Functionally Graded Polymer Matrix Nano-Composites by Solid Freeform Fabrication: A Preliminary Report

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ABSTRACT

A research program has been initiated to develop a Solid Freeform Fabrication (SFF) technology for combining nanosized particulate or fiber reinforcements with a photocurable thermoset matrix resin in order to produce functional graded composites. The composites that are being studied initially are optical components filled with nano-phase ceramic particles that form gradient refractive index lenses (GRIN). The Solid Freeform Fabrication (SFF) method employs an ink-jet deposition (IJD) process to form the composites. The IJD process has the advantage of incorporating nano-reinforcements into a low viscosity matrix resin that is relatively easy to process and rapidly photocures to produce functional polymeric parts. It also has the advantage that major modifications to the basic SFF processing methodology are not necessary.

The emphasis in the program is on demonstrating the feasibility of this approach for fabrication of gradient refractive index lenses (GRIN), which are flat instead of the traditional spherical lens geometry. As a result these lenses will be less costly to produce than conventional curved lenses. SFF is an ideal technique for meeting the needs of GRIN lens fabrication because changes in composition can be made from layer to layer and even within each layer, allowing for the introduction of compositional and structural gradients. Thus it has the potential for creating the spatial material distributions required for designing computer optimized, custom made GRIN lenses. Integral to the SFF process are computer design procedures that specify the exact material deposition patterns that need to be employed in order to optimize the performance of the GRIN lens.

The optical nano-composites will serve as a model system that we will use to work out the many challenges for implementing a viable SFF polymer composites technology. We then will make use of the information obtained and lessons learned from the work on optical composites and extend the development to structural composites that incorporate nano-particulate clays and carbon nanofibers.

POLYMER NANO-COMPOSITES FOR GRIN OPTICAL APPLICATIONS

Background

Optical lenses are traditionally created from blocks of uniform material by grinding curved (usually spherical) surfaces. The spatial contour of the index of refraction change provides optical power when the shape and orientation are appropriately chosen. The non-planar surfaces (Figure 1) of this type of lens are detrimental to many commercial and military applications. The curvature is the source of the glint signature used for detecting covert observation. The curvature also will generate turbulence if the lens forms the window of a detector viewing out from a moving body, such as an aircraft. This situation often necessitates the use of an additional window fitted to the surface curvature, which may adversely affect optical clarity or light transmission.

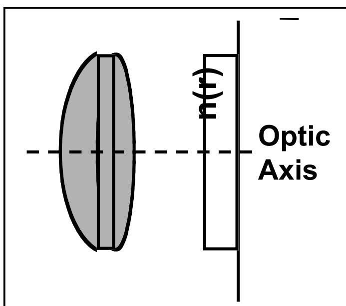

Figure 1 Traditional lens shape and refractive index profile.

Gradient index of refraction lenses (GRIN) present an alternative geometrical format. They provide the multi-dimensional spatial variation of refractive index required for optical power by implementing a non-uniform material distribution. (Figure 2) the use of GRIN techniques decouples the optical power generation from the curvature of the element. GRIN lenses can be fabricated with planar surfaces on either side or both sides. This should greatly simplify and reduce the cost of the fabrication of lenses by eliminating the need for grinding and polishing operations.

The common methods usually used for generating a radial variation in the material properties are chemical diffusion or ion-bombardment, which implant foreign materials into a uniform cylinder or plate of a host material. The implantation density can be varied as a function of radial position. However, with these methods there are technical difficulties in achieving the required axial concentrations of material species. Both of these methods also result in penetration-depth variations of the species introduced. This results in the optical properties changing as a function of distance along the optic axis. Thus independent control of the spatial variation of the material composition is not possible. As a result, the density profiles needed for optimal performance are difficult to achieve. So an SFF, layered manufacturing technique is an innovative, additive approach to the fabrication of GRIN lenses.

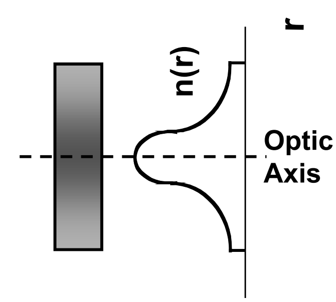

Figure 2 Radial gradient GRIN lens shape and refractive index profile.

