Polymer Matrix Nanocomposites by Inkjet Printing

By

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Abstract

This paper describes work on a continuing project to form functional composites that contain ceramic nanoparticles using a Solid Freeform Fabrication (SFF) inkjet printing method. The process involves inkjet deposition of monomer/particle suspensions in layers followed by curing each layer in sequence using UV radiation. The reactive monomer is hexanediol-diacrylate (HDODA); the polymer forming reaction proceeds by a free radical mechanism. The liquid monomer containing nanoparticles is essentially a printing ink formulation. Successfully suspending the particles in the monomer is critical. We have developed a surface treatment method for forming stable suspensions of the nanoparticles so that they remain discrete throughout the processing sequence.

The SFF process involves careful control of the polymer cure so that the interface between layers is seamless and residual stresses in the composites are eliminated. An immediate use for such composites is in optical applications as gradient refractive index lenses (GRIN). GRIN lenses have planar surfaces, eliminating the need for costly grinding and polishing. The planar surfaces also eliminate optical aberrations that result at the edges of spherical lenses and diminish the accuracy of focus.

If the appropriate nanoparticles are fully dispersed they will modify the polymer's refractive index without interfering with light transmission. The effect is additive with volume concentration. Using 'inks' of different compositions in a multiple nozzle inkjet printer allows the formation of composites with precise composition gradients. Since an object is built one planar layer at a time, changes can be made readily both within each layer and from layer to layer. Inkjet printing with picoliter resolution is ideal for this task.

Working with SiC nanoparticles in HDODA as a model system for demonstrating the inkjet deposition process, nanocomposite films with a linear concentration gradient varying from 0 to 4.5% (wt) were fabricated on Silicon wafers. These composites are 30 layer films, which total 140μm in thickness. Each layer in the composite is about 5 μm in thickness. Analytical methods for characterizing the dispersion of the nanoparticles in the composite and some of the salient optical properties of the composites also were established. The status of the program is reviewed in this paper.

Key Words: polymer matrix nanocomposites, dispersing nanoparticles in polymers, solid freeform fabrication of nanocomposites,

Introduction

Processing Polymer Nanocomposites by Inkjet Printing

A solid freeform fabrication (SFF) process has been developed that provides an effective method for combining nano-sized particles or fibers with a photocurable thermoset matrix resin to produce functionally graded composites. The approach is based on inkjet deposition (IJD) and incorporates the nano-reinforcements into a low viscosity matrix resin that can be processed readily. The resin rapidly photocures under UV light exposure to produce functional polymer composite parts and does not require major modifications to the basic SFF concept [1,2].

This paper considers the initial stages in developing the SFF methodology. The process involves careful control of the polymer cure so that the interface between layers is seamless and residual stresses in the composites are eliminated. The reactive monomer is hexanediol-diacrylate (HDODA); the polymer forming reaction proceeds by a free radical mechanism. The monomer containing nanoparticles is essentially a printing ink formulation. The immediate application is for creating optical composites to be used as gradient refractive index lenses (GRIN). Such lenses have planar surfaces, eliminating the need for grinding and polishing. The planar surfaces also eliminate optical aberrations resulting at the edges of spherical lenses.

The utility of composites containing ceramic nano-particles in producing refractive index tunability without scattering has been addressed in the literature [3-7]. If the appropriate nanoparticles are fully dispersed they will modify the polymer matrix refractive index without interfering with light transmission, since the particles are much smaller than the wavelength of light. The effect is additive according to volume fraction of particles in the composite. Successfully suspending the particles in the monomer is critical. We have developed a silane surface treatment method for forming stable suspensions of the nanoparticles so that they remain discrete throughout the processing sequence [8].

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 specified by depositing appropriate amounts of material from the different writing heads. Using 'inks' of different compositions in a multiple nozzle inkjet printer allows the formation of composites with precise composition gradients. Since an object is built one planar layer at a time, changes can be made readily both from layer to layer and within each layer. Inkjet printing with picoliter resolution is ideal for this task.

