FABRICATION OF PLGA NANOCOMPOSITE USING TWO PHOTON POLYMERIZATION

by

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Presented to the Faculty of the Graduate School of
The University of Texas at Arlington in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

THE UNIVERSITY OF TEXAS AT ARLINGTON

DECEMBER 2009

ACKNOWLEDGEMENTS

I would like to thank my principal advisor, Dr. Panayiotis. S. Shiakolas for the immense support, guidance and support that he has provided throughout the course of my thesis work. I also would like the thank Dr. Jiang Yang and Dr. Seiichi Nomura for their interest in my research and for taking time to serve in my thesis defense committee.

I acknowledge the support which I have received from my colleagues at the MARS and FLM laboratories: Dr. Nitin Uppal, Mr. Mohsin Rizwan, Mr. Vijay Sarathy, Mr. Krishanu Saha and Mr. Joonas Ponkala. I also graciously acknowledge Ms Soujanya Kona for her support in understanding the technical aspects of the polymeric nanoparticles for biomedical applications.

I would like to thank Dr. Kytai Nguyen for allowing access to the sonication machine and Zeta Potential Analyzer and for providing the PLGA nanoparticles. I would also like to thank Dr Jiechao Jiang for allowing access to the SEM and optical microscope for the characterization and measurement of micro/ nano structures.

I would also like to thank the staff of Mechanical Engineering Department, Mr. Tom Leeds, Mr. Sam Williams, Mr. Michael Baker, Mrs Debi Barton for their support, encouragement and assistance throughout my graduate studies.

April 20, 2009

ABSTRACT

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USING TWO PHOTON POLYMERIZATION

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The demand of smaller size 3D structures in scale of several nanometers has significantly increased the need of development of new techniques for micro/nano fabrication. Applications of nanomaterial embedded true 3D micro/nano structures in the field of medicine, tissue engineering, scaffolding, drug delivery, antibacterial implants or catheters, modification of textiles and refinement of polymers has opened new areas of research for fabrication of nanocomposites embedded with engineering nanoparticles.

A novel fabrication process called two photon polymerization (2PP) is employed for the fabrication of polymeric nanocomposites embedded with PLGA nanoparticles. An ultra short pulsed laser source is used to produce laser at high frequency (80 MHz) and pulse width of 150 fs which is conducive for 2PP. A resin mixture of monomer, photo-initiator and nanoparticles is properly prepared. When the laser is scanned in the liquid polymer resin, a polymerization reaction is initiated and during this reaction nanoparticles get trapped in the polymerized structure. This research examined the 2PP process for nanocomposite fabrication for two power levels, three levels of photo-initiator concentration and three levels of nanoparticle concentration. It was found that manoparticles are indeed present in the fabricated structures confirming the viability of the process. The process parameters examined influence the size of the nanocomposite structure.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Nanocomposites are commonly defined as the combination of multiphase materials where at least one of the constituent's materials has one dimension in the nanometer range [1, 2, 3]. The constituent phase can be one dimensional (examples include nanofibre or nanowires), two-dimensional (layered mineral like clay) or three-dimensional (spherical particles in nanoscale range) [2, 3]. The multifunctionality of nanocomposites can be attributed to the combination of the constituent materials. Desired properties can be obtained from a nanocomposite based on the desired application through the selection of the constituent materials and the size of the nanoparticles. Research in the open literature has focused in the areas of manufacturing techniques and material combination for the manufacturing of the nanocomposites.

The technological advances in the field of MEMS have opened new areas of research for fabrication of new devices and applications of existing 3D structures and devices. The demand for smaller size 3D structures in scales of several nanometers has significantly increased the need for the development of new techniques for micro/nano fabrication. The excitement surrounding the nanoscale science and technology gives us unique opportunities to develop and study revolutionary processes and materials.

Applications of nanomaterials embedded with 3D micro/nano structures in the field of medicine, tissue engineering, scaffolding, drug delivery, antibacterial implants or catheters; modification of textiles, refinement of polymers and several optical, electrical and magnetic applications has opened new areas of research for manufacturing nanocomposites with engineered nanoparticles material.

Researchers all over the world have been working on different micro/nano manufacturing techniques. Photo lithography [4, 11], LIGA [7, 8], Electrochemical Fabrication (EFAB) [5] localize electrochemical deposition [6] and laser ablation [12 and 13] are some of the techniques used for micro/nano fabrication. Some of these techniques have been used for fabrication of nanocomposites.

Photolithography is one of the widely used techniques for fabrication of nanocomposites. In photolithography, a light source such as UV light is used to polymerize the photo-responsive resin with suspended nanoparticles through a mask [11]. Depending upon the requirement of the feature, a mask is prepared and the feature is transferred using a UV source light. The removal of the unaffected part by the light source is performed using the secondary process of chemical etching. UV light has been used primarily for transferring the mask, but various other alternatives such as nanoimprint lithography, X-ray lithography, ion projection lithography are being explored [4,5,6,7,8]. This technique has been researched and developed for several decades now but the resolution of the fabricated feature using photolithography is limited due to the limitation of optical diffraction. There is also the need of fabrication of expensive mask and molds for fabrication of structure which is the basic drawback of this method. These methods are effective for fabrication of high resolution features, but they are limited to 2D geometries.

Another method that has been widely used in the manufacturing of nanocomposites is laser ablation technology. In this method of fabrication, a high intensity laser is used to ablate the material and form nanoparticles [28, 29]. This process is performed inside a liquid polymer resin which is then polymerized using UV light to form nanocomposites layers. The main advantage of this method is that metals, non-metals, glass, polymers can be used to fabricate nanocomposites with varying properties [30, 32]. The main disadvantage in this method is that it is mostly limited to planar geometries. Stacking of different layers has been tried, but alignment

and the handling of the layers contribute to the limitation of aspect ratio of the micro device [7, 8].

Multi Photon Absorption (MAP) is a relatively new and evolving technique for manufacturing of micro/nano structures. This technique unlike other methods does not involve any secondary operations or processes for nanocomposite fabrication.

1.1 Multi-Photon Polymerization (MAP)

A relatively new technique called multi photon polymerization (MAP) is an advanced and efficient method for manufacturing micro/nano structures and features using ultrashort laser pulses from a nearly infrared laser source [1, 9, 10]. When an ultrashort laser pulse is focused in a photo responsive polymer resin, a solid voxel (volumetric pixel) is formed. The voxel size defines the minimum resolution of the polymer that is converted into solid form. Complex 2D and 3D structures can be easily formed by scanning the laser in the photo responsive resin [1, 9, 10, 15 and 16].

An active research effort at Laser Zentrum Hannover, Germany is carried on two-photon polymerization (2PP) for fabrication of micro/ nano devices and structures. Research is also performed on 2PP for fabrication of various micro/nano devices for wide application in the field of tissue engineering and scaffolding and in the field of optics for manufacturing micro/nano sensors and devices

Various experiments and research on 2PP for voxel size characterization has been conducted; a mathematical model has been developed for evaluation of length and width of the voxel by Chichkov et al. [12, 17] The study was performed to find the change in voxel size due to changes in concentration of photo-initiator, monomer, and intensity of laser or focusing lens. This study opened new application and areas of research in the medical field that can be carried out for micro/nano device fabrication. There is a need of 2D and 3D devices to be manufactured for controlled drug delivery and tissue engineering and scaffolding applications [21, 24]. For drug delivery applications, there is a need of manufacturing a controlled release pill which can

carry nanoparticles embedded with drug into the body [24, 27]. Also in tissue engineering, nanoparticle embedded structures are required or desired for scaffolding. Thus, there is a need for research in the field of nanocomposite manufacturing using 2PP. Research has explored fabrication of nanocomposites using microstereolithography. Due to advantages of 2PP over other methods, research in manufacturing nanocomposite using 2PP is currently performed at the BioMEMS lab at The University of Texas at Arlington. Representative microparts fabricated using 2PP at the BioMEMS laboratory are shown in figure. 1.1 [1]

