Stereolithography Using Compositions Containing Ceramic Powders

by

Hongmei Liao

A thesis submitted in conformity with the requirements for the Degree of Doctor of Philosophy
Graduate Department of Chemical Engineering & Applied Chemistry
University of Toronto

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ABSTRACT

Stereolithography can now be used to build three-dimensional plastic parts based on the layer-by-layer ultraviolet (UV)-curing of photo-monomers under laser irradiation controlled by Computer Aided Design (CAD) data from a computer. This thesis is an investigation of the extension of stereolithography to allow the fabrication of ceramic components. The issues that are addressed are the dispersion of high volume-fraction ceramic powder in liquid monomer while maintaining a low viscosity, UV-curing of these ceramic suspensions under laser exposure, and fabrication of ceramic parts including the debinding and sintering steps.

Photosensitive suspensions have been developed by dispersing selected ceramic powders in non-aqueous acrylate- or epoxy- based monomer solutions. The highly-loaded ceramic suspensions produced include alumina, mullite and silica dispersions which have shown viscosities and cure depths that are compatible with the stereolithography process. Examples of alumina and silica parts fabricated using a stereolithography apparatus (SLA-250) with a 30 mW He-Cd laser are presented. The alumina parts are fully densified after debinding and sintering at 1600°C. The light scattering that occurs at the interface of the particles and a surrounding medium of a different refractive index reduces the cure depth of the suspensions by limiting the depth of light transmission. The penetration depths for these ceramic suspensions are described by UV diffuse reflectance and transmittance measurements and subsequent Kubelka-Munk analysis. Finally, a two-stream multiple scattering model is applied to the ceramic suspensions to study the fundamental parameters that control the curing behavior. The calculated results are compared with experimental data. The insight gained about the principles of the UV-curing of a concentrated suspension provides guidelines for designing suspensions with controlled curing behavior.
I would like to thank my supervisor Professor Tom W. Coyle for providing research directions, insights, continued support, and many discussion hours concerning the technical and non-technical issues I faced through the course of this work.

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Chapter 1

Introduction

1.1 Overview

Rapid prototyping or as it is sometimes called "solid freeform fabrication", "desktop manufacturing", or "flexible manufacturing", turns a computer aided design (CAD) file into a solid model in a shorter amount of time and at a significantly less cost than conventional fabrication methods. Rapid prototyping, which represents processes known as stereolithography (SLA), selective laser sintering (SLS), laminated object manufacturing (LOM), three dimensional printing (3DP), fused deposition modeling (FDM) and others, offers benefits such as speed, complex models, multiple or scaled models, repeatable accuracy and direct use of CAD data [Jacobs 92; Burns 93]. Each technique essentially involves producing parts by adding layers of material on top of each other to build a complete part additively. Although rapid prototyping is a new technology that has largely been developed in the past ten years [Dickens 95], it has assumed a critical role in the activities of technologically advanced corporations, and it has become increasingly available to small businesses through service bureaus [Mueller 95].

Most rapid prototyping techniques have been developed initially to produce polymer prototypes for evaluation of a design in terms of shapes and functionality. The use of rapid prototyping models can reduce costs and shrink the product development cycle and therefore is bringing significant benefits to the design process [Ashley 91; Ashley 95; Wohlers 91; Muraski 90]. The extension of rapid prototyping from the design field to manufacturing is developing rapidly [Kochan 95]. One direction being taken is the direct rapid prototyping of
components for evaluation under actual service conditions.

Stereolithography (SLA) which claims to be the first of the rapid prototyping technologies [Hull 86], was introduced by 3D systems Inc. who shipped the first commercial machine in 1987. Stereolithography starts with a solid CAD model of an object which is cut horizontally into many cross-sectional thin layers using a slicing algorithm. The part itself is built in a vat of photocurable liquid monomer that hardens on exposure to ultraviolet light. An ultraviolet laser beam is moved across the surface of the polymer to instantly cure the liquid and bond the resulting solid layer to the top of an elevator table positioned just beneath the surface. After a layer is built, the elevator is lowered a programmed distance into the vat, and another layer is drawn by the laser on top of the first one. The process is repeated, layer by layer, until a three dimensional plastic part is produced from the bottom up. When the part is completed, it is removed from the machine and postcured in an ultraviolet oven to complete the polymer solidification process [Jacobs 92].

The most notable feature of stereolithography is that it can simply create a complicated, three-dimensional shape fully automatically in a matter of hours compared to weeks or months by traditional methods. An extension of polymer stereolithography that also utilizes inorganic materials would have a great potential to produce functional parts such as dies, molds, and custom components directly without hard tooling. With ceramic stereolithography, it allows the ceramic industry to take all the advantages that rapid prototyping provides; in the mean time the menu of materials suitable for stereolithography will be expanded. In 1995, a hollow silica box (1 inch × 1 inch × 0.75 inch) fabricated using stereolithography was first reported in the literature [Griffith 95]. In 1996, stereolithography fabrication of dense alumina parts was demonstrated by the author [Liao 96a]. More recently, there have been increased research activities in the area of ceramic stereolithography [Brady 96; Garg 96].

The intent of this work aims at defining the capabilities of stereolithography to produce ceramic parts directly from CAD files. Our approach is based on the photo-induced polymerization of a liquid monomer containing a high volume-fraction of ceramic powder.
The whole process includes: dispersion of high volume-fraction powder in liquid monomer maintaining a low viscosity; polymerization of the photoactive suspension under UV laser irradiation; elimination of the organic phase with shape retention; and sintering the powder compact to high density [Griffith 95; Liao 96b]. The essential issues include rheology of highly concentrated ceramic suspensions, ultraviolet curing of these highly concentrated ceramic suspensions under laser exposure (both experimental and theoretical), and fabrication of dense ceramic parts via stereolithography. It is hoped that this work will produce both theoretical and experimental grounds as a starting point for further research work into a novel method of fabricating ceramic functional parts directly from CAD files without tooling.

We have considered a range of ceramic materials including alumina, silica, mullite, zirconia, tri-calcium phosphate and lead zirconate titanate. These powders were dispersed in acrylate- or epoxy-based non-aqueous monomer solutions to create stereolithography suspensions. Alumina has diverse applications ranging from structural components to micro-circuit substrate. Zirconia is a structural ceramic. Silica and mullite represent advanced refractory ceramics. Silica was chosen as a model material for investment casting applications. It is known that tri-calcium phosphate will undergo a phase transformation upon firing to form hydroxyapatite bio-ceramics. Lead zirconate titanate (PZT) is well known for its piezoelectric property and can be used in sensors and actuators.

The liquid monomer phase present in the ceramic suspension, upon partial polymerization under UV irradiation, acts as the organic binder phase to hold the ceramic particles together to form a green ceramic part. To achieve a dense pore-free sintered ceramic part, solids loading as high as 50 volume percent is desirable, similar to conventional ceramic forming processes. The addition of a large volume-fraction of ceramic particles to liquid monomers creates concerns over the stability and photosensitivity of these highly loaded suspensions.

The ceramic suspension must be fluid enough to ensure proper flow during the recoating step of the stereolithography process. Conventional liquid resins used in stereolithography apparatus (SLA) usually have viscosities less than 5 Pa.s at low shear rates, which can be
considered as a rough criterion in tailoring ceramic suspensions for SLA process. To achieve a thoroughly dispersed inorganic phase, a dispersant/dispersants need to be added to allow the polymeric binder to wet the inorganic solids, giving an agglomerate-free system. The selection of a dispersant for a particular system depends on the photosensitive resin system, the type of ceramic powder (i.e., oxide, non-oxide, and etc.), and solvent used. Generally, a medium solubility of the dispersant in the monomer solution is required to ensure the adsorption of the dispersant from the solution onto the surface of ceramic particles. The amount of dispersant is generally 1-5.0 percent by weight of the amount of the ceramic powder used. In some cases, a solvent or a mixture of solvents is added to the suspension to obtain complete dissolution of the dispersant, the photosensitive resin and other organic components. The amount of solvent used with respect to the amount of photosensitive resin is selected so as to obtain an appropriate fluidity while maintaining polymerizability under UV laser exposure.

Unlike chemical-curable compositions which can be cured more or less evenly throughout the volume provided all ingredients are mixed thoroughly, light-curable compositions are cured only at or near the surface where light reaches them. This means both the intensity of laser light and the attenuation power of the suspension influence cure depth. The ceramic particles, when dispersed in a liquid of a substantially different refractive index, appear opaque. The scattering of light involved at the interface of a dispersed particle and the liquid medium will hinder at least part of the light from travelling directly through the medium containing the powder. The simultaneous light scattering by ceramic particles and absorption by liquid monomer matrix control attenuation of light in the suspension which in turn controls the cure depth of the suspension under laser irradiation [Liao 96c].

The objective of this work is to address major obstacles associated with each step of ceramic stereolithography. In this work, photosensitive suspensions of ceramic powders in non-aqueous monomer solutions were created with suitable rheological properties. Next, the suspensions were cured under UV laser exposure in a commercial stereolithography
apparatus. The measured cure depth for the concentrated suspensions is discussed in combination with the light scattering study using UV diffuse reflectance and transmittance measurements. A multiple light scattering model is applied to study the light scattering and absorption in a ceramic suspension theoretically. The modeling provided insight into the curing behavior of a ceramic suspension which helps to predict the cure depth theoretically and therefore is useful in the design of ceramic suspensions suitable for stereolithography. Finally, we demonstrated with alumina and silica that dense ceramic parts could be fabricated via stereolithography including suitable debinding and sintering steps.

1.2 Thesis Outline

Chapter 1 presented the academic challenges and industrial benefits of stereolithography using compositions containing ceramic powders and hence defined the motivations and objectives for this work. It should be noted that this dissertation investigates the potential of creating ceramic parts based on the photo-polymerization of a liquid monomer containing a high volume-fraction of inorganic powder. The focus here is on addressing the main issues related to the four major aspects of this process: dispersion of ceramic powder in liquid monomer solution, photo-polymerization of the composition under UV exposure, removal of the organic phase and sintering of ceramic powder to high density.

Chapter 2 briefly describes the family of rapid prototyping techniques which builds components via a layer-by-layer process directly from CAD files, with an emphasis on stereolithography which is the subject of this dissertation. The focus is on the state-of-the-art of rapid prototyping techniques to produce parts directly from ceramic and metallic materials.

In Chapter 3, the various issues involved in the creation of ceramic suspensions are addressed. Selection of the dispersant/solvent systems was made in an attempt to control the dispersion stability and therefore the rheology. The viscosity of the ceramic suspensions is discussed according to the rheological criteria imposed by the stereolithography process.
In Chapter 4, experimental results of cure depth for ceramic suspensions as studied in a commercial stereolithography apparatus (SLA-250) using a 30 mW He-Cd laser, are presented. Much attention was devoted to determining the cure depth versus ceramic powder concentration and cure depth versus laser dose. Further, the concept of freeform fabrication is illustrated through building multilayer parts from alumina and silica suspensions. These examples make use of the basic idea but at the same time demonstrate the potential of ceramic stereolithography.

In Chapter 5, the optical properties of the ceramic suspensions as characterized by the scattering and absorption coefficients are discussed. Experimental results of UV diffuse reflectance and transmittance spectra for ceramic suspensions are presented, in combination with the Kubelka-Munk analysis on the experimental data. The computation of cure depth as a result of simultaneous scattering and absorption by the suspension is made based on the Kubelka-Munk model and the results are compared with experimental data.

In Chapter 6, the theoretical predication of the cure depth for highly-loaded ceramic suspensions based on multiple light scattering modeling is investigated. A simple multiple light scattering model is applied to study the fundamental parameters which affect the light transmission and subsequently the cure depth of a ceramic suspension. Cure depth dependence on refractive index difference, particle size, particle content, and laser exposure are highlighted. The calculated results are compared with experiment. Further, the curing behavior for other ceramic powders is predicted.

In Chapter 7, a summary of the thesis contributions is given and suggestions are made for further research.
Chapter 2

Rapid Prototyping Background

With rapid prototyping techniques, components and parts can be built directly from CAD files automatically in significantly less time than by conventional fabrication methods [Jacobs 92; Burns 93]. The major application for this technology has been early verification of product designs and the quick production of prototypes for testing [Cohen 92]. The fabrication of patterns or masters for secondary tooling, for processes such as injection molding and investment casting, has become more common recently [Ashley 95]. With increased competition and technical innovations, rapid prototyping is becoming more affordable for a variety of users.

This chapter briefly reviews the various rapid prototyping techniques with an emphasis on stereolithography which is the focus of this dissertation. The major benefits and application fields for rapid prototyping are discussed. The focus is on the state-of-the-art of rapid prototyping techniques to produce parts directly from ceramic and metallic materials.

2.1 Application Fields

Due to competitive pressures, manufacturers are required to bring their products to market with reduced development costs and in ever shorter development times. Both of these objectives can be achieved through rapid prototyping. The general steps for the development of a product usually include: (1) designing the prototype in a CAD system; (2) building the prototype; (3) inspecting the prototype part for errors; (4) correcting the errors in CAD; (5) verifying the corrected prototype part; (6) iterating to improve the design; (7) building a functional test model; (8) performing functional testing and (9) proceeding to manufacture
The development areas in which rapid prototyping have been put to use are design verification as well as prototype-production.

Figure 2.1 lists the application fields for rapid prototyping. Design models built by rapid prototyping have been used for purposes such as visualization, verification, and iteration. Conventional methods for design verification have been the manual and numerical control (NC) machining of aluminum and machineable plastics. In some industries such as automotive and aerospace, the originality of a design is particularly important and the creation of prototypes via conventional methods is expensive because they require expensive tooling and lengthy manufacturing cycles. In comparing rapid prototyping to the conventional approach for making parts, rapid prototyping can easily create a complicated three-dimensional shape fully automatically in a matter of hours [Chua 94a]. Design verification savings using rapid prototyping vary by firm and application and are best calculated on a case-by-case basis [Jacobs 92]. In general, rapid prototyping is most beneficial for situations where a single unique item or a small number of copies is needed, the optimization of a design is important, and/or the shape of the object is too complex to be generated in any other way.

With the improvement of the technology, rapid prototyping can generate patterns or master models to be used in processes such as investment casting and injection molding [Mueller 91; Innace 94; Gustafson 95]. For this application, an accurate pattern is first built by rapid prototyping techniques. Then a refractory ceramic material is coated on this pattern, and when this is sintered at high temperatures, the plastic prototype is burned out and the ceramic shell forms a mold. When molten metal is poured into this mold, a cast product is created. This concept has been employed to produce patterns from CAD which, when applied to an investment casting operation, yield molds to be used in injection molding of plastics. A process called “QuickCast” based on stereolithography was introduced by 3D Systems Inc. in 1993 [Jacobs 93]. QuickCast rapidly builds precise epoxy-based resin patterns that replace standard wax patterns traditionally used to make high-quality metal castings. QuickCast application examples have been illustrated [Denton 94; Jacobs 94].
Three-Dimensional CAD

Rapid Prototyping Systems

Industrial Fields
- Design Models
  - Visualization
  - Verification
  - Iteration
  - Optimization
- Master Models
  - For Use in
    - Injection Molding
    - Investment Casting
    - Sand Casting
    - Flame Spraying

Medical Fields
- Duplication
- Dental Models
- Surgical Operation Simulation
- Custom Implants

3D Copiers
- For Use in Archeology
- Duplication of Artifacts

**Figure 2.1:** Applications for rapid prototyping techniques

Another application of rapid prototyping is three-dimensional replications. Objects can be scanned by a laser scanner, converted to CAD files from which replicas are fabricated using rapid prototyping techniques [Schuster 93; Godin 93; Chua 94b]. Three-dimensional replications are particularly useful for archeologists and museum curators. Applications in medical fields include valuable three-dimensional representation, surgical operation simulation, and creating custom implants using computer tomography (CT) data [Adachi 93; Burns 93].

### 2.2 Rapid Prototyping Techniques

Rapid prototyping builds three-dimensional parts via a layer-by-layer process. In principle, each technique begins with a CAD file representing a three-dimensional object, which is then sliced into many cross-sectional elements or layers. Then, the three-dimensional model is created by "imaging" each cross-sectional layer, one on top of the other. In practice, the methods of imaging each layer are different among rapid prototyping techniques and can be classified into: (1) solidifying photosensitive liquid resins by a UV laser; (2) cutting
materials in a sheet form by a CO$_2$ laser; (3) melting powders into a fused state by a CO$_2$ laser; (4) spreading layers of powders and ink-jet printing binders; and (5) laminating a wire-shaped plastic by squeezing it through a nozzle [Jacobs 92]. In this section, each of these methods will be briefly described.

### 2.2.1 Stereolithography (SLA)

Among rapid prototyping processes, stereolithography systems pioneered by 3D Systems Inc., Valencia, CA, have been used most widely. This process combines computer aided design with laser-induced photocuring to build three-dimensional parts. The operation employs photomonomomers that change from liquid to solid upon an ultraviolet laser irradiation.

The concept of three-dimensional photo-fabrication was introduced by Munz as early as 1956 [Munz 56]. The process, called “photo-glyph recording” by Munz, used masks, a light source, and a photoresist composition or a silver emulsion. In 1981, Kodama described a process using either a series of photo-masks or an x-y plotter to draw and stack cross-linked layers [Kodama 81]. The use of a computer with a laser and photopolymer was reported in a paper by Herbert in 1982 [Herbert 82].

In a patent by Hull [Hull 86], a stereolithography system was described, which included a platform in a resin vat, a computer, and a laser. During the process, the platform moves down into the liquid resin tank by a pre-determined layer thickness for further solidification. Various approaches for three-dimensional photo-fabrication have been developed in the literature [Fudim 88]. Fudim described a process called “sculpting with light” which uses a series of masks [Fudim 86]. Instead of the use of a movable platform, a patent [Masters 87] described a system which involves the use of a device to “inject” or “spray” droplets of curable material in an imagewise fashion while being irradiated with UV light.

The commercial stereolithography machines based on the patent by Hull were developed by 3D Systems Inc. in 1987. The two stereolithography machines sold by 3D Systems Inc. today are the SLA-250 and the SLA-500 for about $250,000 and $540,000, respectively. The
SLA-250 constructs parts up to $10 \times 10 \times 10$ inches with a 30-milliwatt helium-cadmium laser, while the SLA-500 system features a 200-milliwatt argon-ion laser that builds parts up to $20 \times 20 \times 24$ inches. Part accuracies are $\pm 0.005$ inch.

Other SLA systems developed by Sony (SCS machines), Dupont (SOMOS machines), Mitsubishi (SOUP machines), and Electro-Optical Systems of Germany (Stereos 400) are very similar to SLA units. Cubital Ltd., an Israeli company has developed the Solider system which involves UV light exposure through masks.

Basically, stereolithography builds three-dimensional parts of plastic materials. More recently, stereolithography using photosensitive ceramic suspensions has been reported [Griffith 95; Liao 96a]. This dissertation aims at producing ceramic parts directly from the stereolithography process.

### 2.2.1.1 Basic Operation

Figure 2.2 illustrates the schematic diagram of the stereolithography apparatus, which is comprised of three basic components: a computer, a UV laser, and a resin vat with a movable platform. To build a three-dimensional part, there are three major steps: (1) preparing and slicing a CAD file; (2) part building; and (3) postprocessing [Jacobs 92].

![Schematic diagram of the stereolithography apparatus.](image)

**Figure 2.2:** Schematic diagram of the stereolithography apparatus.
The first step involves the generation of a three-dimensional CAD file of the object, which is then translated to the "STL" format that can be input to the stereolithography machine. Then support structures are selected for this object for the following purposes: (1) to provide temporary support of overhangs and other sections during the time of part building; (2) to facilitate the removing the part from the platform upon its completion; (3) to ensure that the recoat blade will not strike the platform upon which the part is being build; (4) to ensure that any small distortions of the platform will not lead to problems during part building. A separate CAD file is generated for the support structures.

Both the part and the supports are "sliced" using a computer algorithm into a series of cross-sectional layers. During this step, the layer thickness, the build style, the overcure thickness, the line width compensation, and the shrinkage compensation factors are all selected. The sliced files for both the part and the supports are then merged together. Before the beginning of part building, certain operational parameters are selected, such as the number of recoater blade sweeps per layer, the sweep period, and the desired "z-wait" which is the amount of time (in seconds) that the system is instructed to wait after recoating. This pause ensures a smooth and uniform resin surface before polymerizing another layer.

The step of part building is where the liquid resin polymerizes upon the laser irradiation and a three-dimensional object is created by a layer-by-layer process. The building process consists of leveling, recoating, and laser polymerizing.

During the building process, the distance between the laser beam and the surface of the liquid resin is chosen so that the width of laser beam is at its minimum. In the SLA system, there is a unit responsible for level compensation. Upon completion of laser drawing on each layer, the resin level is checked and corrected if necessary before proceeding to the next step.

The recoating step starts at "Deep Dip". Under computer control, the z-stage motor moves the platform down into the vat by a distance of about 0.3 inches for the SLA-250. Under the influence of gravity, the resin fills the depression zone generated by the deep dip. The z-stage, again under computer control, then elevates the most upper part layer above the free resin
surface. When the elevation step is completed, the most upper surface of the previously cured layer is positioned one layer thickness below the bottom edge of the recoater blade. At this point, the recoater blade traverses the vat from front to back, and “sweeps” the excess liquid resin from the part. For the majority of part geometries, the optimum sweep period is about five seconds. Upon completion of sweeping, the z-stage moves downward again until the top of the layer of recoated resin is at the free surface level of the resin in the vat. At this position, the top of the previous layer is now at a depth equal to one layer thickness. Once the platform has moved to the build position, in principle, the resin on top of the previous cured layer should blend with the free surface of the liquid resin in the vat. Unfortunately, due to finite surface tension effects, it is common to notice a small “crease” around the perimeter of the part, at the solid to liquid interface. The amplitude of the crease will decay with time. The so-called “z-wait” which is commonly between 15 to 30 seconds, is intended to eliminate this non-uniformity. Up to this point, the total recoating time is about one minute.

More recently, a new coating apparatus called Zephyr has been developed for the SLA-250 and SLA-500 machines [Edge 96]. With the Zephyr recoating system, the need to “deep dip” and subsequently “elevate” are avoided. Through a special reservoir and channel located within the recoater blade, resin is directly applied on top of the last cured layer, requiring that the part be lowered only one layer into the vat before recoating. The result is shorter times between drawing of subsequent layers and a shorter overall build time.

After the recoating step is completed, the liquid resin is ready for “laser drawing”. Having specified the desired cure depth which is the sum of layer thickness and overcure amount, the laser drawing speed is automatically adjusted so that the energy deposition is sufficient to polymerize the resin to the specified cure depth. During the scanning process, the laser first draws the part borders for the given layer cross-section, then proceeds to “hatch” or “fill-in” those interior areas that will eventually become solidified.

Once the laser drawing is completed for a given layer, the above steps of levelling, recoating, and laser drawing are repeated for subsequent layers until a three-dimensional part
is built from the bottom up. The duration of part building varies according to the complexity of part geometry, part size, and type of resin. Part building can average from 4 to 20 hours.

After completion of building the part, the platform and the attached part are elevated above the free surface of the resin in the vat and excess liquid resin is drained. Then the platform with the attached part is removed from the SLA chamber and excess liquid resin is wiped away from both the part and the platform. The platform and the part can also be further cleaned in a solvent cleaning vat with/or without ultrasonification. After cleaning, the platform and the attached part are dried. Then, the part is removed from the platform.

Finally, the part is postcured in a UV lamp oven to complete the polymerization process and to improve the final mechanical strength of the prototype. Postcuring takes about 1-2 hours, however, large parts may require up to 10 hours. After postcuring, the part is ready for hand-sanding, polishing, painting, and/or spray metal coating.

### 2.2.1.2 Photo-Induced Polymerization

The ultraviolet radiation induced polymerization of acrylate resins has been used in the coating industry for more than 20 years. Applications range from furniture finishes, high gloss paper finishes, printing inks, to reinforcement coatings for fiber optics [Salim 90].

The development of stereolithography resins has taken advantage of the wide range of commercially available photosensitive monomers and oligomers which were originally developed for use in coatings. Basically, a stereolithography resin consists of photosensitive monomers, oligomers, a small amount of photoinitiators, and other additives. The mechanisms of photocuring are free radical polymerization for acrylates and cationic polymerization for epoxies. The general mechanisms of photo-induced polymerization can be found in the literature [Pappas 78; Roffey 82; Decker 90].

