REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)

2. REPORT DATE
2 April 2001

3. REPORT TYPE AND DATES COVERED
Final Progress Report for the period
01 Jun 93 ~~930601 – 970630~~ 31 May 97

4. TITLE AND SUBTITLE
Biomimetic Processing of Ceramic Composites

5. FUNDING NUMBERS
DAAH04-93-G-0098

6. AUTHOR(S)
Ilhan A. Aksay, Daniel M. Dabbs

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Princeton University, Princeton, NJ

RECEIVED
MAY 08 2001
BY

8. PERFORMING ORGANIZATION
REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
ATTN: AMSRL-RO-BI (Technical Reports)
4300 S. Miami Blvd.
Durham, NC 27703-9142

10. SPONSORING / MONITORING
AGENCY REPORT NUMBER
31268.1-MS-AAS

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Three task areas composed the research effort: (i) optimized depth of photocuring in a resin system, (ii) improved resin/ceramic particle compatibilities consistent for use in stereolithography, and (iii) developing the technique of ceramic stereolithography (CSL) for the fabrication of a ceramic matrix composite test structure. The depth of photocuring in a model resin system was investigated as a function of photoinitiator concentration. Polymer solutions were photocured using varying levels of energy and photoinitiator concentration. An optimal photoinitiator concentration maximizing the cure depth was observed. Two regimes were shown to exist in which shrinkage was minimized or maximized. A quantitative model was developed to describe the system's behavior. Good agreement with experiment was obtained and the model predicted both the existence and location of the optimal photoinitiator concentration and corresponding cure depth.

After optimizing the resin/particle system, complex shaped structures were fabricated from ceramic powder compacts constructed using CSL. The main processing parameters in CSL such as layer thickness, resolution, hatch spacing, and overcure were found to depend on the light propagation in a concentrated dispersion, and a model was developed and used to optimize the fabrication of the ceramic structures.

14. SUBJECT TERMS
stereolithography, rapid prototyping, ceramic matrix composites, ceramic/polymer composites, biomaterials, biomimicking, bone implants

15. NUMBER OF PAGES
12

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	**UNCLASSIFIED**	**UNCLASSIFIED**	**UL**

NSN 7540-01-280-5500
Prescribed by ANSI Std. 239-18

Standard Form 298 (Rev.2-89)
298-102

20010516 111

FINAL PROGRESS REPORT

for the

BIOMIMETIC PROCESSING OF CERAMIC COMPOSITES

DAAH04-93-G-0098

April 2, 2001

to

U.S. Army Research Office / AMSRL-RO-BI
4300 S. Miami Blvd.
Durham, NC 27703-9142

submitted by

Ilhan A. Aksay and Daniel M. Dabbs
Department of Chemical Engineering and
Princeton Materials Institute
A313 Engineering Quadrangle
Princeton University
Princeton, NJ 08544-5263

TABLE OF CONTENTS

PROJECT SUMMARY

This is the final technical report for the AASERT project "*Biomimetic Processing of Ceramic Composites*", grant number DAAH04-93-G-0098, for the period 1 June 1993 through 30 June 1997. The project's studies augmented the ARO-sponsored research on "*Layered Nanocomposites by Biomimetic Processing*" a University Research Initiative (URI, DAAL03-92-G0241) program on the biomimetic processing of materials at Princeton University. The URI, a collaboration between Case Western Reserve and Princeton Universities, worked to develop strategies to process novel multilayered hierarchical ceramic-polymer composites at the nano- and micrometer scales. The objective of the URI program was to develop new materials through biomimicking. A significant part of this research effort was the use of student research assistants in the design of novel processing techniques and the use of these to synthesize new materials with hierarchical micro- and nanostructures.