Approach to Solving the Problem

In our research program we are exploring the feasibility of an SFF ink-jet deposition process that creates GRIN lenses from polymer/ceramic composites that have composition tunable optical properties. These composites are based on optically clear, photocurable thermoset resins containing various amounts of nanosized ceramic particles, to provide positionally controlled, tailored refractive indices. The utility of such composites in producing a wide refractive index tunability with little scattering has been demonstrated by Ho, et.al. [1]. The amount of light scattering in the composites is small, since the particles are much smaller than the wavelength of light.

There are four major elements of our GRIN research. These can be delineated as:

1. Polymer and composite development; this includes formulation or synthesis, ceramic particle dispersion, and polymer and composite processing
2. Ink-jet printing and processing of layers;
3. CAD GRIN design implementation;
4. Process feasibility demonstration; characterization of optical properties

Currently we are concentrating on elements 1 and 2 (encompassing the more basic materials processing related issues) in order to validate the viability of the concepts proposed. We are using a standard piezo ink-jet printer head for the initial exploratory work to demonstrate the basic concepts outlined here. The reservoirs in the ink-jet printer head contain a range of polymer/ceramic concentrations, so that the concentration of particles (and the index of refraction) at any location can be controlled by depositing appropriate amounts of material from the different writing heads. Following deposition, the layers are photocured by UV light. The UV light application mode is controlled so as to provide suitable optical and mechanical properties in the final product. Aspects of polymer cure control will include optimizing the cure advancement of each layer precisely so as to achieve a seamless interface and the application of radiation in specific patterns that will minimize the effects of cure shrinkage and residual stress buildup in the cured material.

Ink-jet Printheads

In order to achieve a sufficient refractive index gradient in a lens as large as several inches across, it will be necessary to both increase the material refractive index difference, Δn (as discussed below) by using a higher index ceramic filler and to implement a more sophisticated print system. Present day advanced commercial ink-jet capabilities include high-performance, multichannel printheads. For example, there are multi-nozzle piezo-driven printheads designed specifically for printing UV inks onto polymeric substrates at high deposition rates [2]. Nozzle diameters in these systems are of the order of 20μm or less. The printers also have gray-scale resolution capabilities with greater than 900dpi resolution. In order to work with higher viscosity formulations, the temperature can be controlled by a heating element integrated into the printhead mount that heats both the printhead and the ink supply. An example of the utility of printheads of this type in a related SFF application is micro devices made from a UV curable (cationic) epoxy resin [3].

Printability of Nanoparticle Loaded Polymers; Nozzle Clogging

The photocurable monomer that we have chosen to work with initially is hexanediol-diacrylate (HDODA). HDODA is a low viscosity liquid with viscosity of several cP. At the low solids contents that will be used for this application (<< 20% by volume), the relative viscosity of the loaded polymer systems will remain low [4, 5]. This will insure ease of printability at low temperatures and help to mitigate the potential ink-jet printer nozzle clogging issue. That nozzle clogging should not be an issue is further suggested by the work of Sharp and Adrian [6], who considered particle bridging in particle loaded fluids flowing through microchannels. Their experiments identified 'shear-induced arching' as a mechanism that causes microtube blockage. They found that this mechanism is most likely to occur only when $0.33D < dp < 0.46D$, where dp is the particle diameter and D is the microtube diameter. This was observed for flows of particle-laden fluids with concentrations as low as 0.5%. Since in our case the ink jet nozzle is of the order of 20μm in diameter, dp is around 10^{-3} less than D.

Ceramic Filler Selection

It has been demonstrated that appropriately large optical gradients can be achieved through the use of ceramic particles dispersed in a polymeric matrix [1]. Typical UV cured polymers have refractive indices in the 1.4 to 1.7 range. There are several ceramics that have a considerably higher refractive index than these organic polymer systems, as indicated in Table 1 [7].