The acrylate resins were first formulated for the stereolithography. The free radical polymerization of an acrylate monomer is an energetically favorable or “exothermic” reaction [Hoyle 92].
**Figure 2.3:** Illustration of the free radical polymerization.

The essential steps in polymerization are: initiation, propagation, and termination, as illustrated in Fig. 2.3. When exposed to the appropriate laser light wavelength, the photoinitiator \( I \) absorbs energy and forms free radicals \( R \cdot \), which, in turn, react with the monomer molecules \( M \) to start the chain reaction.

Polymerization does not proceed beyond a limited extent until the laser exposure reaches a level \( E^* \) sufficient to create enough free radicals to overcome quenching by inhibitors such as oxygen or water [Jacobs 92]. Photo-polymerization takes place in microregions near the site of radical initiation, e.g., the polymerization proceeds one spot at a time. The growing macroradical becomes a cross-linked gel at a relatively low degree of conversion. The rate of polymerization steadily decreases as the concentration of unreacted monomer decreases and the viscosity of the gel increases. The mobility of free monomer to the site of the macroradical is thus restricted at higher conversion.

The termination occurs mainly due to recombination and disproportionation. In thin films,
the reaction is strongly inhibited by atmospheric oxygen, which diffuses into the surface of the polymerizing micro-region and interferes with the polymerization by scavenging both the initiating and the polymer radicals [Fouassier 93]. For laser-induced polymerization, the polymerization reaction continues to occur after the radiation by a UV laser stops (i.e., “dark reaction”) [Kotchetov 93]. The dark reaction time for most SLA resins is about one second [Jacobs 92].

It is well recognized [Decker 90; Jacobs 92] that laser-induced polymerization only results in a low degree of monomer conversion. Therefore, laser-cured parts need to be postcured in a UV lamp oven to complete the polymerization process and improve the mechanical strength of the part. In addition, acrylate resins usually shrink about 5-7% by volume, while epoxy resins shrink less (2-3%). Shrinkage, insufficient green strength, and other factors all contribute to the distortion and warpage of the part built by SLA. The origin and control of part distortion and curl have been the subject of extensive studies [Jacobs 92].

In stereolithography, the resin is polymerized layer-by-layer. The polymerization proceeds based on the surface light absorption which follows the Beer-Lambert exponential law. The Beer-Lambert law indicates that there is a gradient of cure from the top to the bottom of a cured specimen. The cure depth depends upon the absorption characteristic of the monomer as well as the laser exposure level (mJ/cm²), as shown in the following equation:

\[ C_d = D_p \ln \left( \frac{E}{E_c} \right) \]  

(2.1)

where \( C_d \) is the cure depth, \( D_p \) is the resin “penetration depth”, \( E \) is the laser exposure on the resin surface, and \( E_c \) is the threshold exposure level of the resin. In practice, the transition from a liquid phase to a solid phase does not occur until the laser exposure reaches a threshold value \( E_c \) \((E_c > E^*)\), where \( E^* \) is the laser exposure level required to overcome the quenching of free radicals due to inhibitors such as oxygen or water.

In general, \( D_p \) and \( E_c \) are two constants of the resin, depending on the composition of the resin, the concentration of the initiator, and the concentration of inhibitors. Equation 2.1, which is fundamental to SLA, indicates a linear relationship between \( C_d \) and \( \ln E \), which is true
at a cure depth range between \( D_p \) and \( 4D_p \) (i.e., \( D_p < C_d < 4D_p \)). For cure depths greater than \( 4D_p \), \( C_d \) versus \( \ln E \) will often begin to exhibit nonlinear behavior [Jacobs 92]. For a resin, measured \( C_d \) is plotted as a function of \( \ln E \) and \( D_p \) and \( E_c \) are then obtained from the slope and intercept, respectively.

Both acrylate- and epoxy- based resins specifically designed for stereolithography are commercially available. Table 2.1 summarizes the characteristics of a variety of resins. In general, epoxy resins require longer part building hours than acrylate resins. However, more accurate parts can be built from epoxy resins due to their lower shrinkage compared with acrylate resins.

<table>
<thead>
<tr>
<th>Company</th>
<th>Trade Name</th>
<th>Product (HeCd laser)</th>
<th>( D_p ) (( \mu \text{m} ))</th>
<th>( E_c ) (mJ/cm(^2)) (HeCd laser)</th>
<th>Viscosity (Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dupont</td>
<td>SOMOS (acrylate-based)</td>
<td>2100/2110</td>
<td>118</td>
<td>3.5</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3100/3110</td>
<td>126</td>
<td>2.5</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5100/5110</td>
<td>102</td>
<td>2.5</td>
<td>5</td>
</tr>
<tr>
<td>Ciba-Geigy/3D Systems</td>
<td>Cibatool SL (epoxy-based)</td>
<td>5081 (acrylate-based)</td>
<td>178</td>
<td>5.6</td>
<td>1.6-2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5149</td>
<td>147</td>
<td>5.5</td>
<td>1.6-2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5154</td>
<td>130</td>
<td>4.2</td>
<td>1.6-2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5170</td>
<td>122</td>
<td>13.5</td>
<td>0.165-0.195</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5180</td>
<td>132</td>
<td>16.2</td>
<td>0.187</td>
</tr>
<tr>
<td>Allied Signal</td>
<td>Exactomer (acrylate-based)</td>
<td>2201 (acrylate-based)</td>
<td>175</td>
<td>27</td>
<td>0.205</td>
</tr>
</tbody>
</table>

2.2.1.3 Laser Exposure Process

The advantage of lasers over conventional light sources lies in the ability to rapidly direct focused radiation of appropriate power and wavelength onto the surface of a liquid photopolymer resin. Helium-cadmium lasers produce UV light at 325 nm at powers of 20-30 mW. One problem with this laser is that the cadmium is consumed and, as a result, there is a
limited useful life. An argon-ion laser delivers 100-500 mW at 351 nm and 364 nm. The power and wavelength of argon ion lasers are better, but, they are more expensive.

For the SLA-250/500 machines, the laser itself remains stationary during the laser drawing process, but a galvanometer mirror scanner guides the light. After passing through a focusing system, the beam is reflected by two mirrors, one moving the beam from side to side on the surface of the vat, and the other moving it from front to back. Galvanometers are used to deflect the mirrors. The angular position of the two mirrors is controlled by CAD data from the computer. During the part building process, the laser scan speed is automatically adjusted by the computer to provide the required exposure (mJ/cm²) necessary to polymerize the material to a pre-selected cure depth.

The lasers are focused to provide an illumination spot between 200 and 300 μm in diameter on the liquid resin surface [Jacobs 92]. The shape of the beam cross-section is circular, and the profile of the intensity of the laser beam is approximately Gaussian. Figure 2.4 shows a schematic view of the curing profile. For a laser scanned in a straight line across a photomonomer obeying the Beer-Lambert law, the cured line width \( L_w \) is found to be directly proportional to the laser spot diameter \( B \) and the square root of the ratio of the cure depth \( C_d \) to the resin penetration depth \( D_p \) by the expression [Jacobs 92],

\[
L_w = B \sqrt{\frac{C_d}{2D_p}}
\]  

(2.2)

Thus, curing deeper will also result in increased linewidth. According to Eq. 2.2, "line width compensation" can be incorporated in the software.

During laser scanning, the borders are drawn first and then the interior is scanned with selected build styles. "Tri-Hatch" uses a scanned line parallel to the \( x \) axis with lines at 60° and 120° to the \( x \) axis. This produces an internal structure of equilateral triangles. The most common spacing between these lines is 1.27mm. Vertical triangular columns are thereby created which contain resin that has not been solidified. This captured resin is cured during postprocessing.
Figure 2.4: Schematic view of the curing profile for laser exposure.

(a) Weave: conventional hatch

(b) Star-weave: staggered hatch

Figure 2.5: Illustration of building styles of (a) weave and (b) star-weave.
More efficient building styles are the so-called “Weave” and “Star-Weave” patterns. “Weave” uses hatch scanned parallel to the x axis and the y axis. The hatch spacing ($h_x$) is approximately 0.3 mm (for a 254 $\mu$m layer thickness) for both the x and y hatch. The spacing must be reduced when building thinner layers. “Weave” leaves very little resin that has not been at least partially cured. “Star-Weave” building style has been developed to compensate for the internal stresses created during the building step. Figure 2.5 compares the two different building styles [Jacobs 92]. With Star-weave, a staggered hatch between layers is used. This reduced the internal stresses dramatically. In addition, alternate sequencing and retracted hatch are employed as well. The alternate sequencing has the laser scanning in opposite directions for each layer which reduces the build up of internal stresses. The retracted hatch reduces the tendency to curl for the part.

The above building methods are intended for the interior of a part. The outside surfaces or skins require a “skin fill”. In this case, the laser must polymerize the complete surface.

### 2.2.2 Laminated Object Manufacturing (LOM)

The laminated object manufacturing (LOM) technique builds parts by laminating and laser-trimming the material delivered in sheet form (i.e., paper and plastics). Commercial LOM machines are sold by Helisys Inc., Torrance, CA. The concepts related to the use of sheet materials in building three-dimensional parts were reported in 1984 [Kunieda 84]. In 1988, the laminated object manufacturing systems were described in a patent [Feygin 88]. Further improvements on the LOM method were suggested by Feygin as well [Feygin 90].

During the part building process, sheet material is supplied from a continuous roll on one side of the machine and taken up on the opposite side. Beneath the sheet is a platform on which the part is fabricated and which can be moved vertically under computer control. The sheets of materials are laminated into a solid block using a thermal adhesive coating. Each sheet is attached to the block using a heated roller to form a new layer. Next, the contours associated with the current cross-section are cut into the layer using a 25 or 50 watt CO$_2$ laser. After the
cut is completed, the laminated layers are lowered, and the next sheet is rolled into place. This process is repeated until all layers have been laminated and cut. Then, the formed part imbedded within a block of supporting materials can be removed.

The LOM process was originally designed to produce parts from paper. In 1994, fabrication of ceramic components via the LOM process has been reported by Griffin et al. at the Lone Peak Engineering Inc., Draper, Utah [Griffin 94]. During the LOM process, tape-cast ceramic sheets were cut by a CO₂ laser to create each cross-section. However, each ceramic tape has to be manually added to the platform before lamination and cut. After completion of the part building, the ceramic green parts are heated up to burn-out the binder phase and sintered to high density. Dense alumina ceramic components have been made using tape-cast alumina sheets with a thickness of about 375 μm [Griffin 94]. More recently, ceramic composites were fabricated by alternating the layers of Ce-ZrO₂ and mixed Al₂O₃/Ce-ZrO₂ tapes in the LOM process [Griffin 96]. The tape thickness was 58 μm or 116 μm. The physical and mechanical properties of the sintered ceramic composites were measured [Griffin 96; Mumm 96].

The fabrication of components from ceramic green tapes was also reported using a cut-then-stack approach which is known as computer-aided manufacturing of laminated engineering materials (CAM-LEM) [Cawley 96]. In CAM-LEM, individual cross-sections are cut from the ceramic tape using a CO₂ laser first. Then these cross-sections are stacked and laminated together using a robotics system to form a solid part. The laminated green object is then heated to remove the organic phase and finally sintered to high density. CAM-LEM technology has been demonstrated for the fabrication of alumina components.

2.2.3 Selective Laser Sintering (SLS)

The selective laser sintering (SLS) system sold by DTM Corp., Austin, TX. generates three-dimensional parts by fusing powdered-thermoplastic materials with the heat from a CO₂ laser. The concept of selective laser sintering was proposed initially by Deckard as a Master's
student at the University of Texas at Austin in 1986 [Deckard 86] and he was granted a patent later [Deckard 89].

During the building process, a uniform thin layer of powder is deposited under controlled temperature and atmosphere using a powder leveling drum. The particles range in diameter from 80 µm to 120 µm and the layer thickness ranges between 75 µm and 250µm for various powders. The first layer of the object is traced with a CO₂ laser coupled to the computer-controlled scanning system. The laser beam scans the powder bed surface and raises the temperature of the powder it contacts, binding the loose powder together to form a solid mass. This process is called fusing or sintering. In areas not sintered, powder remains loose and may be removed once the part building is completed. At the end of the first layer scan, a second layer of loose powder is deposited and then sintered. The process is repeated until a three-dimensional part is built layer-by-layer.

Materials used for SLS include polyvinyl chloride (PVC), polycarbonate, investment wax, and nylon. The SLS processing of metals and ceramics has been under development at the University of Texas at Austin [Bourell 92]. The approaches described included the use of precursor powder mixed with or coated by a polymer. The ceramic materials studied were alumina/ammonium phosphate [Bourell 92], alumina/boron oxide [Lee 94a], calcium phosphate [Lee 94b], and silicon carbide precursors [Tompkins 94]. The green body formed by SLS process is then subsequently heated to remove the binder and sinter the ceramic. However, little success has been achieved so far in producing dense ceramics of structural integrity due to inappropriate powder sizes and compositional problems.

Selective laser sintering of metals has been developed using metal powders coated with a thermoplastic binder and infiltrating the porous metal parts [Bourell 94]. The green metallic part formed by the SLS processing is postprocessed in a furnace where the binder is removed and the metal powders are bonded together to form a porous part. An infiltrant is then added to infiltrate the pores of the metal part to generate a dense part. The infiltrant is usually copper and a hydrogen furnace is required to control the resulting mechanical properties.
2.2.4 Three-Dimensional Printing (3DP)

The three-dimensional printing (3DP) system developed at the Massachusetts Institute of Technology (MIT), generates three-dimensional parts by repetitively spreading a layer of powder and selectively joining the powder within the layer by ink-jet printing of a binder material [Sachs 92]. The 3DP machine, known as the Direct Shell Production (DSP) system, is sold by Soligen Inc., Northridge, CA for the direct fabrication of casting molds.

The solid object is created by printing a sequence of layers. Each layer begins a thin distribution of powder spread over the surface of a bed of loose powder. Particles are then joined by the selective application of a liquid binder material using a technology similar to ink-jet printing. The powder is contained in a flask with a movable piston that allows the part to be lowered at the completion of a given layer, and another layer of powder is spread and selectively joined together. This layer-by-layer process is repeated until the part is completed.

The 3DP process can use a number of powdered materials including those well-known to the investment casting industry in the production of shells: refractory powder, such as silica and alumina, and a liquid colloidal silica binder [Michaels 92; Sachs 93]. The 3DP machine has been used to fabricate ceramic shells using a refractory material based on alumina/colloidal silica. The green body formed by 3DP is subsequently heated to remove the binder and improve the ceramic strength. Currently, the major problem with 3DP-produced molds is inadequate surface finish [Fan 93].

2.2.5 Fused Deposition Modeling (FDM)

The fused deposition modeling (FDM) system developed by Crump [Crump 92], generates three-dimensional parts by dispensing thermoplastic wire-like filaments through a controlled temperature extrusion head. The FDM machine (3D Modeler) is sold by Stratsys Inc., Minneapolis, MN.

During the building process, a spool of the thermoplastic wire-like material is fed into the temperature controlled extrusion head, heating the material to a semi-liquid state. The
semi-liquid resin is then extruded from the head and deposited in a layer-by-layer process. A precision volumetric pump is used to control the material passing through the extrusion head. The model is fabricated upon a piston which is lowered, between layers, to make room for the next layer. The types of resin that can be used in the FDM process are nylon, wax, and acrylonitrile butadiene styrene (ABS).
Chapter 3

Photosensitive Suspensions

A stable suspension of ceramic powder dispersed in liquid monomer at high solids loading with low viscosity is highly desirable in stereolithography. The suspension should contain as much as 50-60 volume percent of ceramic particles to achieve a high green density and minimize the shrinkage upon removal of the organic phase and porosity of the sintered part, while in the mean time, be fluid enough for use in a stereolithography machine.

In this chapter, the preparation as well as rheological properties of photosensitive ceramic suspensions are reported. First, the dispersion of ceramic powders in organic liquids is briefly reviewed. The preparation of highly concentrated non-aqueous ceramic suspensions via adding proper dispersant/solvent systems along with using suitable mixing procedures, is then given. Finally, the rheological characterization of the ceramic suspensions developed is presented. The effects of shear rate and solids loading on viscosity are discussed briefly.

3.1 Dispersing Powders in Organic Liquids: a Brief Review

Dispersion of a powder in a liquid generally consists of three stages: wetting the surface, deagglomerating clumps, and stabilizing the powder against flocculation [Parfitt 81].

The first stage, wetting the powder, is dependent on the characteristics of the powder and the liquid. The wetting occurs to minimize the surface free energy at the interface between the liquid and particle. The degree that liquid wets a solid can be estimated by the contact angle formed by a drop of the liquid on a flat, dense, solid surface. The contact angle is related to the surface tensions via Young’s equation [Nelson 88],
where $\gamma_{sv}$, $\gamma_{sl}$, $\gamma_{lv}$ are the interfacial tensions for the interfaces between the solid and vapor phases, the solid and liquid phases, and the liquid and vapor phases, respectively. A small contact angle indicates the liquid wets the solid.

The second stage, deagglomeration, may require some activation procedure (e.g. stirring or shaking, ultrasonification, or milling). The third stage, stabilization, is determined by the balance of the forces acting between individual particles. Powder particles wetted by liquids may not achieve much dispersion due to van der Waals's attractive forces if no repulsive forces are present between the particles. The sources of repulsive forces between particles include electrostatic repulsion, steric barriers, solvent forces, or their combination [Horn 90].

A dispersion is usually stabilized by adding electrolyte or polymer dispersants to the suspension. The dispersants added may migrate to the solid-liquid interfaces and form a layer of sufficient thickness to provide electrostatic or steric repulsive forces between the solid particles. The stability of aqueous suspensions containing electrostatically charged particles can be described by the well-known DLVO theory which considers the balance between electrical double-layer repulsions and van der Waals attractions [Horn 90]. DLVO theory has been successfully applied in extensive studies of aqueous suspension stability.

In nonaqueous suspensions, there is some evidence for electrostatic stabilization due to charged species on particle surfaces [Fowkes 87]. However, the low dielectric constants of organic solvents result in weak electrostatic interactions. As a result, electrostatic stabilization is not effective in non-aqueous suspensions. Instead, steric stabilization plays the major role in non-aqueous systems. The use of steric stabilization has the advantage that it can be effective under conditions of high volume fractions of solids [Kerkar 90]. Extensive reviews on steric mechanism are available in the literature [Vincent 74; Napper 83]. Steric stabilization originates from entropic and osmotic interactions between adsorbed polymer layers on separated particles. Such layers can form steric barriers around the particles and their
deformation or interpenetration upon collision results in repulsions. The criteria for an effective steric stabilization are strong attachment of the dispersant to the particle surface, a complete coverage of the particle by the adsorbed molecule, and good solvation condition of the loops and tails of the adsorbed polymer [Tadros 82].

To achieve a thoroughly dispersed inorganic phase, a dispersant/dispersants need to be added to promote the wetting of the inorganic solids by the liquid as well as stabilize the suspension against flocculation. The selection of effective dispersants for a particular system is difficult and usually based on the method of trial-and-error. The characteristics of the photosensitive resin systems, ceramic powders, and solvents if used as well as the interactions among them should all be considered in choosing dispersants. The choice of dispersants could be fatty acid, polycarbonates, copolymers, etc. A large number of dispersant copolymers are available on the market, and they are developed for specific media varying from the strongly polar to the nonpolar [Schofield 90]. In the literature, two copolymer dispersants have been used in the dispersion of copper solids in a photosensitive copper conductor composition [Nebe 89]. In this study, a copolymer dispersant used in paints which are acrylate resins filled with pigments was found effective in dispersing ceramic powders in non-aqueous photosensitive resin systems.

In some cases, a solvent or a mixture of solvents is added to the suspension to obtain complete dissolution of the dispersant and provide solvation of the loops and tails of the adsorbed dispersant molecules. The amount of solvent used with respect to the amount of photosensitive resin is tailored to obtain a ceramic suspension which is fluid as well as UV-curable.

Rheological behavior of ceramic suspensions is ultimately determined by the state of dispersion as governed by the interparticle forces [Bergström 94]. Good dispersion allows higher solids loading to be achieved, while still maintaining reasonable viscosity levels necessary for processing. The rheology of concentrated suspensions is concerned with how these materials respond to an applied stress or strain [Barnes 89]. In simple shear, which is the
most common way of determining the rheological behavior, the shear stress $\tau$ can be related to the shear rate $\dot{\gamma}$ by

$$\tau = \eta \dot{\gamma}$$

(3.2)

where $\eta$ is the viscosity.

The different types of response in steady shear can be illustrated by plots of shear stress versus shear rate, or viscosity versus shear rate. Yield stress values are defined as the shear stress intercept obtained by linearly extrapolating the high shear rate portion of the flow curve (shear stress versus shear rate) back to zero shear rate. In the simplest case, so-called Newtonian behavior, the flow curve is a straight line passing through the origin with the slope being equal to the viscosity. In practice, most concentrated suspensions show non-Newtonian behavior where the viscosity is shear dependent. Therefore, rheological characteristics of concentrated suspensions are complex. Factors affecting the rheology of concentrated suspensions include the base rheology of the liquid phase, the volume-fraction of the dispersed solids, the average particle size and particle size distribution of the powder, the structure of the aggregates formed, and the interaction forces among the ingredients of the suspension.

The relative viscosity $\eta_r$ is defined as the ratio of the apparent suspension viscosity $\eta_s$ to that of the liquid phase $\eta_l$ as expressed in the following equation.

$$\eta_r = \frac{\eta_s}{\eta_l}$$

(3.3)

As the ceramic volume fraction of suspensions is increased, the relative viscosity increases but generally remains low until the particle packing hinders the flow of the suspension. When ceramic concentration approaches the maximum packing volume, the relative viscosity shows a steep dependence on solids loading.

### 3.2 Experimental

In this work, photosensitive suspensions were created by dispersion of selected ceramic powders in non-aqueous acrylate- and epoxy- based resin solutions. The rheological properties
of the suspensions were characterized. The goal is to obtain a high solids loading while still maintaining a reasonably low viscosity (less than 5 Pa.s). This section describes the materials and experimental procedures used.

### 3.2.1 Materials

**Ceramic Powders**

Six ceramic powders have been investigated and Table 3.1 shows the characteristics of the ceramic powders used. The silica and mullite powders obtained from the suppliers have large particle sizes and broad particle size distributions. Therefore, a 4 hour attrition milling process was employed to grind both silica and mullite powders, respectively. After attrition milling, particle sizes for silica and mullite were measured and reported in Table 3.1.

**Monomers**

Acrylate- and epoxy- based resins for stereolithography are commercially available and used as the liquid monomer systems in the ceramic suspensions. Table 3.2 shows the resins used and their physical properties according to the suppliers. SOMOS 5100 (SM 5100) is a liquid photopolymer system including components of acrylate monomer, methacrylate monomer, acrylate oligomer, photo-initiator, and other additives. Cibatool SL5170 (CT 5170) is a liquid epoxy resin with additions of acrylate ester and photo-initiator.

**Dispersants**

To help achieve highly loaded suspensions with low viscosity, a range of dispersants was tested (see Table 3.3). Among those dispersants tested, SOLSPERSE 24000 (SP 24000), which is a comb-structured co-polymer with amine “anchor” groups, was found to be the most effective. SP 24000 has been used in the dispersion of pigment particles in paint formulations. The dispersant is expected to be adsorbed on the inorganic particle surfaces and to provide steric barriers. Although the individual bonds between the amine “anchor” groups and the sites
### Table 3.1: Characteristics of ceramic powders

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Mean Particle Diameter (µm)</th>
<th>Density (g/ml)</th>
<th>Refractive Index &amp;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina (Al₂O₃)</td>
<td>Alcoa</td>
<td>0.93</td>
<td>3.98</td>
<td>1.72</td>
</tr>
<tr>
<td>Silica (SiO₂, fused)</td>
<td>C-E Minerals</td>
<td>0.91</td>
<td>2.19</td>
<td>1.48</td>
</tr>
<tr>
<td>Mullite (3Al₂O₃·2SiO₂)</td>
<td>Refractory Minerals</td>
<td>1.38</td>
<td>3.22</td>
<td>1.65</td>
</tr>
<tr>
<td>Zirconia (ZrO₂) (Yttria Stabilized)</td>
<td>Magnesium Elektron</td>
<td>1.31</td>
<td>5.90</td>
<td>2.17</td>
</tr>
<tr>
<td>Lead Zirconate Titanate Pb(Zr,Ti)O₃</td>
<td>Sensor Technology</td>
<td>1.50</td>
<td>7.35</td>
<td>2.38</td>
</tr>
<tr>
<td>Tri-Calcium Phosphate Ca₃(PO₄)₂</td>
<td>Merck</td>
<td>1.00</td>
<td>3.14</td>
<td>1.63</td>
</tr>
</tbody>
</table>

# Horiba Capa-700 Particle Analyzer, McMaster University, Hamilton, ON.

& The values of alumina and silica are at the wavelength of 325 nm [Palik 85; Toon 76]. The values of mullite, zirconia, tri-calcium phosphate, and lead zirconate titanate are at the visible [CerSource 91; Cannon 81; Weast 64; Rogers 42].