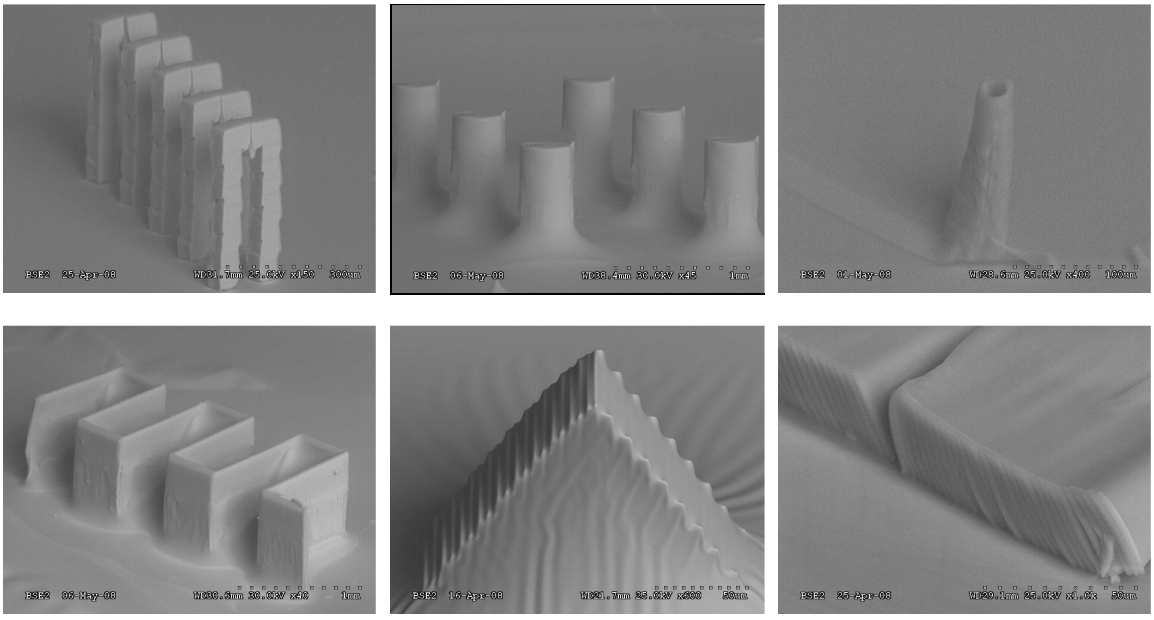


Fig. 1.1 Representative structures fabricated using 2PP at BioMEMS labs at The University of Texas, Arlington.

1.1.1 Two Photon Absorption

In this section, a short description of the 2PP process is presented. Polymerization takes place when the ultrashort laser pulse is targeted in the photo-responsive polymer solution. The laser light is composed of numerous photons carrying energy equivalent to h*v (where h is Planck's constant and v is frequency). When these photons are targeted in the photo-responsive solution, the photons transfer the energy to the photo-initiator molecules and free

radicals are generated. These free radicals are responsible for initiating the polymerization reaction [1].

When one photon has sufficient energy to generate a free radical, the process is called as single photon absorption and when two photons are simultaneously required for generation of free radical, it is termed two-photon absorption process. In multi photon absorption more than two photons are required for radical generation [9, 10].

The Lucirin (photo-initiator) has good absorbance in the long wave region of the UV spectrum which is around 400 nm. Thus, the energy carried by one photon is not enough to generate free radicals from photo-initiator molecule [1]. When two photons target the photo-initiator molecule simultaneously within a time interval of 10^{-15} sec to 10^{-16} sec, a free radical is generated as shown in figure 1.2. The first photon excites the photo-initiator molecule to the transition state and the photo-initiator molecule remains in this state for 10^{-15} sec to 10^{-16} sec. The second photon should hit this molecule between this time span to excite this molecule to the excitation state and lead to generation of free radical.

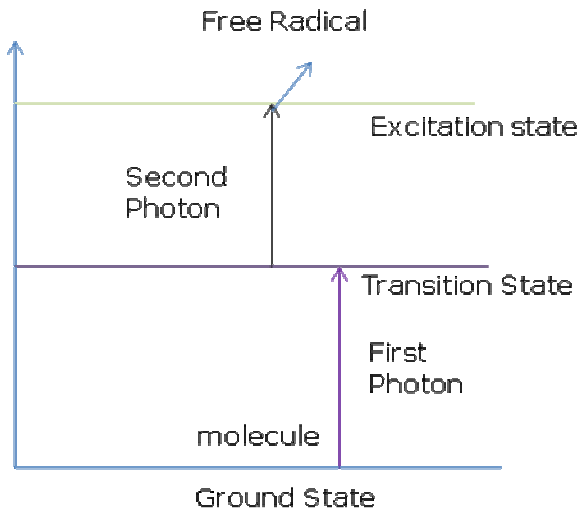


Fig. 1.2 Two photon absorption process

1.1.2 Polymerization

Polymerization is the basic process of fabrication of any micro/nano structure. When a light source is focused on a photo-responsive polymer solution, a cross link reaction takes place between the monomer molecules leading to a polymerization chain reaction. A long polymerized chain results in manufacturing of 2½D and 3D structures. In 2PP there are 3 main stages: Initiation, Propagation and Termination.

Laser light consists of numerous photons which carry energy. When photons come in contact with the photo initiator present in the polymer solution, they transfer their energy to the photo responsive molecules and free radicals generated in the polymer solution [1, 35]. In equation 1, P represents the photo-initiator molecule, hv represents the energy of single photon and R describes the free radical which is generated by the reaction.

$$P + hv \longrightarrow R \tag{1}$$

These free radicals propagate to react with the monomer molecules to form a reactive polymer chain. The reactive polymer chain reacts with other monomer molecules to form an elongated polymerized chain [1, 40]. The reaction of free photo-initiator molecule with the inactive monomer M is described in equations 2 and 3. This allows the active monomer molecule to react with other monomer molecule and form a chain.

$$R^0 + M \longrightarrow M^1 \tag{2}$$

$$M^{n-1} + M \longrightarrow M^n \tag{3}$$

The polymerization chain can terminate by radical combination or by radical trapping [1]. Radical combination occurs when two active monomers react to from a polymer chain and become inactive and do not undergo any further reaction. The polymerization reaction can also terminate due to entrapping of active monomer molecules in the polymer chain. This entrapped monomer molecule then cannot react with other monomer molecules to form chain reaction. Thus, the polymerized chain reaction terminates [41]. The chain reaction of various active monomer molecules, forming a polymerized chain reaction is shows by equation 4.

$$M^n + M^m \longrightarrow M^{n+m} \quad (4)$$

1.2 Nanoparticle embedded micro/nano structures

Micro/nano structures and devices are manufactured with higher accuracy and complexity using 2PP than other prevailing methods of fabrication such as microstereolithography or polymerization for various applications. Research on manufacturing of micro/nano structures from different types of polymers using 2PP has been conducted over a brief span of time [1, 9, 10, 11]. In certain applications there is a need of fabrication of complex nanocomposite structures [17, 18, 21]. The prevailing techniques [4, 5, 6] for nanocomposite manufacturing are good for planar or 2D devices fabrication. For manufacturing 2½D and 3D nanocomposite devices with accuracy and precision there is a need of identifying or perform research towards the development of new fabrication techniques.

In medical applications such as controlled drug delivery for curing various diseases such as cancer or tissue engineering for fabrication of scaffolds or for fabrication of artificial limbs with greater strength and rigidity, there is a need of fabrication of micro/ nano structures with embedded nanoparticles [17, 18, 21, 24, 27]. Engineering nanoparticles are used in nanocomposite and coatings for various biomedical devices, magnetic nanoparticles are used for fabrication of micro strain gauges and sensors for semiconductor industries, polymeric nanoparticles are used for making optical devices with better optical properties [42].

Research has identified different methods for fabricating nanocomposites using various types of nanomaterials. Laser ablation [12] and microstereolithography [11] are two of the most effectively used methods for fabrication of nanocomposite structures. Microstereolithography is a layer by layer method of nanocomposite fabrication. In this method ultraviolet (UV) laser light is used to solidify the UV curable resin mixture with ceramic nanoparticles in the resin. This resin is a mixture of monomer, photo-initiator, ceramic nanoparticles and light absorbing additive. This method is helpful in manufacturing the nanocomposite structures using layer by layer approach for 2D geometries. The main disadvantage of this method is that complex 3D

structures cannot be fabricated. In the nanocomposite manufacturing using laser ablation method, ultra short pulsed laser is used to ablate the target material, leading to the formation of nanomaterials due to laser ablation. These nanoparticles are suspended in a gaseous medium such as gas or vacuum, and can be controlled deposited on a substrate for manufacturing nanocomposite thin film or coating. This is the advantage of this method over other method for thin film manufacturing methods. The main disadvantage of laser ablation is its application manufacturing a complex geometries, 2½D and 3D structures.