Polymer Nano-Composites for GRIN Optical Applications

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 spherical shape itself can be a problem. For example, the dominant abberation in lenses used for laser beam delivery systems is spherical abberation, which causes the light rays at the edge of the lens to be misaimed with respect to the rays at the center of the lens. This results in a larger focused spot. The use of a gradient lens effectively eliminates this type of abberation giving a more accurate focus.

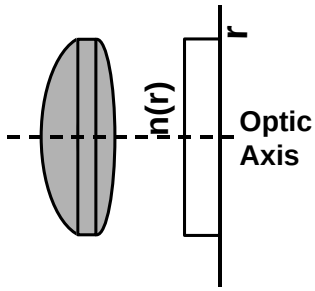

Figure 1: Traditional lens shape and refractive index (n) profile.

The curvature also is the source of the glint signature used for detecting covert observation. This situation often necessitates the use of an additional window fitted to the surface curvature, which may adversely affect optical clarity or light transmission. In addition, the curvature will generate

turbulence if the lens forms the window of a detector viewing out from a moving body, such as an aircraft.

GRIN lenses present an alternative geometrical format. They provide the multi-dimensional spatial variation of refractive index required for optical performance 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 greatly simplifies and reduces the cost of the fabrication of lenses by eliminating the need for grinding and polishing operations.

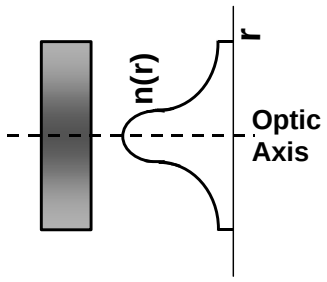

Figure 2: Radial gradient GRIN lens shape and refractive index profile; n

Creating composition gradients in glasses has proved difficult. The common methods usually used for generating a radial variation in 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 it has not proved possible to achieve the required axial concentrations of material species. This results in uncontrolled changes in optical properties as a function of distance along the optic axis. Thus, 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. Optical surface coatings also can be applied as part of the SFF process. Direct inkjet printing of polymer based composites promises to provide a novel, low-cost means for achieving the desired result.

Experimental

Materials; Photocuring

Hexanediol-diacrylate (HDODA) is the monomer that forms the matrix polymer for the nanocomposites. It was supplied by Cytec Surface Specialties, Inc., Radcure Division (Smyrna, Georgia USA). HDODA is a transparent liquid with a viscosity at ambient temperature of ~ 2 cpois. In this study the monomer was activated for UV photocuring using a photoinitiator, 1-hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184, Ciba Specialty Chemicals Corp., Chicago, Illinois USA). The polymer forming reaction proceeds by a free radical mechanism. Irgacure 184 is soluble in the monomer and is non-yellowing; the photoinitiator concentration is 1% by weight.

Nanoparticle powders were obtained from Sigma-Aldrich Chemical Co. (Milwaukee, Wisconsin USA). Both SiC and $BaTiO_3$ particles were surface treated with two different silanes: 3-Acryloxypropyltrimethoxysilane (ACTMS) for the $BaTiO_3$ and 3-Aminopropyl-triethoxysilane (AMPTES). They were obtained from Gelest, Inc. (Morrisville, Pennsylvania, USA). Additional specifics about the surface modification process are provided in another publication [8]. In this paper we concentrate on the results obtained for SiC.

An EFOS Acticure® UV generator (EXFO, Inc. Vanier, Quebec, Canada) with a High Pressure 100 Watt Mercury Vapor Short Arc bulb and a liquid-filled light guide was used as the ultraviolet light source for curing the composites. The Acticure® lightguide is a 1m long, flexible cable, liquid-filled lightguide with a 5 mm diameter output tip. The flexible lightguide made the setup for UV curing very versatile. The Acticure® delivers radiation in the 320-500nm range, which is in the spectral region where the photoinitiator is active.

