a 90° mount to the face of the printed part. The design can be seen in figure 3.9.

While the nature of 3D printing does not allow for the precision which would typically be required in an optical setup, we have designed our models so that minor hand adjustments can be made after assembly in order to allow for fine-tuned alignment, but overall the bulk of the alignment is determined before part fabrication.

One aspect that is notable to discuss within the context of 3D printed components is the poor ability to tap/print threads within plastics such as PLA (it can be done, but the small feature size makes them *very* prone to failure). One solution is to use a through-hole concept, where the plastic components will have either a nut on the other side, or be screwed into a respective mating component. For this setup, we have used a combination of hexagonal slots to hold nuts, and pass-through holes to allow for the attachment of standard 6mm optical cage rails.

Resin Exposition Platform

Due to the effects of oxygen scavenging free radicals from the photopolymer system, it was necessary to expose the resin in an inert gas environment (See section 2.6.1 for discussion of this process). To accomplish this task, a small container was fabricated which uses positive pressure N_2 gas to displace oxygen within the container. The design can be seen in figure 3.10 with both an overview and cutaway profile. The figure does not show the lid of container, which can be seen in 3.4.

The lid of the box contains a coverslip window with a thickness of $250\mu m$ to allow

Fig 3.9: Rendering of the Angled DMD and LED Mounting bracket. The design angles (24° zenith and 45° azimuth) are such that the reflected light from the DMD will be normal to its surface when it is in the “on” state. Two slotted holes are present for mounting with M6 screws.

for exposition. The bottom contains a chamber with two resin pools: One for exposition (figure 3.10, #1) and the other for temporary storage (figure 3.10, #2). Prior to exposition, a cleaned coverslip (procedure in section 4.1) will be placed on the lip of the exposition pool, but the pool itself will be left empty. 1.5mL of resin will alternatively be placed in the temporary storage pool, which is open to the inside of the chamber. After the chamber is closed and nitrogen is flushed through the system, the chamber will be tilted to cause the resin to flow from the temporary storage pool, under the coverslip, into the exposition pool. The coverslip is held in place by a 3D printed compression ring throughout the experiment (not shown in figures).

The temporary pool helps facilitate the quick removal of oxygen from the resin, as initial experiments with a single covered pool showed that even after placing the resin in a nitrogen environment, the oxygen remained trapped in the resin after a considerable amount of time. For example, for one resin mixture of HDDA, it was found that the time decreased from 1 hour to 8 minutes.

Fig 3.10: Top left) Rendering of the exposition platform. Bottom left) Rendered cutaway showing both the exposition pool (1) and temporary storage pool (2). A model glass coverslip sits on top of the exposition pool. Right) Loaded exposition pool after the resin is poured from the storage pool (Actual experiment).

Dust guard and DMD controller mount

Both the dust guard and DMD controller mounting bracket were printed on the Artillery Sidewinder X1 3D printer in our lab. These can be seen in subsection 3.4 as number 8 and 9. They were designed based around the physical constraints of the setup, and both use slotted through-holes to allow for adjustment into their respective positions. The DMD controller mount suspends the controller card by its mounting holes, allowing for air circulation and access to connectors. They will not be discussed further as there are no notable aspects which require further elaboration.

3.3.3 Grayscale Lens Pattern Generation

In order to create a sample which would follow desired shape (that of a convex lens, for example), it was necessary to generate a grayscale pattern which would cure the resin in such a way that it takes into account the non-linear dynamics of how the resin responds

to light. In this section, the development of the pattern generation code will be discussed, and later in chapter 4 experimental results will be shown associated with controlled resin exposition.

Taking into account that the DMD consists of an array of 1920x1080 micromirrors, a bitmap of proportional size is considered, where the x-y plane is defined in the plane of these mirrors. The z-direction is therefore considered normal to the glass coverslip, and increasing with depth into the resin. The line profile of a desired cure shape is then represented by a function $Z = f(r)$, where r is the radial distance from the origin to a point in the x-y plane. Knowing that the resin has a certain maximum cure depth (experimentally determined for a given intensity/exposure time), in order to produce an accurate representation of a shape Z , the maximum height of Z must not exceed the maximum cure depth. It must be noted that the cure depth is governed by a complex relationship between the intensity, initiator concentration, uv absorber concentration, exposure time, monomer type, and temperature. Because of the complexity involved, it is typically determined empirically. For this reason the maximum cure depth is a limitation for a single-step exposure, as it limits the height of a component to that of the maximum cure depth. If the design does require a larger height than a particular resin can support, however, there are several solutions: 1) If the shape allows (such as a simple spherical lens), only a section of Z proportional to the cure depth can be used. 2) The shape can be sliced into multiple layers where the bottom of each layer is considered a value of zero, and the maximum value of each layer is the maximum cure depth (one can imagine a Fresnel type lens on a lighthouse), meaning that the slice height $\Delta Z = C_d$. Examples of both cases can be seen in figure 3.12.

Because we are using an 8-bit DMD with 256 grayscale values available (0-255), the Z function must be normalized to 255, allowing for removal of the depth information, but keeping the basic shape of the function. Furthermore, as the resins have a minimum energy threshold which must be met in order to polymerize, we must scale the values to

not fall below the critical threshold. Finally, we must take into account the magnification of the setup when generating a pattern in order for it to be physically accurate, and to do so we scale the initial r values by the magnification. After being scaled by the magnification, the grayscale value (GSV) of a point r can be determined by:

$$GSV(r) = \frac{255 - GSV_c}{Z_{max} - Z_{min}} * (Z(r) - Z_{min}) + GSV_c \quad (3.2)$$

where Z_{max} is the peak height of the curve, and $Z_{min} = Z_{max} - C_d^*$, with C_d^* being the maximum cure depth of the resin for an intensity value of 255. GSV_c is the critical grayscale value at which polymerization starts. This is equivalent to E_c in equation 2.7 of a cure depth profile which has a varied intensity (via DMD) for a fixed exposure time and fixed LED power. Examples of cure depth profiles for different polymers and exposure conditions can be seen in figure 4.3 of chapter 4.

Equation 3.2 is a linear scaling factor to adjust the exposure range for a particular resin with known curing characteristics. As an example, if a resin has a maximum cure depth of $600\mu m$ after being exposed to $100\mu W/cm^2$ of $\lambda = 405nm$ UV light for 3 seconds, where $100\mu W/cm^2$ corresponds to a GSV of 255 on the DMD, we can then determine the height at any other grayscale value by a linear scaling relationship. Before this, however, we must also consider that a particular polymer needs some minimum intensity threshold exposed over the duration in order to crosslink densely enough to form a solid (experimentally determined). For the above arbitrary example, we can consider a critical intensity of $20\mu W/cm^2$. This corresponds to a critical GSV of $GSV_c = 51$, determined by scaling 255 by the ratio between minimum and maximum intensity. This would mean that there are 199 grayscale values which can be used over the $600\mu m$ curing depth range. If the desired shape of the resin has a function $F(r)$, we can then only use the top $600\mu m$ of the function, regardless of shape. Equation 3.2 captures this aspect by subtraction of

Z_{min} from the function $Z(r)$, where any values which are negative are considered uncured. In order to map the values into a grayscale range, we then normalize away the maximum cure depth and multiply by the usable range of GSV (199 for this case). Because the range desired is from 51-255 instead of 0-199, we then include a linear offset term proportional to GSV_c . One key feature to note in equation 3.2 is that it requires a well characterized resin where C_d^* and GSV_c are known. If incorrect values are chosen, the function will not be properly scaled to GSV space, resulting in an incorrect intensity distribution on the sample and thus form error. This key aspect lead to the in-depth push towards resin characterization in chapter 4.

Our code assumes that the desired output is symmetric about the z -axis, as it will take a two-dimensional line shape in the $z - r$ plane (cylindrical coordinates) and sweep it 360° around the z -axis, and then convert it into Cartesian coordinates. This could be modified for freeform optics by using a surface function $Z(x, y)$ and using the x, y coordinates as input. As our DMD consists of 1980×1080 pixels, we choose an array size of $1080 (x) \times 1080 (y)$, and consider the function $Z = f(r)$ to have its origin in the center. Using the integer pixel number and multiplying by the pixel pitch of the DMD and by the magnification of the setup, we can determine discrete r values and assign them an associated grayscale value. After we assign grayscale values for each $Z - r$ pair, we can sweep this through the $x - y$ plane by using the Midpoint Circle Algorithm[75, 101], which was designed to rasterize a circle with a given radius in a system which is pixelated, i.e. a system which can only contain values within a distinct array. This algorithm is very frequently used in computer graphics to render images on a LCD display where an approximate curve must be used.