Researchers all over the world [1, 9, 12, 13, 15, 18, 19] are investigating 2PP to fabricate micro structures due to its advantages over alternative methods. This is a novel method for fabrication of nanocomposites. An ultra short pulsed laser source is used to produce laser at high frequency of around 80 MHz and pulse width of ~ 150 fs which is conducive for 2PP [1].

A resin mixture of monomer, photo-initiator and nanoparticles is used for fabrication of nanocomposite structures. When the laser is scanned in the liquid polymer resin, the photo-initiator molecules get excited and emit free radicals. These free radicals transfer energy to inactive monomer molecules resulting in a continuous chain reaction of monomer molecules. The uniformly distributed nanoparticles in the resin mixture get trapped in these polymer chains resulting in the formation of solid structure embedded with nanoparticles.

The fabrication steps are shown schematically in figure 1.3. These embedded nanoparticles in the solid structure can be then used for various applications such as optical devices with high refractive index, biomedical applications for drug delivery and formation of mechanical sensors.

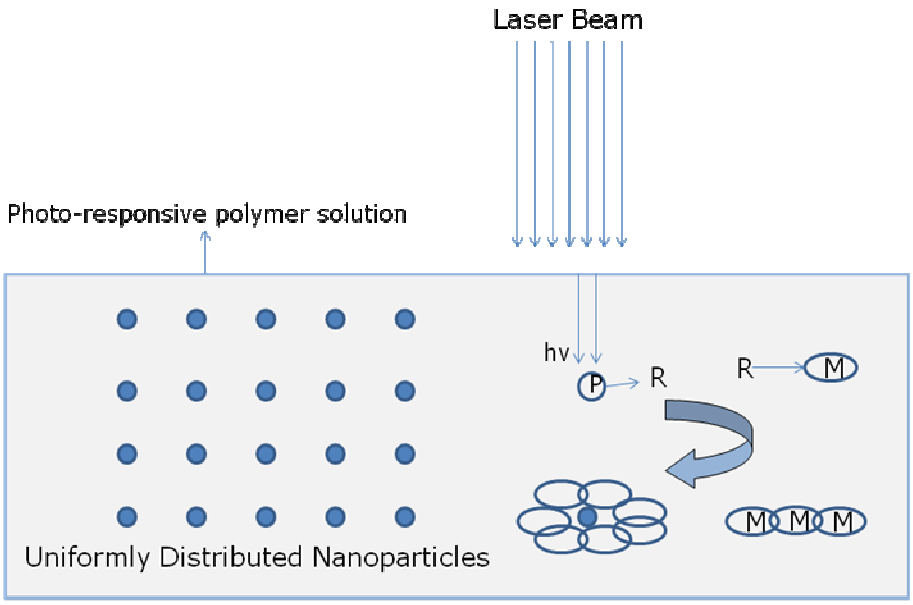


Fig. 1.3 Schematic of the nanocomposite fabrication process using 2PP

1.3 Thesis outline

The outline of this thesis is as follows. Chapter 2 provides a detailed discussion on the femtosecond laser system experimental setup, materials and material characterization equipment used for the research. In chapter 3, the experimental procedures and the results are introduced along with a detailed discussion over the observations of the experiments conducted. Plots providing information about the size of the micro/nano composite structures fabricated with embedded PLGA nanoparticles are also presented and discussed. Chapter 4 presents the conclusions along with recommendations for future work.

CHAPTER 2

DESCRIPTION OF EXPERIMENTAL SETUP

The two most important components for applying the two photon polymerization process are an ultrashort pulse laser source along with the photo-responsive polymer resin (monomer and photo-initiator). In this chapter, a detailed discussion on the laser system used for micro/nano fabrication and the photo-responsive resin along with the devices and setups used for characterization of the fabricated nanocomposite are presented.

2.1 Ultrashort laser pulse system

A Hurricane Femtosecond Ti:Sapphire laser system from Newport-Spectra Physics [38, 39] was used for the experiments for nanocomposite fabrication. This laser system generates ultrashort pulses ranging from 750 nm-850 nm wavelength and pulse width of ~150 fs (femtoseconds) and two different pulse repetition rates; a pulse repetition rate of 1 kHz with average pulse energy of 0.75 μJ/pulse and a pulse repetition rate of 80 MHz with average pulse energy of 0.325 nJ/pulse

The femtosecond laser microfabrication system can be used for both additive and subtractive micro/nano fabrication and is shown in figure 2.1. The chirped laser pulses coming out of Mai Tai [38] which is inside the laser enclosure, has low energy pulses with high pulse frequency of 80MHz. This low energy pulses do not produce energies above the threshold energy required for ablation and for our research are used for two photon polymerization. These low energy pulses are passed through a regenerative amplifier to increase their energy/pulse. The pulse from the regenerative amplifier is then compressed in the compressor circuit. The compressor amplifies the energy of the pulse and reduces the pulse width [38, 39]. These low frequency pulses have high output energy of 0.75μJ/pulse and generate very high peak intensities due to their pulse width of ~150 fs. The high energy pulses are used for micro/nano

fabrication and are used for conducting ablation study on various engineering materials, polymers, composites etc.

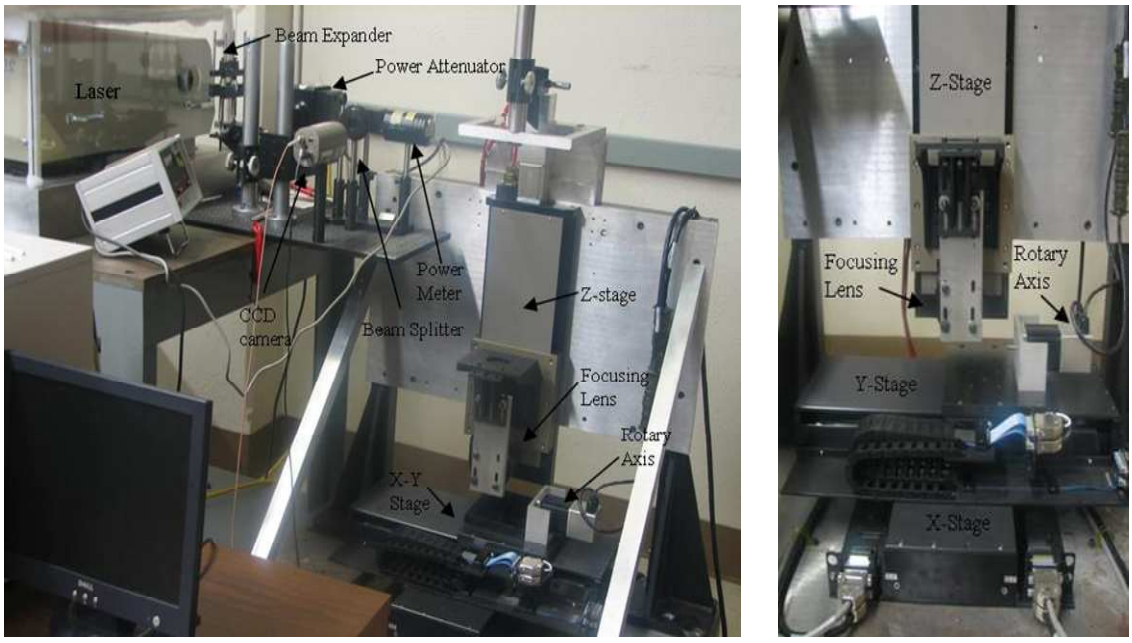


Fig. 2.1 The femtosecond laser microfabrication setup at BioMEMS lab at UTA

A mircomotion stage setup with 3 degrees of freedom having high accuracy and repeatability from Aerotech [37] has been installed for the experimental setup. These stages have a resolution of 0.01μm and are controlled by NL Drives. The A3200 software takes as input industry standard G-codes and traces the path of laser in the polymer resin to fabricate the desired micro/nano structure. The laser was set at 800nm wavelength and 80MHz pulse repetition rate for all the 2PP experiments reported in this work. However, for 2PP, both the amplified and non-amplified systems can be used [1, 20, 37]. Most of the research performed in two photon polymerization uses low energy per pulse (nJ/pulse) and high pulse rates (80 MHz). The laser light coming out of the aperture passes through a Galilean expander to reduce the raw laser diameter from 6.3 to 3.8 mm. The reduced diameter laser light is then passed through an attenuator where the power of the laser beam can be manually adjusted. The laser beam could be directed through a beam splitter where 5% of the energy is diverted to a CCD camera

with a BEAMVIEW® beam analyzer software for real time viewing of the shape of the beam and for studying other Gaussian parameters of the laser beam. The remaining 95% of the laser beam energy is diverted towards the fabrication site through a 90 deg reflection and the focusing lens. A high numerical aperture lens tightly focuses the laser in the container holding the polymer (monomer photoinitiator and nanoparticles) resin on the linear motion X-Y stages. The focusing lens is placed upright on a holder mounted on the Z axis.