Each layer was exposed to UV following a two-step procedure. First a low-intensity UV exposure (0.500 W/cm^2) was rastered across the surface to partially cure and gel each layer in sequence. After all layers were printed, a longer-time, higher intensity (1.5 W/cm^2) exposure was used to slowly advance the cure to a high degree. This final exposure is equivalent to a postcure.

The polymer matrix will be of lower refractive index and the nano particulate ceramic will be of higher refractive index. This arrangement provides maximum flexibility in material selection. The graded refractive index is achieved by varying the ceramic loading in the matrix material. The initial matrix material chosen for this program is HDODA, hexanediol-diacrylate. HDODA has a refractive index, n, of 1.45 and the polymer formed has n = 1.50; SiC has n = 2.68 [9].

Ink Jet Deposition Experiments

For the sake of simplicity (and low cost) in the initial stages of the program we used a standard piezo ink-jet printer to demonstrate the concepts that were delineated above. The piezo systems use a PZT piezo crystal to generate an acoustic wave in the reservoir that both ejects a fluid stream and creates the instabilities that cause the jet tip to break off a well defined, repeatable droplet.

Printing experiments were carried out with neat HDODA and HDODA suspensions using an Epson Stylus Photo 960 printer. This printer accommodates printing on a CD sized flat surface with droplet volumes of 3-10 picoliters and variable droplet size control (gray scale resolution). The reservoirs (seven reservoirs) in the inkjet printer head can be used to 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 print nozzles. Our initial experiments concentrated on processing and photocuring monomer without ceramic as well as processing ceramic dispersions having various concentrations and employed only 2 print nozzles. Printing was done on silicon wafers, which are the same diameter as conventional CDs. Curing was accomplished with the EFOS^{TM} guided UV broadband light source as described above.

Results and Discussion

Results Obtained for SFF processing of GRIN Composites

The major emphasis in the GRIN research thus far has centered on materials and SFF processing issues involving:

1. Polymer and composite development; this includes resin formulation, ceramic particle dispersion, and polymer and composite curing
2. Ink-jet printing and processing of layers
3. Characterization of polymer cure, material and optical properties

The results of the research program thus far are described in the following paragraphs

Ink Jet Deposition Experiments

Using the approach cited previously, in the initial effort we restricted the printing dimensions to less than 3-inches, since we were concerned with proof of concept studies. Ultimately, in order to demonstrate the fabrication of a lens as large as 5-in or greater and to achieve the appropriate differences in refractive index, we will both increase the refractive index difference, Δn, by using a higher index, non-absorbing ceramic filler *and* also implementing a more precise industrial print system with multiple inkjets.

Examples of neat and gradient polymer films produced by the SFF method are shown in Figures 3 and 4. The neat film is shown in an edgewise view in Figure 5. The change in composition in the gradient film appears as a color change.

Figure 3: Neat HDODA printed film 140μm thick, 30 layers; the film is flexible

Figure 4: Gradient printed film containing 0 to 4.5wt% SiC; 140μm thick, 30 layers

These films were printed by filling one blank ink cartridge with a 4.5 wt % SiC suspension and another with pure HDODA. The two 'inks' were printed as individual films as well as a gradient film combining the two in order to demonstrate that a film having multiple layers of HDODA and a gradient in ceramic nanoparticle concentration readily can be formed. The Epson 'Print CD' software was used to create the print program, which was set to form an apparent linear gradient in moving from one end with pure HDODA to the other with 4.5 wt % SiC.

During printing, after each layer was deposited, the silicon wafer in a nitrogen atmosphere was scanned with the UV light intensity set to 0.500 W/cm^2. After 30 layers were deposited, the films were scanned with the UV light set to 1.5 W/cm^2. The films then were allowed to remain on the wafer for an extended time period before being removed. They were easily removed from the wafer by lifting with a razor blade. Each film was approximately 140μm (0.14 mm) thick.