The algorithm is based on the following logic: If a pixel to be drawn is represented by its coordinates (x, y) , the next point to be drawn can be represented by either $(x, y + 1)$ or $(x - 1, y + 1)$. In order to determine which of these should be drawn, the midpoint between the two, $p = (x - 0.5, y + 1)$ is computed and if the midpoint falls inside or on

Fig 3.11: A representation of the Midpoint Circle Algorithm, where the yellow line represents the perimeter of an ideal semicircle of radius r . The grayscale value is set based on $Z = f(r) = f(x)$, and is swept counterclockwise from the x axis to the y , and then mirrored to the other three quadrants.

the desired curve, $(x, y + 1)$ is chosen. If the point falls on the outside, then $(x - 1, y + 1)$ is used instead. This process will continue from $x = r$ to $x = 0$, in reverse order, until the entire first quadrant has been computed, which after completion will be mirrored to the other three quadrants.

One artifact of this algorithm is that there tend to be unfilled pixels left within the generated pattern. The reason for this is that if you take two adjacent pixels, one at slightly smaller radii, and rotate them to form circles, there are certain pixels between these two circles which will remain unfilled by either iteration of the algorithm. This is corrected in our code by taking the nearest neighbor average to fill the empty cells.

After filling empty cells, the array can be exported as a bitmap image. If it is sought to create a Fresnel lens type of pattern described above, we can perform multiple iterations with discrete steps and after add the results. Examples of patterns generated can be seen in figure 3.12, where a) shows a pattern for a convex lens of radius of curvature

Fig 3.12: a) Grayscale pattern radius of curvature $R = 7.0mm$ at a slice height (max resin cure depth) of $310\mu m$, and b) pattern for a Fresnel lens of $R = 3.5mm$ with a slice height of $290\mu m$. Both shown before non-linear resin correction or intensity correction.

$R = 7.0mm$ at a slice height (max resin cure depth) of $310\mu m$, and b) shows the pattern for a Fresnel lens of $R = 3.5mm$ with a slice height of $290\mu m$.

These patterns generated will then be modified in a different script to take into account the non-linear response of the resin, and have a pattern applied to correct for inhomogeneity in the spatial intensity distribution.

3.3.4 Non-linear Resin Correction

After generating a grayscale pattern, the non-linear effects of the resin must be taken into account in order to produce a desired shape. Knowing that for specific exposure conditions, the resin will follow the logarithmic shape of the Jacobs cure depth equation[22].

$$C_d = D_p \ln(E_o/E_c) \quad (3.3)$$

where D_p is the penetration depth, E_o is the incident energy, and E_c is the critical energy. We can then draw parallel between the logarithmic shape, and create a mapping function:

$$GSV_{Res} = \ln\left(\frac{GSV_{in}}{GSV_c}\right) * \frac{255}{\ln(255/GSV_c)} \quad (3.4)$$

where GSV_{Res} is the interpreted value of how the resin will behave according to the shape of equation 3.3, GSV_{in} is an input grayscale value, and GSV_c is the critical grayscale value determined experimentally from the critical energy for specific dose conditions. The term on the right-hand side serves to normalize to a maximum value of 255.

Equation 3.4 predicts how the resin will behave under a given input, but in order to for the resin follow a pattern as we design, we must now require that $GSV_{Res} = GSV_{Pattern}$, and we compute the input required. Rearranging equation 3.4 and simplifying yields

$$GSV_{in} = GSV_c \left(\frac{255}{GSV_c} \right)^{(GSV_{Pattern}/255)} \quad (3.5)$$

It is important to note that this equation simply solves the non-linearity issue, and does not imply anything about the maximum cure depth of the resin. This is taken into account in the previous section during the initial creation of a pattern. The final shape will be governed by the pattern generated, the curing characteristics of the particular resin, and the exposition parameters, all being of equal importance.

figure 3.13 provides a reference for the application of equation 3.5. The double black line serves two purposes: as an uncorrected pattern reference, which would produce a cure depth proportional to the blue line, and as a cure depth which would result from exposure with a pattern from the orange line.

In figure 3.14 we then offer experimental validation of equation 3.5, where we exposure a deoxygenated sample of HDDA with 2%wt photoinitiator and 15%wt UV absorber. We expose the pattern shown in the subset graph, which consists of fourteen solid rectangles

Fig 3.13: The linear center line represents both the uncompensated intensity profile and how the resin will behave after correction. The orange line shows the compensated intensity profile, and the blue shows how the resin will behave with no compensation.

with increasing grayscale values from 10-255. For the points shown in red, we apply the correction, and for those in brown we expose “as is”. We determined the critical energy of this particular mixture to be approximately $600\mu J/cm^2$, and corrected accordingly. This experiment was performed after spatial intensity correction, which is discussed in the next section. The resin mixture, along with acronyms, can be found in tables 4.1 and 4.2.

3.3.5 Spatial Intensity Correction

In our system we take advantage of our spatial light modulator during resin exposition, allowing us to homogenize our beam without additional diffusers. This is done by applying a correction pattern to any patterns which we wish to expose. In this section we will discuss the code which generates this correction.

We start with removing the resin exposition platform, and placing a CMOS camera (Xinema xiQ series) in the focal plane mounted on the z -stage. We then display a flat white square of 850x850 pixels on the DMD, and recording the real intensity distribution on the CCD. We have created a Matlab script which will display this image, and allow a

Fig 3.14: Experimental results for an exposition of HDDA/2%wt Irgacure 819(Initiator)/15%wt BDO(UV Absorber) with the pattern shown in the subset image. The x -axis shows the position number of each block, where the y -axis shows the associated cure depth at that location with both the corrected (red) and uncorrected profile (brown). The fittings are for reference, and show how the trend changes from logarithmic to linear.

user to adjust manually for any difference in angle, and to mark the outline of the square on the screen. After input, the script will then take these parameters to center and scale the acquired image, allowing it to adjust for differences in magnification and mechanical offset. The acquired image will then be smoothed using Gaussian and averaging filters in order to remove noise and pixel lines, and then rotated and cropped to fit a 850x850 square.

After smoothing and cropping, the image will have its maximum value adjusted to 255 to account for camera exposure settings, and then will be used as an adjustment mask by dividing the original pattern by the adjustment, and multiplying by 255. This image will then be re-displayed on the DMD, and the process repeated through several iterations. We typically choose 30 iterations, where the pattern with the least standard deviation is chosen as the correction mask.

figure 3.15 shows the intensity distribution of our configuration before (a) and after (b) running the correction algorithm, where it can be seen that the standard deviation of the pixels reduces from 8.49 to 2.40 in an 850x850 square. Both of the images have

Fig 3.15: Panels labeled a) show the intensity distribution of an uncorrected 850x850 square imaged on to a CMOS camera. The range has been adjusted to show a 55 pixel spread centered on the mean. Panels labeled b) show the same square after spatial intensity correction. Comparatively, the standard deviation reduces from 8.49 to 2.40 pixels. Images are time averaged over 1 second.

had their pixel ranges reduced to 55 in order to better show variation. Discontinuities seen in the center of the corrected image are manifestations of an inherent issue with the chosen DMD, and will be discussed further in section 5.3. figure 3.16 shows an intensity map of a pattern which has had the intensity correction of figure 3.15 applied to it by normalized multiplication. The edge of the pattern is left uncorrected for comparison, where the central region has been corrected. It is important to note that this correction is very susceptible to alignment and thermal stability of the LED over time. For this reason, correction masks are created new before every experiment after the LED has been allowed to warm up for thirty minutes. It is also very susceptible to dust on the DMD, and to artifacts generated by the DMD itself (Section 5.3), as it will try to overcompensate for a defect which can not be corrected, resulting in a propagated error. Finally, the incident beam on the DMD must be sufficiently expanded such that the variation between edge and center is minimal, as this would lead to correction which is too aggressive. We typically

Fig 3.16: 3D intensity mapping for the homogenization of the pattern shown in the bottom left by the correction pattern on the bottom right. The frame around the pattern was left uncorrected for comparison, where the Gaussian nature of the original profile can be seen. Arbitrarily scaled for visualization.

choose a difference of approximately 25%.

Chapter 4

Methods and Results - Resins

Characterization

This chapter will be dedicated to discussion of the methods and results obtained via use of the instrument and techniques described in the previous chapters. Various photoactivated resins will be analyzed for their suitability via study of the cure depth under various exposure conditions and chemical composition (concentration of photoinitiator). The models described in Chapter 2 will also be tested for their validity, and where they fail an alternative will be suggested based on the experimental behaviors observed. Finally, proof-of-concept lenses will be shown which were fabricated with the previous information in mind. These will be analyzed for their surface quality, along with shape conformity.