### Table 3.2: Physical properties of liquid resins

<table>
<thead>
<tr>
<th>Parameters</th>
<th>SOMOS 5100 (SM 5100)</th>
<th>Cibatool SL 5170 (CT 5170)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplier</td>
<td>Dupont, New Castle, DE</td>
<td>3D Systems, Valencia, CA</td>
</tr>
<tr>
<td>Monomers</td>
<td>acrylate-based</td>
<td>epoxy-based</td>
</tr>
<tr>
<td>Form</td>
<td>oily liquid</td>
<td>oily liquid</td>
</tr>
<tr>
<td>Color</td>
<td>milky white</td>
<td>light amber</td>
</tr>
<tr>
<td>Viscosity (Pa.s)*</td>
<td>7</td>
<td>0.2</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.3</td>
<td>1.14</td>
</tr>
<tr>
<td>Solubility in Water</td>
<td>negligible</td>
<td>slight</td>
</tr>
</tbody>
</table>

* Measured at room temperature using a rotary viscometer (Haake Rotovisco 12, Fisons Instruments, Inc., Valencia, CA).
of the particle surfaces may not be very strong, the large number of anchor groups in the comb-structured co-polymer ensures that the dispersant is firmly attached to the inorganic surface [Solsperse 95]. Thus, SP 24000 is effective for a variety of inorganic surfaces. In this work, SP 24000 was used as the dispersant in ceramic/liquid resin suspensions. In the preparation of silica suspensions, another dispersant (Triton X-100) (2 wt% /silica powder) was added in addition to SP 2400.

Table 3.3: Dispersants tested for non-aqueous systems of ceramic/resin

<table>
<thead>
<tr>
<th>Name</th>
<th>Material</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearic Acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{16}$COOH</td>
<td>Anachemia, Montreal, Canada</td>
</tr>
<tr>
<td>Aluminum Stearate</td>
<td>Al(C$<em>{18}$H$</em>{35}$O$_2$)$_3$</td>
<td>Anachemia, Montreal, Canada</td>
</tr>
<tr>
<td>Darvan 7</td>
<td>sodium polyacrylate</td>
<td>R.T. Vanderbilt Co., Norwalk, CT, USA</td>
</tr>
<tr>
<td>Titanate Coupling Agents</td>
<td>R'O-Ti(O-X-R-Y)$_3$ (where R', X, R, Y are functional groups)</td>
<td>Kenrich Petrochemicals Inc., Bayonne, NJ, USA</td>
</tr>
<tr>
<td>(LICA 38 and KR 55)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triton X-100</td>
<td>octylphenoxy polyethoxyethanol</td>
<td>Union Carbide, Danbury, CT, USA</td>
</tr>
<tr>
<td>Pluronic F87</td>
<td>block copolymer of ethylene oxide and propylene oxide</td>
<td>BASF Co., Parsipany, NJ, USA</td>
</tr>
<tr>
<td>SOLSPERSE 2400</td>
<td>co-polymer with amine “anchor” groups</td>
<td>Industrial Colors &amp; Chem. Ltd., ON, Canada</td>
</tr>
</tbody>
</table>

3.2.2 Procedures

In the preparation of a ceramic suspension with high solids loading, the viscosity of the liquid resin is an important factor to be considered in choosing an appropriate mixing procedure. The pure liquid resin SM 5100 has a relatively high viscosity (7 Pa.s) that makes it difficult to directly mix a large volume-fraction of ceramic powder with the liquid resin to produce a homogenous suspension because the viscosity of the liquid is so high that ball milling
is no longer effective in breaking up the agglomerates present in the suspension. Figure 3.1 shows the viscosity of alumina/SM 5100 suspensions prepared without ball milling. It was shown that the viscosity was so high that a new procedure was required to prepare the suspensions with low viscosity. Therefore, the ceramic powder was first dispersed ultrasonically in a mixture of SP 24000 (at a level of 2 percent of neat SP 24000 based on the ceramic powder weight as recommended by the supplier), methyl ethyl ketone (MEK) (Anachemia, Montreal) and tripropylene glycol methyl ether (TPM) (Dow Chemical Co., NY) at a solids content around 50 wt%. The suspension was then ball milled for 4 h in a polyethylene jar with Al₂O₃ media to assure uniform mixing. Then, a very low level of heat was applied to the suspension using a hot plate with stirrer to facilitate the evaporation of MEK from the suspension, resulting in a highly concentrated dispersion of alumina in TPM with the dispersant. The prepared concentrated dispersion was finally mixed with the liquid resin SM 5100 to produce the suspensions of alumina in non-aqueous monomer solution. Tripropylene glycol methyl ether (TPM) was selected as the organic solvent due to its compatibility with the liquid resin and MEK as well as its moderate solubility for the dispersant used. The amount of TPM added was in the range of 26 to 50 percent based on the weight of the liquid phase. The viscosity of alumina/SM 5100 suspensions prepared using above procedures as shown in Fig. 3.2 was lowered compared to that of suspensions made without ball milling (see Fig. 3.1). The alumina/SM 5100 suspensions showed shear thinning behavior.

Unlike SM 5100, the liquid resin CT 5170 has a low viscosity (0.2 Pa.s) and the suspensions were prepared by dispersing ceramic powders ultrasonically in the liquid resin with or without MEK in the presence of the dispersant followed by 8 h ball milling in polyethylene jars with Al₂O₃ media (no TPM was added).

The viscosity of the suspension was measured with a rotary viscometer (Haake Rotovisco 12, Fisons Instruments, Inc., Valencia, CA) using a cone-plate geometry over a range of shear rates at 25°C. The radius of the cone is 14 mm with a cone angle of 1 degree. A sample size of 1 ml was used for each measurement.
Figure 3.1: Viscosity vs. shear rate of alumina/SM 5100 suspensions at the indicated solids loading prepared without ball milling.

Figure 3.2: Viscosity vs. shear rate of alumina/SM 5100 suspensions at the indicated solids loading prepared via a ball milling based procedure.
3.3 Rheology of Concentrated Suspensions

The important features for a stereolithography resin are a low apparent viscosity at shear rates between 1 and 100 per second, and a negligibly small apparent yield stress to allow for leveling during the recoating step as well as draining after the part building stage is completed. In this section, the measured rheological properties of the ceramic suspensions are presented and discussed with emphasis on the rheological limits imposed by the stereolithography process.

3.3.1 Alumina

A low viscosity at a high solids loading is essential for fluid based forming processes, especially for the stereolithography of ceramics. Figure 3.3 shows the viscosity-shear rate characteristics of the alumina/CT 5170 suspensions at various solids loadings. At a low solids loading of 21 v/o, the suspension viscosity remains almost the same over the range of shear rates measured, implying a Newtonian flow behavior. The observations of Newtonian behavior and low viscosity indicate the 21 v/o suspension is well dispersed. As the solids loading increases, the suspension viscosity decreases with increasing shear rate, indicating a shear thinning flow behavior which is typical for concentrated ceramic suspensions [Tadros 90]. In stereolithography, the estimated maximum shear rate is about 100 l/sec during the recoating process.

The flow resistance of the suspension depends on the viscosity of the liquid resin itself as well as the resistance generated by particle-particle interactions. Due to the much lower viscosity of the pure CT 5170 resin itself, the viscosity of CT 5170 based suspensions is expected to be lower than that of SM 5100 based suspensions (see Fig. 3.2).

Conventional liquid resins used in stereolithography apparatus (SLA) with a “deep dip” coating process usually have viscosities less than 5 Pa.s at low shear rates, which can be considered as a rough criterion in tailoring ceramic suspensions for SLA process. As seen from Fig. 3.3, the viscosities at shear rates below 10 l/s are around 1 Pa.s for 37 v/o suspension and
**Figure 3.3:** Viscosity vs. shear rate of suspensions of alumina/CT 5170 solution at the indicated solids loading.

**Figure 3.4:** Relative viscosity as a function of volume fraction for alumina suspensions at a shear rate of 12 s\(^{-1}\). The data was fitted using Chong’s equation (Eq. 3.4) with \(\phi_{max} = 0.62\).
3 Pa.s for 45 v/o suspension, respectively. Therefore, the alumina suspensions are within the usable limit for stereolithography. Actually, the 45 v/o alumina suspension was used to fabricate multilayer parts via stereolithography and was sintered to full density (Chapter 4).

The yield stress values, defined as the shear stress intercept obtained by linearly extrapolating the high shear rate portion of the flow curve back to zero shear rate, were about 3 Pa for 37 v/o suspension and 5 Pa for 45 v/o suspension, respectively. There was no apparent yield stress for 21 v/o alumina suspension. There was no apparent leveling problem for 45 v/o alumina suspension. However, the yield stress for 45 v/o alumina suspension could create difficulty in draining and cleaning the cured multilayer parts. Thus, iso-propanol was used in the cleaning process.

There is a very large number of empirical models linking relative viscosity to particle volume-fraction [Edirisinghe 86], such as the Krieger-Dougherty equation, the Eilers equation, and Chong’s equation. Among them, Chong’s equation has been used successfully to fit the data at high volume loadings and is expressed as

\[ \eta_r = \left( 1 + \frac{0.75 \phi / \phi_{max}}{1 - \phi / \phi_{max}} \right)^2 \]

(3.4)

where \( \phi \) and \( \phi_{max} \) are the volume fraction and maximum volume fraction, respectively and \( \eta_r \) is the relative viscosity (Eq. 3.3). Attempts were made to fit the viscosity results using Chong’s equation (Eq. 3.4). It was found that the viscosities at a shear rate of 12 l/sec. as a function of volume-fraction, could be fitted to Eq. 3.4 with \( \phi_{max} = 0.62 \), slightly below the volume-fraction for random close packed uniform spheres \( \phi_{max} = 0.64 \) (see Fig. 3.4).

Traditionally, photosensitive resins used in stereolithography process are preferably low in viscosity. This is typically true for all apparatus that employ low shear coating methods. More recently, there have been reports of new coating methods developed for the stereolithography process which could tolerate non-Newtonian resins with a higher viscosity. At 3D Systems Inc., a newly developed coating system called Zephyr (see Section 2.2.1.1) is available for shipment [Edge 96]. This new coating system applies a new layer of liquid resin
through a special reservoir and channel located within the recoater blade and therefore more viscous resins with some apparent yield stresses can be used in stereolithography.

In a patent assigned to Dupont [Fan 92], methods and apparatus have been described to apply shear-thinning non-Newtonian photosensitive compositions of high viscosity in thin layers quickly and uniformly in the process of stereolithography. These coating methods are based on the utilization of a doctor blade or linear extrusion head in which high shear rates (100 l/sec-1000 l/sec) are applied. The shear-thinning compositions used in these coating apparatus exhibit viscosities greater than 7 Pa.s at a very low shear rate of less that 0.3 l/sec. In addition, the coating methods appropriate for compositions with very high yield stress values are described in this patent as well [Fan 92]. Therefore, with these new coating methods and apparatus, there is no question that ceramic resins can be coated quickly and uniformly, making ceramic stereolithography feasible in practice.

3.3.2 Silica

Figure 3.5 shows the viscosity-shear rate characteristics of the silica/CT 5170 suspensions at the indicated solids loading. These suspensions also exhibited shear thinning behavior. As seen from Fig. 3.5, the viscosities at shear rates below 10 l/sec are below 5 Pa.s for silica suspensions, which are within the usable limit for ceramic stereolithography. There was no apparent yield stress for 45 v/o and 50 v/o silica suspensions. In fact, the 45 v/o silica suspension was used to fabricate multilayer parts via stereolithography (see Chapter 4).

Chong's equation (Eq. 3.4) was used to fit the viscosity results as a function of volume fraction. It was found that the viscosities at a shear rate of 12 l/sec could be fitted to Eq. 3.4 with $\phi_{max} = 0.64$ (see Fig. 3.6), implying that the suspension was well dispersed.

3.3.3 Other Powders

Tri-calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ was dispersed in the CT 5170 solution as well. However, the maximum volume fraction attainable was very low (around 20 v/o).
Figure 3.5: Viscosity vs. shear rate of suspensions of silica/CT 5170 solution at the indicated solids loading.

Figure 3.6: Relative viscosity as a function of volume fraction for silica suspensions at a shear rate of 12 s\(^{-1}\). The data was fitted using Chong's equation (Eq. 3.4) with \(\phi_{\text{max}} = 0.64\).
The 20 v/o tri-calcium phosphate suspension showed shear-thinning behavior with a viscosity of about 2.5 Pa.s and a yield stress around 7 Pa at very low shear rates (see Fig. 3.7). Further work needs to be conducted to select new dispersant/solvent systems for tri-calcium phosphate in order to achieve a high solids loading with a relatively low viscosity.

Mullite powder was dispersed in the CT 5170 solution and the maximum volume fraction achievable was 48 v/o. The rheological properties of mullite suspensions were not studied in detail. However, the 48 v/o mullite suspension exhibited a viscosity of about 2 Pa.s at a shear rate of 12 1/sec, within the usable limit for stereolithography.

Zirconia and lead zirconate titanate (PZT) powders were dispersed in the CT 5170 solution. The 26 v/o zirconia and 38 v/o PZT suspensions were usable in the stereolithography machine (SLA-250). However, they had very limited photosensitivity towards UV light (see Chapter 5).

![Figure 3.7: Viscosity vs. shear rate of 20 v/o tri-calcium phosphate/CT 5170 solution.](image-url)
3.4 Summary

Photoactive ceramic suspensions have been developed by dispersing fine ceramic powders in non-aqueous acrylate- or epoxy- based monomer solutions with the presence of effective dispersants.

Rheological characterizations studied up to a shear rate of 200 l/sec showed shear-thinning behavior and relatively low viscosity at low shear rates. Concentrated non-aqueous ceramic resins including 45 v/o alumina, 50 v/o silica, and 48 v/o mullite suspensions have been achieved with viscosities less than 5 Pa.s at low shear rates, which are within the usable limit for stereolithography machines. A good degree of dispersion was implied by the low relative viscosity at high solids loading. The relative viscosity as a function of ceramic volume fraction for alumina and silica suspensions can be fitted using Chong’s empirical model with a maximum volume fraction approaching 0.64.
Chapter 4

UV Curing of Filled Monomer Solutions

With a photosensitive monomer solution filled with a high volume-fraction of ceramic powder, three-dimensional ceramic green shapes can be built automatically layer-by-layer using the technique of stereolithography. During the process, this suspension is at least partly cured or solidifies via appropriate exposure to ultraviolet light. After fabrication, the ceramic green part is heated to burn-out the cured polymeric phase while retaining the component and subsequently sintered to high density.

In this chapter, UV-curable compositions filled with inorganic materials are briefly reviewed. The measured curing behavior for the ceramic suspensions developed via dispersing ceramic powders in non-aqueous monomer solutions, is then presented. Finally, fabrication of multilayer parts from alumina and silica suspensions via ceramic stereolithography including debinding and sintering steps, is discussed.

4.1 Review of UV Curable Filled Compositions

Radiation curable photopolymers are widely used in industry. The advantages of liquid photocurable resins include lower energy consumption than thermal curing, fast cure speed and low overall cost. A variety of properties can be achieved for different applications using the wide range of existing monomers and oligomers.

4.1.1 Related Arts

UV curable paints, adhesives and inks are a group of compositions usually containing inorganic additives. For example, paints use inorganic ceramic powders as pigments which are
dispersed in acrylate resins, but the ceramic content is low (less than 10 vol%) and therefore these ceramic resin systems can not be used for ceramic stereolithography. However, the monomers, oligomers, photoinitiators, and dispersants developed for these applications are commercially available and can be used in the development of ceramic-containing resins for stereolithography.

UV curable compositions filled with metals or ceramics have been used in the formation of thick-film patterns in circuit technology [Nebe 89; Haertling 90]. These photosensitive compositions are pastes. They are applied to a substrate in the form of layers by means of screen printing. The films are subsequently patterned using a UV lamp and a mask and the unexposed portions of the layer are removed by solvent. The patterned films are then fired to remove all remaining organics and to sinter the inorganic materials. This technology as described above has expanded into the field of micromachining where a UV laser is used to solidify the composition instead of the UV lamp and mask [Shan 94a; 94b]. Resins loaded with 30 v/o alumina were cured with a cure depth around 90 microns and alumina micro-structures on the order of 1.0 mm have been made from these 30 v/o alumina resins. This technology was aimed at fabricating very tiny metal or ceramic structures with dimensions smaller than 1.0 mm for micromachines. These compositions can not be used in stereolithography due to low solids loading and low cure depth. However, they demonstrate that ceramic patterns or structures can be created from UV curable ceramic-containing resins.

There is extensive literature on using visible or UV light curing of composite dental restorative materials which are polymers reinforced by ceramic particles. Reinforced dental restorative materials consist of four general components which are monomer, reinforcing ceramic particles, initiators, and other additives. The percent volume filler in dental restorative materials is typically above 50 v/o [Pilliar 84; 87]. The filled paste can be easily cured under visible or UV light with a cure depth as large as 2 mm [Swartz 83; McCabe 89]. Ceramic filler particles are added to photosensitive monomer systems to increase mechanical properties, reduce polymerization shrinkage, control rheological behavior, and improve thermal
properties. There is no doubt that the polymeric network formed from the amount of monomer present upon polymerization acts well to bond the ceramic particles together. These dental compositions are thick pastes and can not be used in SLA. However, they demonstrate that large cure depth can be achieved in highly loaded ceramic compositions.

Gel casting is a ceramic forming technique introduced in 1990 [Janney 90]. In this method, the aqueous system containing a high volume fraction of ceramic powders is poured into a mold and then gels with the aid of thermal initiators to produce a ceramic green body. The green part is then subjected to debinding and sintering. This technique is based on the conventional slip casting method. Two aqueous systems used for gel casting have been reported in the literature. One is an acrylate system which has proved to be difficult to work with in practice. Another is an acrylamide aqueous system [Young 91].

The aqueous acrylamide gel casting system can be extended to be UV-curable by replacing the thermal initiators with appropriate photo-initiators working in the ultraviolet range. A 45 v/o alumina/acrylamide suspension has been reported to be cured in a test tube using a UV lamp [Chu 94]. This paper emphasizes fiber spinning, fiber coating, and spray drying, and does not discuss rapid prototyping or stereolithography.

4.1.2 Stereolithography

Raw stereolithography resins are transparent to the laser beam. Additions of an inert particulate phase, which is transparent to the radiation in the environment of the composition, have certain recognized advantages, such as reduction of shrinkage upon polymerization, improvement of the cured specimens, and often increase in photospeed due to the reduction of the amount of active component. In one case, in order to increase the opacity of the composition, hollow glass or ceramic microspheres up to 70 percent by weight, were added to a photosensitive resin as radiation deflection matter in order to limit the depth of photocuring with a simultaneous increase in the width of photocuring, so that the resolution was better balanced in all directions [Fan 89]. Transparent hollow spheres of glass or ceramics were
added to the photosensitive resins mainly for the purpose of reducing the cure depth.

Aqueous UV curable systems intended for stereolithography have been first reported by Griffith et al. in 1994 [Griffith 94]. Their system was based on the acrylamide aqueous composition initially developed for the technique of gel casting. The aqueous system comprises acrylamide, methylene bis-arylamide and water. The amount of water present in the liquid phase was in the range of 50-70 v/o. The cure depths for silica and silicon nitride suspensions were studied using an ultraviolet lamp emitting UV light at 312 nm and 366 nm. It was reported that 55 v/o silica suspension had a cure depth of 330 μm and 30 v/o silicon nitride suspension had a cure depth of 60 μm [Griffith 94]. In 1995, they reported cure depths larger than 200 μm for 50 v/o silica and 50 v/o alumina suspensions [Griffith 95]. In this paper, a hollow silica box (1 inch x 1 inch x 0.75 inch) was fabricated using the SLA-250 machine with an argon-ion laser.

The benefit of using an aqueous acrylamide system is the low viscosity of the liquid and the ease of dispersing oxide ceramic powders. However, acrylamide is known to be both neurotoxic and carcinogenic. In addition, the large amount of water present introduces problems such as drying and cracking of the green body. The aqueous acrylamide solutions reported [Griffith 95] had low refractive indices ranging from 1.38 to 1.44 and therefore the refractive index differences between the ceramic powders and the liquid solutions were large. The large refractive index mismatch can preclude increasing the cure depth of the suspension and therefore limit the choice of ceramic powders to be considered for stereolithography.

In this research, non-aqueous systems of commercial stereolithography acrylate- and epoxy- based resins are used. Commercial stereolithography resins were chosen for their well balanced compositions (such as the type of photoiniator and monomer to oligomer ratio) as well as suitable photosensitivity towards UV laser. Thus, the ceramic compositions developed based on the commercial resins are relatively simple and can be easily accepted by SLA users.

The acrylate- and epoxy- based resins have larger refractive indices (1.47-1.55) than those of aqueous acrylamide solutions. This is very beneficial because even a small increase in
refractive index of the monomer solution can result in a dramatic increase in cure depth. Therefore, a lower laser dose is required to achieve a given cure depth, resulting in a faster building time. In our work, dispersants and solvents have been added to the composition in order to maximize the solids loading while maintaining relatively low viscosity, provided that the organic solvents added do not interfere with the photo-curing of the suspension. In practice, non-aqueous systems are also preferred in the processing of nonoxide ceramics due to the difficulties arising from hydrolysis and oxidation of non-oxide fine particle surfaces in aqueous systems. By utilizing the non-aqueous resin systems, suspensions containing different ceramic powders have been developed with useful cure depths.

4.2 Results of Polymerization under Laser Irradiation

To make a three-dimensional object via stereolithography, it is necessary to polymerize the monomer solution layer by layer. The dependence of the cure depth upon the incident laser exposure at the resin surface represents a useful characterization of photosensitivity [Jacobs 92]. This section presents the experimental results of curing behavior for ceramic suspensions studied in a commercial stereolithography apparatus (SLA-250) using a 30 mW He-Cd laser.

4.2.1 Definition of Cure Depth

When a laser scans on the surface of a liquid raw resin, the laser exposure which is defined as radiant energy per unit area (mJ/cm²) will decrease exponentially with depth $z$ according to the Beer-Lambert law [Jacobs 92]:

$$E_z = E \exp \left( -\frac{z}{D_p} \right)$$

(4.1)

where $E_z$ is the laser exposure at a depth of $z$ and $E$ is the laser exposure at the resin surface ($z = 0$). $D_p$ is the penetration depth of the resin. It is evident that $D_p$ is actually the depth where the laser exposure reduces to $1/e$ of the original value at the surface. For the resin to polymerize, $E_z$ must reach at least the critical threshold exposure $E_c$, where $z=C_d$. 
from which we obtain the well-known cure depth equation for stereolithography raw resin as shown in Eq. 2.1 (Chapter 2) and included here again for convenience:

\[ E_c = E \exp \left( -\frac{C_d}{D_p} \right) = E_c \]  \hspace{1cm} (4.2)

Both \( E_c \) and \( D_p \) are two constants of a resin. For a raw resin, experimentally measured \( C_d \) is plotted as a function of \( \ln(E) \) and \( E_c \) and \( D_p \) are then obtained from the slope and intercept of the linear fit.

In practice, the cure depth of the polymerized resin is measured with a micrometer, however, the definition of the cure depth is not clear in the literature. The Beer-Lambert law predicts that there is a gradient of cure as one goes from the top to the bottom of a cured specimen. From Eq. 4.2, it is evident that the critical threshold level \( E_c \) is the laser exposure delivered at the depth \( z = C_d \).

Suspensions containing a high volume-fraction of ceramic particles will no longer obey Eq. 4.3, which is valid only for raw monomers. However, the cure depth of the ceramic suspension can still be defined in a similar way, i.e., the maximum depth at which sufficient polymerization has occurred to increase the viscosity enough to yield solid-like behavior. It follows that \( E_c \) is still the value of \( E \) at the depth \( z = C_d \).