The primary goal of the AASERT project was to illustrate the feasibility of using stereolithography in the synthesis of biogenic materials. The approach was to pattern photocurable resins containing a high volume fraction of ceramic particles, using the resin as a matrix for highly loaded (>50 volume %) suspensions and to then apply this technology to the processing of hierarchically structured ceramic matrix composites. Two graduate students, G. Stephen Burpee and Jim H. Lee were the researchers on the project, working with co-advisors Profs. Ilhan A. Aksay and Robert K. Prud'homme, Chemical Engineering and Princeton Materials Institute. Related studies were performed by Rajeev Garg under the sponsorship of the URI project.

Coincident with the latter portion of the AASERT program were the first two years of a ARO-sponsored Multidisciplinary University Research Initiative (MURI, grant number DAAH04-95-1-0102) on "*Smart Materials Systems through Mesoscale Patterning.*" This project built upon the results of the preceding URI as well as complemented and supported studies in the AASERT program.

Three task areas composed the research effort: (i) optimized depth of photocuring in a resin system, (ii) improved resin/ceramic particle compatibilities consistent for use in stereolithography, and (iii) developing the technique of ceramic stereolithography (CSL) for the fabrication of a ceramic matrix composite test structure. In the first task area, the depth of photocuring for a model resin system was investigated as a function of photoinitiator concentration. Polymer solutions were photocured using varying levels of both photonic energy and photoinitiator concentration. An optimal photoinitiator concentration that maximized the gel cure depth was observed. Additionally, two regimes were shown to exist in which the shrinkage (upon solvent removal) was minimized or maximized. A quantitative model was developed to describe the observed behavior in the system. Good agreement with experiment was obtained, and the model was employed to predict both the existence and location of the optimal photoinitiator concentration and the corresponding cure depth.

After optimizing the resin/particle system, complex shaped structures were fabricated from ceramic powder compacts constructed using CSL. The main processing parameters in CSL such as layer thickness, resolution, hatch spacing, and overcure had been found to depend on the light propagation in a concentrated dispersion, and the model developed in the first task area was used to optimize the fabrication of the ceramic structures.

INTRODUCTION

Stereolithography is a sequential layering process that converts a "virtual" object into a real structure.[1,2] A 3-dimensional, computer-aided design (CAD) model is computationally sliced into a series of 2-dimensional, thin patterns. Each 2-D pattern is then transmitted to another computer that controls a scanning laser. The laser is rastered across the surface of a photocurable monomer resin to solidify the layer in the shape of the 2-D pattern. A new layer of resin is swept across the surface, and the process repeated. By sequentially depositing layers in this layer-additive fashion, the entire structure is replicated in solid form.

By their very nature, composite materials encompass a wide range of applications. Since stereolithography lends itself especially well to the fabrication of complex shaped objects, the focus of this project was on the processing of organic/inorganic hybrids for use as biomaterials. A specific goal was to produce bone graft or implant materials with complex internal geometries tailored by computer design. Ultimately, it is desired to produce composites that are immunologically compatible and mechanically functional in supporting loads, replicating the form and function of natural bone. Practically, this would result in an enhanced bone graft or implant structure. Current bone graft techniques suffer from a series of drawbacks: Autogenous strategies are limited by finite supply and issues of morbidity. Allografts often involve issues of immunogenicity (potential for viral transmission) as well as efficacy, depending on the method of sterilization.[3] Commercial products such as ultra high molecular weight polyethylene lack bone inductivity and/or strength.

In processing of organic/inorganic composites by stereolithography, a two-pronged approach was taken: first, we built on developed techniques used to produce fully ceramic compacts, then used a commercial stereolithography apparatus (SLA), designed to build organic polymer structures, to instead fabricate ceramic/polymer composites. To synthesize these materials it was found necessary to develop monomer resins not available commercially, then to optimize these systems with respect to the curing depth, which was found to be controlled by the photoinitiator concentration.

TECHNICAL APPROACH

This work focused on fabricating organic/inorganic composites composed of submicron size alumina (Al_2O_3) powder[*] as the inorganic phase (15% by volume) and a multi-functional monomer, *2,2-bis(4-(2-hydroxy-3-methacryloxypropoxy)phenyl) propane* (Bis-GMA)[†] as the organic matrix. Parts were fabricated using a commercial SLA unit.[‡] Bis-GMA is a commonly employed monomer in the dental industry, and alumina is used by virtue of its extensive history as a biocompatible material.[3] The photoinitiator used was *2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone* (DBMP)[§] (Fig. 1).