The primary motivation driving the resin characterization results herein lies in an attempt to find a unified model which can accurately predict how a resin mixture will behave under different exposure conditions. Precise control of the cure depth is critical for production of optical components, where aberration can be generated with surface sag deviation as little as $\lambda/14$, where λ is the illuminating wavelength (see section 3.3.3 and 5.3 for discussion). Furthermore, since bottom-up frontal polymerization is limited by the cure depth of the resin in terms of maximum part height, it is of great interest to

be able to quickly determine optimal resin formula/dose parameters. We investigate four of the most commonly used acrylate based photopolymers in the 3D printing and dental industry with two primary features in mind. First, from these four we determine a resin to use for further experimentation with optical fabrication based on ease-of-use (lowest viscosity) and high cure-depth to dose ratios. Secondly, we are able to demonstrate both the high throughput of the collection technique for those developing their own resins, and we show the failure of several commonly used models to accurately predict curing parameters over multiple resins. Based on these experiments, we can also note that literature claiming cure depth information with Jacob’s style working curves ([14, 37, 42, 43] as select examples) should only be considered under a very specific set of exposure conditions. To the best of our knowledge, robust cure depth data is not presently reported for these particular mixtures (and under-reported in general for others as well), but this is likely of little importance due to the numerous possibilities for monomer/additive/initiator combination. A common practice for this field is to determine this data as a mixture is made, and utilization of a DLP-based technique can greatly decrease time required to fine-tune a formula for printing. In this aspect, our primary objective with the following analysis is not to provide data on a specific resin formula, but to provide a methodology which can be reproduced for those whom seek the same information for their own mixture.

4.1 Substrate Preparation

Throughout our experiments, we extensively use $250\mu m$ thickness coverslips. Before use, they are cleaned via sonicating in acetone, followed DI water, and then further via a 37% hydrochloric acid bath with a two hour soak time. After soaking, they are washed with DI water, and then silanated by soaking in a bath of 20:1 toluene:3-(trimethoxysilyl)propyl methacrylate(TPM, a silane). Prior to use, the substrates are blown dry with compressed nitrogen. Silanation is done to increase the adhesion properties of our prepolymers. This

occurs because the silicon component in the organic/inorganic TPM attacks the hydroxyl groups on the surface of the glass, forming covalent $Si - O - Si$ bonds. After bonding, the acrylate portion of the molecule is left dangling to bond with any prepolymers on the surface, therefore increasing wetting of our photopolymers.

4.2 Photopolymer Preparation

All photopolymers were prepared a day in advance of polymerization, and allowed to mix for at least three hours on a heated hotplate at $50^{\circ}C$ with a magnetic stir bar. They were protected from accidental UV exposure by being wrapped in aluminum foil. The mixtures tested are compiled in table 4.2, while the chemical abbreviations are listed in table 4.1. In preparation for exposure, $1.5mL$ of the room temperature solution is pipetted into the temporary resin pool as described in section 3.10. After exposition of each sample, the pools are emptied and refilled with fresh solution, regardless of mixture being used. This ensures that the initial concentration of photoinitiator remains constant.

Prior to exposition, the LED was allowed to stabilize for thirty minutes and after which a calibration mask was made. The irradiance was then measured with a power meter. We performed all measurements through the thickness of two microscope coverslips to take into account reflectance from the substrates (one for the box window, and one from the actual substrate). This was typically a 10% reduction. As the thickness of the coverslips could sometimes vary, and therefore the transmission, we used the exact slips which we would later fabricate the samples on. The transmission varies with thickness due to the slight absorption of the glass coverslips in the UV range. This could likely be reduced by using either quartz or fused silica substrates, but cost becomes an issue as after polymerization the slide is very difficult to clean should the sample fail. For this reason, it is more feasible to measure each slide individually.

Class	Chemical (Supplier: Merck)	Abbreviation
Prepolymer	1,6-Hexanediol diacrylate	HDDA
Prepolymer	Trimethylolpropane triacrylate	TMPTA
Prepolymer	Bisphenol A glycerolate dimethacrylate	BisGMA
Prepolymer	Pentaerythritol tetraacrylate	PETA
Diluent	2-Hydroxyethyl methacrylate	HEMA
Photoinitiator	Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide	BAPO
UV Absorber	2-(2H-Benzotriazol-2-yl)-6-dodecyl-4-methylphenol	BDM
Silane	3-(Trimethoxysilyl)propyl methacrylate	TPM

Table 4.1: List of chemicals used. All chemicals were used as supplied.

Constituents	Percent Weight(%w)
TMPTA:BAPO	98:2
BisGMA:HEMA:BAPO	59:39:2
PETA:BAPO	98:2
HDDA:BAPO	98:2
HDDA:BDM:BAPO	(93,88,83):(5,10,15):2
HDDA:BDM:BAPO	(84.75,84.5,84,83,81):15:(0.25,0.5,1,2,4)

Table 4.2: List of polymer mixtures tested. Brackets mean that the same constituents were used in multiple ratio pairs. They correspond element-wise. BisGMA is mixed with HEMA as a diluent, as BisGMA itself has a molecular weight of $512g/mol$, with a viscosity comparable to tree sap.

4.3 Sample cleaning / post processing

One of the notable aspects to using a method of bottom-up fabrication is that there will always be a layer of partially cured polymer on the surface of the part, as this is the critical point of conversion where there is not quite enough energy to fully cure the polymer. This means that after exposition of any sample, it is necessary to remove excess resin. In other instances this is done by washing the cured component with isopropyl alcohol or another organic solvent. We found, however that this will destroy the surface quality by roughening the gel layer, and often result in cracking of the part on a small scale. What we desire to do is to remove the excess resin, but still leave the gel matrix partially saturated, enough to allow for a second exposure to set the remaining gel into a hard, solidified layer.

We have found that the best way to do this is to take advantage of capillary action using a very sharp pair of tweezers. Typically an annoyance for those working with small samples, capillary action will draw any liquid from a surface which comes near it. By first poking a sharp tweezers through a small piece a standard laboratory KemWipe, and placing the tip just near the edge of the sample, capillary action will wick away excess resin. After several wipe replacements, a cleaned sample is left behind without use of solvents. A pictorial depiction of the cleaning process is given in figure 4.1. We should mention that this will only work with low viscosity prepolymers, and for those prepolymers with high molecular weight (high viscosity) we would heat the sample to 60C on a hotplate during the wicking process.

After cleaning, all samples were exposed to a final round of exposition with the same parameters as the pattern which created them. They were placed right-side-up in the exposition chamber, allowed once again to be exposed to a nitrogen environment for 30 minutes, and were exposed with the correction pattern described in section 3.3.5.

Fig 4.1: Pictorial depiction of wicking process for cleaning gel samples. Sharp tweezers are brought to the meniscus of the uncured resin, where upon touching, capillary action will draw the droplet up the tweezers into the small fibers of the wipe, removing excess resin from the gel.

4.4 Resin Characterization Pattern

In order to characterize the resins shown within this thesis, a cross-mixed pattern of 8 x 15 grayscale bars is used. It can be seen in figure 4.2, along with a number associated with the typical order which it is exposed. Each row of the matrix is exposed at a constant time, where each bar within a row is at a different intensity. We use a mixing of the orders to reduce any unexpected effects to the resin cure process (namely, leftover oxygen within the resin scavenging free radicals). As can be seen in figure 3.10, the inlet for the resin (and thus oxygen) lies at the side of the pool. If there are any of these such effects, they present themselves as a gradient with a stronger scavenging effect near the inlet. Cross-mixing thus allows for discerning between these effects and others. We can, however, determine if the resin is completely deoxygenated by performing all exposures simultaneously with the same parameters, and observing any such gradient being present. One strong benefit to performing resin characterization with projection based polymerization is that it allows for the simultaneous capture of multiple Jacob's working curves (equation 2.7) on a single chip (i.e the same experimental conditions). This allows for more accurate results and reduces sample preparation/measurement time required. By doing this method, we are able to analyze a resin's characteristics in mass (120 individual doses per chip compared

Fig 4.2: Multi-dose patterns which are exposed in numeric order, individually.

to 1).

References [55] and [92] have implemented similar techniques configuration wise, with the exception that [55] utilized a laser at fixed power, and both do not consider the effects of deoxygenation. However, it is likely that the oxygen in the experiments of [92] is depleted while exposing due to the small volume involved, but this is unclear based on their reporting. The method of [55] is also less efficient in terms of modifying beam intensity, as they would have to either adjust the laser manually or carefully tune the scan velocity. Reference [92] assumes that the resin will obey the Jacobs working curve, and goes no further than this. This would be equivalent to measuring a single set of 15 bars in 4.2, and is insufficient to describe a photopolymer system. In the next section we will describe this phenomenon further.