In the stereolithography process, the layer thickness is controlled by the distance the elevator is lowered into the vat each time and subsequently the amount of liquid recoated onto the part. A sufficient amount of exposure to induce cure is delivered to the bottom of the layer, and any excess laser radiation that penetrates this layer only acts to slightly increase the curing of the previous layers. The layer thickness for raw resins is usually in the range from 120 to 500 \( \mu \text{m} \). The most difficult part for stereolithography of ceramics is the limited cure depth after adding a large volume-fraction of ceramic particles. A cure depth larger than 200 \( \mu \text{m} \) is required for a high solids (40-50 v/o) suspension.
4.2.2 Experimental

In this work, the cure properties of ceramic suspensions were studied in a stereolithography apparatus (SLA-250, 3D systems, Inc., CA) using a He-Cd laser which emits UV light at a wavelength of 325 nm. The preparation of the ceramic suspensions was given in Section 3.2. The suspension was poured into a vat and unsupported rectangles of 10.2 mm × 3.8 mm were drawn on top of the liquid surface by laser at controlled levels of laser dose for each suspension tested. The laser power during the experiments was 28 mW. After exposure, the solidified sample was removed from the remaining uncured suspension and cure depth was measured by a micrometer. Five measurements were made for each sample and the mean values were determined. The range error for each sample (i.e., the maximum value minus the minimum one) was reported.

4.2.3 Alumina

Both acrylate (SM 5100) and epoxy (CT 5170) based alumina suspensions were at least partially cured under the irradiation of UV laser. Typical solidified single layers are shown in Fig. 4.1, where samples were made from an alumina/SM 5100 suspension at a solids loading of 27 v/o. Though the single layer shrank a lot after debinding and sintering due to a low solids loading, it demonstrated the idea of shape retention after post processing steps.

As mentioned before, a cure depth larger than 200 μm for a highly concentrated (40-50 v/o) suspension is the principal requirement for the stereolithography of ceramics. The measured cure depth for alumina/CT 5170 is plotted against laser dosage in Fig. 4.2. It can be seen that at laser doses greater than 1500 mJ/cm², cure depths larger than 200 μm for 45 v/o alumina/CT 5170 suspension are achievable. At a solids loading of 37 v/o, the sample cure depth increases nearly linearly with exponentially increasing laser dosage. However, at a solids loading of 45 v/o, cure depth first increases nearly exponentially with an increasing laser dosage, but at laser dosages greater than approximately $4 \times 10^3$ mJ/cm² the rate of increase declines and cure depth tends to level off around 250 μm.
Figure 4.1: Photograph of typical solidified layers made from 27 v/o alumina/SM 5100 suspension, (left) as-cured and (right) as-fired.
Figure 4.2: Cure depth versus laser dose for alumina/CT 5170 at the indicated solids loading.
The curing behavior of alumina in a non-aqueous solution which is comprised of CT 5170 and MEK in a 80:20 volume ratio was investigated. The cure depth for alumina/CT 5170 solution at selected solids loadings was measured at a range of laser doses (Fig. 4.3 and Fig. 4.4). In general, at a given level of solids loading, the sample cure depth increases nearly linearly with exponentially increasing laser dosage. However, at a high solids loading of 45 vol%, cure depth first increases nearly linearly with exponentially increasing laser dosage, but at laser dosages greater than approximately $3 \times 10^3$ mJ/cm$^2$, the cure depth increases slowly and tends to level off around 280 μm at higher laser doses.

The effect of solids loading on cure depth was investigated as well. It was found that at a low laser dose range (less than $10^3$ mJ/cm$^2$) there is no significant change of cure depth with solids loading. At a medium to high laser dose range (more than $10^3$ mJ/cm$^2$), the cure depth decreases with increasing solids loading. However, at a solids loading roughly above 35 v/o, the cure depth at the same laser dose remains almost unchanged. The reasons for this behavior are not clear; however, it may be interpreted by considering the mechanism of polymerization.

At low laser doses, there is a lesser dependence of cure depth on the laser dose due to the presence of inhibitors such as oxygen and water. Therefore even the depth where the laser can penetrate varies with the concentration of ceramic particles; however, it may not be reflected in the cure depth significantly. At medium to high laser doses, the rate of polymerization is accelerated, thereby creating large changes in cure depth with solids loading. At high laser doses, the system generates more free radicals than can be used for polymerization, producing a saturation effect. The free radicals react with each other rather than form polymer.

### 4.2.4 Mullite

Figure 4.5 shows the curing behavior of mullite dispersed in a solution consisting of CT 5170 and MEK in a 80:20 volume ratio. The curing behavior of mullite suspensions is similar to that of alumina suspensions; however, the laser dose needed to achieve a cure depth larger than 200 μm is much lower—around 500 mJ/cm$^2$ for 48 v/o mullite suspension.
**Figure 4.3:** Cure depth versus laser dose for suspensions of alumina/CT 5170 solution at solids loadings of 5 v/o and 22 v/o, respectively.
Figure 4.4: Cure depth versus laser dose for suspensions of alumina/CT 5170 solution at solids loadings of 35 v/o and 45 v/o, respectively. For comparison, cure depth for 5 v/o suspension is re-plotted in this graph.
**Figure 4.5:** Cure depth versus laser dose for suspensions of mullite/CT 5170 solution at the indicated solids loading.
In general, cure depth for mullite suspensions increases nearly linearly with exponentially increasing laser dosage. However, at a solids loading of 34 v/o and 48 v/o respectively, cure depth first increases with exponentially increasing laser dosage, but at laser dosages greater than about $5 \times 10^3$ mJ/cm$^2$ the rate of increase progressively declines.

At low laser doses (less than $10^3$ mJ/cm$^2$) there is no significant change of cure depth with solids loading. At a medium to high laser doses (more than $10^3$ mJ/cm$^2$), the cure depth decreases with increasing solids loading. However, at a solids loading roughly above 34 v/o, the cure depth remains almost unchanged.

### 4.2.5 Silica

Figures 4.6 and 4.7 show the curing behavior of silica dispersed in the same non-aqueous epoxy-based solution as used for alumina and mullite. As expected, the 50 v/o silica suspension has a larger depth of cure, 500 μm at 150 mJ/cm$^2$ and 740 μm at 1500 mJ/cm$^2$. All layers were transparent before and after photocuring. The large cure depth obtained for the silica suspensions is primarily because the refractive index difference between the fused silica (1.48) and the monomer solution (1.473) is almost zero. The close refractive matching almost eliminated the scattering of light by silica particles, as indicated by diffuse reflectance and transmittance measurements and subsequent Kubelka-Munk analysis (See Chapter 5).

The cure depth of 50 v/o silica suspension also increases nearly linearly with exponentially increasing laser dosage, but at laser dosages greater than approximately $6 \times 10^3$ mJ/cm$^2$ the rate of increase declines. Similar results were observed for both 35 v/o and 46 v/o silica suspensions as well (Fig. 4.6).

It was found that as the solids loading increases from 35 to 50 v/o, the cure depth increases. However, a comparison of the curing behavior between 5 v/o and 35 v/o silica suspensions (Fig. 4.7) showed that at low laser doses ($<600$ mJ/cm$^2$), cure depth of 5 v/o silica suspension is smaller than that of a 35 v/o silica suspension. At higher laser doses ($>600$ mJ/cm$^2$), the cure depth of 5 v/o silica suspension is larger than that of 35 v/o silica suspension.
Figure 4.6: Cure depth versus laser dose for suspensions of silica/CT 5170 solution at solids loadings of 5 v/o and 35 v/o, respectively.
Figure 4.7: Cure depth versus laser dose for suspensions of silica/CT 5170 solution at solids loadings of 46 v/o and 50 v/o, respectively. For comparison, cure depth for 35 v/o suspension is re-plotted in this graph.
In general, at a solids loading of 5 v/o, the cure depth increases approximately linearly with exponentially increasing laser dosage with a slope significantly larger than those of the other suspensions. For 5 v/o silica suspension, its curing behavior should be close to that of the raw monomer solution and therefore its cure depth is expected to be larger than other suspensions containing a significant amount of silica particles.

For silica suspensions, absorption by the monomer solution mainly controls the laser penetration depth since scattering by silica particles is very small. As the solids loading increases, i.e., the monomer solution is more diluted, the absorption by the monomer solution is reduced which may cause a larger depth of cure.

In the literature, an increase in light transmission with increasing solids content at high solids loadings has been reported once for a ceramic suspension intended for stereolithography [Garg 96]. This may imply an increase in cure depth with increasing solids content, although no cure depth was reported in that paper [Garg 96].

Griffith et al. reported a decrease in cure depth with increasing solids loading for quartz dispersed in an aqueous acrylamide solution studied using a UV lamp. However, as the solids loading was above 30 v/o, the dependence was less significant as seen from the graph presented in the paper [Griffith 95]. In their case, the refractive index difference between quartz (1.56) and the acrylamide solution (1.38) was much larger than that of our silica suspension; therefore, the scattering by quartz particles was large and controlled the cure depth. As the solids loading increases, scattering power increases due to increased content of particles, resulting in a reduction in cure depth.

4.2.6 Other Powders

a) Tri-Calcium Phosphate

Figure 4.8 shows the cure depth as a function of laser dose for tri-calcium phosphate dispersed in the same non-aqueous CT 5170 epoxy solution. It indicated a nearly linear dependence of cure depth on the logarithm of laser dosage.
Figure 4.8: Cure depth versus laser dose for 20 v/o tri-calcium phosphate/CT 5170 solution.
Figure 4.9: Cure depth versus laser dose for 26 v/o zirconia/CT 5170 solution.
As expected, the 20 v/o tri-calcium phosphate suspension has a large depth of cure, 257 μm at 163 mJ/cm² and 439 μm at 2196 mJ/cm². This is mainly because the refractive index difference between tri-calcium phosphate (1.63) and the monomer solution (1.473) is small. All tri-calcium phosphate layers were transparent before and after photocuring.

It was difficult to disperse tri-calcium phosphate in the CT 5170 based non-aqueous solution at a high solids loading and still maintaining a reasonably low viscosity. Therefore, more effective dispersants need to be identified for tri-calcium phosphate powder in order to achieve a solids loading above 40 v/o. However, it can be predicted that the cure depth of tri-calcium phosphate suspensions at high solids loadings (above 40 v/o) may be still large enough (above 200 μm) to be useful for stereolithography.

b) Zirconia

Figure 4.9 shows the cure depth as a function of laser dose for zirconia dispersed in the same non-aqueous CT 5170 epoxy solution, indicating an approximately linear dependence of cure depth on the logarithm of laser dosage. All zirconia layers were opaque before and after photocuring.

The 26 v/o zirconia suspension has a very small depth of cure (below 100 μm) primarily due to the large refractive index difference between zirconia (2.17) and the monomer solution (1.473). No further experiments were attempted for zirconia suspension due to the very small cure depth.

c) Lead Zirconate Titanate (PZT)

A suspension of 38 v/o PZT dispersed in the same non-aqueous epoxy-based solution was prepared and tested under UV laser irradiation. However, it was found that the suspension did not solidify under laser exposure.

This is primarily due to the large refractive index difference between PZT (2.38) and the monomer matrix (1.473). In addition, PZT powder may absorb UV light. Therefore, no further tests were performed for PZT powder.
4.2.7 Summary

Table 4.1 summarizes all the cure depth results for the ceramic suspensions tested. The penetration depth $D_p$ which is the slope of the linear fit of $C_d \text{ vs } \ln(E)$ is included as well. In conducting the linear fit, the non-linearity at high laser doses which was exhibited by some high solids loading suspensions was ignored. Table 4.1 shows no values for the critical exposure $E_c$. The ceramic suspension tends to deviate from Beer-Lambert behavior and the critical exposure can not be determined from extrapolating the linear fit to low laser dose ranges (<100 mJ/cm$^2$).

As seen from Table 4.1, a cure depth larger than 200 $\mu$m has been achieved for alumina, mullite, silica and tri-calcium phosphate suspensions. At a laser dose around 2200 mJ/cm$^2$, the cure depth obtained was about 231 $\mu$m for 45 v/o alumina suspension, 330 $\mu$m for 48 v/o mullite suspension, 885 $\mu$m for 50 v/o silica suspension, and 439 $\mu$m for tri-calcium phosphate suspension, respectively. Therefore, the ceramic suspensions developed are suitable for stereolithography in terms of photosensitivity.

Base on the criteria of larger than 200 $\mu$m cure depths for stereolithography, the practical laser dose ranges needed were around $10^3 - 10^4$ (mJ/cm$^2$) for alumina/CT 5170 solution or $5 \times 10^2 - 10^4$ (mJ/cm$^2$) for mullite/CT 5170 solution, respectively. For both alumina and mullite suspensions, it was found that the cure depth decreased with increasing solids loading at the working laser dose range, implying a scattering-limited curing behavior. For silica suspensions, the cure depth was very large and the working laser dose range was significantly lower - around $10^2 - 10^3$ (mJ/cm$^2$). As the solids loading increased from 35 v/o to 50 v/o, it was found that the cure depth increased, suggesting an absorption-limited curing behavior.

In the stereolithography process, the layer thickness is controlled by the distance the elevator is lowered into the vat each time and subsequently the amount of liquid recoated onto the part. As long as the laser doses used are sufficient to initiate photocuring with a cure depth larger than the predetermined layer thickness, a three-dimensional part can be fabricated layer-by-layer automatically.
Table 4.1: Experimental results of cure depth for ceramic suspensions studied in the stereolithography apparatus (SLA-250) with a He-Cd laser emitting UV light at 325 nm

<table>
<thead>
<tr>
<th>Powder</th>
<th>Monomer Solution</th>
<th>Solids Loading (vol%)</th>
<th>Dp (µm)</th>
<th>Cd (µm)</th>
<th>E=440 (mJ/cm²)</th>
<th>E=2200 (mJ/cm²)</th>
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<td></td>
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<tr>
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<td>58</td>
<td>152</td>
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<td>48</td>
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</table>
4.3 Building of Multilayer Ceramic Parts

After a preliminary determination of the curing parameters of concentrated ceramic suspensions, three-dimensional green parts were fabricated via stereolithography using the same procedures as used for plastics. The green parts produced were then heated to remove the organic phase and finally sintered to the required density. This section first presents the important issues which need to be considered in fabricating ceramic parts via stereolithography. The building of multilayer parts from alumina and silica suspensions including the debinding and sintering steps, is then demonstrated.

4.3.1 Background

Three-dimensional ceramic components have been traditionally fabricated using the suspension-based forming techniques including tape casting, injection molding, and slip casting. In slip casting, a suspension of the powder in a liquid is prepared and a compact layer of the powder is deposited on the surface of a porous mould, into which the liquid is drawn by capillary action. Tape casting has been used to produce large quantities of ceramic substrates. In this technique, the powder is dispersed in a liquid containing solvent, binders, plasticizers and dispersants, the dispersion is spread over a flat surface, and then when the solvent is removed, the powder and binders form a ceramic green tape. Injection molding is a method capable of producing complex ceramic parts in high volume production. In this process ceramic powders are added to a polymer based binder phase (polypropylene, polyethylene, etc.) at solids loadings approaching 65 volume percent. The mixture is then injection molded using procedures and equipment similar to that used for plastics. In each of these techniques, the ceramic green body formed is subsequently heated to eliminate the binders and finally sintered to high density.

In comparison to these conventional forming methods, stereolithography can offer benefits such as complex geometries without the need of a mold. Essentially, the part building strategies developed in the stereolithography of plastics such as drawing style, generating
support structures, and methods of reducing curl problem, can be directly applied to the stereolithography of ceramic green parts. Therefore, for short run manufacturing where few ceramic components are need, stereolithography should be most useful. The success of stereolithography technology should enable the fabrication of ceramic functional parts directly from CAD files without tooling.

4.3.1.1 Fabrication of Green Parts

The pre-requisites for ceramic stereolithography are appropriate rheological and curing properties of the photosensitive ceramic suspension used, which have been investigated in Section 3.3 and Section 4.2, respectively. In principle, building green parts from the concentrated ceramic suspensions can take advantage of the procedures developed for raw resins. In general, appropriate SLA parameters are needed in order to build a part with accuracy. This is particularly true when a new resin is used the first time, such as a ceramic suspension. In most cases, SLA parameters are obtained experimentally. Here, several issues including the interlayer adhesion, the problem of warp and curl, and accuracy of the green body are briefly addressed.

At the beginning of part building, the layer thickness as well as overcure depth are specified. The total cure depth which is the sum of the layer thickness and overcure depth determines the laser dose. Then the correct laser scan velocity is calculated automatically based on the laser power, spot size and required laser dose. The overcure parameter assures that a sufficient laser dose is delivered to not only cure the layer to the desired thickness but also attach the cured layer to the previous one. The overcure parameter is usually chosen based on the type of resin used. The principle is that the laser dose should be large enough to promote proper adhesion between layers. However, too large a laser dose will not only slow down the scanning speed but also may cause curling and warping of the cured part. The absence of individual layers in the exterior or interior of the green body indicates good adhesion between layers.
In stereolithography using raw resins, curling or warping is a common problem due to the shrinking of the monomers upon polymerization. This is usually minimized by using resins with little shrinkage (e.g. epoxies), choosing an appropriate draw style, and generating suitable support structures. For highly concentrated ceramic suspensions, shrinkage during photocuring is not a problem due to the lowered amount of monomer present in the composition. The draw style, discussed in Section 2.2.1.3, plays an important role in reducing shrinkage and residual stresses during the fabrication of the part. The support structure links the green part and the metal platform. As long as the support structure adheres to the platform, it will reduce the tendency to curl.

It is known that stereolithography can build parts with good accuracy and resolution from raw resins, particularly epoxy-based resins. The ceramic particles added usually have lower thermal conductivities than that of a photopolymer. For example, the thermal conductivities ($cal/cm \cdot s \cdot K$) of ceramic materials are about 0.05 for alumina, 0.004 for fused silica, and 0.01 for mullite, respectively [CerSource 91], which are significantly lower than that of an acrylate polymer which is about 5.1 ($cal/cm \cdot s \cdot K$) [Cabrera 90]. Therefore, the addition of ceramic particles is not expected to cause a loss in resolution due to diffusion of heat away from the microregion of polymerization.

This dissertation did not investigate accuracy in any detail. However, the multilayer alumina and silica parts fabricated had well defined edges and angles, suggesting a high degree of accuracy is achievable with proper control of SLA parameters during part building.

### 4.3.1.2 Debinding and Sintering

The three dimensional green part formed via stereolithography needs to be cleaned and postcured. Postcuring involves applying heat or ultraviolet light to fully solidify the uncured liquid trapped in part cavities. To obtain a dense ceramic article, it is necessary to eliminate the organic binder phase in a furnace prior to sintering. This stage is similar in principle to the debinding procedure encountered in ceramic powder tape casting and injection molding.
The mechanisms and procedures for binder removal have been well established in the field of ceramic powder injection molding. The dominant criteria for the selection of the organic binder system are suitable rheological characteristics and decomposition in a non-catastrophic manner to facilitate its removal from the ceramic body. The binder phase is a multicomponent system which usually comprises a major binder, a minor binder and other processing aids. In principle, the minor binder should burn out at a lower temperature and provide pore channels for the escape of gas produced on decomposition of the major binder. The major binder provides strength while gaseous products from the minor binder diffuse through the low permeability structure without generating an internal vapor pressure that might cause failure. In general, any thermoplastics which are themselves routinely injection molded and simultaneously satisfy the fluidity criteria can be used in the binder system. Various kinds of waxes have been effectively used as the minor binder due to their low melting temperatures, short molecular chain lengths and high volatility.

In stereolithography, the polymerized organics act as the binder phase to hold the ceramic particles in the shape. In this work, ceramic suspensions have been developed based on commercial acrylate or epoxy resins widely used in SLA. To investigate the decomposition behavior of photopolymers at high temperature, several solidified commercial acrylate (SM 3110 and SM 5100) and epoxy (CT 5170 and XB 5149) resins were characterized by thermal gravimetric analysis (TGA-50-H, Shimadzu, Japan) and the TGA results are summarized in Fig. 4.10 and Fig. 4.11.

The TGA results indicated that all the photopolymers were completely decomposed after heating to a temperature around 600°C. For acrylate polymers, the first major weight loss occurred at a temperature range of 209-389°C for SM 3110 or 204-306°C for SM 5100, then a second occurred at a temperature range of 389-469°C for SM 3110 or 306-471°C for SM 5100, followed by a third minor decomposition at a temperature around 550°C (see Fig. 4.10). Epoxy polymers decomposed in a similar behavior (see Fig. 4.11).
Figure 4.10: The TGA graph of pure solidified acrylate resins studied in air at a flow rate of 40 ml/min (above) SM 3110 and (below) SM 5100.
Figure 4.11: The TGA graph of pure solidified epoxy resins studied in air at a flow rate of 40 ml/min (above) CT 5170 and (below) XB 5149.
For epoxy-based polymers, the first major weight loss occurred at a temperature of 419°C for CT 5170 or 430°C for XB 5149, followed by a second minor burn out at a temperature around 530°C.

The alumina and silica green parts made from CT 5170 based suspensions were heated up and the binder phase was eliminated with shape retention. However, the green parts fabricated had dimensions around 2 cm. For larger and thicker samples, in order to effectively eliminate the polymeric phase without failure, two component binders may be required in the formulation of a photosensitive mixture. This can be achieved by adding inert thermoplastic or wax materials provided that they will not interfere with the photo-polymerization process. In a patent [DeSoto 89] to avoid shell mould cracking in the application of investment casting, the use of a photosensitive liquid which solidifies to a thermoset shape upon UV exposure in a mixture with a substantially inert low temperature thermoplastic material is described. The thermoplastic component of the photopolymer composition becomes somewhat bound within the solidified polymer matrix. During binder burn-out, the thermoplastic component is melted and thereby weakens the binder structure, and so aids in the complete burn out during subsequent heating. Although it was not investigated in this work, a thermoplastic which may melt and pyrolyze at a low temperature may be incorporated into the photosensitive composition in order to meet the requirement of successful removal of the polymeric phase.

After the removal of the polymeric phase from the ceramic green body, the component is finally ready to be sintered to high density in a furnace. The ceramic sintering principles and procedures are well established and can be used in this work directly.

**4.3.2 Preliminary Results**

Attempts were made to build multilayer alumina and silica parts from the suspensions of alumina or silica/CT 5170 solution. One design is a box (20 mm × 20 mm × 2 mm) having a maple leaf footprint and both alumina and silica parts were made using this design. Another design used for silica is a box (10 mm × 10 mm × 1 mm) having nine small rods on top of it.
Each rod has a diameter of 2 mm and the center to center distance between two rods is 1.5 mm. The green shapes were accurately fabricated using SLA-250 with a 30 mW He-Cd laser. The laser dose used was 3276 mJ/cm² for alumina and 1205 mJ/cm² for silica, respectively. The thickness of each layer is 152 µm. Twelve layers were built for the alumina part, while ten layers were built for each of the silica parts. Underside support structures of five layers were built only for silica parts. For the object with a maple leaf footprint, the times required for drawing a layer by laser were several minutes for alumina and silica suspensions. For the silica object with small rods, to draw a layer took about 1 minute for the base and several seconds for the rods. After exposure, the polymerized parts were removed from the remaining uncured suspension, then cleaned using iso-propanol and postcured in an ultraviolet oven. The green parts were then subjected to binder burn-out followed by sintering. Table 4.2 gives the heating schedules for binder burn-out and sintering for both alumina and silica parts.

### 4.3.2.1 Alumina

The TGA graph for cured 45 v/o alumina/CT 5170 solution is shown in Fig. 4.12. The sample underwent a major weight loss at a temperature around 264°C and then a minor weight loss in a temperature range of 384-500°C. Compared to the decomposition behavior of fully solidified raw resin CT 5170, the temperature ranges where weight loss occurred for the sample containing alumina powder were lower probably due to the lower degree of conversion for the monomers filled with ceramic particles. The total weight loss for the cured sample is comparable to the amount of liquid resin present in the composition, indicating a nearly complete elimination of polymeric phase.