Because Bis-GMA has a viscosity of approximately 1200 Pa·s, trichloroethylene (TCE) was used as a diluent solvent for the monomer in a 40/60 weight ratio. The resin was pipetted into cylindrical wells and filled to the brim. A glass cover slide placed in contact with the top of the solution acted as a substrate for attachment during the polymerization. Samples were cured by writing a cross-hatched pattern with dimensions shown in Fig. 2(a). Solid composites were formed at energy dosages of 1.702 J/cm^2 and 22.255 J/cm^2.

In the fabricated composites, the CAD cross-hatched pattern was replicated successfully (Fig. 2(b)). Use of the glass cover slide facilitated removal of the gel for thickness measurements. Because of operating constraints with the SLA, individual layer thicknesses should have an order of magnitude of 100 μm to achieve successful layer lamination and adhesion. As clarified in earlier work, the introduction of ceramic filler particles into the photocurable resin results in scattering effects, which effectively decrease the mean transport length of photons through the resin.[4,5]. Thus, it is desirable to maximize the curing depth in the homopolymer resin before the addition of ceramic to ensure suitable cure depths are obtained in the composite material.

The "standard design equation" for stereolithography presented by Jacobs provides a relationship between cure depth and energy dosage:[1,2]

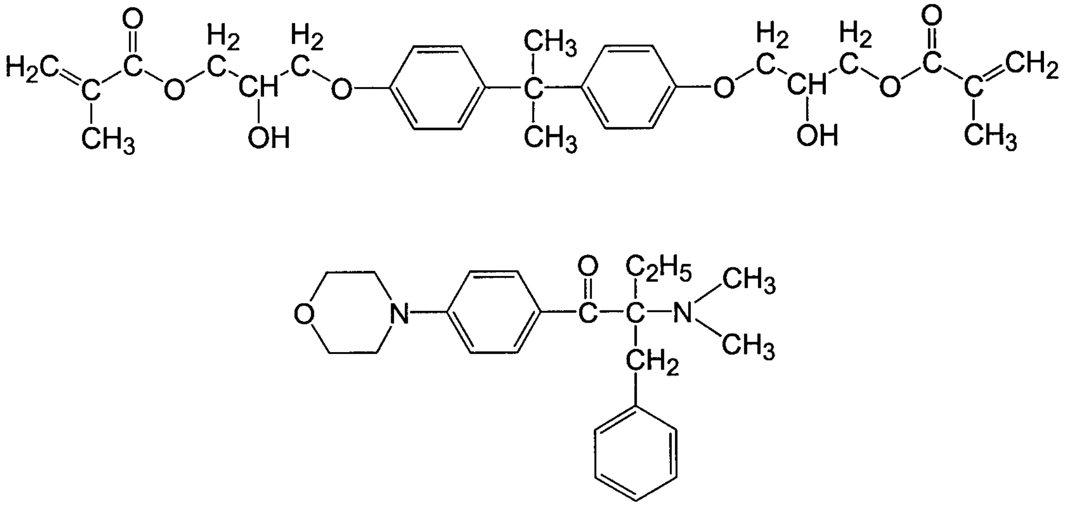

***Figure 1**: Chemical structures for* 2,2-bis(4-(2-hydroxy-3-methacryloxypropoxy)phenyl) propane (Bis-GMA) *and* 2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone *(DBMP).*