4.5 Resin Characterization Results

While conducting experiments to determine which polymer to use to attempt to fabricate optics, it was noted that the curing characteristics of the resins used did not follow the Bunsen-Roscoe reciprocity law. This law states that for a given dose (energy x times), a proportional photochemical reaction should always follow. This means that for any pair

of time and energy, as long as the product is the same, the reaction will be the same. As described in section 2.5, the cure depth of a photoinitiated reaction is often described by the Jacob’s working curve equation $C_d = D_p \ln(E_o/E_c)$, with D_p and E_c the penetration depth and critical energy. This equation predicts compliance to the Bunsen-Roscoe law, and is therefore insufficient.

We will first show how this fails for several different Type-I photopolymer systems (Type I systems are discussed in section 2.6.3). Figure 4.3 shows cure depth measurements for the first four mixtures in table 4.2, shown as a function of a series of constant energy exposures. For these measurements all mixtures were allowed to sit under flowing nitrogen for thirty minutes as described in section 3.3.2, before transferring the resin to the exposition chamber. They were exposed in sequential order according to figure 4.2, and after post processed as described in 4.3. Cure depth measurements were performed on a Taylor Hobson Talyscan 150 stylus profilometer where the peak sample height was taken as the cure depth. In figure 4.3 it can be seen that for all systems, the cure depth is a decreasing function of time, where each constant time set is represented by a different color. It should be noted that the independent variable in figure 4.3 is the dose, and not the intensity. This means that for longer exposure time, a proportionally weaker peak exposure intensity was used. The PETA system exhibited the weakest effect, but is nonetheless still present. We chose to continue further analysis on HDDA of the four combinations, as the low viscosity of this photopolymer yields shorter working time and more reproducible results in the cleaning stage of processing. The low viscosity also allowed diffused oxygen to be removed from the resin quicker, where a sample could be deoxygenated in as little as five minutes. We did not choose to continue with the PETA system for the same reason, as it has nearly double the molecular weight. We would likely need to create a new chamber to reliably work with overly viscous polymers in a deoxygenated environment.

Fig 4.3: Cure depth vs exposure energy for four prepolymers with 2w% photoinitiator at different exposure times. For all mixtures, the cure depth is a decreasing function of time.

4.6 Analysis of the cure depth relation to energy

We will now proceed to fit the data according to exposure time and irradiance in order to approximate the cure depth for a given set of parameters. A typical approach would be to use the Jacobs equation for cure depth (equation 2.7), but as these are complex chemical reactions, the Jacobs working curve is an oversimplification of the governing photochemistry, and neglects many key aspects such as the concentration of photoinitiator (which will be investigated in the next section). Furthermore, as discussed in Chapter 2, the cure depth, intensity, and initiator concentration all make up a set of coupled differential equations which can not be expressed simply. Setting this aside, we find that the best fit can be achieved by using time with an exponent of 0.5. We have modified the Jacobs equation to:

$$C_d = D_p \ln \left(\frac{I_o t^b}{c} \right) \quad (4.1)$$

where D_p is same penetration depth as in the Jacobs equation, and b and c are fitting constants. Noting however, that the units of c would need to be such that they cancel the $s^{0.5}$ unit for time. Figure 4.4 shows the data of figure 4.3 panel 4 with a surface fitting performed by equation 4.1. It is fit as a function of intensity and time, and yields the parameters of $D_p = 316.2\mu m$ and $c = 9.2$ with an R^2 value of 0.99. The parameters of TMPTA, PETA, and BisGMA/HEMA were $D_p = 237.1, 204.3, 255.6\mu m$; $c = 123.7, 64.3, 28.55$; and $R^2 = 0.97, 0.93, 0.98$, respectively. We note that the poor fitting of PETA was likely due to experimental error related to the difficulty involved with cleaning excess resin from viscous samples.

Fig 4.4: Experimental data from HDDA+2%w BAPO at various intensities and times. Surface fitting is performed with equation 4.1, with parameters $D_p = 316.2$ and $c = 9.2$. Same data set as shown in the fourth graph of 4.3

4.7 Effects of initiator concentration

The equation used in the previous section fits well to a particular polymer blend with a defined concentration of photoinitiator, but it does not include effects of changing the initial concentration included in the blend. The work of J. H. Lee et. al.[55] offers a prediction to account for this in the form of approaching the experiment from a basic kinetic analysis point of view. They predict $C_d \propto 1/\epsilon[PI]$, where ϵ is the molar extinction coefficient and $[PI]$ is the concentration of photoinitiator. Similarly, they also predict that $E_c \propto \alpha\beta/[PI]^{0.5}$, where α and β are processing parameters.

After fitting to data we find that the model of equation 2.10 failed to appropriately describe our system of HDDA+BAPO+BDO. We found such a poor fitting that data is not show, as it returned fitting errors. We then release the constraints of the exponents for initiator concentration to perhaps identify extent of dependence. Equation 2.10 then becomes

$$C_d = \frac{a}{[PI]^d} \ln(c * E_o * [PI]^b) \quad (4.2)$$

where E_o is the exposure energy, and a , b , c , and d are fitting parameters. a and c assume that all constants are known, while d and b describe a power law behavior for the initiator concentration. In figure 4.5 we show equation 4.2 applied to fit a series of five initiator concentrations in HDDA+15%w BDO. The parameters obtained for a , b , c , and d are 12.8, 1.64, 0.69, and 0.72, respectively. The obtained fitting had $R^2 = 0.91$, suggesting that the fitting performed still does not effectively describe the behavior, even with released constraints. We use a fixed time of exposure for all concentration dependence measurements to negate the effects described in the previous section regarding breakdown of Bunsen-Roscoe reciprocity law for different dose condition. Further studies would need to be carried out for a simplified model for predictive purposes.

Fig 4.5: Experimental results for the dependence of cure depth on both exposure energy and initial initiator concentration. Polymer blend contains 15%w BDO, with remainder HDDA. a) shows the curing characteristics with guide lines for the maximum and minimum cure depth. b) Shows fittings as proposed by [55] using a constant exposure time of $t = 25s$. The model does not fully describe the curing characteristics.

There are several reasons which this model may have failed, the first being documented by the original author. They mention that equation 2.10 predicts the cure depth in the 'wet' state, meaning before shrinkage is accounted for. They state that at lower initiator concentration, the crosslinked density for the bulk of the gel is lower, and therefore results in higher shrinkage than a gel cured with high initiator concentration when the gel transitions to the dry state. They also predict that at higher initiator concentration, this effect becomes less apparent. While there is currently no data for our particular polymer system on what quantifies as high or low initiator concentration, we argue that we should not see this effect as strongly in our system because we use a two-step curing process, where first a 'wet' gel is formed with the experimental exposure conditions, and then a second cure is performed on the monomer-saturated sample to harden the delicate gel for measurement (see procedure in section 4.3). We would expect to see similar shrinkage across the board for all concentrations.

Another possibility, if considering the initial derivation of equation 2.10, is that it uses a steady state approximation for the initiator concentration. It is likely that the local concentration of initiator depletes faster than it can be replenished by diffusion, especially at high light intensity. Similarly, as the gel forms, the viscosity increases drastically, also reducing diffusion. This model also does not take into effect temperature, which will ultimately affect the entire system viscosity as well[47].

4.8 Kinetic Analysis approach

In Chapter 2 another method was shown which makes use of a kinetic analysis approach to determine the degree of conversion of a polymerizing system based on the irradiance, exposure time, and initiator concentration (equations 2.26 and 2.8). It will now be used to fit experimental data. Noting that the determination of the rate constants k_p and k_t for any given system is non-trivial, and often requires methods such as photo-differential scan-

ning calorimetry (photo-DSC), nuclear magnetic resonance (NMR), or Fourier Transform Infrared Spectroscopy (FTIR) for their determination[21]. Furthermore, it has been noted that the rate constants of a reaction change as a function of temperature and viscosity[47, 107], where there is a sharp increase in viscosity at the gel point. The equation describing the S -function (equation 2.26), and therefore the conversion, makes use of constant values for $K = k_p/k_t^{0.5}$. We perform this analysis with the knowledge that we can determine most experimental parameter required with exception of the rate constant K and critical gel transition point. For those not readily determined, well-documented values from literature will be used. the S -function would be constant for the set of parameters used to create that particular Z_c . a' , b' , ϕ , and λ are all constants within these equations, and the independent experimental variables will be C_o , I_o , and t , with dependent variable $z = C_d$. With all other parameters known, we can then gain information about our system based on the ratio of S/K . We normalize to K because due to the linear relationship between S and K in equation 2.26, it is not possible to decouple the two without other experimental techniques. Through analysis of S/K , we can still, however, elude to some information about our system.

Molecular dynamics and graph theory calculations[97] have predicted that the critical gel point for HDDA is not static, and in fact can range from 0.18 to 0.33 depending on the initial amount of radicals in the system. This occurs because as the amount of radicals increases, the system transitions from chain-like polymerization to step-like polymerization. The amount of radicals is related to both the intensity irradiating the polymer, and to the concentration of photoinitiator. It has been shown by Starker *et. al*[82] and Kardar *et. al*. [47] that higher light intensity increases the critical gelation point.