Figure 4.13 shows a densified alumina object with a maple leaf footprint made from 45 v/o alumina/CT 5170 solution. The maximum linear shrinkage was about 20%. The bumps shown on the surface of the sintered part as seen from Fig. 4.13, were due to the left-over residues resulting from the cleaning process. Incomplete cleaning around the edges of the maple leaf was evident as well.
Table 4.2: Binder burn-out and sintering conditions used for alumina and silica parts

<table>
<thead>
<tr>
<th></th>
<th>Binder Burn-out (in air)</th>
<th>Sintering (in air)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>25°C -&gt; 300°C, dwell for 2 hours</td>
<td>25°C -&gt; 1600°C, dwell for 2 hours</td>
</tr>
<tr>
<td></td>
<td>300°C -&gt; 550°C, dwell for 1 hours</td>
<td>1600°C -&gt; 25°C, no dwell</td>
</tr>
<tr>
<td></td>
<td>Heating Rate: 0.1°C/minute</td>
<td>Heating/Cooling Rate: 3.7°C/minute</td>
</tr>
<tr>
<td>Silica</td>
<td>25°C -&gt; 300°C, dwell for 2 hours</td>
<td>25°C -&gt; 1100°C, dwell for 2 hours</td>
</tr>
<tr>
<td></td>
<td>300°C -&gt; 530°C, dwell for 1 hours</td>
<td>1100°C -&gt; 25°C, no dwell</td>
</tr>
<tr>
<td></td>
<td>Heating Rate: 0.1°C/minute</td>
<td>Heating/Cooling Rate: 5°C/minute</td>
</tr>
</tbody>
</table>

Figure 4.12: The TGA graph of cured 45 v/o alumina/CT 5170 solution studied in air at a flow rate of 40 ml/min.
Figure 4.13: Photograph showing a densified alumina object with a maple leaf footprint made from 45 v/o alumina/CT 5170 solution.
To study the adhesion between individual layers, the fractured surface of the sintered alumina part was examined under scanning electron microscope (SEM). It was found that the layers were barely noticeable, indicating the strong knitting of the individual layers. In Fig. 4.14, a SEM micrograph shows side surface, while a small fraction of the top surface is included as well. The line in the micrograph represents the corner between the top and the side regions. As seen from Fig. 4.14, there was no distinguishable signs of individual layers. A close-up around the corner region is shown in Fig. 4.15. The edge was uniform as suggested by the straight line. The microstructures at the top and side regions of the part were dense and consistent. Another close inspection on the side region of the fractured surface showed that the particles are uniformly and randomly distributed (see Fig. 4.16).

Figure 4.17 shows the microstructure of the sintered alumina, indicating a completely densified part with very little porosity. The grain size is 1-2 microns. Abnormal grain growth which is common for alumina during firing, was implied by the larger grains present in Fig. 4.17 and this is easily overcome by addition of a small amount of magnesium oxide.

Though the part is far from perfect, it demonstrates the potential capability of ceramic stereolithography to produce complex-shaped dense components.

### 4.3.2.2 Silica

Figure 4.18 shows a cured silica part with a maple leaf footprint fabricated from 45 v/o silica/CT 5170 solution. In comparison to the green part made from alumina, the cured silica part had better quality in terms of stiffness and layer adhesion. The edges of the box as well as the maple leaf were well defined. The cured silica part had a green strength as good as that of the cured raw resin without ceramic particles. The crack at the upper left region of the box was caused by the improper handling of the cured part. The several pores present on the surface were due to the air bubbles present in the suspension. Gas holes which are formed from air bubbles are observed during laser-curing of raw resins [Lu 95].

Figure 4.19 shows the maple leaf in the silica box at a larger magnification.
Figure 4.14: SEM micrograph of the fractured surface of the densified alumina part.

Figure 4.15: SEM micrograph showing the corner between the top and side regions.
Figure 4.16: SEM micrograph of the fractured surface, showing uniformly and randomly distributed alumina particles.

Figure 4.17: SEM micrograph showing the dense microstructure of the sintered alumina part.
Figure 4.18: Photograph showing a cured silica object with a maple leaf footprint made from 45 v/o silica/CT 5170 solution.
Figure 4.19: Photograph showing the cured maple leaf in the silica part at a larger magnification.

Figure 4.20: Photograph showing the maple leaf in the silica part after binder burn-out and calcination.
It can be seen from Fig. 4.19 that the maple leaf edges were very sharp, though roundness around some of the maple leaf edges was observed. This could be attributed to the too large a laser dose used in the silica part building process. At the laser dose used for silica (1205 mJ/cm²), the cure depth is estimated to be around 720 µm (see Fig. 4.7) which is obviously much larger than the layer thickness (152 µm). Using a laser spot size of 250 µm and a penetration depth for 45 v/o silica suspension of about 154 µm, the line width at a cure depth of 720 µm is estimated to be around 0.4 mm according to Eq. 2.2 (see page 18). Therefore, the large line width introduced by using an excessive laser dose, may be responsible for the roundness around some maple leaf edges.

Figure 4.20 shows the maple leaf in the silica box after debinding and calcination. As expected, the silica part did not shrink upon firing due to phase transformations of silica particles at high temperature. Therefore, sintering did not improve either part strength or density. The silica stereolithography suspension was intended as a model system of slurry used in investment casting. In the mixture used in investment casting, a small amount of colloidal silica is added which will bind the large silica particles together upon firing. In our case, no colloidal silica was added; however, the green part still kept its shape after elimination of the organic phase. Indeed, the edges of the maple leaf were still sharp after calcination.

Figure 4.21 shows another cured silica part with nine small rods fabricated from 42 v/o silica/CT 5170 solution. It can be seen that the edges of the rods were well defined. This demonstrates the potential of building parts with fine features. The same silica part after debinding and calcination is shown in Fig. 4.22. It was found some silica particles became loose after removal of the binder phase and subsequent calcination. However, the green part still kept its shape after elimination of the organic phase.

The calcined silica parts were examined under SEM. Good knitting of the individual layers was observed. Figure 4.23 shows the side wall of a small rod built on the silica part at low and high magnifications, indicating individual layers. Figure 4.24 shows the microstructure of the calcined silica parts.
Figure 4.21: Photograph showing a cured silica part with nine small rods fabricated from 42 v/o silica/CT 5170 solution.

Figure 4.22: Photograph showing the silica part with nine small rods after binder burn-out and calcination.
Figure 4.23: SEM micrograph showing the side wall of a small rod built on the silica part at low (above) and high (below) magnifications.
Figure 4.24: SEM micrograph of the microstructure of the calcined silica parts.
As expected, the silica parts were not densified upon firing. The silica particles are about 2 microns in average and are randomly distributed.

4.4 Conclusions

The photosensitivity of ceramic suspensions has been studied in a stereolithography apparatus (SLA-250) with a 30 mW He-Cd laser. by measuring the cure depth vs. laser dose and the cure depth vs. solids loading for each kind of ceramic suspension. After a preliminary determination of SLA parameters, alumina and silica multilayer parts were fabricated via stereolithography including the steps of debinding and sintering.

Cure depths larger than 200 μm have been achieved for alumina, mullite, silica and tri-calcium phosphate suspensions. At a laser dose around 2200 mJ/cm², the cure depth obtained was about 231 μm for 45 v/o alumina suspension, 330 μm for 48 v/o mullite suspension, 885 μm for 50 v/o silica suspension, and 439 μm for tri-calcium phosphate suspension, respectively. Therefore, the ceramic suspensions developed are suitable for stereolithography in terms of photosensitivity.

Multilayer parts were fabricated from 45 v/o alumina and silica suspensions, respectively. The cured parts demonstrated well defined edges and good layer adhesion. Nearly complete elimination of the polymerized organic phase was suggested by the results of thermal gravimetric analysis (TGA). The subsequently sintered parts as examined using SEM showed no signs of individual layers. The alumina part was fully densified after sintering at 1600°C. As expected, silica parts did not shrink upon firing. However, the SEM micrograph of the calcined silica part indicated that the silica particles were uniformly and randomly distributed.
Chapter 5

UV Diffuse Reflectance and Transmittance

One of the main issues for ceramic stereolithography is the cure depth, because the penetration of laser light into the ceramic suspension is limited by the absorption and scattering of light caused by ceramic particles [Liao 96a]. Consequently, it is very important to study the optical properties of the ceramic suspension which is the major concern of this chapter.

The monomer solution used in stereolithography which is usually called a "resin", consists of monomers, oligomers, a small amount of photo-initiator, and other inert additives. The monomer solution is considered optically homogeneous and its absorption of a monochromatic beam of light is usually described by the Beer-Lambert law [Guillet 85].

\[ I = I_0 \exp(-\varepsilon cl) \]  

(5.1)

where \( I_0 \) represents the incident light intensity, \( I \) is the distance between the column containing the sample and the light source, \( c \) and \( \varepsilon \) are the concentration and absorption coefficient of a single absorbing species respectively, and \( I \) is the transmitted light intensity. The monomers and oligomers do not absorb much of the laser emitted photons, while initiators absorb them efficiently [Cabrera 90]. Under the irradiation of a UV laser, initiator molecules absorb the laser emitted photons and form free radicals, which, in turn, start the chain reaction of polymerization. In other words, the liquid resin solidifies. According to Eq. 5.1, the penetration depth of the laser light into the resin depends on the concentration of the initiator and on its absorption coefficient at the selected wavelength.

On the other hand, a suspension containing a large volume-fraction of ceramic particles
having a refractive index substantially different from that of the monomer matrix is no longer optically homogeneous, instead, it appears translucent or opaque. Therefore, the Beer-Lambert absorption law is no longer valid due to the scattering of light at the interface of the dispersed particle and the medium. According to the scattering theory [van de Hulst 57], the two variables which most strongly affect scattering and can be controlled are the particle size and refractive index relative to the surrounding medium. Particle shape and volume fraction have some effects as well.

If a beam of laser light enters a ceramic suspension, it is partially absorbed and partially scattered. For a suspension containing a sufficiently large number of ceramic particles, the radiation can be expected to be scattered in all directions uniformly due to the multiple light scattering involved [Kortüm 69]. In other words, the scattering distribution is isotropic.

The optical properties of the ceramic suspension can be studied by UV diffuse reflectance and transmittance measurements [Kortüm 69]. To describe radiation transfer in such a simultaneously scattering and absorbing medium, a number of theories have been developed. The widely used is the Kubelka-Munk theory representing the conventional continuum theory [Wendlandt 66; Kortüm 69]. Kubelka-Munk theory divides the radiation field into two opposite streams. The transmittance and reflectance of a layer of finite thickness can be expressed in terms of two constants, the absorption coefficient and the scattering coefficient. These two constants are regarded as characteristic properties of the layer per unit thickness and may be determined from measurements of reflectance and transmittance on such layers.

Another theory that should be mentioned here is the Melamed model [Melamed 63]. More recently, Mandelis et al. [Mandelis 91] proposed a discontinuum theory based on the Melamed model. The discontinuum theory is based on statistical summation over discrete particles reflecting light diffusely according to the laws of geometrical optics. Therefore, this discontinuum theory relates measured reflectance and transmittance to optical properties of the particle. However, it is only valid for particle sizes very large compared to the exciting wavelength.
In this chapter, both Kubelka-Munk theory and discontinuum theory are briefly reviewed. The measured UV diffuse reflectance and transmittance spectra for alumina, mullite and silica suspensions are then presented. The scattering and absorption coefficients of the ceramic suspensions obtained by the Kubelk-Munk analyses of the spectra are discussed. Finally, the cure depths for ceramic suspensions are predicted using the Kubelka-Munk model and the results are compared with experimental values.

5.1 Absorption and Scattering of Tightly Packed Particles

In ceramic stereolithography, ceramic particles are added to the liquid monomer solution in large quantity (more than 40% by volume). The particles are so tightly packed that multiple scattering is involved at the interface of the particles and the surrounding medium. To describe radiation transfer in such a simultaneously scattering and absorbing medium, there are generally two categories of theory in the literature: (1) continuum theory (i.e., the Kubelka-Munk model) in which coefficients of absorption and scattering are considered as properties of the irradiated layer; and (2) discontinuum theory (i.e., the Melamed model) in which the scattering and absorption of the particle are used as optical constants.

5.1.1 Kubelka-Munk Theory

The Kubelka-Munk (K-M) theory is a two-stream approximation that simplifies the radiation field into radiation fluxes in only the forward and backward directions. This theory treats the sample as a continuum medium and introduces only two constants (i.e., the absorption and scattering coefficients) by means of which transmittance and reflectance of a layer of finite thickness may be expressed. A complete review of Kubelka-Munk theory has been given by Kortüm [Kortüm 69].

In this theory, the optical properties of a material can be described by the two constants, $S$ and $K$, which are the scattering and absorption coefficients as per unit thickness of the irradiated layer, respectively. The diffuse reflectance can be expressed as [Wendlandt 66],
\[ R = \frac{(1 - \beta^2) \exp(\alpha z) - (1 - \beta^2) \exp(-\alpha z)}{(1 + \beta^2) \exp(\alpha z) - (1 - \beta^2) \exp(-\alpha z)} \] (5.2)

where \( z \) is the thickness of the layer and \( \alpha \) and \( \beta \) are two constants that are each dependent on both \( K \) and \( S \),

\[ \alpha = \sqrt{K(K + 2S)} \] (5.3)

\[ \beta = \frac{\sqrt{K}}{\sqrt{K + 2S}} \] (5.4)

The transmittance of the layer is given by the following equation,

\[ T = \frac{4\beta}{(1 + \beta)^2 \exp(\alpha z) - (1 - \beta)^2 \exp(-\alpha z)} \] (5.5)

If the layer is infinitely thick, i.e., \( z \to \infty \), then the equations become

\[ T_x = 0 \] (5.6)

\[ R_x = \frac{1 - \beta}{1 + \beta} = \frac{1 - \sqrt{K}}{1 + \sqrt{K + 2S}} \] (5.7)

From Eq. 5.7, it is evident that the reflectance of an infinitely thick layer is a function of \( K/S \). It is, therefore, impossible to determine the true value of either \( K \) or \( S \) from reflection measurements alone. However, as long as only the calculation of reflectance is desired, only the relative values of the constants are necessary. The true or absolute constants may be determined from a transmission measurement. The respective advantages of the relative and absolute sets of constants depend on the case of interest.

By re-arranging Eq. 5.7, the widely used K-M function, \( F(R_x) \) is obtained,

\[ F(R_x) = \frac{(1 - R_x)^2}{2R_x} = \frac{K}{S} \] (5.8)

For diffuse reflectance spectrometry, a dilution method is usually employed in which the sample is mixed with a non-absorbing and highly scattering matrix of an alkali halide, such as
KBr or KCl. In this case, $K$ is related to the absorption of the sample alone as expressed in the following equation [Frei 73],

$$K = 2.303ac$$  \hspace{1cm} (5.9)

where $a$ is the absorptivity and $c$ is the concentration of the substance, respectively.

From Eqs. 5.8 and 5.9, it can be seen that the K-M theory indicates that linear plots of band intensity versus concentration should result when intensities are plotted as the K-M function. The Kubelka-Munk equation for quantitative analysis by diffuse reflectance spectrometry is common for measurements made in the ultraviolet to visible [Kortüm 69; Wendlandt 66] and infrared [Fraser 90; Boroumand 92] regions of the spectrum. A wide variety of practical applications has been based on the K-M theory in the literature. Generally, the reflectance and transmittance spectra of the simultaneously absorbing and scattering medium are used to determine the absorption spectrum of the substance in question. Materials such as paints, papers, plastics and opal glasses have been studied by the K-M theory using diffuse reflectance measurements for optical properties such as typical color curves, contrast gloss, and so on [Wendlandt 66].

The application of the Kubelka-Munk model in combination with diffuse reflectance measurements on visible-light curable dental materials has been reported recently [Taira 95]. These materials are photopolymer resins reinforced by ceramic or glass particles. In this study, the K-M theory was used to evaluate the optical transmittance in the visible light region of a commercial dental resin by two optical constants, the scattering and absorption coefficients. The prediction of the color of the dental resins using the Kubelka-Munk theory was reported in the literature as well [Cook 85].

Despite its wide application, the K-M theory remains only an approximation to the solution of realistic scattering problems because it considers the scattered radiation only in the forward or the backward directions. In addition, the K-M theory assumes: the scattering distribution is isotropic; the particles in the layer are randomly distributed and very much smaller than the thickness of the layer itself; and that the scattering and absorption coefficients
are uniform throughout the sample.

Advanced ceramic powders available commercially are generally of micron size. The particle diameter \( d \) is in the range of 0.5-2 \( \mu m \). In the ultraviolet region (specifically, \( \lambda_0 = 0.325 \mu m \)), the ceramic particle size is less than \( 7\lambda \). Therefore, Kubelka-Munk theory which treats the medium as continuum, is employed here for the study of the optical properties of stereolithography ceramic suspensions. For very large particles (\( d > 10\lambda \)), discontinuum theory has to be used.

### 5.1.2 Discontinuum Theory

Kubelka-Munk theory treats the homogeneous layers as a continuum and therefore does not provide a direct connection between the optical properties of the particles and that of the ceramic suspension. A theory is needed in order to relate the optical properties of the particles directly to the measurable quantities and this is the so-called discontinuum theory. Discontinuum theory (i.e., the Melamed model) is built on statistical summation of reflected light intensity fractions over one layer of discrete particles reflecting light diffusely according to the laws of geometrical optics. Therefore, this discontinuum theory relates measured reflectance and transmittance to optical properties of the particle. However, it is only valid for particle sizes very large compared to the exciting wavelength. The discontinuum theory was first proposed by Melamed in 1963 [Melamed 63] and further developed by Mandelis et al. [Mandelis 91].

Mandelis’ theory begins with expressions for diffuse reflectance and transmittance on the single particle level which were initially put forth by Melamed. An important feature is that the summation of scattered rays which results in the expressions for diffuse reflectance \( R \) and transmittance \( T \) is performed on an individual particle basis. \( R \) and \( T \) are expressed in terms of the parameters of the individual particles,

\[
R = 2y\bar{m}_e + (1 - 2y\bar{m}_e) \left[ \frac{(1 - \bar{m}_i \bar{m}_M)^2}{1 - (\bar{m}_i \bar{M})^2} \right]
\]

\((5.10)\)
\[
T = (1 - 2y\bar{m}_e) \left[ \frac{(1 - \bar{m}_i) M}{1 - (\bar{m}_i) M} \right]^{2}
\]  

(5.11)

where \( M \) is the non-absorbed fraction and can be expressed as,

\[
M = \frac{2}{(kd)^2} \left[ 1 - (kd + 1) \exp(-kd) \right]
\]

(5.12)

where \( k \) is the particle absorption coefficient at the specified wavelength, \( d \) is the particle diameter (for non-absorbing particles, \( k = 0 \) and \( M = 1 \)) and \( \bar{m}_e \) and \( \bar{m}_i \) are the external and internal reflection coefficients, respectively, and both are functions of the particle refractive index. Another parameter which appears in the theory is the fraction of radiation scattered in the upward direction (i.e., \( y \)).

\[
y = \frac{y_u}{1 - (1 - 2y_u) T_{\text{avg}}} \quad \text{(5.13)}
\]

where \( T_{\text{avg}} \) is the average particle transmission:

\[
T_{\text{avg}} = \frac{(1 - \bar{m}_i) M}{1 - \bar{m}_i M} \quad \text{(5.14)}
\]

\( y_u \) is a constant representing the probability for diffuse scattering in the upward direction.

Once the single particle reflectance and transmittance have been determined, diffuse reflectance and transmittance of layers of discrete particles of arbitrary shape can be obtained as a function of the particle absorbance \( kd \), via multilayer transfer functions [Mandelis 91].

### 5.2 UV Diffuse Reflectance and Transmittance Spectra

The optical properties of the ceramic suspensions were investigated by diffuse reflectance measurements using a double-beam ultraviolet/visible (UV-Vis) light spectrophotometer (Cary 3, Varian Australia Pty. Ltd., Victoria, Australia) equipped with a 73 mm diameter integrating sphere attachment. Traditionally, the accessory used to measure diffuse reflectance is the integrating sphere. It is also adequate for measuring the transmission of turbid, translucent or opaque materials where standard techniques prove inadequate due to loss of
light resulting from the scattering effects of the sample.

In the experiments, uncured suspensions of alumina, mullite and silica in liquid monomer solutions were mounted in a single cell (12 mm x 45 mm x 1 mm) (Quaracell Products, Inc., Baldin, NY) with sample cavity of dimensions 10 mm x 38 mm x 0.2 mm. During diffuse reflectance measurements, a white Al₂O₃ plate and a black SiC plate were used as a white or black background, respectively. Diffuse reflectance spectra of the 0.2mm thick specimens with white and black backgrounds were obtained under the following experimental conditions: band width = 2.0 nm; time constant = 2 s; wavelength set = 200 - 400 nm; scan rate = 30 nm/min. The diffuse reflectance spectra of the white and black backgrounds were recorded as well. All the measured spectra were normalized using pressed polytetrafluoroethylene (PTFE) powder. The optical transmittances of the suspensions were also examined using the same experimental conditions as mentioned above.

The UV diffuse reflectance and transmittance spectra were obtained for alumina, mullite and silica suspensions. For each kind of ceramic suspension, spectra were obtained for samples at the specified ceramic volume fraction. In addition, spectra were measured for alumina dispersed in both acrylate- and epoxy- based monomer solutions. The measured spectra allow the calculation of the scattering and absorption parameters using the K-M model.

5.2.1 Alumina

The optical properties of alumina suspensions were studied by UV diffuse reflectance and transmittance measurements on alumina powder dispersed in (1) an acrylate-based monomer solution containing a commercial resin (SM 5100), tripropylene glycol methyl ether (TPM) solvent, and a very small amount of other additives (the volume ratio of SM5100 to TPM is 50:50); (2) a commercial epoxy-based resin (CT 5170) with a small amount of dispersant; and (3) an epoxy-based monomer solution containing CT 5170 resin, methyl ethyl ketone (MEK), and a small amount of dispersant (the volume ratio of CT 5170 to MEK is 80:20). The refractive indices \( n_{D}^{20} \) of the monomer solutions were measured at room temperature with an
An Abbe refractometer at a wavelength corresponding to the emission line of sodium ($\lambda = 589$ nm) and the results are summarized in Table 5.1.

**Table 5.1: The measured refractive index ($n_D^{20}$) of the monomer solution ($\lambda = 589$ nm)**

<table>
<thead>
<tr>
<th>Monomer Solution</th>
<th>Ingredients</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT 5170</td>
<td>Epoxy-based Resin</td>
<td>1.4895</td>
</tr>
<tr>
<td>CT 5170 Solution</td>
<td>80 v/o CT 5170: 20 v/o MEK</td>
<td>1.4729</td>
</tr>
<tr>
<td></td>
<td>70 v/o CT 5170: 39 v/o MEK</td>
<td>1.4633</td>
</tr>
<tr>
<td></td>
<td>52 v/o CT 5170: 48 v/o MEK</td>
<td>1.4515</td>
</tr>
<tr>
<td>SM 5100</td>
<td>Acrylate-based Resin</td>
<td>1.4986</td>
</tr>
<tr>
<td>SM 5100 Solution</td>
<td>50 v/o SM 5100: 50 v/o TPM</td>
<td>1.4650</td>
</tr>
</tbody>
</table>

In general, the reflectance spectra directly reflect the scattering and absorption properties of the irradiated material. In this work, the reflectance spectra of each specimen with the white and black backings were obtained, which allows the later calculation of secondary constants of Kubelka-Munk theory at a selected wavelength (see Eq. 5.20 and Eq. 5.21). In addition, corrections are introduced to account for the internal and external surface reflections (see Eq. 5.16 and Eq. 5.17) before the application of the K-M theory.

The reflectance spectra of specimens with the white backing are shown for alumina dispersed in the SM 5100 solution, CT 5170, and the CT 5170 solution at the indicated solids loadings in Fig. 5.1-5.3, respectively. It was found that the diffuse reflectance of each alumina specimen with the black backing was close to that measured with the white backing, particularly at solids loadings above 30 v/o. This suggests that the specimen thickness (0.2 mm) was so large that the background did not influence the diffuse reflectance. In other words, the specimen thickness (0.2 mm) is probably approaching the infinite thickness limit. Thus the measured diffuse reflectance is close to $R_c$ as defined in Eq. 5.7.

Diffuse reflectance is a direct measurement of scattering in the irradiated material. A specimen with a higher solids loading would be expected to have more scattering leading to a larger reflectance as is seen in Fig. 5.1-5.3.
Figure 5.1: UV diffuse reflectance spectra of uncured specimens of alumina/SM 5100 solution at the indicated solids loading with white backing.
Figure 5.2: UV diffuse reflectance spectra of uncured specimens of alumina/CT 5170 at the indicated solids loading with white backing.
Figure 5.3: UV diffuse reflectance spectra of uncured specimens of alumina/CT 5170 solution at the indicated solids loading with white backing.
Diffuse reflectance is defined as the fraction of the incident radiation which has penetrated and been reflected by at least one particle. Thus, diffuse reflectance is related to the absorption properties of the material as well, because absorption of the light by the irradiated material could reduce its chance to be reflected by a particle. Light absorption by either the particles or the liquid monomer solution would reduce the diffuse reflectance.