A primary problem that we encountered in printing was the rapid deterioration of the polymeric inkjet nozzle cone in the Epson inkjet cartridges, when exposed to the HDODA monomer. The cone is used to penetrate the ink cartridge and feed the ink-jet nozzle. In all cases, the cone fractured, resulting in failure of the nozzle system to function properly after a few hours of operation.

Another problem encountered (as expected) is the inability to cure the thin monomer layers (~5μm) deposited during processing. This is due to oxygen inhibition of the free radical reaction. The problem was corrected by carrying out printing in an enclosure with an N_2 atmosphere. The O_2 inhibition is effectively eliminated by this means.

Importance of Controlled Polymerization for the Layered Deposition of HDODA

Interlayer diffusion and bonding is essential in the design and fabrication of a gradient refractive index lens, since the radial (or axial) variation in concentration of ceramic nanoparticles creates the desired light refraction. The goal is to have a lens formed by layered deposition, which exhibits no optical or mechanical artifacts imparted by the processing methods used to form the lens.

When a thin film of HDODA is deposited on the silicon wafer and partially cured, this layer (L_i) then becomes the substrate for the subsequent layer. Thus, L_1 is deposited on the wafer and then becomes the substrate for L_2. As a substrate, L_1 must be adequately gelled. Since it is also desired to have seamless adhesion between every layer, L_1 must also have adequate reactivity on the surface of L_1. Because of this UV exposure of L_1 is controlled so that only a partial cure is imparted, so that reactive sites are present on the surface. The surface of each layer, after being partially cured, in fact is 'tacky'. L_2 is then deposited onto L_1. We observe that the newly deposited monomer wets the surface and interdiffusion then occurs at the interface. When L_2 is exposed to UV, the polymer

network will extend through the interface between L_1 and L_2. Polymer molecules in L_2 are then covalently bonded to the polymer matrix in L_1 to form a continuous polymer matrix. This interphase reaction joins the two layers and makes the bonding permanent. The dynamics of the bonding process creates a seamless polymer matrix which provides both improved mechanical strength at each individual interface and the desired optical properties for the composite as a whole. After all the layers have been deposited, an extended exposure to UV has the effect of advancing the cure of the entire sample. Upon completion of this extended postcure, it is not possible to distinguish, either mechanically or optically, any interface indicative of the layered deposition process used to create the polymer composite.

Characterization of the Printed Films

AFM Results on Particle Dispersion in IJD Composites

Atomic Force Microscopy (AFM) was found to be a useful tool for quickly assessing the particle dispersion in cured HDODA composites. While it may not give a complete picture of the particle dispersion in the bulk of the polymer, it gives useful results that indicate whether particle aggregates have been successfully eliminated and also provides a qualitative idea of the particle distribution in the bulk of each sample.

Figure 5: Neat HDODA printed film 30 layers, 140µm thick

Figure 6 is an AFM scan of a reference HDODA nanocomposite sample containing dispersed silica (SiO_2). This sample was produced from a commercial silica nanoparticle suspension in HDODA supplied by Clariant Corp. (designated as product OG 103-53). Here a very uniform flat surface is obtained over a 5µm^2 area as indicated by the color bar. This is the common result obtained for all of the samples prepared on a silicon wafer. Note that the images obtained were enhanced by using a shading option