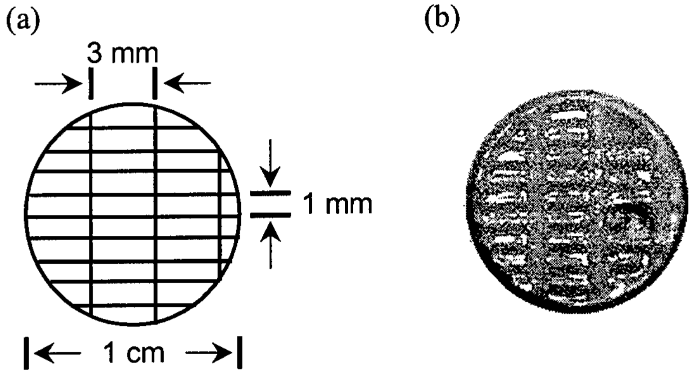

Figure 2: *(a) CAD schematic of UV-cured disc. Black lines represent cross-hatched laser rastering pattern (laser beam diameter of 250 μm and wavelength of 325 nm); (b) Bis-GMA/alumina (10/90 by volume) thin film composite formed in the SLA. Note that the designed architecture of the CAD file has been reproduced successfully.*

$$C_d = D_p ln\left(\frac{E_{\max}}{E_c}\right), \qquad (1)$$

where C_d is the cure depth, D_p is the depth of penetration of the laser beam into the solution, E_{max} is the energy dosage per area, and E_c represents the critical energy dosage. This empirical equation is used to fit experimental data on cure depth versus energy dose (E_{max}) to determine values for D_p and the empirical constant E_c. These values are then used to determine layer thicknesses of each layer for stereolithographic fabrication. Thus, one way to increase cure depth is to increase energy dosage. Noting, however, that the energy dosages employed in fabrication of the Bis-GMA/alumina composites described above are higher than those typically required for the commercially available resins the commercial SLA unit was designed for. In consideration of this design limitation, another method of increasing cure depth was desirable. Controlling the photoinitiator concentration was found to provide suitable control on cure depth.

To investigate the effect of photoinitiator concentration on cure depth, solutions of Bis-GMA and TCE were prepared in the manner described above. Photoinitiator (PI) concentration was varied from 0.3×10^{-3} to 5.1×10^{-3} moles/liter, corresponding to 0.010 to 0.150 weight percent of total solution and 0.0167 to 0.2500 weight percent based on Bis-GMA monomer weight. These values are comparable to typical industrial formulations. Samples were cured at 3 dosage levels: 0.931, 1.702, and 22.255 J/cm^2. The dosage levels were controlled by changing the laser beam writing speed on the SLA. The cure depth was then measured using a micrometer.

RESULTS

The experimental results are shown in Fig. 3 for the patterned photopolymerized films. The ordinate is the gel thickness in millimeters and the abscissa the photoinitiator concentration from 0.3 to 5.1 mM, which corresponds to 0.017 to 0.250 weight percent based on Bis-GMA monomer weight. The corresponding weight percent photoinitiator (0.01 to 0.15) based on total weight of solution is shown above. The three data curves correspond to three different laser energy dosages.

It might be expected that cure depth should increase with increasing photoinitiator concentration[6–,7,8] but this is not the case. The experimental data show that an optimal photoinitiator exists for which the cure depth is maximized. Furthermore, this dependence is not adequately explained by the standard design equation for stereolithography, which only directly considers the effect of energy dosage on cure depth. Extended data points (not shown) were taken for higher photoinitiator concentrations to confirm that the curve continues to decrease monotonically.