2.2 Experimental setup for 2PP

The laser beam is focused using a focusing lens which is mounted on the Z-axis of the motorized stage and the translation of the motorized X-Y stages provides an equivalent laser scanning motion in the container holding the photo-responsive polymer resin. The schematic for the 2PP setup for the fabrication of micro/nano structures is shown in figure 2.2.

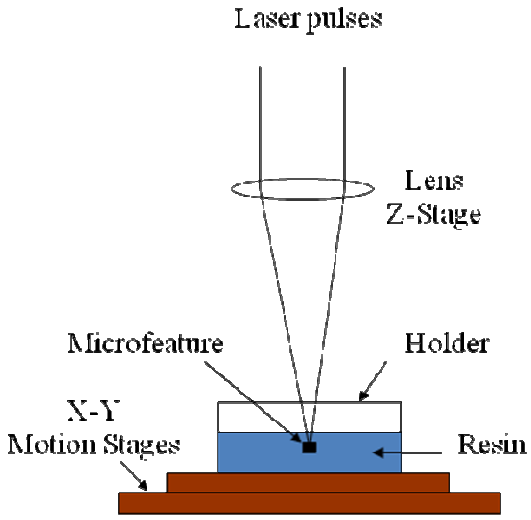


Fig. 2.2 The experimental setup for 2PP

The Z-axis is translated such that the laser focuses on the bottom surface of the container holding the liquid resin mixture so that the structure to be fabricated in achored at the bottom and starts fabricated from a bottom to top approach in a layer by layer process. The motorized stages are programmed using G-codes to move the container with the resin in such a manner that, the laser scans a specific path inside the resin mixture. The area scanned by the

laser polymerizes or solidifies and thus the desired nanocomposite structures are formed. The size of polymerized structure depends on power levels, scanning speed and photo-initiator concentrations and the focusing lens. Modulation of these parameters will result in control of width and height of the voxel. The photo-initiator concentrations do not have significant effect at higher scanning speeds on the width/diametre of the voxel [1]. The voxel is the smallest size that can be polymerized using the 2PP process. It depends on the focusing lens, power levels and concentration of the photo-initiator. The voxel defines the resolution of the 2PP process. Thus it becomes necessary to study the change in voxel size of nanocomposite structures.

2.3 Materials used in this Research

The materials used for polymerization play a very important role in the fabrication. The polymer structures manufactured in which the monomer molecules are linked to each other is a result of crosslinking of the polymer molecules. High degree of crosslinking in the polymer results in the formation of 2½ D and 3D structures. Crosslinking can occur during the polymerization process by use of appropriate selection of monomer and photo-initiator. Monomer alone cannot develop as many radicals required for polymerization to occur. Thus, photo-initiator is used which decomposes to free radicals when energy is transferred to it from incident photons. In 2PP, radicals are generated only when two photons are incident on the photo-initiator molecule simultaneously to excite the free radicals in the resin. Commercially available monomer and photo-initiator and polymeric nanomaterial were used for the experiments of this research.

The monomer used in the experiments is Ethoxylated (6) trimethyl triacrylate which is commercially available with trade name as SR-499 from Sartomer [39]. Due to its low skin irritation, fast curing, low shrinkage and low formulation viscosity it is used for free radical polymerization with its chemical structure shown in figure 2.3. When the free radical of photo-initiator molecules react with the inactive monomer, the carbon double bond with oxygen breaks

to form active monomer molecule which is involved into chain reaction with other active monomer molecules to form polymer chain reaction [1, 40].

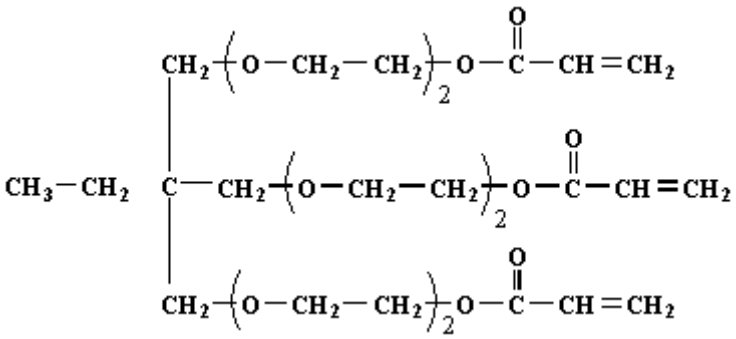


Fig. 2.3 Molecular structure of monomer SR499 (Ethoxylated(6) trimethyl triacrylate) [35]

The photo-initiator used is Ethyl 2, 4, 6 Trimethylbennzoyldiphenylphosphinate and is commercially available with a trade name Lucirin TPO-L from BASF [35]. The molecular structure of the photo-initiator molecule is shown in figure 2.4. This inactive photo-initiator molecule becomes active when acted upon by an incident photon. The photon transfers the energy and breaks the carbon-phosphorus bond to emit free radicals [1, 35]. This free radical reacts with monomer molecules to form chain reaction. Lucirin TPO-L is a liquid initiator and thus is easy to add into all formulations. Due to its low volatility, it is suitable for experiments with low odor.

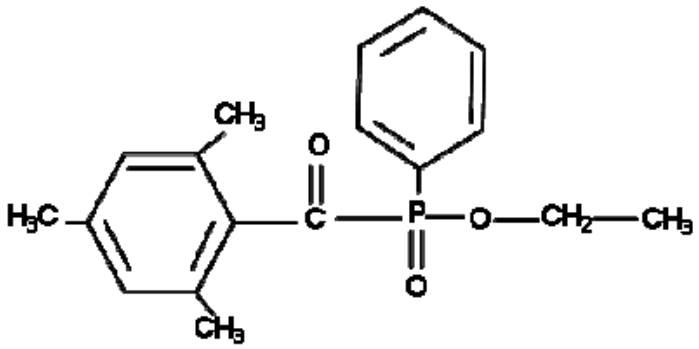


Fig. 2.4 Molecular structure of photo-initiator (Lucirin TPO-L) [36]

The nanomaterial used is poly (lactic-*co*-glycolic acid) PLGA provided by Professor Ngyuen of the Biomedical Engineering Department at The University of Texas, Arlington. The nanomaterials were spherical in shape with an average approximate size of 200nm and a deviation of 50 nm. The PLGA nanomaterial is biodegradable and is made with 5% PVA (Poly Vinyl alcohol) as a surfactant. The nanoparticles tend to attract to each other due to the Van der Waals forces when suspended in the polymeric solution. If there is no counteractive repulsive force acting on these nanoparticles, they would coagulate. Surfactant is used for stabilizing these nanoparticles and reduces the forces acting between them and thus increases the coagulation time.

2.4 Material Characterization

Once the nanoparticles are added in the polymer resin, sonication of the polymer resin is performed to ensure uniform distribution of nanoparticle throughout the solution. A sonicator is a device which supplies acoustic (sound) energy at a particular power which disintegrates the PLGA particles to the smallest form and disperses them uniformly in the polymer resin. Sonication decreases the nanoparticle coagulation rate and gives more time for experiments to be conducted in the polymer resin.

The uniform distribution of the nanoparticles and the study of aggregation of these nanoparticles in aqueous solution were performed using ZetaPALS manufactured by Brookhaven Instruments Corporation and shown in figure 2.5 [43]. This study provides a detailed report on the average size of the nanoparticles with standard deviation along with the polydispersity index. The setups for ZetaPALS and for sonication were available in Professor Ngyuen's research laboratory.