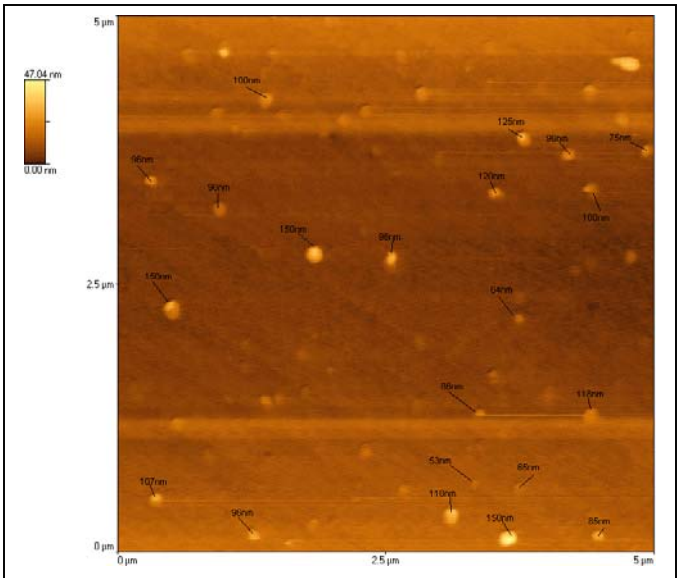

Figure 6: AFM scan of SiO_2 suspended in HDODA (OG 103-53 from Clariant Corp.)—Baseline nano-composite (50 wt% SiO_2) with discrete, well- dispersed nanoparticles; view 0-5µm

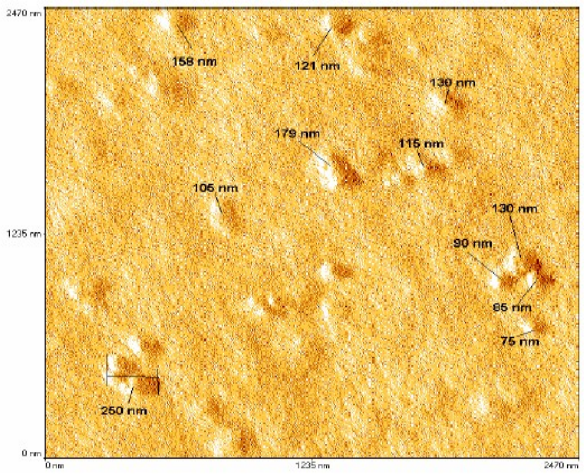

Figure 7: AFM scan of sample containing dispersed SiC particles (16.2 % wt); view 0-2.5µm

in the AFM analysis software. This gives better contrast and presents the surface as it might appear if a light source were present on one side of the sample. The silica dispersion is 50 wt % silica, or approximately 30 vol %. Judging by the above image, it is apparent that the most evident particles likely are the largest in the distribution, since they average over 100nm in diameter. These are the ones most likely to show up on a surface scan. Clariant reports a mean particle size of 50nm. The smallest silica particles are seen only as specs on the image.

Figure 7, is a representative AFM scan of the surface of a SiC composite (16.2 wt %). The particles are well dispersed and appear to be discrete. The particle sizes are similar to those of the neat particles characterized separately by transmission electron microscopy [8].

Optical Characteristics of Composites

In the graded film of Figure 4 the change in composition appears as a color change. The SiC nanoparticles are well dispersed as indicated in the AFM scan in Figure 7. So light scattering is not a factor but transmission is hindered by the filler's light absorption. The neat polymer and composite light transmission characteristics are compared in Figures 8-10.

Printed film samples were analyzed using UV/VIS spectroscopy. The pure HDODA film (blue curve) and 4.5 wt % SiC film (red curve) were scanned from 600 nm to 200 nm (see Figure 8). 300 nm was then chosen as a fixed wavelength for analysis of the composition gradient for the graded film shown in Figure 4. The graded film was moved, incrementally, across the beam of the UV/VIS sample field and absorbance readings were taken at several points. Figure 8 also shows the effectiveness of using an inkjet printer to create a film having a controlled gradient in particle concentration. The green data points indicate the variation in absorbance at 300nm with position along the gradient. Figure 9 shows more clearly the absorbance values at 300nm as a function of position for the graded film. It begins on the left with the absorbance of neat monomer and ends on the right with 4.5 wt % SiC. It is clear that the Epson 'Print CD' software sets a linear color gradient in the middle of the film, while printing the solid colors on either end. In this case the color designation corresponds to particle concentration.