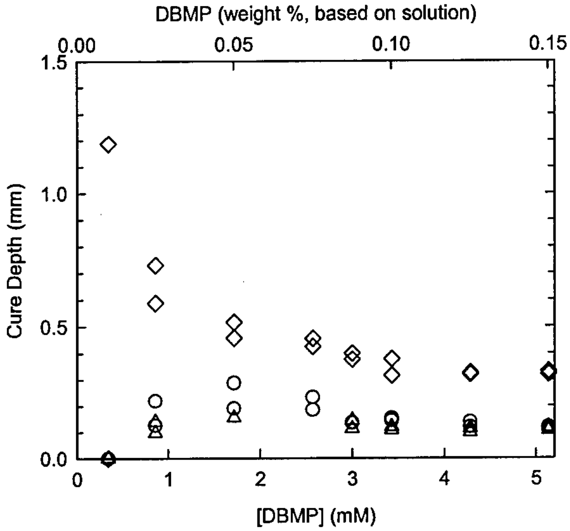

Figure 3: *Gel thickness versus photoinitiator concentration. The three data curves correspond to the three different laser energy dosages (◇ 22.255 J/cm^2, O 1.702 J/cm^2, and △ 0.931 J/cm^2). Photoinitiator concentration is given in millimoles/liter on the bottom abscissa, and as weight percent based on total solution on the top abscissa. Note the existence of an optimal photoinitiator concentration that maximizes cure depth.*

Returning to the filled resin, the degree of attenuation of the laser beam as it penetrates into the colloidal suspension medium is exacerbated by a multiple scattering effect. As filler is introduced into the system, the mean transport path of photons into the solution decreases, thereby altering the curing properties of the resin.[4,5] With the assumption that interference effects in the medium (modeled here as semi-infinite) can be neglected, a complete description of photon transport can be made in terms of the number of photons per unit volume per unit direction. In this diffusion model for scattering, two length scales are characteristic of the medium and are important in describing the photon density in the medium:[4] The absorption length, l_a, represents the average distance traveled by the photon before being absorbed. For purely absorbing resin this represents the penetration depth. The transport mean free path-length, l_{tr}, is the average distance the photon travels before its propagation direction is completely randomized. Using a Percus-Yevick structure factor, $S(\theta)$, for hard sphere scatterers, l_{tr} may be calculated as:[4]

$$l_{tr} = (n\sigma_{tr})^{-1}, \tag{2}$$

where n is the number density of scatterers and σ_{tr} is the transport scattering cross-section of a single scatterer, found as:

$$\sigma_{tr} = \int \frac{d\sigma}{d\Omega}(1 - \cos(\theta))S(\theta)d\Omega\,, \tag{3}$$

where $d\sigma/d\Omega$ is the differential scattering cross-section scaled by (1-cos(θ)) to account for anisotropic scattering. This in turn allows the calculation of the actinic intensity profile as a function of l_a. Solution of the diffusion equation gives expressions that allow for the rescaling of the absorption length in medium without particles, l_m, based on volume fraction filler, ϕ, as:

$$\frac{1}{l_a} = \left(\frac{\phi}{\phi_m}\right)^{1/3}\left(\frac{\phi_m{}^{1/3} - \phi^{1/3}}{\phi^{1/3} l_m} + \frac{1}{l_p}\right), \tag{4}$$

where ϕ_m is the maximum packing fraction for the colloidal dispersion and l_p is defined as the length scale where the light intensity decays by a factor e^{-1} traveling through the particle. Support for this determination of the absorption length for photon propagation through dense colloidal dispersion was provided by pulse-chase dye experiments to simulate the actinic absorption of the photocuring resin.[4,5] Figure 4 summarizes the results of the experiment.[4] As the data show, the transport length decreases dramatically with increasing filler volume fraction. Note that without correction for multiple scattering, the deviation between actual transport length and calculated value grows as volume fraction rises. Thus, rescaling of the transport length by Eq. (4) is necessary in order to accurately predict the curing profile for ceramic resin.

While the model describes the dependence of the curing profile on filler fraction, it does not suggest the shape of the cure depth versus photoinitiator concentration curve seen in Fig. 3.