Fig. 2.5 ZetaPALS analyzer [43]

The fabricated nanocomposite structure characterization was performed using a Scanning Electron Microscope, a Hitachi – S3000N shown in figure 2.6, and an optical microscope FT-IR Nicolet 6700 with a resolution of 0.1 μm available in the Materials Characterization Center of the Materials Science and Engineering Department at The University of Texas, Arlington. The characterization consisted of measuring the height and wall thickness of the fabricated nanocomposite structures and confirming the presence of nanoparticles in the fabricated structures.

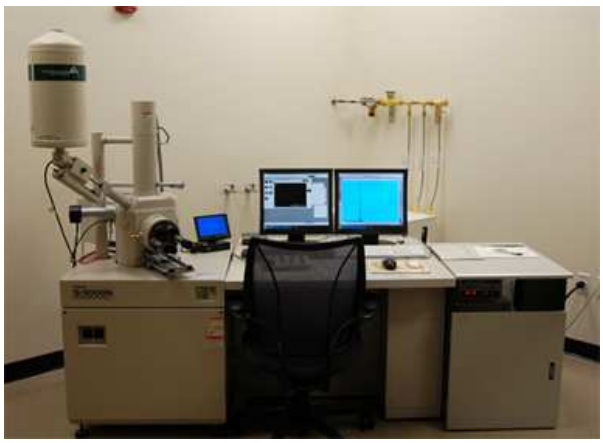


Fig. 2.6 Hitachi-S3000N scanning electron microscope at Materials Characterization laboratory at UTA

CHAPTER 3

EXPERIMENTAL PROCEDURES AND RESULTS

3.1 Experimental Identification

Experiments were conducted to study the effects on the dimensions of the fabricated structure with and without the presence of nanoparticles in the photo-sensitive resin. The observations of the experiments were measurement of the width and height of walls fabricated with and without nanoparticles. The walls were fabricated by changing controlled process parameters such as input power of the laser beam, concentration of nanoparticles, and concentration of photoinitiator. All the experiments were contacted at a constant pulse repetition rate of 80 MHz and a constant scanning speed of 3 mm/min using a 0.4NA focusing lens. The resin with the nanoparticles was sonicated for 3 min to assure uniform distribution. Two levels of power (20mW and 30mW), three levels of photoinitiator concentration (3.34%, 4.99% and 6.56%) by weight, and three levels of nanoparticle concentration (0.01%, 0.1% and 0.5%) by weight were selected for the experiments. These parameters were selected from previous work [1, 20, 37] conducted by Dr. Uppal and Dr. Shiakolas at BioMEMS laboratory at The University of Texas, Arlington. The experimental parameters and their values as used in this research are presented in table 3.1

A mixture of monomer (Ethoxylated (6) trimethyl triacrylate) and photoinitiator (Lucirin) is prepared with a concentration of 6.56% by weight in 2.981grams of monomer. The PLGA nanomaterial was added to the solution with a concentration of 0.01% by weight. The prepared solution is kept for sonication in an ice cold bath for 3 min (45 sec cycle time and an interval of 15 sec rest time). The sonication process causes the polymer solution to heat up which might initiate the polymerization reaction due to high reactivity of the photoinitiator at high temperatures. Thus the solution container is placed in an ice bath while it undergoes sonication

to ensure that no polymerization reaction is initiated while the nanoparticles are uniformly dispersed in the resin mixture.

Table 3.1 Experimental Parameters and their values

Parameters	**Values**
Wavelength	800 nm
Pulse Repetition Rate	80 MHz
Pulse Width	120 fs
Output Power	20 mWatt and 30 mWatt
Concentration of Photo-initiator	3.34%, 4.99% and 6.56% (by weight)
Concentration of Nanomaterial	0.01%, 0.1% and 0.5% (by weight)
Speed of Scanning	3 mm/min
Sonication time	3 min
Focusing lens	0.4NA

The laser is tightly focused using a 0.4NA lens (placed on the Z-axis stage through a custom designed holder) yielding a spot diameter of 1.5 μm [1] evaluated according to equation 5 where f represents the focal length of the lens, D the diameter of the unfocussed beam and w the wavelength of the light source.

$$Spot\ Diameter = \frac{4*w}{\pi} * \left(\frac{f}{D}\right) \quad (5)$$

The polymer resin is poured in a container that occupies a volume of 87.12 mm³ and placed under the laser focusing lens on the motorized X-Y stages for fabrication. The laser scanning speed is set at 3 mm/min which ensures 99.97% overlap of the laser pulses [1]. The system was programmed using G-codes to fabricate 8 walls 100 μm long at a separation distance of 10 μm at the substrate of the container as shown in figure 3.1. A total of six sets were fabricated for each combination of process parameters. When the process was completed, the excessive resin was carefully drained leaving the fabricated walls standing on the substrate.

The polymer structure was then washed with ethanol which has the unique property of dissolving any remaining liquid polymer. After complete removal of the liquid polymer, the walls in the container are kept for drying at room temperature. These structures are then studied using optical microscopy by measuring their width and height and also using scanning electron microscopy to examine for the presence of nanoparticles inside the fabricated walls.

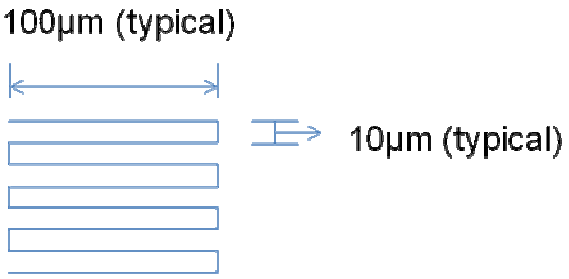


Fig 3.1 Schematic of the set of walls (top view)

3.2 Experimental Results

The experiments were conducted by analyzing the dimensional changes in the structure when manufactured with and without nanoparticles in the resin. Optical microscopy was used to measure the width and height for all the fabricated walls. The measurements of width were taken as the average for several walls standing/attached on the substrate. In order to guarantee that the correct height was measured, the height was measured for free floating walls fabricated with the same settings and configuration of laser setup. The container having the polymer resin mixture was placed on the X-Y stages under the laser for fabricating the walls on the substrate of the container. Due to the high aspect ratio of the height to width of the walls which is around 1:30, the walls tend to be wavy in nature. Also the walls at their extreme ends were not straight as compared to the walls on the inside due to the movement of the resin in the container caused by the movement of the stages [1]. Thus, the width was measured at the inside walls as shown in figure 3.2 (a). The measurements were obtained from the inside walls, at 5 different places at regular intervals and then noted as the average of the readings.

The height measurements were performed for the free floating walls. Six sets of walls each at a height increment (laser re-focusing) of 20 μm were fabricated for all the process parameter combinations. The first sets of walls are fixed on the substrate and hence are truncated. As the laser is refocused the truncation height tends to reduce and finally a free floating wall is fabricated. A schematic of the process is shown in figure 3.2. This process is required as the depth of focus of the focused laser spot is not exactly known in order to compensate for it. These free floating walls are the ones with no truncation and should be the maximum height for the particular set of process parameters. Representative free floating walls fabricated for one of set of parameters are shown in figure 3.3 (c).