Furthermore, we must also consider that the rate constants do not necessarily need to remain constant. The work of Torres-Knoop *et. al*. [97] shows that both k_i and k_p can depend on the light intensity used for polymerization, and also the temperature.

Furthermore, one may expect to see rate constants change proportional to viscosity of the system[59, 60, 106]. The works of Li *et. al.*[57] shows that viscosity is an increasing function of conversion. For samples with a higher cure depth, which in turn have a large gradient in conversion from bottom to top, we could expect to see lower rates as sample height increases, even if the critical point for two samples was the same. We could also expect some reduction in viscosity from sample temperature following an Arrhenius relationship, where as the sample heats, mobility would increase. The temperature would increase proportional to higher light intensity and longer exposure times.

4.8.1 Experimental Results

We first started by determining the required experimental constants for equation 2.26. Using a LED with a wavelength of $\lambda = 405nm$ at an intensity of $I = 70\mu W/cm^2$, we measure an absorbance of $A = 0.16$ by recording the transmission through a $500\mu m$ thick region of 15%w BDM+HDDA. The negative natural logarithm divided by the cure depth is then taken to determine an absorbance of $Q = 36cm^{-1}$ for the prepolymer blend. We take the molar extinction coefficient for our initiator. BAPO, from literature, with a value of $\epsilon = 0.5mM^{-1}cm^{-1}$ [68]. It is assumed that there is no photolysis product ($b' = 0$). All units of length are given in cm , units of concentrations given in mM , and units of energy in mJ/cm^2 . We also assume that oxygen inhibition does not contribute to a decrease in free radical concentration, as all experiments were performed under flowing nitrogen after a 30 minute induction period.

The results for two different experiments are presented in figure 4.6, where a) shows the dependence of K/S determined from equation 2.26 on irradiance and exposure time with constant initial initiator concentration, and b) shows the dependence on initial initiator concentration and irradiance at constant exposure time. For figure 4.6a we use time $t = (2, 4, 13, 26, 65)s$ and irradiance $I_o = (50 - 800)\mu W/cm^2$ at an initiator concentration

Equation List	Eqn. #
$[M]/[M_o] = \exp(-S_{analytic})$	2.8
$S_{analytic} = G(z, t) \sqrt{\left(\frac{83.6a'\phi\lambda C_o I_o (k_p)^2}{2k_t} \right) \exp(-2.3z(a'C_o + Q))}$	2.26
$G(z, t) = \frac{1 - \exp[-0.5t(B'(z) - 0.5A_1(z)t)]}{0.5(B'(z) - 0.5A_1(z)t)}$	2.27
$I(z, t) = I_o \exp(-A'z)$	2.17
$C(z, t) = C_o \exp(-B't)$	2.18
$A'(z, t) = 2.3(a'C_o + Q) - A_1t$	2.19
$A_1(z) = 2.3(a' - b')C_o I_o z(83.6a'\phi\lambda)$	2.20
$B'(z) = (83.6a'\phi\lambda)I_o \exp(A''z)$	2.21
$A'' = 2.3\left(\frac{a' + b'}{2} + Q\right)$	2.22

Table 4.3: Tabulated equations used for this sections analysis which are explained in 2.6.6.

Fig 4.6: a) shows S/K as a function of irradiance over various cure time as calculated by equation 2.26 for $t = (2, 4, 13, 26, 65) \text{ s}$ and irradiance $I_o = (50 - 800) \mu\text{W/cm}^2$ at an initiator concentration of $C = 49 \text{ mM}$. A general increase of K/S with both time and intensity is observed. b) shows S/K as a function of initiator concentration $C = (6, 12, 24, 49) \text{ mM}$ and irradiance $I_o = (50 - 800) \mu\text{W/cm}^2$ at a fixed time $t = 25 \text{ s}$. A similar dependence on intensity is observed, but the effect of PI concentration is less pronounced.

of $C = 49mM$ and for 4.6b we use initiator concentration $C = (6, 12, 24, 49)mM$ and irradiance $I_o = (50 - 800)\mu W/cm^2$ at a fixed time $t = 25s$

We note the increase of K/S with increasing irradiance, time, and (slightly) with PI concentration. This is in agreement with the discussion at the end of the last section, where if we consider weaker effects on K than S , S would shift higher with increasing irradiance and PI concentration. However, based on the nature of the experiment, interpretation of results is left up to speculation, where we can not tell which of the above points plays the key role. Further techniques would therefore need to be developed to sufficiently decouple K and S .

4.9 Kinetic Analysis Conclusions

In this chapter we have experimentally investigated three different models for frontal polymerization, all of different complexity. For the first we tested the simple Jacob's working curve. We found that this equation works well for a specific set of dose conditions, but will fail if any initial parameters are changed. Similarly, the second model tried to account initiator concentration, but failed to accurately describe concentration based experiments along with the dependence on dose. The third model, while taking into account varying initiator concentration and irradiance as a function of time, did not consider the effects of variable rate constants or that for gelation, the critical transition point is not always the same. The prior two models had not been experimentally validated to a great extent, with the third not being validated experimentally whatsoever. While we do not intend to pursue creation of new models in this thesis, we do highlight the need for development of future models to fully understand the curing process of these photopolymer systems. As it stands, to the best of our knowledge there is currently no model which can fully describe a frontal polymerizing system at varied initial conditions which has been experimentally validated. With the introduction of this low-cost methodology we

hope that other researchers may be able to help fill the gap within this field of study, where prior it was impractical to collect experimental data such as that obtained due to large time constraints involved with measuring samples one-at-a-time instead of on a bulk chip.

Chapter 5

Methods and Results - 3D Printed Lenses

After investigation of the curing characteristics of the various resins in section 4.7, we could now, with a known set of parameters, attempt to fabricate lenses. These were fabricated with the same methods as described in section 4.1-4.3, with the only difference being the pattern used (with the patterns used similar to the one shown in figure 3.12a). The total time to produce one lens is approximately 30 minutes, including deoxygenation and post-treatment. The actual exposure time to form the shape is around 45 seconds to 2 minutes, depending on thickness desired and maximum irradiance.

We show a selection of different lenses from our preliminary investigation, and then proceed to analyze thoroughly the best of these in terms of surface conformity. In figure 5.2 we show three lenses of designed focal length $10mm$, $15mm$, and $20mm$, along with white light from a distant LED source focused on to a sheet of paper. We demonstrate with this figure that we have rough control over the shape of the surface enough such that the focal point is in the general region. However, this does not mean that the lenses are perfectly spherical and defect free, and only serves as demonstration. We must further analyze their optical properties with a combination of surface profiler, optical simulation,

and wavefront sensor, which will be shown later in the chapter. Figure 5.2 shows three more lenses of focal length $4mm$, $7mm$ and $10mm$, where the $4mm$ lens is made using a fresnel-style pattern as discussed section 3.3.3 and shown in figure 3.12b. We note that the cloudiness seen in this lens is due to the lens being over-cured during fabrication, where the cloudiness is imprints of the pixels of the DMD on the back surface of the lens. This can be corrected by using lower intensities, or slightly defocusing the pattern during fabrication, as was conducted with the other samples. In figure 5.3 we show the lenses of figure 5.2a focusing light on to a sheet of paper at distances of $4mm$ and $10mm$, providing approximates of their focal lengths. In figure 5.4 we show images taken from a smart phone camera through three different lenses, where a) shows a cotton swab imaged through the $f = 10mm$ lens in figure 5.2a, b) shows a human hair through the $f = 7mm$ lens in figure 5.2b, and c) the tip of a pen imaged through the $f = 15mm$ lens in figure 5.1.

After initially determining the approximate focal length, we can then begin to analyze the surfaces in more detail. We begin with the plano-convex lens shown in figure 5.5a along with its accompanying surface data. The top portion of figure 5.5 depicts three curves related to a horizontal cross-section of the center of the lens. The blue line is the shape of a) as measured via single scan stylus profilometer. The key to creating a lens as designed lies in appropriately generating the pattern according to a specific cure depth. This was explained in section 3.3.3, and for this particular resin we determined that the appropriate height for the exposure conditions was $310\mu m$ with a critical energy at a grayscale value of 15. After generating a pattern with equation 3.2 and curing the lens, it was found that the maximum height was in fact closer to $340\mu m$. Based on these two sets of conditions, if the cure depth of the sample would have been correct at $310\mu m$, the shape would be that shown by the gray line. Since it was incorrect, we can apply a correction factor proportional to ratio between the desired and actual cure depth, and another scaling factor for the difference between the maximum grayscale value (255) and

Fig 5.1: White light focused through three lenses from a distant radial LED source. From left to right, lenses of focal lengths $f = 10, 15, 20\text{mm}$ can be seen. The diffraction along the edges is caused by excess resin along the edges of the sample.