Table 1: Average Refractive Index of Some Common Ceramic Systems [7]

Material	Average Refractive Index
Alumina (corundum)	1.75
Quartz (SiO_2)	1.55
Zircon ($ZrSiO_4$)	1.95
Spinel ($MgAl_2O_4$)	1.72
Rutile (TiO_2)	2.71
Silicon Carbide (SiC)	2.68
Galena (PbS)	3.9
Barium Titanate ($BaTiO_3$)	2.4
Zirconia (ZrO_2)	2.3
Iron Oxide (Fe_2O_3)	3.0
Zinc Oxide	2.0

The use of a high refractive index ceramic (>2.0) in an organic matrix provides for a wide range of refractive index in the GRIN optics. The refractive index in the graded optics can be controlled by varying the concentration of the dispersed ceramic. (To avoid optical scattering from the dispersed particles, the ceramic powders used in the GRIN system should be nano-particulate (5nm – 40nm) and should be very well dispersed.) A greater difference in the refractive index between the ceramic particle and the organic matrix will allow a wide gradient to be achieved with a minimum amount of ceramic particles. In calculating the necessary GRIN optical parameters it is found that the larger is Δn, the easier it becomes to fabricate GRIN lenses with shorter focal lengths as well as thinner cross-sections.

In summary, the polymer matrix will be of lower refractive index and the nano particulate ceramic will be of higher refractive index. The graded refractive index can be achieved by varying the ceramic loading in the matrix monomer as well as the deposition pattern and drop size for deposition. The initial matrix material chosen is HDODA, which, when polymerized, has a refractive index of ~1.6. Initial experiments will be performed using a ceramic such as zirconia due to its commercial availability and relatively high refractive index. After the feasibility of using nano-particulate zirconia has been demonstrated using the ink-jet printing method, the use of higher refractive index ceramics, for example, rutile, barium titanate, and iron oxide will be explored in order to increase the Δn window.

We noted above that ceramic loadings of 20% by volume will be a maximum limit. Assuming a linear rule of mixing to estimate refractive index of ceramic dispersed systems (worst case), the effective refractive index of a 20% zirconia loaded HDODA system will be approximately 1.74. Using appropriate optics design methods, the resultant Δn of 0.14 is found to be adequate for fabricating GRIN test optics of dimensions up to a few inches in size.
For Fe_2O_3 the Δn is 0.28, which provides much greater latitude in GRIN fabrication. The initial goal for proof of concept is to fabricate an optical wedge with a linear radial refractive index gradient.

Particle Stabilization and Dispersion

A key factor in the printed optics fabrication of GRIN elements with ceramic particle index modifiers is complete deagglomeration and dispersion of the nano-ceramic particles. Agglomeration and poor dispersion of ceramic particles in the organic matrix will result in scattering, degrading the GRIN optic's performance. Traditional deagglomeration and dispersion techniques are ultrasonication and surface treatment of the powder during synthesis [8]. Significant progress has been made in the synthesis of nano-particulate ceramic powders in recent years. Spherical nano-particulate ceramic powders with narrow particle size distributions are commercially available. Significantly, the same sources that synthesize the nano-particle ceramic powders have been able to develop surface treatments to keep the powders deagglomerated and with a high degree of dispersability. Such surface treatments are applied to the powder particles during the synthesis process. The treatments are of various types, which effectively functionalize the surface with an adsorbed monolayer, resulting in steric-stabilization that prevents agglomeration of the powder. These coatings are tailored so that appropriate wetting of the particles by an organic monomer is achieved. The surface functionalized ceramic particles are dispersed in the monomer by mixing using an ultrasonic vibration technique. Because of the small size of the particles and relatively large surface tension forces, settling of the particles is not expected.

Numerous references to steric stabilization of nanoparticles by surface functionalization by different approaches are available in the literature. Specific examples of this are contained in references [9-15]. These include grafting polymers such as silanes onto the particle surfaces [9-11, 15] or using adsorbed monolayers of a polymer or surfactant [13-15].

Polymer Matrix: Photocuring and Residual Stresses; Chemical Stability; Air Bubbles

A key issue in photocuring is that the effects of residual stresses must be minimal so as to effectively eliminate dimensional distortion and spurious stress-induced refractive index gradients. This can be addressed in two ways: 1) by implementing random segmented cure patterns [16], where UV radiation is applied to small areas separated from each other, in a sequential pattern until the entire layer is cured, and 2) applying radiation in incremental doses small enough such that cure is carried out slowly. By combining these two principles the polymer will retain rubbery characteristics long enough so that much of the cure-induced residual stress can relax before full vitrification of the resin occurs [17]. The use of incremental curing methods has been shown to be quite effective in minimizing residual stresses by allowing each small area to undergo a high degree of stress relaxation before being joined to other cured areas.