This dependence has been investigated using the homopolymerization reaction of Bis-GMA and a model developed from first principles incorporates the photoinitiator dependence.[9]

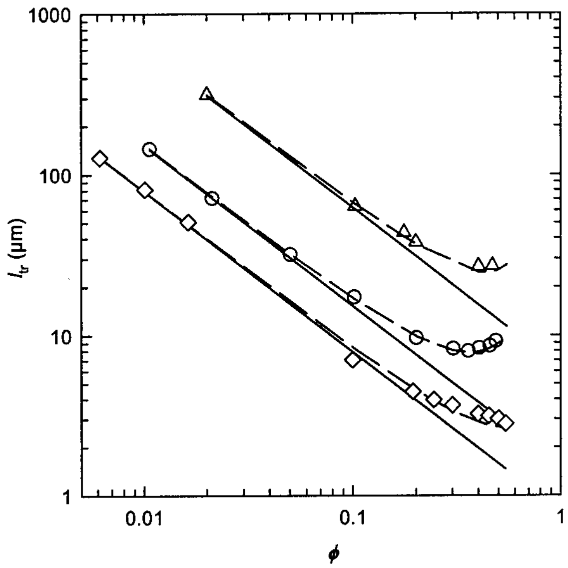

Figure 4: *Transport mean free path versus volume fraction, φ, of scattering particles on log-log scale. Solid curves are computed values without correlation and σ_{tr}; dashed curves are computed values obtained by using equations (2)-(4) and S(θ) from Percus-Yevick theory. Symbols represent transport lengths obtained from experiment: ◇ 0.51 μm alumina, △ 0.46 μm silica, and ○ 0.32 μm alumina, and. The curve for 0.51 μm alumina has been shifted up by log(3) for clarity. (reprinted by permission[4])*

CONCLUSIONS

We have successfully processed Bis-GMA/alumina organic/inorganic biocomposites using stereolithography. Additionally, controlled patterning of the composite has been demonstrated through replication of designed architecture via CAD. In obtaining feasible cure depths to enable fabrication of multi-layered objects, the cure depth has been controlled using an route other than simply increasing energy dosage: controlling the concentration of the photoinitiator. A model for the role of volume fraction ceramic filler on the curing profile was developed and corroborated by experiment. The dependence of the curing depth on photoinitiator concentration has been demonstrated and the existence of an optimal photoinitiator concentration for which cure depth is maximized has been found. A model derived from first principles to explain the experimental results quantitatively has been developed. Once clarified, dependence of the cure depth on photoinitiator concentration should provide implications to fields as diverse as industrially cured coatings and dental fillings, in addition to 3-dimensional fabrication techniques described in this report.

REFERENCES

1. P.F. Jacobs, *Rapid Prototyping and Manufacturing*, (Soc. of Manufacturing Engineers, Dearborn, MI:1992).
2. P.F. Jacobs, *Stereolithography and other RP&M Technologies* (Soc. of Manufacturing Engineers, Dearborn, MI:1996).
3. L.L. Hench, "Bioceramics," *J. Am. Ceram. Soc.* **81** [7] 1705-28 (1998).
4. R. Garg, R.K. Prud'homme, I.A. Aksay, F. Liu, and R. Alfano, "Optical Transmission in Highly-Concentrated Dispersions," *J. Opt. Soc. Am.* **15** [4] 932-35 (1998).
5. R. Garg, R.K. Prud'homme, I.A. Aksay, F. Liu, and R. Alfano, "Absorption Length for Photon Propagation in Highly Dense Colloidal Dispersions," *J. Mater. Res.* **13** [12] 3463-67 (1998).
6. G.A. Brady and J.W. Halloran, "Differential Photo-calorimetry of Photopolymerizable Ceramic Suspensions," *J. Mater. Sci.* **33** [18] 4551-60 (1998).
7. F.A. Rueggeberg, P.E. Lockwood, and J.W. Ergle, "Effect of Post-cure Heating and Photoinitiator Level on a Model Resin System," *J. Dental Res.* **76** 472-72 (1997).
8. F.A. Rueggeberg, J.W. Ergle, and P.E. Lockwood, "Effect of Photoinitiator Level on Properties of a Light-cured and Post-cure Heated Model Resin System," *Dental Materials* **13** [5-6] 360-64 (1997).
9. J.H. Lee, R.K. Prud'homme, and I.A. Aksay, "Cure Depths in Photopolymerization: Theory and Experiments," *J. Mater. Res.* submitted (2000).