Fig 5.2: Three different lenses are shown, where a) shows a plano-fresnel $f = 4\text{mm}$ lens (made with a pattern similar to that shown in figure 3.12b) on the left, and a plano-convex lens of $f = 10\text{mm}$ on the right. b) shows another plano-convex lens of focal length $f = 7\text{mm}$.

Fig 5.3: White light focused through two lenses from a distant radial LED source. These lenses are shown in figure 5.1a on the same substrate, where the stage is varied between $f = 4mm$ and $f = 10mm$, alternating between which lens focuses light tightly on the paper below.

Fig 5.4: Three different images acquired by a combination of smart-phone camera and printed lenses. a) shows a cotton swab imaged through the $f = 10mm$ lens in figure 5.2a, b) a human hair through the $f = 7mm$ lens in figure 5.2b, and c) the tip of a pen imaged through the $f = 15mm$ lens in figure 5.1.

Fig 5.5: The top plot shows a surface profile from the center of a) (blue line) compared to theoretical predictions for the shape *as-designed* (gray line) and corrected for incorrect cure depth assumption (orange). The bottom plot shows the subtraction of the surface profile and the corrected prediction. a) shows a $f = 10\text{mm}$ plano-convex lens (designed profile), and b) shows 8 point printed font imaged through a smart phone camera with a).

the critical energy (in this case 15). These applied to the gray line are shown in the orange line of the figure. The reason that the correction factors are necessary is that an incorrect cure depth prediction is equivalent to introducing scaling in the vertical direction (and not the horizontal), which results in stretching of the profile. As mentioned, the primary drawback to this method is that it then becomes critical to determine the curing depth with a high degree of precision in order to fabricate suitable optical components. The cure depth, as shown in the resin analysis sections, is governed by a complex relationship of temperature, exposure time, initiator concentration, oxygen concentration, viscosity, intensity, post processing practices, defocusing of the light with depth, or a combination thereof. In an attempt to quantify the uncertainty, we measure the standard deviation of the cure depth from the idealistic fitting of equation 2.7. As a sample set, we use the data shown in figure 4.5, and after fitting each set of data individually, we determine an average standard deviation over the whole set. We present this data in the histogram of figure 5.6, where all deviation measurements across different samples are combined. We determine the standard deviation of the cure depth for HDDA to be $\sigma = 25.8\mu m$ over a total count of 220 measurements.

It was also noted by [12] and [7] that self-focusing of the polymers can alter the curing characteristics due to a gradient refractive index, but we do not anticipate that this effect is prominent with the scale of our samples being in the several *mm* range. It can also be minimized by using a lower curing intensity. In the bottom portion of figure 5.5 we show the subtraction between the surface profile (blue) and corrected theoretical profile (orange), and in b) we show a business card imaged through this lens with a smart phone camera on to text of 8 point font to show practical applications. The lens was designed to have a focal length of $f = 10mm$. We will now proceed to offer more in-depth analysis of this lens from both a surface quality perspective by scattering theory, and from an optical simulation perspective for the overall lens characteristics.

Fig 5.6: Histogram showing the deviation of cure depth from idealistic model $C_d = D_p \ln(E_o/E_c)$, where D_p and E_c are determined individually per sample. The distribution shows a standard deviation of $25.8\mu m$ with a total count of 220 data points.

5.1 Determination of surface roughness and waviness

**The following results were determined using the theory discussed in section 1.4.1.*

For our polymer lenses in particular, it was originally thought to use frontal polymerization to produce optics when it was noticed that the surface roughness of a part cured with a thin gel layer on the surface was in the single digit nanometer range. In figure 5.7a we offer experimental validation of this by showing a contact surface profilometer measurement performed on the apex of the cured sample in figure 5.5. We note a line roughness of $R_a = 5.45nm$ and line waviness of $W_a = 36.68nm$. To determine these values, we first remove form through subtraction of a 9 degree polynomial fitting from the extracted profile, calling it the combined profile, which consists of the summation of the roughness and waviness. We then perform convolution between the combined profile and the Gaussian weighting function discussed in section 1.4.1 (equation 1.3), choosing a cutoff value of $\lambda_c = 13.25\mu m$, where the result is the waviness profile. The roughness profile is then the subtraction of the waviness from the combined profile, and the resulting root-mean-squared values are determined from each respective profile to determine

Fig 5.7: Roughness measurements performed on a section of the lens in figure 5.5. a) shows the extracted profile after removal of form via subtraction of 9 degree polynomial fitting, and the result of filtering with an optimal cutoff value of $\lambda_c = 13.25 \mu\text{m}$. b) shows the RMS value of roughness (R_a) and waviness (W_a) as a function of filter cutoff wavelength. c) shows the first and second second gradient of the R_a line in b), where the first inflection point serves as a separator between clusters of different wavelength components

R_a and W_a .

As mentioned much earlier in section 1.4.1, ISO 16610 provides recommended cutoff values for filtering, and the value of $\lambda_c = 13.25\mu m$ used for this sample differs from those suggested. We avoid the values listed in ISO 16610 because they are only chosen based on typically present features in machined parts, and are arbitrary/subjective in nature. In order to quantify the RMS values of roughness and waviness, we instead calculate both parameters over a range of cutoff wavelengths which are shown in Figure 5.7b. To choose the optimal filter wavelength, we then take the first and second derivative of the R_a line to find the first inflection point (Figure 5.7c). This point serves as a fair choice for cutoff because it marks the location where the filtered waviness profile is best fit to the combined profile. For example, at higher cutoff wavelengths the waviness profile will be “*over smoothed*”, not accurately following larger peaks and valleys. This will push the ill fit regions into the roughness profile after subtraction, therefore increasing the roughness. Furthermore, when the cutoff is just below the inflection point, the roughness starts to be pushed disproportionately into the waviness profile, overall reducing the roughness at a faster rate. The inflection point thus serves as a fair choice for separation of two clusters of different wavelength components.

The resolution of the ball probe used is $2nm$ on the height axis (z), and has a tip radius of $2\mu m$ with 60° contact angle. Another consideration aside from the resolution of the stylus in the z direction is how the spacing of surface elements affects the measurement. Taking a sinusoidal surface feature with wavelength λ and a ball probe of radius R , in order for the measurement to remain unaffected by the probe (meaning that the probe radius is not too large to reach the bottom of a small feature), the probe radius should adhere to the following standard:

$$R \leq \frac{\lambda^2}{4\pi^2 A} \quad (5.1)$$

Fig 5.8: Minimum wavelength for data validity as a function of sinusoidal amplitude using a probe radius of $2\mu m$.

where A is the amplitude of the feature. Rearranging we can then calculate a critical wavelength λ_t where below this value, the measurement has been modified by the probe:

$$\lambda_t = 2\pi\sqrt{RA} \quad (5.2)$$

Considering a probe of radius $R = 2\mu m$, using equation 5.2 we can perform a simple sanity check on the data shown in figure 5.7a. Taking a sinusoid with amplitude equal to approximately two times the RMS value (the average peak-to peak-separation) of the roughness and waviness, for $R_a = 5.45nm$ and $W_a = 36.68nm$ minimum wavelengths λ_t are determined to be $0.9\mu m$ and $2.4\mu m$, respectively. Comparing to our measurement resolution of $0.5\mu m$, we note that λ_t is within 2 and 5 data points, approaching the resolution of the profiler, and does not contribute significantly to the measurement.

Nonetheless, we also performed Atomic Force Microscope (AFM) measurements for further validation. In figure 5.9 we see a surface roughness of $S_a = 3.95nm$ for a section of this same lens, consistent with the stylus profiler measurements. We use tapping mode to prevent sample damage, and use a $20\mu m \times 20\mu m$ measurement area. Filtering was performed as previously described. These results are comparable to the $S_a = 6.5nm$ described in [14] over similar sample area, although direct relation is not possible due to the difference in surface measurement techniques used. We also note less than that claimed

Fig 5.9: Measurements performed in tapping mode on a central section of the same sample shown in figure 5.7, exhibiting a surface roughness $S_a = 3.95nm$.

by Nanoscribe's two-photon systems[49] of $10nm$, however no information is provided on measurement technique or sampling area.