The diffuse transmittance spectra of the suspensions were measured separately and are shown in Fig. 5.4-5.6, respectively. A specimen with a lower solids loading has a larger transmittance mainly due to less scattering from the reduced content of ceramic particles. Light absorption by the Al₂O₃ powder or the liquid monomer solution depends on the wavelength of UV light, which is reflected in the dependence of diffuse reflectance on wavelength observed in Fig. 5.1-5.3. Al₂O₃ absorbs UV light only at wavelengths below 300 nm [Toon 76]. At wavelengths above 370 nm, light scattering by alumina powder is the only contributor to the diffuse reflectance detected. Over the wavelength region of 370 - 300 nm, the absorption by the monomer solution begins to contribute to the decrease in reflectance.

The Argon-ion laser or He-Cd laser used in stereolithography emits UV light at 365 nm or 325 nm, respectively. Thus the diffuse reflectance and transmittance in a wavelength region roughly between 370 nm and 325 nm are ultimately the major concerns.

5.2.2 Mullite

The optical properties of mullite dispersed in the epoxy monomer solution containing CT 5170 resin (80 vol%), MEK (20 vol%), and a small amount of dispersant were studied. The diffuse reflectance and transmittance spectra of the mullite specimens are shown in Figs. 5.7 and 5.8, respectively. Diffuse reflectance increases while transmittance decreases with increasing solids loading in the region of 370-320 nm, similar to that of alumina suspensions.

5.2.3 Silica

Silica was dispersed in the same monomer solution as used for both alumina and mullite.
**Figure 5.4:** UV transmittance spectra of the uncured specimen of 27 v/o alumina/SM 5100 solution.
Figure 5.5: UV transmittance spectra of uncured specimens of alumina/CT 5170 at the indicated solids loading.
Figure 5.6: UV transmittance spectra of uncured specimens of alumina/CT 5170 solution at the indicated solids loading.
Figure 5.7: UV diffuse reflectance spectra of uncured specimens of mullite/CT 5170 solution at the indicated solids loading with white backing.
**Figure 5.8:** UV transmittance spectra of uncured specimens of mullite/CT 5170 solution at the indicated solids loading.
Figure 5.9 shows the diffuse reflectance spectra of the 50 v/o silica specimen with the white and black backing, respectively. It was found that diffuse reflectances at the wavelength of 325 nm for all silica samples were very low, suggesting very limited scattering due to the close match of refractive index between the silica powder (1.48) and the monomer solution (1.473).

The diffuse reflectance of a silica specimen with the white backing is larger than that measured with the black backing at a wavelength above 325 nm. This indicates that there is a portion of light that has penetrated and reached the backing.

With the white backing, this penetrating light is partly reflected backward and passes through the whole specimen and therefore contributes to the diffuse reflectance. With the black backing, this penetrating light is simply absorbed by the backing. At a wavelength below 325 nm, the light that both penetrated and was reflected backward was significantly reduced by the absorption of the specimen and therefore there is almost no difference in the reflectances with white and black backings.

The transmittance spectra for silica suspensions at the indicated solids loadings are included in Fig. 5.10. Compared to alumina and mullite, the transmittances for silica suspensions are much larger.

5.3 Optical Properties of Photosensitive Suspensions

The Kubelka-Munk analysis of diffuse reflectance and transmittance data enables calculation of the scattering ($S$) and absorption ($K$) coefficients of the irradiated layer, assuming that the ceramic particles are uniformly distributed and randomly oriented.

Corrections are introduced to account for the internal and external surface reflections before application of the K-M theory. The scattering and absorption coefficients characterize the optical properties of the photosensitive suspensions which control light transmission and in turn limit the cure depth achieved under laser irradiation.
Figure 5.9: UV diffuse reflectance spectra of uncured specimens of 50 v/o silica/CT 5170 solution with white and black backings, respectively.
Figure 5.10: UV transmittance spectra of uncured specimens of silica/CT 5170 solution at the indicated solids loading.
5.3.1 Kubelka-Munk Analysis

When light falls on the surface of a material, it is reflected in two distinct ways. One is the external reflection of light from the macroscopically flat surface of the sample, i.e., the specular or Fresnel regular reflection. Another is the “diffuse reflection” which describes the re-emission of that fraction of the incident radiation which has penetrated the surface and then been reflected back out of the sample following partial absorption and scattering in the specimen. The second contribution to the sample reflectance is the one the K-M model treats.

Internal and external surface reflection corrections to the experimental reflectance and transmittance data were performed as described by Saunderson [Saunderson 42]. The same corrections were applied to diffuse reflectance measurements on visible-light or UV curable dental resins reinforced by ceramic or glass particles [Cook 85; Taira 95]. The relation between the reflection $R$ from a sample as measured by the spectrophotometer, and the “reflectance” $R'$ which the sample would have if measured in a transparent medium having the same index of refraction as the sample, can be expressed as [Saunderson 42].

$$R = \frac{k_1}{2} + (1 - k_1) (1 - k_2) \frac{R'}{1 - k_2 R'}$$  \hspace{1cm} (5.15)

where $k_1$ is the fraction of the incident light (from air) reflected from the sample front surface according to the Fresnel law. As a consequence, only a fraction $(1 - k_1)$ of the incident intensity does in fact penetrate the layer and undergoes diffuse reflection. The fraction of the light incident diffusely upon the surface from inside the sample which is reflected is $k_2$, so that the fraction $(1 - k_2)$ emerges from the sample and reaches the detector of the spectrophotometer. In the expression, $\frac{k_1}{2}$ represents the half of the specularly reflected light measured by the instrument used by Saunderson. However, for the instrument used in this study, the entire specular component is directed out of the spectrophotometer and therefore the term $\frac{k_1}{2}$ can be ignored. The corrected reflectance $R'$ is therefore,
\[ R' = \frac{R}{k_2 R + (1 + k_1 k_2 - k_2 - k_1)} \] (5.16)

Diffuse transmittance measurements should, in a similar way, take into account the attenuation of the incident light by a factor of \((1 - k_1)\). The real transmittance of the sample layer, \(T'\), can therefore be obtained from the measured value \(T\) [Boroumand 92]:

\[ T' = \frac{T}{1 - k_1} \] (5.17)

In Saunderson’s study, the values of \(k_1\) and \(k_2\) were estimated to be 0.05 and 0.04, respectively for pigmented plastics. The same corrections including the same values of \(k_1\) and \(k_2\) were applied to diffuse reflectance measurements on visible-light or UV curable dental resins reinforced by ceramic or glass particles [Cook 85; Taira 95].

As defined above, \(k_1\) is the fraction of the light incident from an optically thin medium (air) into an optically thick medium (the sample) reflected at the interface according to the Fresnel law. Similarly, \(k_2\) is the fraction of the light incident diffusely from an optically thick (the sample) into an optically thin medium (air) reflected at the interface. For diffuse incident radiation, \(k_1\) and \(k_2\) can be expressed in terms of the refractive index of the sample [Mandelis 90].

\[ k_1 = \frac{n^4 - \frac{8}{3} n^3 + 2 n^2 - \frac{1}{3}}{2(n^2 - 1)^2} + \frac{8 n^6 - 8 n^4 + 6 n^4 + 1 - \frac{2 n^3}{2(n^2 + 1)^2}}{(n^2 - 1)^2} \left[ \frac{8 n^4 (n^4 + 1)}{(n^2 + 1)^3 (n^2 - 1)^2} \right] \ln(n) - \left[ \frac{n^2 (n^2 - 1)}{(n^2 + 1)^3} \right] \ln\left(\frac{n + 1}{n - 1}\right); n \geq 1 \] (5.18)

\[ k_2 = 1 - \frac{1}{n^2} + \frac{1}{2(n^2 - 1)^2} \left( \frac{n^2 - \frac{8}{3} n + 2}{3 n^2} - \frac{1}{3 n^2} \right) - \frac{2 n}{(n^2 + 1)^2} + \frac{n^6 - 8 n^4 + 6 n^2 + n^{-2}}{2(n^2 + 1)^2 (n^2 - 1)^2} \left[ \frac{8 n^2 (n^4 + 1)}{(n^2 + 1)^3 (n^2 - 1)^2} \right] \ln(n) - \left[ \frac{n^2 (n^2 - 1)}{(n^2 + 1)^3} \right] \ln\left(\frac{n + 1}{n - 1}\right); n \geq 1 \] (5.19)
where \( n \) is the refractive index of the sample relative to that of the surrounding medium (air). For suspensions, particles are dispersed in a liquid medium. The volume-averaged value using the refractive indices of the particle and the monomer solution can be used to estimate the refractive index of the suspension. Therefore, \( k_1 \) and \( k_2 \) can be approximated using Eq. 5.18 and Eq. 5.19. The estimated values of \( k_1 \) and \( k_2 \) were used to obtain the correction equations (Eqs. 5.16 and 5.17) for both diffuse reflectance and transmittance for different ceramic suspensions.

The corrected reflectances of the specimens on the white or black background were used to compute the two secondary constants of Kubelka-Munk theory [Kortüm 69; Taira 95] (see Appendix 1):

\[
a_c = \frac{R'_{sw}R_wR_b - R'_{sw}R_wR'_{sb} + R_b - R'_{sb} - R_wR'_{sb}R_b - R_w + R'_{sw}R'_{sb}R_b + R'_{sw}}{2(R_bR'_{sw} - R_wR'_{sb})} \tag{5.20}
\]

\[
b_c = \sqrt{a_c^2 - 1} \tag{5.21}
\]

where \( R'_{sw} \) and \( R'_{sb} \) refer to the corrected reflectances of the specimen on white or black backing respectively. \( R_w \) and \( R_b \) are the un-corrected reflectances of the white and black backings respectively. The measured diffuse reflectance spectra of the white and black backings are included in Appendix 1. If \( R'_{sw} \equiv R'_{sb} \equiv R_s \), then \( a_c \) is.

\[a_c = \frac{R_s^2 + 1}{2R_s} \tag{5.22}\]

In this case, \( R_s = R_\infty \) according to Kortüm [1969].

These secondary constants \((a_c \text{ and } b_c)\) were then used in conjunction with the corrected transmittance of the specimen \((T')\) to calculate the scattering \((S)\) and absorption \((K)\) constants from the following equations,

\[S = \frac{\text{sinh}^{-1}b_c - \text{sinh}^{-1}b_c}{b_c} \tag{5.23}\]

\[K = S(a_c - 1) \tag{5.24}\]
where \( z \) is the specimen thickness.

### 5.3.2 Scattering and Absorption Coefficients

Table 5.2 shows the calculated scattering (\( S \)) and absorption (\( K \)) coefficients for the specimens based on the procedures described in the above section (Section 5.3.1) using reflectance and transmittance measured at a wavelength of 325 nm for the ceramic suspensions (see Section 5.2).

**Table 5.2: Calculated scattering (\( S \)) and absorption (\( K \)) coefficients using Kubelka-Munk theory based on the diffuse reflectance and transmittance measured at a wavelength of 325 nm**

<table>
<thead>
<tr>
<th>Powder</th>
<th>Monomer Solution</th>
<th>Solids Loading (vol%)</th>
<th>( S ) (1/mm)</th>
<th>( K ) (1/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>alumina</td>
<td>SM 5100 solution (50:50)</td>
<td>27</td>
<td>45</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>CT 5170 resin</td>
<td>21</td>
<td>13</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37</td>
<td>28</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>CT 5170 solution (80:20)</td>
<td>5</td>
<td>3</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22</td>
<td>14</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35</td>
<td>23</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>28</td>
<td>3.2</td>
</tr>
<tr>
<td>mullite</td>
<td>CT 5170 solution (80:20)</td>
<td>5</td>
<td>0.3</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22</td>
<td>4</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>34</td>
<td>5</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>43</td>
<td>9</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48</td>
<td>10</td>
<td>5.0</td>
</tr>
<tr>
<td>silica</td>
<td>CT 5170 solution (80:20)</td>
<td>5</td>
<td>0.4</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22</td>
<td>0.4</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35</td>
<td>0.6</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>46</td>
<td>0.8</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>0.6</td>
<td>3.3</td>
</tr>
</tbody>
</table>
In the case of alumina, it can be seen that as solids loading increases, the scattering coefficient increases due to an increase in the amount of ceramic particles, while the absorption coefficient remains nearly unchanged. Further, the scattering coefficient is larger than that of absorption coefficient for suspensions at a solids loading above 20 v/o, indicating that light transmission is mainly controlled by the scattering by the particles. The SM 5100 based suspensions tend to scatter more light than CT 5170 based systems. Mullite suspensions indicate similar behavior.

In the case of silica, the scattering coefficients are very small, suggesting very little scattering due to the close match of the refractive index of silica particle to that of the monomer solution. Therefore, light transmission for silica suspensions is essentially limited by the absorption from the monomer solution.

5.4 Prediction of Cure Depth Using Kubelka-Munk Theory

Cure depth is a very important issue in ceramic stereolithography. Although the effect of light scattering by ceramic particles on cure depth has been discussed [Griffith 95], there is no quantitative prediction of cure depth reported in the literature so far. In this section, a quantitative prediction of cure depth is developed based on Kubelka-Munk theory. This approach considers the contributions from the multiple scattering by the particles as well as the absorption by the monomer solution. A cure depth equation for a simultaneously scattering and absorbing material is derived. Calculation of the cure depth is made for alumina, silica and mullite suspensions based on their measured optical properties and the results are compared with experimental data.

5.4.1 Derivation of Cure Depth Equation

In practice, the polymerization does not proceed beyond a limited extent where the laser dose is below a threshold value $E_c$ [Jacobs 92]. The incident exposure at depth $z$ ($E_z$) is,

$$E_z = ET_z$$

(5.25)
where $E$ is the laser exposure at the suspension surface ($z=0$). $T_z$ is the light transmittance at sample depth $z$ which can be obtained from Eq. 5.5. For the suspension to polymerize, $E_z$ must reach at least the critical threshold exposure $E_c$, where $z=C_d$ (cure depth):

$$E_z = ET_z = E_c$$

(5.26)

from which we obtain:

$$\frac{E}{E_c} = \frac{1}{T_z}$$

(5.27)

Substituting $T_z$ with Eq. 5.5 where $z=C_d$ (cure depth), we obtain the cure depth equation.

$$(1 + \beta)^2 \exp(\alpha C_d) - (1 - \beta)^2 \exp(-\alpha C_d) = 4\beta \frac{E}{E_c}$$

(5.28)

where $E$ is the laser exposure at the suspension surface, $E_c$ is the critical laser exposure and $C_d$ is the cure depth. The constants $\alpha$ and $\beta$ are defined in Eqs. 5.3 and 5.4 respectively and depend on the absorption coefficient ($K$) and the scattering coefficient ($S$) of the suspension.

The cure depth equation derived for a scattering and absorbing suspension (Eq. 5.28) is the first to allow prediction of the curing behavior based on the optical properties of the suspension as determined by UV diffuse reflectance and transmittance measurements and the subsequent K-M analysis.

### 5.4.2 Comparison between Modeling and Experiment

The cure depth equation derived using Kubelka-Munk theory (Eq. 5.28) is valid not only for ceramic suspensions but for any simultaneously scattering and absorbing media in general. Based on the optical properties of the suspension as determined by diffuse reflectance and transmittance measurements, the cure depth at a given laser dose incident on the surface can be inferred provide that the critical exposure $E_c$ for the suspension is known. In this section, the cure depth as a function of $E/E_c$ is calculated for alumina, silica and mullite suspensions based on the scattering and absorption coefficients shown in Table 5.2 (Section 5.3.2). The calculated results are compared with experimental values.
5.4.2.1 Scattering-limited Suspensions

The cure depth as a function of $E/E_c$ for alumina dispersed in the epoxy monomer (CT 5170) solution was calculated (Eq. 5.28) using the measured scattering and absorption coefficients. It was found that the calculated cure depth for the alumina suspension was nearly linearly dependent on the logarithm of laser dose. As solids loading increases, the cure depth decreases, suggesting that the cure depth is largely controlled by the scattering by alumina particles instead of the absorption in the liquid matrix. The slope of the calculated $C_d$ vs. $\ln E$, e.g., the penetration depth $D_p$ for the suspension, is included in Table 5.3. For comparison, the observed values of $D_p$ determined as described in Sect. 4.2.6 are included as well.

Figure 5.11 shows the measured cure depth as a function of laser dose for the 45 v/o alumina suspension and a line whose slope $D_p$ is determined by the K-M model and whose position was chosen to yield the best fit with the linear portion of the experimental results. Such obtained values of $E_c$ for ceramic suspensions studied are included in Table 5.3.

Table 5.3: Calculated cure parameters using Kubelka-Munk theory for the ceramic powders dispersed in the epoxy-based monomer solution.

<table>
<thead>
<tr>
<th>Solids Loading (vol%)</th>
<th>Slope of $C_d$ vs. $\ln E$ (the K-M Model)</th>
<th>Slope of $C_d$ vs. $\ln E$ (observed)</th>
<th>$E_c$ (mJ/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>152</td>
<td>78</td>
<td>108</td>
</tr>
<tr>
<td>22</td>
<td>86</td>
<td>52</td>
<td>93</td>
</tr>
<tr>
<td>35</td>
<td>72</td>
<td>51</td>
<td>75</td>
</tr>
<tr>
<td>45</td>
<td>70</td>
<td>41</td>
<td>62</td>
</tr>
<tr>
<td>Mullite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>119</td>
<td>80</td>
<td>68</td>
</tr>
<tr>
<td>34</td>
<td>99</td>
<td>60</td>
<td>62</td>
</tr>
<tr>
<td>48</td>
<td>89</td>
<td>66</td>
<td>51</td>
</tr>
<tr>
<td>Silica</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>315</td>
<td>219</td>
<td>92</td>
</tr>
<tr>
<td>35</td>
<td>240</td>
<td>126</td>
<td>56</td>
</tr>
<tr>
<td>46</td>
<td>242</td>
<td>154</td>
<td>50</td>
</tr>
<tr>
<td>50</td>
<td>252</td>
<td>150</td>
<td>50</td>
</tr>
</tbody>
</table>
Figure 5.11: The calculated cure depth using the K-M model (line) and the measured cure depth (dot) for the 45 v/o alumina/CT 5170 solution ($E_c = 62$ mJ/cm$^2$).

Figure 5.12: The calculated cure depth using the K-M model (line) and the measured cure depth (dot) for the 48 v/o mullite/CT 5170 solution ($E_c = 51$ mJ/cm$^2$).
As seen from Table 5.3, the calculated penetration depth is typically larger than the observed. This may be partially because the model assumes all light is reflected either forward or backward, whereas light scattered sideways during the process of laser scanning is actually lost and does not contribute to the total light transmission.

It can also be seen from Table 5.3 that the values of $E_c$ for the alumina suspensions are in the range of 62-108 mJ/cm$^2$, which are significantly larger than that of the raw resin CT 5170 (13.5 mJ/cm$^2$). In addition, as solids loading increases, the value of $E_c$ for ceramic suspension decreases. Basically, $E_c$ is the threshold laser dose needed to generate the critical number of radicals required to consume the inhibitors and then cause sufficient polymerization to reach a “gel” state. Therefore the threshold exposure $E_c$ is mainly determined by the concentrations of inhibitors and the concentration of photoinitiator [Jacobs 92]. The viscosity of the suspension may affect the value of $E_c$ as well.

As the concentrations of inhibitors increases, $E_c$ increases since more radicals are needed to consume the inhibitors. It is also known that $E_c$ increases with decreasing the photoinitiator concentration [Jacobs 92]. The non-aqueous epoxy monomer solution used for ceramic powders consists of raw resin CT 5170 and methyl ethyl ketone (MEK) in a 80:20 volume ratio. The addition of MEK into the resin CT 5170 causes a reduction of the photoinitiator concentration due to dilution, resulting in an increase in the value of $E_c$. Further, the addition of ceramic powders into the monomer solution may introduce some impurities which include inhibitors such as water and hydroxyl-containing compounds, causing an increase in the value of $E_c$. Hence, a larger value of $E_c$ for 5 v/o alumina suspension than that of raw resin itself can be understood. As solids loading increases, the value of $E_c$ decreases, which may be related to the viscosity of the ceramic suspension. As solids loading increases, the suspension viscosity increases and less polymerization is required to obtain a solid-like behavior.

The calculation of cure depth using the K-M method has been performed for mullite dispersed in the epoxy monomer (CT 5170) solution and the results are summarized in Table 5.3. The calculated cure depth for mullite suspensions indicates the scattering-limited curing
behavior, similar to alumina suspensions. However, at a high solids loading of 48 v/o, the observed value of penetration depth was comparable to that for 34 v/o suspension, which may be contributed to dependent scattering at high solids loadings (see Section 6.1.2). Figure 5.12 shows the calculated and the measured cure depth for the 48 v/o mullite suspension, where the value of critical laser dose \(E_c\) is chosen so as to give the best fit with the linear region of the experimental results. The values of \(E_c\) for the mullite suspensions at solids loadings above 20 v/o, are in the range of 51-68 mJ/cm².

5.4.2.2 Absorption-limited Suspensions

Figure 5.13 shows the calculated cure depth as a function of \(E/E_c\) for silica dispersed in the epoxy monomer (CT 5170) solution. The cure depth for silica suspensions is much larger than that of the alumina and mullite suspensions. The calculation results for the silica suspensions are included in Table 5.3.

The cure depth for silica suspensions increases as solids loading increases from 22 to 50 v/o, suggesting an absorption-limited curing behavior. The absorption by the monomer solution mainly controls the laser penetration depth since scattering by silica particles is very limited. As solids loading increases, i.e., the monomer solution is more diluted, the absorption by the monomer solution is reduced which may result in a larger cure depth. However, the 5 v/o silica suspension had a larger cure depth than the other silica suspensions. The best fit between the calculated cure depth and the linear region of the experimental results yielded \(E_c\) values for the silica suspensions which were in the range of 50-92 mJ/cm². Figure 5.14 shows the calculated and measured cure depth for the 46 v/o silica suspension (\(E_c = 50\) mJ/cm²).

Non-linear behavior at high laser doses was observed for several concentrated ceramic suspensions experimentally (see Figs. 5.11, 5.12 and 5.14). The reasons for this are not clear. In stereolithography, the average laser dose at the resin surface \(E_{av}\) is controlled by the laser power \(P_L\) and laser scan speed \(V_s\) as shown in the following equation [Jacobs 92],

\[
E_{av} = \frac{P_L}{(h_s V_s)}
\]  

(5.29)
Figure 5.13: The calculated cure depth as a function of $E/E_c$ for the silica/C151 51/0 solution at the indicated solids loading using Kubelka-Munk theory.
Figure 5.14: The calculated cure depth using the K-M model (line) and the measured cure depth (dot) for the 46 v/o silica/CT 5170 solution ($E_c = 50 \text{ mJ/cm}^2$).

where $h_x$ is the line spacing (usually around 100 $\mu$m).

Reciprocity (i.e., twice the power for half the time will produce the same results) (Eq. 5.29) is assumed for stereolithography process, and is true for most conditions. However, if the scan velocity becomes so low at very high laser doses that the exposure duration becomes comparable to the characteristic time for inhibitors to diffuse back into the scanned region, reciprocity may fail, which might cause non-linear behavior at high laser doses.

In stereolithography, polymerization proceeds one spot at a time and the thermal heat released can be conducted into the surrounding materials, causing an increase in the local temperature when the laser light moves into that region. The increase in the local temperature may result in a reduced refractive index of the monomer matrix [Lightman 91], which implies an increase in the refractive index difference between the particle and the matrix. Therefore, a decrease in the laser penetration depth $D_p$ (i.e., the slope of $C_d$ vs. $\ln E$) is expected due to more scattering by ceramic particles. At higher laser doses, the increase in the local temperature may
be more significant and therefore result in a larger decrease in the laser penetration depth $D_p$, which may also contribute to the non-linear behavior observed at high doses.

5.5 Summary

The characterization of the optical properties for photosensitive ceramic suspensions and its use in the prediction of the cure depth have been studied in this chapter.

UV diffuse reflectance and transmittance spectra for alumina, mullite and silica suspensions at selected solids loadings were measured. The optical properties of the suspensions as characterized by the scattering and absorption coefficients have been inferred using Kubelka-Munk theory, taking into account external and internal reflection corrections. As expected, for alumina and mullite suspensions, the scattering coefficient increases with increasing solids loading. However, for silica suspensions, the scattering coefficient is very small and the absorption by the monomer solution mainly controls the light transmission.