Note that the absorbance of the 4.5% SiC film (red curve) decreases with increasing wavelength (transmittance increases). Although the spectral data of Figure 8 do not continue into the infrared, the IR absorption spectra shown in Figure 10 indicate that the composites are quite transparent to light in the infrared 2-5 micron range. This is consistent with the idea that the dispersed particles indeed have little effect on light transmission in the spectral range where they do not absorb light strongly. Thus the SiC formulations may be suitable for lenses operating in the IR even though they would not be effective in the UV or visible range. Where the absorbance is great in regions beyond 5 microns, the polymer matrix itself is contributing strongly.

Refractive Index of HDODA-SiC Nanocomposites

Cured HDODA- SiC nanocomposite samples having a concentration of 16.3 *weight* % SiC or 5.7 *volume* % were prepared and analyzed for refractive index by ellipsometry. Ellipsometry provides an accurate measurement of refractive index both in bulk and thin film samples by measuring the change in polarization of a light beam reflected from a surface at a specific angle of incidence. A laser is used as the illumination source. Linearly polarized light (of known polarization) is reflected off of a sample, and the change in polarization is measured using a spectrometer equipped with polarizing prisms and retardation plates. The angle of the polarizers is adjusted to obtain the null condition where no more light reaches the detector. The value of refractive index of the sample can be extracted from the angles of the polarizers and the angle of incidence.

A typical literature value for the refractive index of silicon carbide is 2.68 [9]. HDODA monomer has a refractive index of 1.45; we have determined that the fully cured polymer has a refractive index, n = 1.50. Based on this, assuming a linear relationship between ceramic volume concentration and refractive index, adding 5.7 volume % SiC corresponds to a refractive index increase, Δn, of 0.068. The refractive index would be 1.568 for an HDODA-SiC nanocomposite of this composition. However, it was found that the measurements for such a composite yield a refractive index value of 1.550. The difference is attributed to the presence of under cured polymer in the actual composite rather than fully cured polymer. The composite samples were determined to have an extent of cure of 77 % [2]. When we take this into account, then the expected composite n value is 1.557, which is close to the measured value.

Conclusions

The current emphasis in the GRIN research has centered on materials and SFF processing issues. We list below in summary form the major conclusions of the program thus far:

- Optically transparent layered photopolymers can be formed by ink-jet printing
- A basic understanding of the mechanism for UV curing is essential to establishing a successful process for polymer formation; the cure of each layer must be controlled so as to insure good adhesion of the layers and eliminate effects of layer interfaces
- Appropriate cure parameters were established for producing optical quality multilayer samples with a seamless interface between layers
- The presence of dispersed nanoparticles was found not to have a significant effect on the cure
- Atmospheric oxygen inhibits the cure of the thin printed layers but a nitrogen atmosphere was easily implemented to successfully eliminate the problem
- Stable dispersions of nanoparticles in monomer can be prepared using an appropriate silane surface treatment and initially dispersing particles with an intensive high-shear mixer/homogenizer; dispersion concentrations of particles up to 16.5wt % were produced and tested in the ink-jet process; dispersed ceramics included SiO_2, SiC, and $BaTiO_3$
- An ellipsometry method for measuring refractive index was developed
- Particle dispersion in the cured composites was effectively verified by atomic force microscopy (AFM)
- Processing multilayer polymer samples with a commercial off-the-shelf ink-jet printer was demonstrated
- While the off-the-shelf printer was satisfactory for proof of concept studies it was determined not to be robust enough for continuous processing of an organic ink; a printer designed specifically for this purpose is required; suitable printers are readily available
- A broadband UV light source for curing was adopted for establishing the feasibility of the method
- Silicon wafers provided a uniform high quality substrate for part building
- Multilayer composites with linear optical gradients (an optical wedge) were produced using as few as 2 inkjets; test composites were 30 layers in thickness measuring
- 140 μm with each layer approximately 5μm in thickness; nano-particles were silicon carbide; particle concentrations varied from 0 to 4.5 wt%; this provided substantive proof of concept for the SFF method
- An effective method for measuring optical densities in the composites by UV-Vis and FTIR absorption spectra was implemented