The chemical stability of the proposed system is important because we wish to develop optical properties that are stable over long time periods. HDODA cures to produce transparent, water-white optical qualities. The presence of residual photoinitiator quantities could cause yellowing to develop during aging that occurs over a period of time after the GRIN lens is produced. In collaboration with a supplier of photoinitiators we have identified an effective non-yellowing photoinitiator that is stable in the cured resin.

In order to minimize dust contamination and reaction inhibition (due to presence of oxygen) of the samples, we are forming GRIN samples under a nitrogen blanket in a 'clean' environment. We do not anticipate problems with imperfections introduced through bubble formation. There are several reasons for this. First of all, previous SFF ink-jet deposition work [3] has shown that void free spherical micro -lenses can be formed with such printheads using a photocured cationic epoxy resin. Epoxy resins have higher viscosities than the HDODA formulations of interest here. If an epoxy can be processed without bubble formation, it is most likely this will not be a problem with HDODA. Further we will be working with very thin layers (<25μm in thickness) and very small droplets. Also, there will be substantial overlap of droplets as the material is being deposited. All of these are factors that will promote dissipation of air bubbles. However, if we do find that micro-bubbles are a problem, we will add small amounts of an organic soluble surfactant to the resin formulations. This method of bubble suppression is very effective and is used frequently in chemical systems to prohibit bubble formation.

Substrates

The type of substrate to be employed for the proposed application will affect the face of the lens and might compromise the quality of light transmission. Three types of substrates will be considered as working surfaces. In preliminary trial studies of the concepts proposed here, we formed thin films around .002" thick, using a conventional ink-jet printer with a mylar film as a substrate, (film similar to those used for overhead transparencies). The results indicated that both material deposition and the surface of the films produced were of good quality (by simple visual inspection). We have not yet looked at any quantitative measure of surface clarity, and roughness. Also, if mylar should not prove totally effective, we will work with silicon and sodium chloride single crystal substrates. Silicon has been used previously in RP fabrication of micro-ceramic components by other workers [18] and is commonly used for preparing AFM (Atomic Force Microscopy) specimens. We have used NaCl single crystals [19] as substrates for producing extremely smooth thermoset epoxy resin samples for AFM characterization. An advantage in using NaCl is that the substrate can be simply dissolved away from the deposited polymer after the polymer has been cured, leaving an ultra smooth surface behind.

Previous Research on Inkjet Printing of Ceramic Filled Polymers

Ink-jet deposition methods have been used previously for SFF of ceramic particle-filled resins and have proved useful because of their improved resolution relative to other SFF methods. Relevant prior work of other research groups on SFF of ceramics using drop-on-demand ink-jet deposition is reviewed here to provide additional background information for those who would care to explore the topic in more detail. All of the previous studies concern SFF and deposition of monomers (and resins) containing high loadings of ceramic particles of appreciably larger dimensions than the nanoparticles of interest here. The object in these former studies has been using the ceramic slurries to construct green-forms for making ceramic components. The resins in these compositions then serve as a binder for the ceramic powder, which is subsequently burned out prior to densification of the ceramic. Various references that concern ink-jet deposition of monomers containing high- loadings of ceramic particles (greater than 40% by volume) are noted in the list of references [20-29]. These are representative of the work being done by three different research groups, those at the University of Michigan [20-22], University of Manchester (England) [21-23, 28,29], and UCLA [24-27].

Additional research of note that relates specifically to GRIN lenses is that being done by the Cima-Sachs 3-D Printing group at MIT. A recent publication of theirs [30] discusses the use of the slurry based 3-D Printing process for fabricating complex structured materials by printing organic binders in selected positions on each printing layer. This process was modified in an effort to fabricate GRIN lenses by depositing polymers containing different concentrations of an alumina dopant at various positions in a silica powder bed. Two different dopant concentration profiles, which had maximum alumina concentrations of 1.63 mol% and 2.50 mol%, were printed into the silica powder beds. The doped ceramic powders then were sintered at 1650°C into optical transparency, and the magnifying effects of GRIN lenses with gradient profiles of alumina were observed. This work is only in an exploratory state and the method requires extensive post-processing. It will be interesting to learn whether sufficient resolution and control of concentration gradients for producing effective GRIN lenses can be achieved in this method, even though there are problems with spreading of the droplets due to the porous nature of the substrate [31].

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