5.2 Scattering Theory for optical surfaces

Drawing on the theory described in section 1.4.2, we will now proceed to analyze the data described in the last section from a scattering perspective. We first calculate the spectral density function (Eq. 1.4) of the profile used for figure 5.7 and show the result in figure 5.10 . An RMS value for the roughness is obtained with a value of $\sigma = 36.1nm$, comparable to the previous waviness profile value $36.7nm$. We note that once again, the roughness described in this section (σ) is determined over the entire bandwidth of the system, and makes no distinction between waviness and roughness. It is clear from this that the low spatial frequencies dominate the RMS value over contribution from higher frequencies. Spatial frequency limits of $f_{min} = 0.0016\mu m^{-1}$ and $f_{max} = 1\mu m^{-1}$ were used,

Fig 5.10: PSD calculated from the same profile used to determine roughness/waviness from figure 5.7. We determined $\sigma = 36.1nm$ for equation 1.5, $m = 29.6$ from equation 1.6, and $\ell = 7.67\mu m$ from equation 1.7.

with sample spacing of $0.5\mu m$ in the spatial domain and 1200 data points. A slope of $m = 29.6nm^{0.5}$ was determined as well (Eq. 1.6), yielding $\ell = 7.67\mu m$ for the average spatial separation (Eq. 1.7).

To evaluate the effects of only surface scattering, we will consider a flat surface (form removed), and will not consider scattering from the back surface, defects on the surface, or from the bulk. For the PSD shown in figure 5.10, we calculate the angle resolved scattering function shown in figure 5.11 at $\lambda = 1046nm$ and $633nm$. These two wavelengths are used as the surface is still considered relatively optically smooth for higher wavelengths, giving a σ/λ ratio of 0.034 and 0.056, respectively. We note that this ratio is not a limit of usable wavelengths for illumination for the surface, which would be dependent on application, but a limit at which the approximations of equation 1.8 break down for accurate prediction of scattering. For rougher surfaces which approach $\sigma/\lambda = 1$, Mie scattering theory would be more appropriate. More discussion of this ratio is given in section 1.4.2.

In section 1.4.2 we discussed the scratch-dig standard, MIL-PRF-13830B, often used in the optics industry to determine the quality of an optical piece. We do not use these specifications for analyzing optics created with frontal polymerization because scratches

Fig 5.11: Angle resolve scattering as a function of scattering angle at wavelengths $\lambda = 1046nm, 633nm$ for the one dimensional data shown in figure 5.10. We have used $\theta_i = 0^\circ$ to avoid polarization specific Q . We use an index of refraction of $n = 1.456$ for HDDA. Due to the inherent $\sigma = 36.1nm$ roughness of this sample, we did not lower the wavelength below $633nm$, as this is towards to edge of where the surface is considered optically rough.

are not present due to the non-contact fabrication method and parts with *any* bubbles/pits/trapped dust are immediately discarded due to the short fabrication time. We do not intend to say that the pieces created with frontal polymerization are defect-free however-there *are* defects, but they are of a different nature. As mentioned in the experimental section, the DMD is imaged on to the back surface of a coverslip (the base of the lens) in order to ensure that the light distribution matches that which is predicted (defocus would generate a different intensity distribution in the sample plane). While more accurately reproducing the light distribution, it also allows high enough resolution that the individual pixels on the DMD can be seen on the back focal plane of a lens due to inhomogenous curing of the resin between pixels. One possible cause for this is that a local stress in the resin is created upon cure, therefore modifying the index of refraction, creating localized optical defects. Another possible cause is that because the back focal plane is the region which sees the highest UV light intensity, and therefore sees the highest absorption, that photolysis begins to occur where the newly formed long polymer chains begin to once again break down (the effect which we have all seen in plastics which have

sat out in the sun for a long time). This effect can be reduced, and nearly eliminated, but at the cost of adding defocus to the pattern, altering the predicted shape. A solution would be to predict during pattern generation the defocus effect based on the point spread function of the system, and compensate beforehand as was done to correct resin nonlinearity and non-uniform intensity distribution in section 3.3.4 and 3.3.5. This will be left to future experiments, as it adds a layer of complexity (and therefore a layer of error), and the more challenging and critical aspect is to accurately reproduce the form of the optics.

5.3 Form analysis

After verification of the basic shape and quantifying the roughness/waviness, we naturally must check how well the lens conforms over the entire surface in regards to shape replication. In order to do this, we will profile the surface using a stylus profilometer, and then load the surface data into Zemax OpticStudio for simulation. Due to the time involved with profiling a large surface, we use a high resolution x -direction scan with a step size of $0.5\mu m$ paired with a lower resolution y -scan of $25\mu m$ step size. Once our matrix is generated, we then use Zernike polynomials to determine optical aberration.

After placing our surface data in OpticStudio, we determine the effective focal length (EFL) of the lens to be $9.11mm$, compared to the design focal length of $10mm$. At the EFL we then calculate the Huygens PSF for on-axis rays (figure 5.13), and on inspection can see that it is heavily aberrated with an ill defined spot size of approximately $100\mu m$. Further conducting a 37 Zernike polynomial fitting to this PSF, we determine the Zernike coefficients seen in the bar graph of figure 5.12, along with the peak-to-valley (PV) and root-mean-squared (RMS) wavefront error, also denoted W_{pv} and W_{rms} , in terms of illumination wavelength after piston and tilt have been removed. We determine a W_{pv} and W_{rms} of 21.74 and 2.41 Waves at an illumination wavelength of $\lambda = 550nm$, respectively.

W_{rms} falls drastically outside the typically considered Marechal criterion for diffraction limited optics of $W_{rms} < \lambda/14$. Given the nature of the experiments, we can quantify some of these. The original pattern was for a spherical lens which we can expect to see spherical aberration from. This is noted in figure 5.12 for Z_{11} (using Noll index notation) with a value of -1.1 . Furthermore, due to the variability from sample to sample of approximately $30\mu m$, we can expect to see some astigmatism ($Z_5 = -1.75$ and $Z_6 = 0.25$) because improper prediction of the curing depth of the resin will lead to stretching along the z-axis of the lens. It is possible that coma is also introduced ($Z_7 = 0.7$ and $Z_8 = 0.25$) due to a slight tilt in the exposition platform with respect to the incident illumination, causing, on average, a lower amount of curing on the higher portion of the plane, and a higher amount on the lower portion with respect to the normal of the illumination. Any of these aberrations can also be enhanced due to uncured resin not being fully wicked away before post cure, temperature fluctuation while curing (due to the exothermic nature of polymerization), or stress inhomogeniously building in the lens during polymerization. In the inset of the top of figure 5.12 we see a geometric image reconstruction of alphabetical text with lettering size to that match that of 5.5b. In the bottom of figure 5.12 we show the configuration used for simulation of the PSF, where we load surface sag data directly into OpticStudio. We consider an object at infinity, and use an aperture of radius $r = 1.3mm$. We use a smaller aperture than the diameter of the lens because contact surface profilometer can not accurately measure a steep angled surface, and we therefore discard this data.

Finally, with the realization that the lens does not meet standard, we performed a simple comparison between defocused point-spread function in both experiment and in simulation. The purpose of this test was to determine if the poor optical quality was indeed coming from internal factors (over curing, defects, etc.), or from poor form on the convex surface. In figure 5.14 we show both sets of data, where similarity can be seen between the caustic outline of both intensity distributions. This would suggest that

Fig 5.12: Top) The first 37 Zernike coefficients determined from fitting the wavefront at the focal point. The piston term has been set to zero. Top inset) Simulated geometric imaging of alphabetical text with an image width of 10mm. The simulated image can be visually compared to figure 5.5b. Bottom) Optical configuration for simulation with lens shape input from profilometer data. An aperture of radius $r = 1.3mm$ was used to remove edges of the lens, as edges are not properly measured by the stylus profilometer due to high contact angle. An EFL of 9.11mm was determined (Designed for EFL = 10mm). Wavefront aberration is the same as on the surface of the lens for the case of a plano-convex lens, with exception of Z_1 and Z_4 (piston and defocus). PV and RMS errors were determined to be 21.74 and 2.41 Waves after removal of piston and tilt, and all simulations were performed at $\lambda = 550nm$.

Fig 5.13: Huygens point-spread-function for the profiled lens at the focal point of $EFL = 9.11\text{mm}$. Strong aberration is noted, with spot size not reducing below $100\mu\text{m}$.

Fig 5.14: a) shows the geometric PSF calculated at $D = 10mm$ from the lens, slightly out from the focal point of $EFL = 9.127mm$. b) shows experimental PSF data collected by imaging a HeNe laser at low power on to a CCD. Similarities can be seen between the high intensity caustics, suggesting that poor optical quality is due to lens structure.

a large degradation of optical quality is currently due to form defects. Simulation and experimental measurement were performed with a $633nm$ collimated light source incident on the convex side of the lens with aperture excluding the outer edges.

Chapter 6

Conclusions and Future Work

In this thesis we have presented a summary of various optical fabrication techniques, and then introduced an alternative method which may compliment these technologies in the medium scale optical component range (several millimeter diameter). We introduce a low-cost design which may be implemented with mostly off-the-shelf components consisting of a simple two lens imaging system, and allows for rapid characterization of different polymer blends as well. We also introduce an algorithm for beam homogenization and for shape correction based on the curing depth of a given resin. This could not only be useful in our particular 3D printer, but for other configurations as well.