The cure depth behavior for a simultaneously scattering and absorbing media can be described with an equation derived using the Kubelka-Munk model. The prediction of cure depth has been made for alumina, mullite and silica suspensions using the optical properties as determined by the K-M model based on UV diffuse reflectance and transmittance measurements. The calculated cure depth is nearly linearly dependent on the logarithm of the laser dose. For scattering-limited suspensions (i.e., alumina and mullite), cure depth decreases with increasing solids loading. For absorption-limited suspensions (i.e., silica), cure depth for suspensions at high solids loadings increases with increasing solids loading due to decreased absorption from the monomer solution.

The calculated cure depth for each suspension has been compared to the experimental data. The calculated slope of $C_d$ vs. $lnE$ is typically larger than the observed. This is probably because the model assumes all light is reflected either upward or downward, whereas light scattered sideways during the process of laser scanning is actually lost and does not contribute to the total light transmission. The best fit between the calculated cure depth using
Kubelka-Munk theory and the linear region of the experimental results yields the value of the critical laser dose $E_c$ for the suspension. The critical laser doses obtained for the ceramic suspensions are in the range of 50-110 mJ/cm$^2$, which are larger than that of the raw resin itself.

A ceramic suspension is suitable for the stereolithography process as long as the cure depth is larger than 200 μm. It should be kept in mind that Kubelka-Munk theory is only a two-stream approximation based on the assumptions that the particle sizes are smaller than the thickness of the irradiated layer and the particles are uniformly distributed and randomly oriented. However, the calculation of cure depth proves that UV diffuse reflectance and transmittance measurements and subsequent Kubelka-Munk analysis can be a convenient tool for obtaining the curing behavior for a ceramic suspension.
Chapter 6

Light Scattering by Ceramic Particles

This chapter discusses the scattering of light by ceramic particles added into UV-curable monomer solutions in an attempt to predict the cure behavior of highly concentrated ceramic suspensions. The goal is to understand the fundamental parameters which most strongly affect the light transmission and subsequently the cure depth of a ceramic suspension. The scattering and absorption will be studied using a simple analytical model based on multiple light scattering theories. The effects of refractive index difference, particle size, and particle volume fraction will be shown. The insight gained about the principles of the UV-curing of a concentrated suspension can form guidelines for designing suspensions with controlled curing behavior.

6.1 Brief Review of Light Scattering Theories

Light scattering problems have been studied for more than a century. Researchers from a variety of disciplines such as solid state physics, meteorology, chemistry, and astronomy have studied the scattering phenomenon. Each of these diverse groups is interested in different practical problems and prefers its own conventions, notation, and terminology. Therefore, it is beyond the scope of this thesis to present a complete review of all theories and applications, though a fundamental knowledge of the field is necessary. In the literature, there are many books on scattering among which are those of van de Hulst [1957] and Kerker [1969].

The phenomenon of scattering is usually described by single or multiple scattering. Single scattering describes scattering by independent particles which are so far from each other that each of them is exposed to the original external light and has sufficient room to form its own
scattering pattern, undisturbed by the presence of other particles. Therefore, the total scattered field is just the sum of the fields scattered by the individual particles, each of which is acted on by the external field in isolation from the other particles. It is difficult to state precise conditions under which the single scattering criterion is satisfied. In general, in the UV wavelength region, the distance between particles must be greater than twice the particle radius which corresponds to suspensions having particle volume fractions lower than about 10 percent.

In other cases, for a sufficiently large number and a sufficiently thick layer of closely packed particles, multiple scattering comes to predominate, i.e., each particle is exposed to light scattered by the other particles, whereas the light of the original beam may have suffered extinction by the other particles.

In this section, a brief review of the literature concerning both single and multiple light scattering is given to permit the later discussion of this thesis work within that context.

6.1.1 Single Light Scattering

For a material with dispersed solid particles, if the incident radiation flux is designated as $I_0$, and the transmitted, non-scattered radiation flux by $I$, then by analogy to the Beer-Lambert Law (see Eq. 5.1), we have [Kortum 69]

$$I = I_0 \exp (-k_{ext}z)$$

in which $k_{ext}$ is the extinction coefficient and $z$ is the thickness of the illuminated layer.

The light extinction (i.e. attenuation) is the sum of scattering and absorption both of which remove energy from a beam of light traversing the medium,

$$k_{ext} = k_{sca} + k_{abs}$$

where $k_{ext}$, $k_{sca}$, and $k_{abs}$ are coefficients of extinction, scattering and absorption, respectively. Scattered light, in contrast to absorbed light, is not lost from the system. Instead, it merely changes direction and is lost from a beam propagating in a particular
direction and, therefore, contributes to other directions.

The extinction coefficient in reciprocal unit thickness is described by single light scattering theories [van de Hulst 57]:

\[ k_{ext} = nC_{ext} \]  \hspace{1cm} (6.3)

where \( n \) is the number of particles per unit volume and \( C_{ext} \) is the particle extinction cross section efficiency factor. \( C_{ext} \) has the dimension of area. The dimensionless extinction efficiency factor \( Q_{ext} \) is defined as the ratio of the optically effective cross section to the geometrical cross section of the spherical particle,

\[ Q_{ext} = \frac{C_{ext}}{\pi r^2} \]  \hspace{1cm} (6.4)

where \( r \) is the particle radius. By substituting particle volume fraction (\( \phi \)), we obtain

\[ k_{ext} = \frac{3\phi}{4r} Q_{ext} \]  \hspace{1cm} (6.5)

Since the cure depth \( C_d \) is the depth where the UV beam is attenuated from the incident dose \( E \) to the minimum dose required to achieve photocuring \( E_c \) for the particular suspension, then we have

\[ C_d = \frac{4r}{3\phi Q_{ext}} \ln \frac{E}{E_c} \]  \hspace{1cm} (6.6)

A cure depth equation similar to Eq. 6.6 was reported for ceramic suspensions for stereolithography [Griffith 95]. However, it must be pointed that this cure depth equation is based on the theory of single scattering which is only valid for suspensions with particle volume fractions lower than about 10 percent.

Single light scattering models depend on the size of the particles relative to the wavelength of the incident light. Rayleigh scattering applies to particles of arbitrary form which are much smaller than the wavelength. The Rayleigh-Gans method can be employed if these particles, are suspended in a medium with a similar refractive index. For larger spherical particles or those for which refractive index mismatch is large, Mie theory has to be applied [Johnson 93].
6.1.1.1 Rayleigh Scattering For Small Particles

The Rayleigh scattering method can be applied to isotropic particles whose linear dimensions are much smaller than the wavelength of the light scattered \((d < \frac{\lambda}{5})\). The scattering occurs over a wide angle. The intensity loss and commensurate increase in background intensity are the important considerations. When the particle diameter \(d\), the absorption coefficient \(k_{abs}\), and the difference in the refractive indices of the particle \(n\) and matrix \(n_0\) are all small, the expression for \(k_{ext}\) in Eq. 6.1 can be expressed as [Cannon 81]:

\[
k_{ext} = \frac{16\pi^4\phi n_0^4}{9\lambda_0} \left(\frac{d}{\lambda_0}\right)^3 \left(\frac{n-n_0}{n_0}\right)^2 + \phi k_{abs}^p + (1-\phi) k_{abs}^m
\]

where \(k_{abs}^p\) and \(k_{abs}^m\) are the absorption coefficients of the particle and the medium, respectively, and \(\phi\) is the volume fraction of particles. The first term in Eq. 6.7 gives the loss in transmission from scattering and the second and third terms indicate the transmission loss due to the absorption of the particles and the liquid media, respectively. Equation 6.7 is valid for isotropic particles for which \(d < \frac{\lambda}{5}\). Also, the volume fraction of ceramic particles added must be kept low so that single scattering dominates \((\phi < 0.1)\). For quantitative treatments, the effect of the particle size distribution must be considered.

6.1.1.2 Rayleigh-Gans Method

The Rayleigh-Gans method can be employed when the following three assumptions are satisfied:

(1) The particle refractive index relative to the surrounding medium is close to 1. The relative refractive index, which may be complex, is defined as

\[
m = \frac{n}{n_0}
\]

where \(n\) and \(n_0\) are the refractive index of the particle and the medium, respectively.

(2) The particles are not too large, e.g., \(2x (m - 1) < 1\), where \(m\) is the relative refractive index as shown above and \(x\) is the particle size parameter defined by,
where \( r \) is the particle radius, and \( \lambda \) is the wavelength (\( \lambda = \frac{\lambda_0}{n_0} \), \( \lambda_0 \) the wavelength in a vacuum and \( n_0 \) the refractive index of the medium).

(3) The extinction efficiency factor is very small \( (Q_{\text{ext}} \ll 1) \).

Applications for Rayleigh-Gans scattering include small-angle X-ray scattering and scattering by most opal glasses. Within the validity of the theory, the extinction efficiency factor \( (Q_{\text{ext}}) \) for non-absorbing particles is a function of relative refractive index \( m \) (Eq. 6.8) and particle size parameter \( x \) (Eq. 6.9) in a very simple formula [van de Hulst 57].

For small particles \((x \ll 1)\),

\[
Q_{\text{ext}} = \frac{32}{27} (m - 1)^2 x^4
\]  

(6.10)

For large particles \((x \gg 1)\),

\[
Q_{\text{ext}} = 2 (m - 1)^2 x^2
\]  

(6.11)

6.1.1.3 Mie Theory

The scattering of single wavelength incident light by a spherical particle is given by Mie theory, which is based on exclusively two parameters, e.g., the relative refractive index (Eq. 6.8) and particle size parameter (Eq. 6.9). Extensive reviews of this subject are available [van de Hulst 57; Kerker 69; Bohren 83]. Mie theory represents a fundamental application of the Maxwell electromagnetic equations, taking account of the refractive indices of the media and spherical particle as well as the particle dimension. In developing the equations for scattering, the boundary conditions at the particle-medium interface must be specified. These equations are quite complex involving spherical Bessel functions and Legendre polynomials. Calculation based on Mie theory can be performed using existing computer programs [Bohren 83]. In the literature, compilations of extinction and scattering functions for spherical particles over a range of relative indices and particle sizes are available [Wickramasinghe 73].

The main single scattering characteristics are the albedo \( a \) and the asymmetry parameter
g described below. The single scattering albedo gives the ratio of scattering to extinction,

\[ \alpha = \frac{C_{sca}}{C_{ext}} = \frac{Q_{sca}}{Q_{ext}} = \frac{k_{sca}}{k_{ext}} \]  \hspace{1cm} (6.12)

where \( C_{sca} \) and \( C_{ext} \) are the scattering and extinction cross section efficiency factors, \( Q_{sca} \) and \( Q_{ext} \) are the scattering and extinction efficiency factors, and \( k_{sca} \) and \( k_{ext} \) are the scattering and extinction coefficients per unit thickness, respectively.

Let us designate the angle between the incident light direction and the scattered direction of a radiation beam as \( \alpha \). Then the intensity of scattered radiation as a function of \( \alpha \) is defined as a phase function \( \Phi (\cos \alpha) \). The average cosine of the scattering angle \( \alpha \) over the phase function is called asymmetry parameter \( g \),

\[ g = \frac{\cos \alpha}{\alpha} \]  \hspace{1cm} (6.13)

The asymmetry factor is a useful parameter with which to characterize the relative importance of forward-to-backward scattering. If the particle scatters more light toward the forward direction, \( g \) is positive; \( g \) is negative if the scattering is directed more toward the back direction. From the rigorous Mie theory, both the albedo and the asymmetry factor can be computed for particles with a particular relative refractive index and size parameter.

In Mie theory, one important parameter is the refractive index of particles relative to the surrounding medium \( m \). The refractive index of absorbing materials can be formally expressed by the complex quantity [van de Hulst 57].

\[ n' = n - i\kappa \]  \hspace{1cm} (6.14)

where \( n \) and \( \kappa \) are the real and imaginary parts of the complex refractive index \( n' \), respectively, and \( \kappa \) (which is dimensionless) is defined by the Lambert absorption law:

\[ I = I_0 \exp \left( -\frac{4\pi\kappa x}{\lambda} \right) \]  \hspace{1cm} (6.15)

where the quantity \( \frac{4\pi\kappa}{\lambda} \) is the absorption coefficient \( k_{abs} \) whose dimension is \( \text{cm}^{-1} \), e.g.,

\[ k_{abs} = \frac{4\pi\kappa}{\lambda} \]  \hspace{1cm} (6.16)
For a non-absorbing medium, the relative refractive index as expressed in Eq. 6.8 is in real form for non-absorbing particles ($\kappa = 0$) or in complex form for absorbing particles ($\kappa \neq 0$). The Mie theory has been successfully applied for absorbing spheres embedded in a non-absorbing medium, using the complex form of the relative refractive index.

For particles dispersed in an absorbing medium, in general, no theory exists in the literature. Basically, scattering and absorption by the particle as well as absorption by the medium contribute to the total light extinction.

### 6.1.2 Multiple Light Scattering

For high particle concentrations, multiple light scattering predominates. The problem of multiple scattering (or as it is sometimes called “radiative transfer”) is complex and has been investigated theoretically, particularly in the field of atmospheric remote sensing [Lenoble 77; Fouquart 80]. As mentioned in Section 6.1, single scattering describes scattering by independent particles which are so far from each other that each of them is exposed to the original external light and has sufficient room to form its own scattering pattern. Multiple scattering basically treats single scattering in an optically thick medium. However, if the particle concentration is so high that the scattering pattern of an individual particle is influenced by the presence of other particles, dependent scattering has to be considered.

With an assumption that each particle has enough room to develop its own scattering pattern, multiple light scattering under a wide variety of practical situations is treated extensively in a book by van de Hulst [1980]. The methodology used by van de Hulst is illustrated in Fig. 6.1. Prior to the solution for the main problem of multiple scattering, scattering parameters at the single particle level have to be obtained, usually via appropriate single scattering theory. Foremost among these are the albedo and asymmetry factor as defined in Eq. 6.12 and Eq. 6.13, respectively. In practice, we are usually confronted with a plane-parallel layer of arbitrary material embedded in a medium, which is called a slab. The reflection and transmission by a slab are the main concerns in many practical situations.
Figure 6.1: Illustration of calculation steps using multiple scattering theory.

Ceramic suspensions contain scattering and absorbing particles immersed in a medium. Other similar materials are pigments, paints, papers, aerosol dust, opal glass, and synthetic plastics. The color and brightness of these materials when applied in a layer of a certain thickness are usually of practical interest. In principle, the theory of multiple scattering or radiative transfer can provide insight into the relation between the particle properties and the bulk properties of the product. However, if the particle volume fraction $\phi$ approaches 40 v/o, the interparticle distance $\delta$ is much less than the particle diameter $d$ ($d=1\mu m$, $\delta =92$ nm; $d=0.1\mu m$, $\delta =9.2$ nm). In these cases ($\phi \geq 0.4$), the particles touch or nearly touch each other, therefore the assumption of independent scattering used in conventional multiple scattering theory is no longer valid. For this reason, most of the examples mentioned above can not be treated rigorously by the normal multiple scattering techniques [van de Hulst 80]. In the literature, two-stream methods in which scattering is divided into strictly forward and backward scattering, have been developed and used widely for these layered materials such as paints, papers and etc. [Kortum 69]. In Chapter 5, the well-known Kubelka-Munk theory which is a two-stream method has been used in combination with the diffuse reflectance and transmittance measurements on ceramic suspensions in order to predict the cure depth.
However, Kubelka-Munk theory treats the layers as a continuum and therefore does not directly relate the properties of the particles to those of the ceramic suspension.

A two-stream model developed by van de Hulst basically uses the same procedures as illustrated in Fig. 6.1 [van de Hulst 80]. This model depends on scattering parameters at the single particle level which can be obtained via appropriate single scattering theory. Therefore, this model provides a direct connection between the optical properties of the particles and that of the suspension. Recently, this model has been used on the investigation of multiple scattering by kaolin dust dispersed in air [Ben-David 93].

6.2 Computational Results

The multiple light scattering involved at the interface of the particles and the surrounding liquid medium of a different refractive index reduces the cure depth of the suspension by limiting the depth of light transmission. In this section, a two-stream multiple scattering model is used to simulate the cure depth of a ceramic suspension based on the properties of the particle and the monomer solution that constitute the suspension. The calculation has been carried out to evaluate the fundamental parameters governing the magnitude of the cure depth of a ceramic suspension. The theoretical results have been compared with experimental.

6.2.1 Methodology

The calculation of diffuse transmission for a layer of ceramic particles embedded in a medium is based on a simple two-stream multiple scattering model [van de Hulst 80]. The parameters of the model are the single scattering albedo \( a \), the asymmetry parameter \( g \), and the total optical depth of the layer \( b \). The single scattering albedo \( a \) (i.e., the ratio of scattering to extinction, Eq. 6.12) and the asymmetry parameter \( g \) (i.e., the average cosine of the single scattering angle, Eq. 6.13) are scattering parameters treated by single scattering theories. The total optical depth of the layer \( b \) is directly proportional to actual thickness of the layer \( z \).

\[
b = k_{ext}z
\]  

(6.17)
where $k_{ext}$ is the extinction coefficient per unit length.

The widely used Mie theory which is based on two parameters, e.g., the relative refractive index $m$ (Eq. 6.8) and particle size parameter $x$ (Eq. 6.9), treats exactly the scattering by spheres of arbitrary size and yields the scattering and extinction factors. For a ceramic powder which may reasonably be described as a collection of particles of random shape, randomly oriented in space, Mie calculation for equivalent spheres provides an excellent description of average single particle scattering properties in real powders. This approach incorporates within a single particle the average scattering properties of the particles in the powder, by essentially assuming a random distribution of particle orientations in space. For the particle radius, a reasonable value of $r$, can be obtained by estimating the average volume of a particle and taking as $r$ the radius of a sphere of equal volume.

A ceramic suspension intended for stereolithography is composed of ceramic particles dispersed in a weakly absorbing monomer solution. The ceramic particles used in this study do not absorb UV light [Palik 85; Toon 76] except PZT powder. The absorption coefficient of the monomer solution (i.e., the imaginary part of the complex refractive index $\kappa$) is unknown; however, it can be estimated from the penetration depth $D_p$ of the raw resin via the Lambert absorption law. A comparison between Eqs. 4.1 and 6.15 yields,

$$\frac{4\pi\kappa}{\lambda} = \frac{1}{D_p} = k_{abs}$$  \hspace{1cm} (6.18)

where $k_{abs}$ is the absorption coefficient per unit length for the matrix. For raw resin CT 5170 where $D_p = 122\mu m$, $\kappa$ is estimated to be about $1.4 \times 10^{-4}$ at a wavelength of 325 nm. The relative refractive index can be expressed,

$$m = \frac{n}{n_0 - i\kappa}$$  \hspace{1cm} (6.19)

Thus for $\kappa \sim 10^{-4}$, the imaginary part of the refractive index can be neglected while computing the scattering and extinction parameters at the single particle level. Thus, the extinction efficiency factor $Q_{ext}$ and asymmetry parameter $g$ at given values of particle size
parameter and relative refractive index (in real form) can be obtained via Mie tabulations [Wickramasinghe 73].

For an absorbing matrix, the single scattering albedo \( \alpha \) is unknown in the literature. For non-absorbing ceramic particles dispersed in a weakly absorbing medium, the single scattering albedo can be estimated using the ratio of scattering to the total extinction,

\[
\alpha = \frac{k_{sca}}{k_{ext}}
\]  

(6.20)

where \( k_{ext} \) is the sum of the scattering by the particles \( k_{sca}^p \) and the absorption by the matrix \( k_{abs}^m \). Thus, if we assume that \( k_{sca}^p = \frac{3\Phi}{4r}Q_{sca}^p \) (see Eq. 6.5), then substituting it into Eq. 6.20, we obtain.

\[
\alpha = \frac{3\Phi Q_{sca}^p}{3\Phi Q_{sca}^p + (1 - \phi) k_{abs}^m}
\]  

(6.21)

where \( Q_{sca}^p \) is the particle scatter efficiency factor, \( k_{abs}^m \) is the matrix absorption coefficient per unit thickness, \( r \) is the particle radius, and \( \phi \) is the particle volume fraction. For scattering-limited suspensions (i.e., alumina and mullite), the estimated values of \( \alpha \) using Eq. 6.21 are in the range of 0.950-0.997 (see Table 6.1) which are consistent with the fact of a weakly absorbing matrix.

Based on van de Hulst's two-stream multiple scattering model, the probability for forward scattering can be expressed in terms of single scattering albedo \( \alpha \), asymmetry parameter \( g \),

\[
p = \frac{1}{2} \alpha (1 + g)
\]

(6.22)

The probability for backward scattering is,

\[
q = \frac{1}{2} \alpha (1 - g)
\]

(6.23)

The probability for absorption is \( 1 - \alpha \) and \( 1 - \alpha + p + q = 1 \).

For \( \alpha < 1 \) and \( g \) arbitrary, the transmitted fraction of energy \( T_b \) from the layer is expressed as [van de Hulst 80],
\[ T_b = \frac{2h}{(1-p+h) \exp(hb) - (1-p-h) \exp(-hb)} \]  

(6.24)

where \( h = \sqrt{(1-p)^2 - q^2} \), \( p \) and \( q \) are defined in Eq. 6.22 and Eq. 6.23, respectively, and \( b \) is the total optical depth.

To relate the optical depth to the actual thickness of the layer, we need to know the extinction coefficient per unit length of the layer (Eq. 6.17). However, this is not treated in the two-stream multiple light scattering theory. For non-absorbing ceramic particles dispersed in a weakly absorbing medium, the optical thickness can be estimated using the following empirical equation in analogy of Eq. 6.7,

\[ b = k_{ext}^p z + k_{abs}^m z = \frac{3\phi}{4r} Q_{ext}^p z + (1-\phi) k_{abs}^m z \]  

(6.25)

where \( Q_{ext}^p \) is the extinction efficiency factor for the particles, \( k_{abs}^m \) is the absorption coefficient per unit length for the medium, \( \phi \) is the particle volume fraction, \( r \) is the particle radius, and \( z \) is the actual thickness of the layer. The first term in Eq. 6.25 considers the extinction by particles and the second term indicates the contribution from the weakly absorbing matrix. If the total scattering by the particles is significantly larger than the total absorption by the matrix, then the second term in Eq. 6.25 can be ignored.

The transmitted fraction of energy \( T_b \) (Eq. 6.24) depends on the materials' properties (i.e., extinction parameters) as well as the layer thickness \( z \). In addition, \( T_b \) can be related to the laser dose at the layer surface through the definition of cure depth \( C_d \) (see Section 5.4.1),

\[ \frac{E}{E_c} = \frac{1}{T_b} \]  

(6.26)

where \( z = C_d \). \( E \) and \( E_c \) are the laser dose at the layer surface and critical laser dose for a ceramic suspension, respectively.

It must be stressed, however, that the methodology proposed in this section does not pretend to give a solution to the problem of multiple scattering, but rather presents a simple analytical model to assess qualitatively important parameters that affect the transmission and therefore the cure depth of a ceramic suspension.
6.2.2 Parameter Dependence Studies

Calculation using the two-stream multiple scattering model has been performed according to the procedures described in the above section (Section 6.2.1). The assessment of the fundamental parameters controlling the cure depth, which are the refractive index difference, particle size, particle volume fraction, and laser dose, has been made and applied to the ceramic suspensions studied in this work.

6.2.2.1 Refractive Index Difference

Low scattering and subsequently large cure depth can be achieved by minimizing the refractive index mismatch between the ceramic particle and the monomer solution. The calculated cure depth (normalized) at a specified level of $E/E_c$ as a function of relative refractive index is shown in Fig. 6.2, where the particle volume fraction $\phi = 0.45$, and the particle size parameter $x = 13$, e.g., the particle diameter $d = 0.9 \mu m$ ($n_0 = 1.473$, $\lambda_0 = 325 nm$). It can be seen from Fig. 6.2 that the cure depth decreases quickly when the relative refractive index $m$ increases from 1.1 to 1.3, followed by a shallow decrease in cure depth with further increase in the relative refractive index above 1.3.

To describe the effect of refractive index difference, the calculated cure depth is plotted as a function of $1/\Delta n^2$, where $\Delta n$ is expressed as

$$\Delta n = \frac{n}{n_0} - 1 \quad (6.27)$$

$n$ and $n_0$ are the refractive index of the particle and the medium, respectively. It was found that the plot of $C_d$ vs $1/\Delta n^2$ yielded a nearly linear fit as shown in Fig. 6.3.