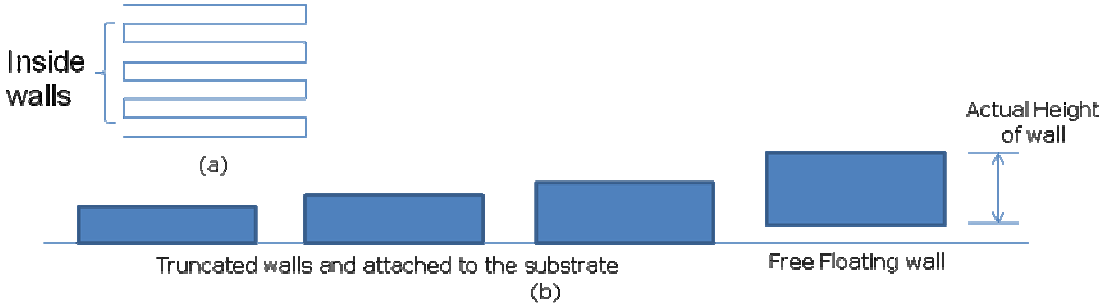
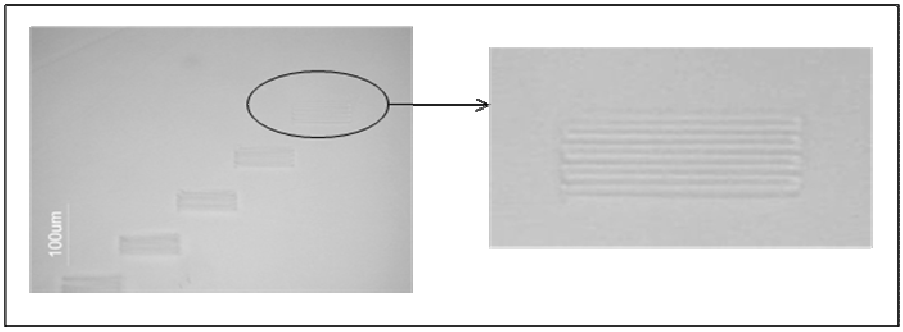
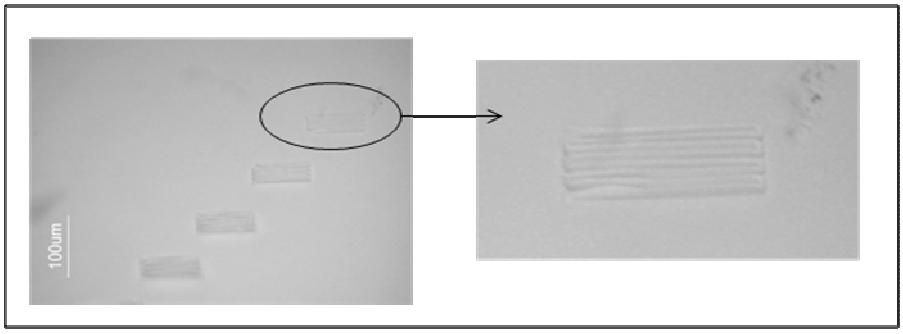


Fig 3.2 Schematic of walls with (a) top view and (b) front view
of the walls formed for each set.

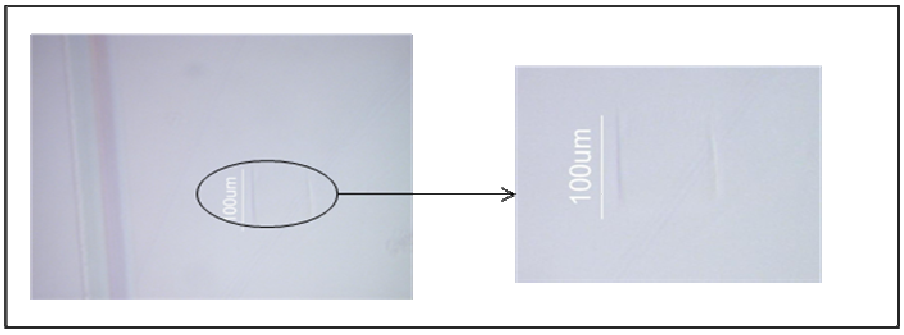
The same sets of experimental parameters were used for the experiments when PLGA nanoparticles were included in the resin. A representative set of free floating walls fabricated with the same power and without PLGA nanoparticles is shown in figure 3.3 (a) where representative walls with two of the PLGA nanoparticle concentrations examined in this study are shown in figure 3.3 (b) and (c). The height and width of the walls with all PLGA nanoparticle concentrations were measured using optical microscopy for comparison and analysis purposes with the results presented in table 3.3.



(a)



(b)



(c)

Fig. 3.3 Walls fabricated with 6.56% concentration of photo-initiator at 20mWatt power and pulse energy of 0.32 nJ/pulse (a) without PLGA, (b) with 0.1% concentration of PLGA and (c) with 0.01% concentration of PLGA.

Table 3.2 Results for polymeric walls (no nanoparticles) fabricated using 2PP

Power (mW)	%PI (by weight)	Width (μm)	Height (μm)
20	3.34	2.55	79
	4.99	2.78	89
	6.56	3.15	122.5
30	3.34	2.85	108
	4.99	3.1	146
	6.56	3.45	169

Table 3.3 Results for nanocomposite polymeric walls embedded with PLGA nanoparticles fabricated using 2PP

%PLGA (by weight)	% PI (by weight)	Power (mW)	Width (μm)	Height (μm)
0.01	3.34	20	2.4	69
	4.99	20	2.75	77
	6.56	20	3.05	96
	3.34	30	3.7	80
	4.99	30	3.9	120
	6.56	30	4.2	159
0.1	3.34	20	3.65	62
	4.99	20	3.9	85
	6.56	20	3.4	117
	3.34	30	3.9	101
	4.99	30	4.1	130
	6.56	30	4.1	166
0.5	3.34	20	3.75	61
	4.99	20	4	90.5
	6.56	20	4.25	135
	3.34	30	4.65	129
	4.99	30	3.9	155.5
	6.56	30	4.9	170

3.3 Discussion of Experimental Results

The proper dispersion of nanoparticles in their smallest size inside the resin mixture is desired for uniform distribution of nanoparticle in the micro/ nano composite structures. The Zeta potential device was used for the analysis of the average size of nanoparticles and their distribution in the aqueous solution. This study was performed after the sonication of the resin solution. Representative results of a detailed analysis of the distribution of PLGA nanoparticles in the aqueous solution of monomer with 0.01% of nanoparticles using the Zeta potential is shown in figure 3.4. Note that no photoinitiator is included as the light of the Zeta potential equipment causes the resin to polymerized.

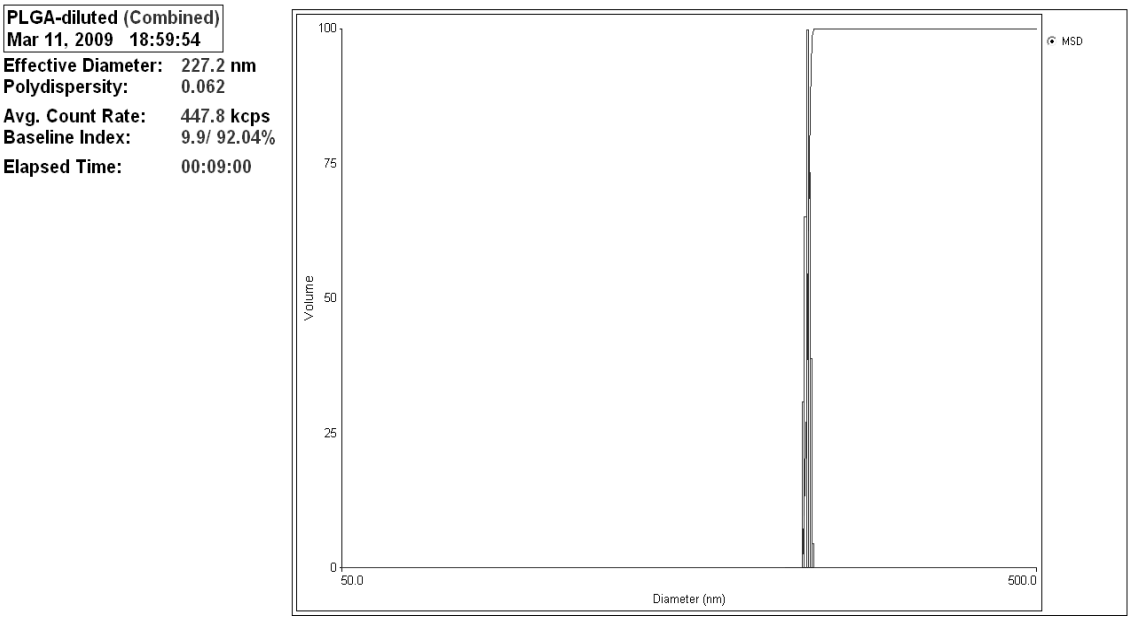


Fig 3.4 The average size of PLGA nanoparticles and their distribution in the aqueous solution as obtained from Zeta potential.