- The ceramics used thus far absorb enough light in the UV and visible spectral range, so that they are not fully suitable for GRIN lenses; however, they are non-absorbing in the infrared, so that the composites produced are transparent in the 2-5μm spectral range

While much remains to be done the principal features of using inkjet printing to form viable graded nanocomposites has been demonstrated.

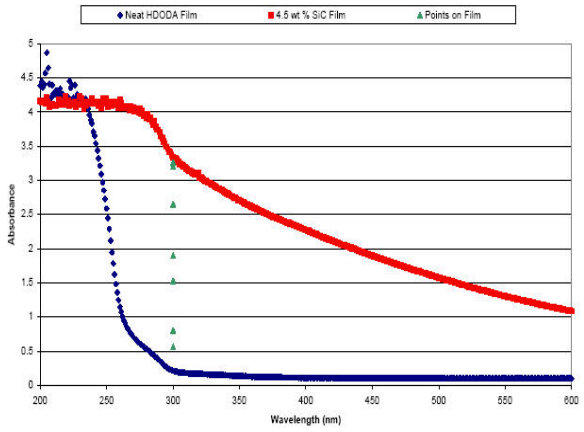

Figure 8: UV/VIS spectra of neat HDODA polymer film (blue) and 4.5wt% SiC film (red); absorbance at individual points across the length of the graded film at 300nm (green)

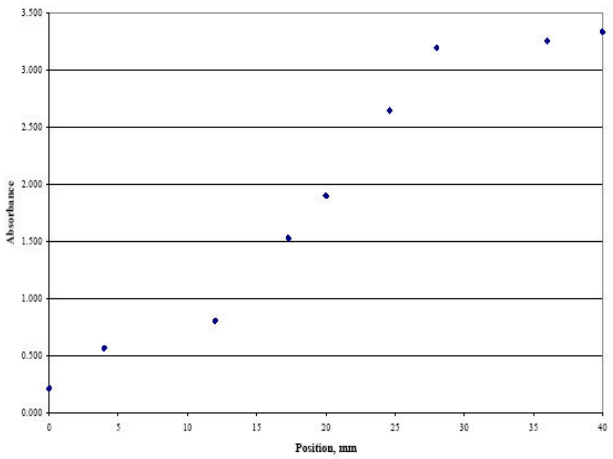

Figure 9: Optical absorbance vs distance (in mm) at 300nm for optical gradient printed film; shows approx. linear gradient from left (0%) to right (4.5%); film is HDODA containing SiC

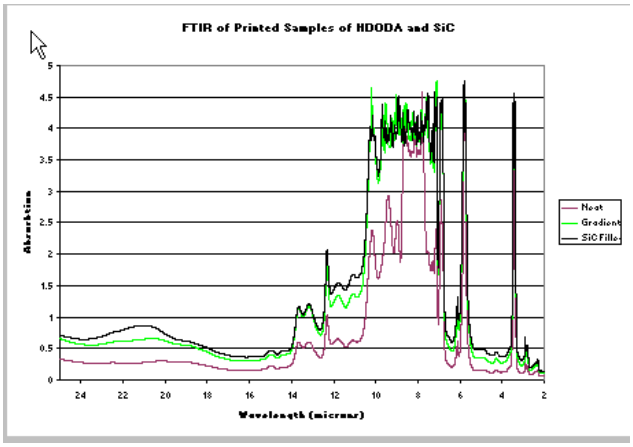

Figure 10: Infrared absorbance spectrum of nanocomposites with different concentrations of nanoparticles

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