A nearly linear relationship of $C_d$ vs $1/\Delta n^2$ was reported for 50 v/o silica (quartz) dispersed in the aqueous acrylamide solutions [Griffith 95]. In that work, the refractive index of the matrix solutions was changed by adding organic solvents and the relative refractive index between the silica and the aqueous solution varied between 1.1 and 1.2. Therefore, the nearly linear relationship of $C_d$ vs. $1/\Delta n^2$ obtained here by the light scattering calculation agrees with the work reported by Griffith et al.
**Figure 6.2:** The calculated cure depth (arbitrary unit) as a function of relative refractive index at the specified level of $E/E_c$ (particle size parameter $x = 13$, the particle volume fraction $\phi = 0.45$).

**Figure 6.3:** The nearly linear dependence of the calculated cure depth (arbitrary unit) on $1/\Delta n^2$ (particle size parameter $x = 13$, the particle volume fraction $\phi = 0.45$).
6.2.2.2 Particle Size

Ceramic particles available commercially are generally in the size range of 0.5-2micron with different shapes. In the ultraviolet region (specifically, $\lambda_0 = 0.325\mu m$), the calculated size parameters $x$ (Eq. 6.9) are between 5-30 for most monomer solutions, indicating that ceramic particles are medium to large in size as compared to the wavelength. In Mie theory, $Q_{ext}$ as well as $g$ approach asymptotic values as the size parameter increases. $Q_{ext}$ oscillates around 2 at very large particle sizes. The asymptotic value of $Q_{ext}$ at an infinitely large particle size is 2 (i.e., $\lim_{x \to \infty} Q_{ext}(x, m) = 2$) [Bohren 83]. For very large particles, an asymptotic form of the Mie equation is valid [Irvine 65].

Figure 6.4 shows the calculated cure depth (arbitrary unit) as a function of particle size. The values of relative refractive index used were 1.1 and 1.2, representing the cases for most ceramic suspensions intended for stereolithography.

![Figure 6.4](image-url)

**Figure 6.4:** The calculated cure depth (arbitrary unit) as a function of particle size at the indicated values of relative refractive index.
It was found that the calculated cure depth increased with particle size; however, at large particle sizes, the calculated cure depth increases only slightly with particle size and tends to level off. In the literature, there was no report on the influence of the particle size on the cure depth for ceramic suspensions suitable for stereolithography. The cure depth equation derived based on the single scattering theory (Eq. 6.6) indicates the cure depth is directly proportional to the particle diameter. However, the two-stream multiple scattering calculation performed here shows that the cure depth increases with the particle size only when the size parameter $x$ is less than about 10-20. The results indicate that the cure depth for a ceramic suspension can be improved by using large particles. However, the effect may be less significant for ceramic particles larger than approximately 1-2 µm. The calculations made here did not include the effects of particle shape and particle size distribution. For quantitative treatments, the particle size distribution has to be considered.

6.2.2.3 Particle Volume Fraction

For scattering-limited suspensions, it is expected that the cure depth decreases as the particle volume fraction increases. Figures 6.5 and 6.6 show the measured cure depth $C_d$ as a function of the inverse of particle volume fraction $1/\phi$ for alumina and mullite powders dispersed in the epoxy-based monomer solution, respectively. Approximately linear fits of $C_d$ vs. $1/\phi$ were obtained for both alumina and mullite suspensions. Griffith et al. also reported the nearly linear relationship between $C_d$ and $1/\phi$ for silica and alumina powders dispersed in aqueous acrylamide solutions [Griffith 95]. Basically, the single scattering theory predicts nearly linear dependence of cure depth on the inverse of particle volume fraction (see Eq. 6.6). In the case of multiple scattering with the assumption of independent scattering, the results of calculation indicated a linear fit of $C_d$ vs. $1/\phi$ as well.

Table 6.1 summarizes both the experimental and computational results for the ceramic suspensions. The slope of $C_d$ vs. $1/\phi$ calculated using the two-stream multiple scattering model was roughly comparable to those observed in experiment.
Figure 6.5: The measured cure depth for alumina suspensions as a function of the inverse of particle volume fraction.

Figure 6.6: The measured cure depth for mullite suspensions as a function of the inverse of particle volume fraction.
Table 6.1: Comparison between calculated and observed values of the slope of \( C_d \) vs. \( 1/\phi \) for the ceramic suspensions

<table>
<thead>
<tr>
<th>Monomer Solution</th>
<th>Alumina</th>
<th>Mullite</th>
<th>Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT 5170 (epoxy-based) Solution</td>
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<td></td>
</tr>
<tr>
<td>( E ) (mJ/cm(^2))</td>
<td>2200</td>
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<td></td>
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<td>( E_c ) (mJ/cm(^2))</td>
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<td>55-70</td>
<td>50-92</td>
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<td>31-40</td>
<td>24-44</td>
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<td>1.005</td>
</tr>
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<td>Particle Size Parameter ( x )</td>
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<td>13</td>
</tr>
<tr>
<td>Asymmetry Parameter ( g )</td>
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<td>0.97</td>
<td>0.90</td>
</tr>
<tr>
<td>Extinction Efficiency ( Q_{ext} )</td>
<td>3.06</td>
<td>2.80</td>
<td>0.01</td>
</tr>
<tr>
<td>Single Scattering Albedo ( \alpha )</td>
<td>0.969-0.998</td>
<td>0.951-0.997</td>
<td>0.095-0.665</td>
</tr>
<tr>
<td>Slope of ( C_d ) vs. ( 1/\phi ) (observed) (( \mu )m)</td>
<td>2.1</td>
<td>23.0</td>
<td>-204</td>
</tr>
<tr>
<td>Slope of ( C_d ) vs. ( 1/\phi ) (calculated) (( \mu )m)</td>
<td>5.4</td>
<td>12.3</td>
<td>-211</td>
</tr>
</tbody>
</table>

Figure 6.7: The measured cure depth for silica suspensions as a function of the inverse of particle volume fraction.
In the case of silica suspensions where the scattering by silica particles is very limited ($Q_{ext} \ll 1$), the absorption by the monomer solution becomes the dominant factor controlling the light transmission and subsequently the cure depth (i.e., absorption-limited suspensions). Figure 6.7 shows the cure depth $C_d$ vs. the inverse of particle volume fraction $1/\phi$ for silica dispersed in the epoxy monomer solution, indicating a nearly linear fit with a negative slope (i.e., cure depth increased with volume fraction at high solids loadings).

For silica particles dispersed in the epoxy monomer solution, the assumptions of Rayleigh-Gans scattering (i.e., $m \to 1, 2x(m-1) < 1, Q_{ext} \ll 1$) are valid. Therefore, single scattering parameters were calculated for silica suspensions using the Rayleigh-Gans method.

The calculation for silica suspensions predicted an increase in cure depth with particle volume fraction due to the dilution of the monomer matrix. The calculation for silica suspensions also resulted in a nearly linear fit of $C_d$ vs. $1/\phi$ with a negative slope which was comparable to that observed in the experiment. The results for the silica suspensions are included in Table 6.1 as well.

In summary, the effect of the particle volume fraction on cure depth first depends on the scattering power by the particles as compared to the absorption effect due to the monomer solution. For scattering-limited suspensions (i.e., alumina and mullite), cure depth increases nearly linearly with increasing $1/\phi$. For absorption-limited suspensions (i.e., silica), cure depth decreases approximately linearly with increasing $1/\phi$. The conditions for absorption-limited suspensions should be that scattering by the particles can be ignored (i.e., $Q_{ext} \ll 1$). For ceramic powders of micron sizes (i.e., $x \approx 10$), the estimated relative particle refractive index using the Rayleigh-Gans equation (Eq. 6.11) is about 1.02 to achieve $Q_{ext} = 0.1$. Thus, the rule of thumb for an absorption-limited ceramic suspension is that the relative refractive index is very close to 1, preferably $m \leq 1.02$.

6.2.2.4 Laser Dose

The nearly linear dependence of cure depth $C_d$ on the logarithm of laser dosage $\ln E$ has
been observed for the ceramic suspensions, although non-linearity at very high laser doses has been shown for some concentrated ceramic suspensions (Chapter 3). In chapter 4, the Kubelka-Munk model using UV diffuse reflectance and transmittance measurements also indicated the nearly linear behavior between the cure depth and the logarithmic laser dosage.

The calculation based on the two-stream multiple scattering method predicted an approximately linear fit of cure depth as a function of \( \ln E \). Table 6.2 summarizes both the experimental and calculated slopes of \( C_d \) vs. \( \ln E \) for the ceramic powders dispersed in the CT 5170 monomer solution containing MEK. For comparison, the slope of \( C_d \) vs. \( \ln E \) obtained via the Kubelka-Munk model based on UV diffuse reflectance and transmittance measurements was included as well. The slope calculated by the two-stream multiple scattering model was larger than that observed in the experiments. The slope of \( C_d \) vs. \( \ln E \) predicted by the K-M model, although still larger than that observed, was closer to the measured one.

Table 6.2: Comparison between the calculated and the observed values of the slope of \( C_d \) vs. \( \ln E \) for the ceramic powders dispersed in the epoxy-based monomer solution.

<table>
<thead>
<tr>
<th>Solids Loading (vol%)</th>
<th>Slope of ( C_d ) vs. ( \ln E ) (( \mu m ))</th>
<th>Observed</th>
<th>Kubelka-Munk Method</th>
<th>Multiple Scattering Model</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alumina</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>78</td>
<td>152</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>52</td>
<td>86</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>51</td>
<td>72</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>41</td>
<td>70</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td><strong>Mullite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>80</td>
<td>119</td>
<td>216</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>60</td>
<td>99</td>
<td>171</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>66</td>
<td>89</td>
<td>153</td>
<td></td>
</tr>
<tr>
<td><strong>Silica</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>219</td>
<td>315</td>
<td>294</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>126</td>
<td>240</td>
<td>411</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>154</td>
<td>242</td>
<td>481</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>150</td>
<td>252</td>
<td>512</td>
<td></td>
</tr>
</tbody>
</table>
In genera, both the multiple scattering model and Kubelka-Munk theory are two-stream approximation methods. During the process of laser scanning, light scattered sideways is actually lost and does not contribute to the total light transmission. The calculation showed the layer thickness which the laser light penetrated so that energy sufficient to initiate the solidification was delivered to the bottom of the layer. In addition, the increase in the local temperature of the resin as a result of the thermal heat released during polymerization may cause a reduced refractive index of the monomer matrix, suggesting an increase in the refractive index difference between the particle and the matrix. Thus, a decrease in the laser penetration depth \( D_p \) (i.e., the slope of \( C_d \) vs. \( \ln E \)) may be obtained due to increased scattering.

For alumina suspensions, the light extinction calculated using the two-stream multiple scattering method was comparable to that obtained by the K-M model. However, for mullite and silica suspensions, the light extinction calculated using the two-stream multiple scattering method was lower than that obtained by the K-M method. This is understandable because the suspensions were highly idealized to facilitate the calculation of multiple scattering. For scattering-limited suspensions, the absorption from the monomer matrix was ignored in the calculation of single scattering parameters. In addition, the effects of particle shape and particle size distribution were not included in the multiple scattering calculation and therefore contributed to the error. Alumina and silica powders used were of high purity (>99%), but the refractory grade mullite powder contained some amount of other particles as impurities. The impurities as well as voids or flocs due to incomplete dispersion, can all introduce light absorption and scattering and therefore make contributions to the total light extinction.

### 6.2.3 Predicting Cure Depth for Other Powders

Figure 6.8 shows the refractive index for a variety of ceramic and metallic powders. The values are at a wavelength of 325 nm [Palik 85; Toon 76] except those for \( \text{Ca}_3(\text{PO}_4)_2 \), mullite, ZrO\(_2\), and ZrSiO\(_4\) which are at a wavelength corresponding to the emission line of sodium (\( \lambda = 589 \text{ nm} \)) [CerSource 91; Cannon 81; Weast 64].
Most white insulating ceramics do not absorb UV light, but silicon carbide (SiC) and colored oxides (e.g., transition metals) can have specific absorptions in the UV region. Most metallic powders absorb UV light.

Fused silica has a low refractive index and the refractive index mismatch Δn (Eq. 6.27) for silica dispersed in the epoxy monomer solution \( n_0 = 1.473 \) is less than 1%. Therefore, large cure depths have been achieved for concentrated silica suspensions at low laser doses. In practice, glasses can be added into the raw resin in order to minimize the shrinkage upon polymerization and increase the strength of the cured parts, without limiting the cure depth.

Alumina, mullite, and tri-calcium phosphate powders have intermediate refractive indices. The refractive index differences Δn for these powders suspended in the epoxy monomer solution are between 10-20%. Cure depths greater than 200 μm have been obtained for these suspensions. Most investment casting ceramic compounds are based on fused silica (n=1.48) and zirconium silicate (n=1.97) in a roughly 50:50 weight ratio. The weight-averaged refractive index for the mixtures is about 1.72 and the estimated Δn is about 17%. It can be
predicted that cure depths larger than 200 μm can be obtained in principle for core mixtures used in investment casting.

Cure depths larger than 200 μm were not achieved for zirconia suspensions where Δn was more than 45%. The estimated refractive index mismatch for silicon nitride and most liquid stereolithography resins (n₀ = 1.45 – 1.55) is between 35-45%. In order to achieve cure depths of 200 μm for zirconia and silicon nitride, monomer solutions with a refractive index larger than 1.67 have to be used. This can be done in theory by adding solvents or oils of high refractive index to the monomer solutions. For example, methyl naphthalene has a refractive index of 1.66.

Metals such as copper and nickel have low to medium refractive indices, but they are absorbing in the ultraviolet range as represented by the imaginary parts of the refractive indices. The absorptions by the inorganic powders will contribute to the light extinction and therefore limit the cure depth. However, useful cure depths may be still achievable for absorbing metals such as copper and nickel by using monomer solutions with refractive indices closely matching that of the powders.

Silicon carbide and titania (rutile) not only have high refractive indices but also tend to absorb UV light. Therefore, these suspensions will not have the required cure depths for ceramic stereolithography.

### 6.3 Summary

The simulation of curing behavior for ceramic suspensions has been performed using a two-stream multiple scattering model. The fundamental parameters controlling the cure depth have been evaluated and applied to the ceramic suspensions studied in this work.

The multiple scattering calculation indicated that the cure depth increased nearly linearly with the inverse of Δn^2 (Δn the refractive index difference defined in Eq. 6.27). Therefore, a large cure depth can be achieved by minimizing the refractive index difference. It was found that the calculated cure depth increased with particle size; however, for micron-sized ceramic
powders, the calculation showed that the particle size dependence of cure depth was weak.

The calculated cure depth showed approximately linear dependence on the logarithm of laser dose. For suspensions with a refractive index mismatch greater than 10%, the simulation showed the linear dependence on the inverse of particle volume fraction. This scattering-limited curing behavior was observed for alumina and mullite suspensions in experiments. In the case of silica suspensions where the particle scattering is very limited, $Q_{ext} \ll 1$, the absorption by the monomer solution is dominant. The calculation made for silica suspensions resulted in an increase in cure depth with particle volume fraction, which was shown in the experimental data. The rule of thumb for an absorption-limited ceramic suspension as obtained via the Rayleigh-Gans method is $\Delta n < 2\%$. 
Chapter 7

Conclusions & Suggestions for Future Work

7.1 Summary

This work has demonstrated that dense ceramic components can be produced based on the layer-by-layer UV-curing of photosensitive ceramic suspensions under laser irradiation controlled by CAD data from a computer. The polymerized organic phase can be eliminated by heating in a conventional furnace and the ceramic part sintered to high density. Only one other report [Griffith 95] describing this process has been published, arising from a study conducted largely in parallel with, but independent of, the work reported here.

Alumina (Al₂O₃), mullite (3Al₂O₃·2SiO₂), and silica (SiO₂) powders were dispersed in non-aqueous acrylate- or epoxy- based monomer solutions at high solids loadings. The highly loaded ceramic suspensions developed had low viscosities (<5,000 cps) and large cure depths (>200 μm) as required by the stereolithography process. Fabrication of ceramic components was demonstrated with the building of alumina and silica parts. The green bodies were built from 45 v/o alumina and 45 (or 42) v/o silica suspensions in a stereolithography apparatus (SLA-250) with a 30 mW He-Cd laser. The alumina part was fully densified after debinding and sintering at 1600°C.

The dispersion of ceramic powders in the liquid monomers was accomplished by adding proper dispersants and solvents. Non-aqueous alumina, mullite and silica suspensions at solids loadings above 45 v/o exhibited viscosities within the usable limit for a stereolithography machine.

The curing behavior of the ceramic suspensions was studied both experimentally and
theoretically. Cure depths larger than 200 μm were achieved under the He-Cd laser exposure for alumina, mullite and silica dispersed in non-aqueous epoxy-based monomer solutions. A cure depth larger than 200 μm was also obtained for tri-calcium phosphate Ca₃(PO₄)₂ suspensions. However, the maximum solids loading achieved for tri-calcium phosphate in an epoxy-based solution was too low to be useful. Zirconia (ZrO₂) had a cure depth less than 100 μm in the epoxy-based solution.

The cure depth for these highly loaded suspensions is controlled by the light transmittance of the suspensions which is limited by the light scattering and absorption in the irradiated layer. The optical properties of the suspension, as characterized by the scattering and absorption coefficients, were obtained by UV diffuse reflectance and transmittance measurements and subsequent Kubelka-Munk analysis. Trends in the penetration depths for these ceramic suspensions could be predicted based on the Kubelka-Munk model, but the predicted values were typically larger than the experimental data. This may be partially because the model assumes that all light is reflected either forward or backward, whereas during the process of laser scanning, light scattered sideways is actually lost and does not contribute to the total light transmission. The best fit between the cure depth calculated using the Kubelka-Munk model and the linear region of the experimental results yielded the value of the critical laser dose for the suspension, which was found in the range of 50-110 mJ/cm².

The fundamental parameters controlling the cure depth were evaluated using a two-stream multiple scattering model. The calculations indicated the cure depth should increase nearly linearly with the inverse of Δn², where Δn is the refractive index difference between the particle and the liquid matrix (Eq. 6.24), in agreement with literature results. For micron-sized ceramic powders, the calculation predicted a weak particle size dependence of cure depth. For scattering-limited suspensions where the refractive index differences were large (i.e., alumina and mullite suspensions), the decrease in cure depth with increasing particle volume fraction observed was reflected in the model calculation. When the particles' refractive index closely matched that of the liquid matrix (i.e., silica suspensions), the calculated cure depth indicated
that the absorption from the monomer solution was dominant.

In summary, stereolithography of ceramics was demonstrated by the fabrication of alumina and silica parts, where the rheology and cure depth behavior were suited to stereolithography conditions. With further development, stereolithography processing of ceramics with controlled microstructures should become a viable technique for producing complex-shaped components.

### 7.2 Suggestions for Future Work

Stereolithography of ceramic components is a young and exciting technology, which has received significant attention recently both from academia and industry.

The rheological properties and curing behavior are two major issues for ceramic suspensions intended for stereolithography. The non-aqueous ceramic suspensions developed in this work had the required viscosities at high solids loadings. These properties could be enhanced by identifying more effective dispersants, optimizing the amount of dispersants added, and using optimum monomer to solvent ratios. Efforts can be made to interpret rheological data in terms of the composition of the suspension and the interactions among the constituents. This will help in designing and optimizing the rheological behavior of a photosensitive ceramic suspension.

The photo-induced polymerization of filled monomer systems needs to be studied. UV curing is based on the absorption of the laser radiation by the photoinitiators. For filled monomer solutions, the optimal concentrations of photoinitiators are unknown in the literature. In this work, the addition of a large volume-fraction of ceramic powders into a raw resin did not prevent the solidification of the liquid matrix; however, the optimal range of photoinitiator concentration needs to be understood. In addition, efforts can be made to investigate possible inhibition of polymerization as a result of the addition of ceramic powders and organic solvents.

The prediction of cure depth behavior can be made based on the modelling of the light
scattering and absorption in the irradiated layer. Efforts can be made to improve the model of light transmission using more complex multiple scattering models which consider the interaction among the particles as well as account for light scattered out of the laser path.

Further research to incorporate suitable high refractive index solvents into the liquid resin to increase the refractive index of the UV-curable solution is important to expand the menu of ceramic materials for use in stereolithography.

In terms of improving the dimensional accuracy of ceramic green bodies fabricated using stereolithography, the mechanical properties of cured layers need to be addressed. The stiffness of cured layers depends on the composition of the liquid monomer solution, the degree of cross-linking, the shrinkage, and the volume-fraction of the ceramic powder added. Stereolithography of ceramic components will also lead to research on the debinding and sintering steps to obtain the final ceramic parts with controlled microstructure.

### 7.3 Conclusions

- Commercially available monomer solutions can be used as the basis of photo-polymerizable ceramic suspensions, as demonstrated by the alumina, tri-calcium phosphate, mullite and silica suspensions developed in this study.

- High solids loading can be achieved in these suspensions with the use of appropriate dispersants and solvents, while maintaining rheological behavior compatible with commercial stereolithography machines.

- The suspensions can be polymerized to form complex-shaped articles using commercial stereolithography machines. The limits on shapes, dimensions, and tolerances are expected to be similar to those for standard stereolithography of plastics.

- Critical laser doses are higher for the suspensions than for the raw monomer solutions, resulting in slower building times.
• Polymerized organic phases can be eliminated by heating in a conventional furnace and ceramic compacts sintered to near theoretical density.

• Kubelka-Munk analysis can be applied to these suspensions. This analysis demonstrates the relative importance of scattering and absorption phenomena, and allows stereolithography suspensions to be developed and characterized without performing trials on the stereolithography machine itself.

• The results of applying multiple-particle scattering theories to these suspensions indicate that in developing optimum systems: particle size is relatively unimportant; light scattering is nearly linearly dependent on $\Delta n^2$ ($\Delta n$ is the refractive index difference in percentage); penetration depth decreases with increasing particle volume-fraction for $\Delta n > 10\%$; penetration depth increases with particle volume-fraction for $\Delta n < 2\%$ for non-absorbing particles.
In Kubelka-Munk theory, diffuse reflectance of a specimen with a backing can be expressed as [Kortüm 69],

\[ R = \frac{R_0 - R_g (2a_c R_0 - 1)}{1 - R_0 R_g} \]  \hspace{1cm} (A.1)

where \( R \) is the diffuse reflectance of a specimen, \( R_g \) is the reflectance of the backing itself, \( R_0 \) is the diffuse reflectance of the sample with an ideal black non-reflecting background (i.e., \( R_g = 0 \), then \( R = R_0 \)), and \( a_c \) is a constant used in the K-M theory.

In this work, the diffuse reflectances of an uncured specimen with white and black backgrounds were measured, respectively. Therefore, we have,

\[ R_{sw} = \frac{R_0 - R_w (2a_c R_0 - 1)}{1 - R_0 R_w} \]  \hspace{1cm} (A.2)

\[ R_{sb} = \frac{R_0 - R_b (2a_c R_0 - 1)}{1 - R_0 R_b} \]  \hspace{1cm} (A.3)

where \( R_{sw} \) and \( R_{sb} \) refer to the reflectances of the specimen on white or black backings respectively. \( R_w \) and \( R_b \) are the reflectances of the white (a \( \text{Al}_2\text{O}_3 \) plate) and black (a SiC plate) backings respectively (see Fig. A.1). Solving Eq. A.2 and Eq. A.3 for \( a_c \), we obtain,

\[ a_c = \frac{R_{sw} R_w R_b - R_{sw} R_w R_{sb} + R_b - R_{sb} - R_w R_{sb} R_b - R_w + R_{sw} R_{sb} R_b + R_{sw}}{2 (R_b R_{sw} - R_w R_{sb})} \]  \hspace{1cm} (A.4)

which is identical to Eq. 5.20. In this work, \( R_{sw} \) and \( R_{sb} \) were corrected to account for the internal and external surface reflections (Eq. 5.16). The corrected values of \( R_{sw} \) and \( R_{sb} \) (i.e., \( R'_{sw} \) and \( R'_{sb} \)) are used in Eq. A.4.
Using the reflectance and transmittance at a wavelength of 325 nm, the scattering ($S$) and absorption ($K$) coefficients for the ceramic suspensions were calculated using Kubelka-Munk analysis (see Eq. 5.20-5.24, pp. 106).

**Figure A.1:** UV diffuse reflectance spectra of the white and black backings.
References


[Hull 86] C. Hull, “Apparatus for Production of Three-dimensional Objects by