The average size of the PLGA nanoparticles was estimated to be 227.2 nm with a polydispersity index of 0.062. The polydispersity index value of 0.062 shows that the deviation of the size of nanoparticles measured in different volumetric locations of the solution is very small and thus ensures that the nanoparticles are uniformly dispersed in the solution. This study was also conducted 3 times in a time interval of 3 minutes to evaluate the change in the

distribution of the nanoparticles as a function of elapse of time with the results tabulated in table 3.4. The results show that after 9 min, the estimated size of the nanoparticles is 225.3 nm compared to 227.2 nm at 3 min. The polydispersity index for the PLGA nanoparticles indicates that they are uniformly dispersed in the polymer solution even after 9 min elapsed time from sonication. This is important for this research as the sonication and laser fabrication equipment are in research laboratories in different buildings and it takes a few minutes to travel between the two laboratories.

Table 3.4 Average size of nanoparticles and polydispersity index for PLGA nanoparticle in aqueous phase

Run	Effective Diameter (nm)	Polydispersity Index	Time (min)
1	227.2	0.072	0-3
2	229.2	0.028	3-6
3	225.3	0.083	6-9

The Gaussian intensity of the laser beam defines the shape of the voxel (volumetric pixel) which the smallest volume that is polymerized by a single laser pulse. The focal spot of the Gaussian laser beam, as seen in figure 3.5, has a spot diameter and specific depth of focus and hence the distribution of the intensity is more in longitudinal direction as compared to lateral direction. This governs the shape of the voxel (volumetric pixel). The voxel shape also depends on the focusing lens used but in this presented research, a focusing lens of 0.4NA is being used throughout the experiments, so the dimension of the voxel is independent of focusing lens. The voxel dimensions will depend upon the concentration of photo-initiator, number and size of nanoparticles and the power or energy/pulse used for the 2PP process.

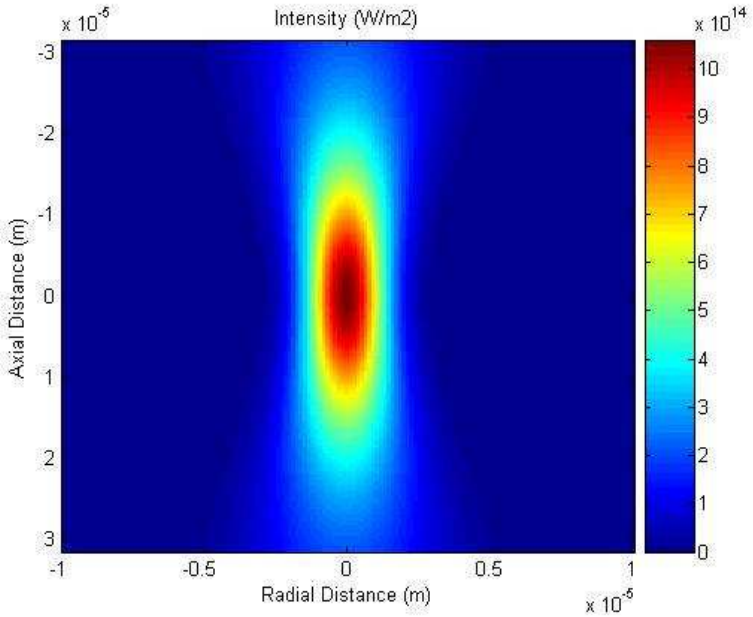


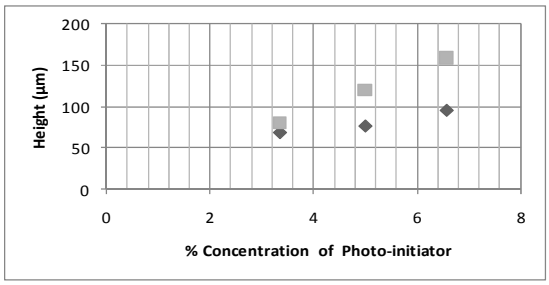
Fig. 3.5 Gaussian intensity distribution [1]

The results in tables 3.2 and 3.3 indicate that there are changes in the width and height of the walls fabricated with and without the presence of PLGA nanoparticles. The results also show that the width and height of the walls are dependent on the process parameters examined; concentration of nanoparticles, concentration of photo-initiator and power level (energy per pulse).

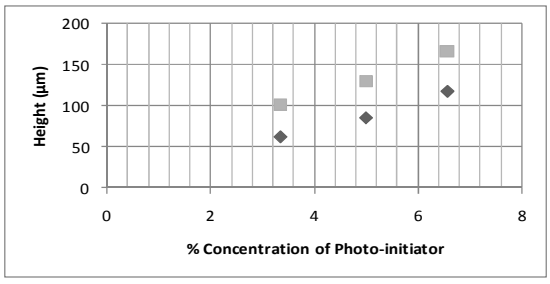
The experimental analysis shows that there is a significant change in the height of the polymerized nanocomposite walls as the power level increases from 20 mW to 30 mW for all different concentrations of nanoparticles and photo-initiator. This increase can be attributed to the Gaussian intensity distribution of the laser beam. As the power level increases, the energy /pulse increases, causing more photons to target the photo-responsive resin and initiate polymerization [1].

The concentration of nanoparticles also changes the trend of increase in height of the nanocomposite walls. The height changes with a different rate with change in concentration of the nanoparticle and hence is a function of concentration of nanoparticle as shown in figure 3.6

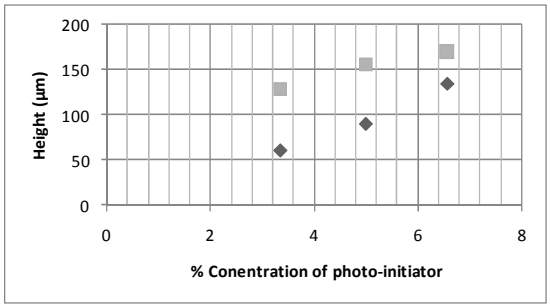
(a), (b) and (c). The same behavior of increased wall height was also observed for the pure polymeric structures without nanoparticles as shown in figure 3.6 (d).