We show some applications of our low-cost printer to determine the curing characteristics of several polymer blends involving the prepolymers of HDDA, HEMA, PETA, TMPTA, and BisGMA in a deoxygenated environment, and compare these to known theory. In terms of future experiments towards this end, we would later seek to integrate a temperature controller in our exposition platform, as this directly relates to the propagation rates in the resin (and therefore the extent of polymerization)[47]. This would also provide further insight into how the temperature would modify the resin cure depth. The theory would suggest that higher temperature would lead to lower viscosity, yielding an increase in the chain propagation and termination rates, and therefore greater cure

depths. This would similarly have applications in the shape of lenses.

We next attempt to fabricate said lenses, which ultimately did not meet the standards set out to achieve in terms of surface conformity (form). On the other hand, considering ideal form, they did show excellent surface microroughness to that of finely polished optics, but had a waviness profile which approaches the Marechal criterion limit in the visible range ($W_a = 36.1nm * 14 = 505nm$ limit). It is possible that waviness features can be reduced by using longer crosslinking time (and therefore lower intensity), allowing for a more controlled chain growth. Also towards controlling the form, we would seek to reduce the variability from sample to sample. While the exact cause could be several different phenomenon, such as the stability of the LED over time, temperature of the resin, oxygen not being completely depleted in the resin, excess resin remaining on the part surface, or the gel being damaged by the force exerted by excess fluid while removing it from the bath. For the aspects relating to the system, the LED stability could be actively monitored by photodiode added into the system, and the DMD adjusted accordingly in a feedback loop. Oxygen issues, if present, could be solved by working in a glove box, allowing longer purging times, or moving away from free radical photopolymer systems which exhibit the oxygen inhibition effect. Some alternatives would be hybrid ionic initiator systems such as those described in [45]. In terms of issues related to the monomers themselves, appropriate blend could create harder gels on initial polymerization, reducing susceptibility to outside forces during the cleaning step.

Appendix A

A.1 Derivation of equation 1.2

Equation 1.2 can be derived based on the use of the paraxial approximation considering a ray reflecting from a spherical surface. The spherical surface is centered about the z -axis, and has an object point B and image point B' . We start with the well-known mirror equation

$$\frac{1}{s'} + \frac{1}{s} = \frac{2}{R} \quad (\text{A.1})$$

where s and s' are the distances along the optical axis to B and B' as measured with respect to the origin, and R is the radius of curvature in the paraxial limit, two times the distance to the focal point. We can then use Fermat's principle to determine the relations

$$l + l' = (-s + s'), \quad l^2 = y^2 + (-s - \Delta)^2, \quad l'^2 = y^2 + (-s' - \Delta)^2 \quad (\text{A.2})$$

where l and l' are the minimum distances from B and B' to a point on the element's surface as by Fermat's principle for the conjugate points. Δ is the z separation between the same point and the apex of the element. If we consider our origin at the apex, we can define $\Delta = -z$. Using the equations of A.2 to eliminate l and l' we determine the

equation:

$$y^2 - 4z \frac{ss'}{s + s'} + 4z^2 \frac{ss'}{(s + s')^2} = 0 \quad (\text{A.3})$$

We can then rearrange equation A.1 to obtain

$$\frac{ss'}{s + s'} = \frac{R}{2}. \quad (\text{A.4})$$

If we are now to consider a conic section with elliptical shape of vertex radius R , we can define the eccentricity e by $e = c/a$, where c is the distance from one foci to the center, and $c^2 = a^2 - b^2$. Considering these in terms of s and s' , the relationships

$$1 - e^2 = \frac{4ss'}{(s + s')^2}, \quad e^2 = \frac{(s - s')^2}{(s + s')^2} \quad (\text{A.5})$$

can be determined, which in combination with equation A.4, can be substituted in equation A.3 to yield

$$y^2 - 2Rz + (1 - e^2)z^2 = 0. \quad (\text{A.6})$$

Using the quadratic equation to solve for $z(y)$, and substituting in the conic constant $K = -e^2$, we determine:

$$z(y) = \frac{\frac{1}{R}y^2}{1 + \sqrt{1 - (1 + K)(\frac{y}{R})^2}}. \quad (\text{A.7})$$

while noting that for a rotationally symmetric system about the z -axis, $z(y) = z(\rho)$. From this base shape, deviation can be added to create an aspheric surface through the addition of polynomial terms, often even due to the inherent symmetry involved, giving

our final solution and the derivation of equation 1.2 as[87]:

$$z(\rho) = \frac{\frac{1}{R}\rho^2}{1 + \sqrt{1 - (1+k)\left(\frac{\rho}{R}\right)^2}} + A_4\rho^4 + A_6\rho^6 + A_8\rho^8 + H.O.T \quad (\text{A.8})$$

Appendix B

B.1 Derivation of equation 2.10, 2.11, and 2.12

The following derivation is reproduced from the work of J. H. Lee et. al.[55], where more detailed descriptions can be found in his work.

Starting from a generic kinetic equation for polymerization,

$$-\frac{d[M]}{dt} = R_i + R_p \approx R_p \quad (\text{B.1})$$

and

$$R_p = k_p[M][M\cdot]. \quad (\text{B.2})$$

The steady state approximation (where radical initiation equals radical termination) is then used to give R_p as

$$R_p = k_p[M] \left(\frac{R_i}{2k_t} \right)^{1/2}. \quad (\text{B.3})$$

Considering a bifunction free radical initiator, the initiation rate R_i is related to the

photon flux I_z by:

$$R_i = 2\phi\epsilon[PI]I_z \quad (\text{B.4})$$

Using Beer's Law, we can relate the flux at depth z to the surface flux ($z=0$) by:

$$I_z = I_o(10^{-\epsilon[PI]z}). \quad (\text{B.5})$$

Rewriting equation B.4 using this relationship we get

$$R_i = 2\phi\epsilon[PI]I_o(10^{-\epsilon[PI]z}), \quad (\text{B.6})$$

which can then be substituted into B.3 to obtain:

$$-\frac{d[M]}{dt} \approx R_p = K_p[M] \left[\frac{\phi\epsilon[PI]I_o(10^{-\epsilon[PI]z})}{k_t} \right]^{1/2}. \quad (\text{B.7})$$

We can then separate variables and integrate, assuming a linear time relationship to get:

$$\ln \left(\frac{[M]_o}{[M]} \right) = \left[\frac{k_p^2\phi\epsilon[PI]I_o(10^{-\epsilon[PI]z})}{k_t} \right]^{1/2} t. \quad (\text{B.8})$$

The term within the logarithm on the left side is the inverse of the degree of polymerization, defined by:

$$X_n = \frac{[M]}{[M]_o}. \quad (\text{B.9})$$

X_n can be related to the extent of polymerization C_{eff} by:

$$X_n = 1 - C_{eff}. \quad (\text{B.10})$$

As the polymerization reaction continues and C_{eff} increases, a gel begins to form at the critical value C_T . This point corresponds to the edge of a solid being formed, and a critical depth of $z = C_d$:

$$\left[\frac{k_t}{k_p^2 \phi \epsilon I_o} \right] [\ln \left(\frac{1}{1 - C_T} \right) / t]^2 = [PI] I_o (10^{-\epsilon [PI] C_d}). \quad (\text{B.11})$$

The energy exposure per unit area on a surface by a scanning laser is given by:

$$E = \left(\frac{2}{\pi} \right)^{1/2} \frac{P}{W_o V_s} = \left(\frac{ch N_{av}}{\lambda} \right) I_o t \quad (\text{B.12})$$

where V_s is the laser scan velocity. Substituting equation B.12 into equation B.11, eliminating V_s , we can then determine:

$$\left[\frac{k_t \ln \left(\frac{1}{1 - C_T} \right)^2 ch N_{av} P}{k_p^2 \phi \epsilon \lambda W_o^2 (2\pi)^{1/2}} \right] \left(\frac{1}{E^2} \right) = [PI] (10^{-\epsilon [PI] C_d}) \quad (\text{B.13})$$

By then collecting variables by their properties, we can use the two parameters of:

$$\alpha^2 = \frac{k_t [\ln \left(\frac{1}{1 - C_T} \right)]^2}{k_p^2 \phi \epsilon} \quad (\text{B.14})$$

and

$$\beta^2 = \frac{ch N_{av} P}{\lambda W_o^2 (2\pi)^{1/2}} \quad (\text{B.15})$$

to represent the photochemical properties and sterolithography process parameters, respectively. We can then substitute equation B.14 and B.15 into B.13, and then rearrange to solve for C_d to get the final result:

$$C_d = \frac{2}{2.303 \epsilon [PI]} \ln \left(\frac{E [PI]^{1/2}}{\alpha \beta} \right) \quad (\text{B.16})$$

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