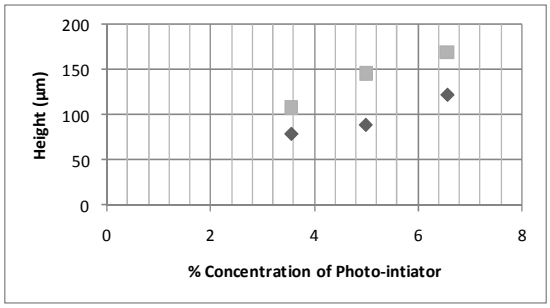
(a) ■ 30mWatt; ♦20mWatt



(b) ■ 30mWatt; ♦20mWatt



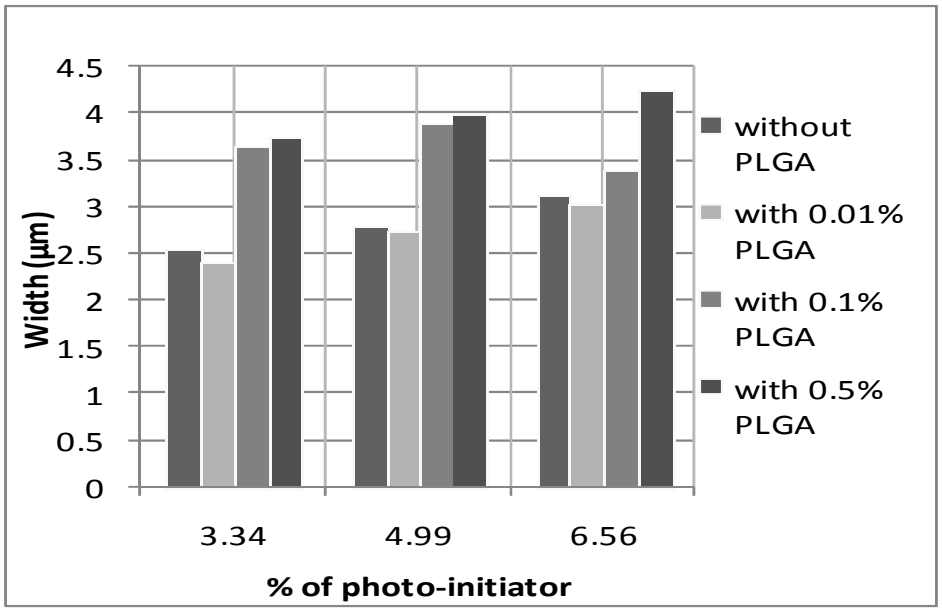
(c) ■ 30mWatt; ♦20mWatt



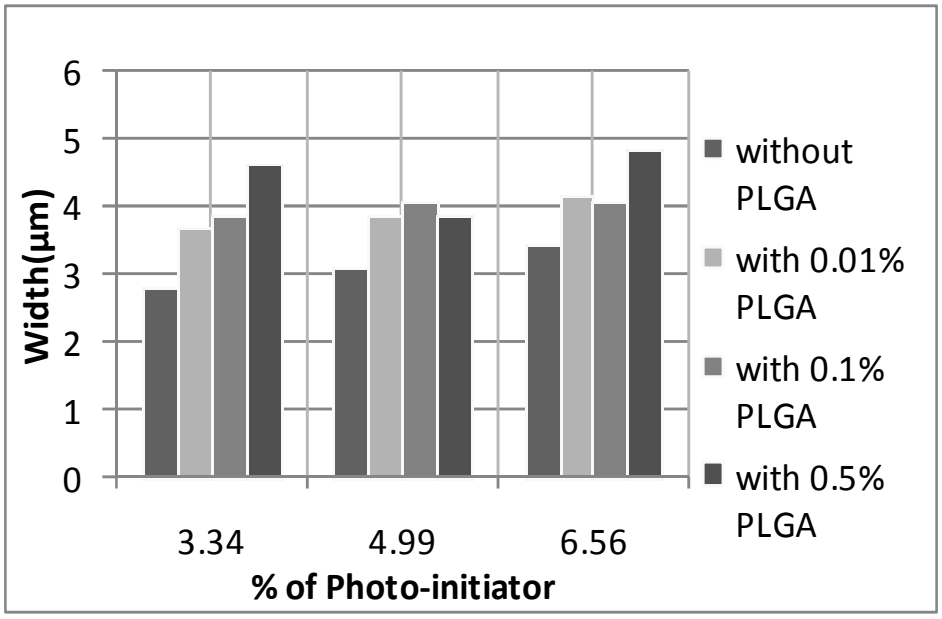
(d) ■ 30mWatt; ♦20mWatt

Fig. 3.6 Height of walls fabricated with (a) 0.01% PLGA, (b) 0.1% PLGA (c) 0.5% PLGA and (d) with no PLGA nanomaterial.

The width of the nanocomposite walls increases with an increase in power level as shown in figure 3.7 (a) and (b). This can be attributed to the Gaussian intensity distribution of the laser beam. However, the change in the width of the polymerized structure is not as significant as the change in the height, as shown in table 3.3



(a)



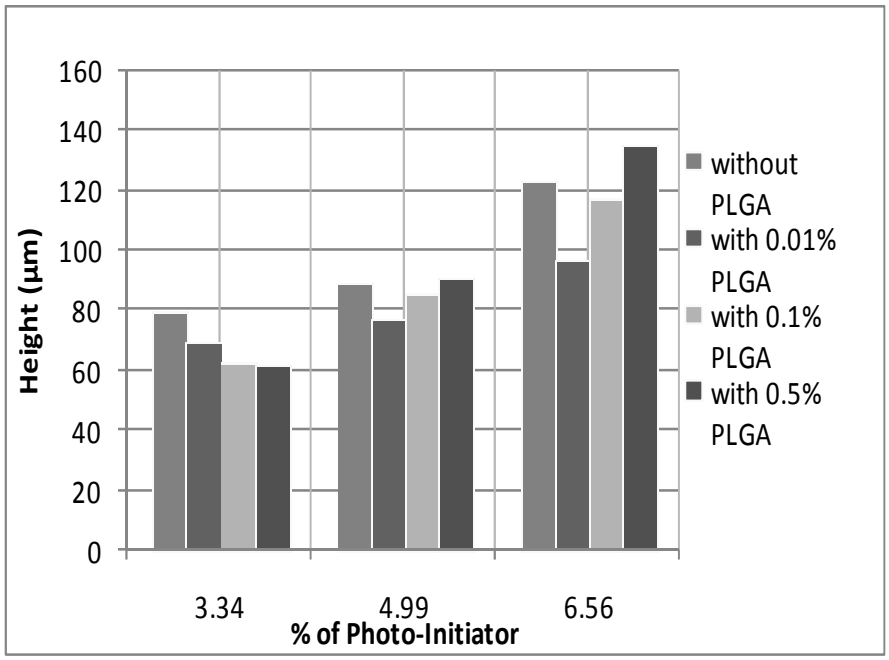
(b)

Fig 3.7 Width of walls fabricated at (a) 20 mW and (b) 30 mW.

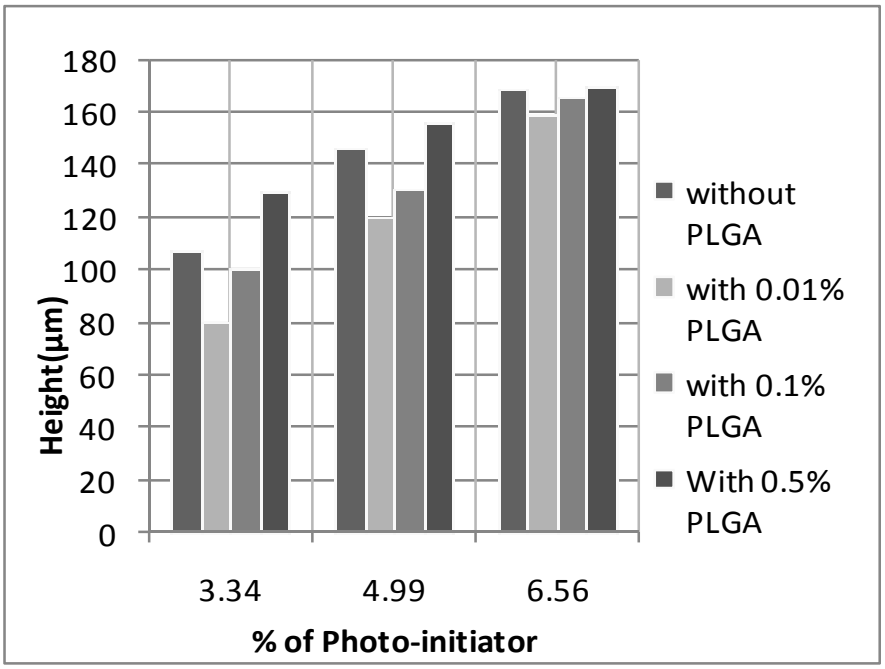
Another observation is that the concentration of photo-initiator affects the dimension of the polymerized structures. The photo-initiator molecules in the resin mixture govern the radical generation and polymerization chain reaction. The incident photons transfer the energy to the photo-initiator molecule to generate free radicals which are responsible for polymerization [1, 35]. Thus, if the number of photo-initiator molecules available in the resin increases the probability of more molecules interacting with the incident laser beam increases which will cause an increase in the polymerization chain reaction resulting in changing the dimensions of the structure. The results show that for lower power (20 mW), the width of the walls increases with an increase in concentration of photo-initiator when the concentration of the nanomaterials is kept constant. At higher power the change in the width of walls fabricated with nanomaterials with increasing concentration of photo-initiator is not large. Thus the effect of photo-initiator on the change in width is significant in lower power or lower energy/pulse. Similar behavior is observed for the walls fabricated without nanomaterials.

The rate of change of dimensions also depends upon the concentration of the nanomaterial present in the resin. The results show that there is a change in width and height of the polymerized walls with and without the nanoparticles. The experimental analysis shows that the width of the polymerized walls increases as the concentration of the nanoparticle increases and is larger than the width increase for the pure polymeric fabricated walls, as shown in figure 3.7 (a) and (b). According to figure 3.7, for the higher power level, the increase in width of the nanocomposite walls is larger when the concentration of nanoparticles increases as compared to the lower power level. At the lower power level the width still increases but not at the same values.

The height of the nanocomposite wall is dependent on the concentration of the nanoparticles as shown in figure 3.8. At higher power (30 mW) and lower nanoparticle concentrations (0.01% and 0.1%), the height of the nanocomposite walls is smaller than that of the walls made without nanoparticles. However, at higher nanoparticle concentration (0.5%) the



(a)



(b)

Fig. 3.8 Height of walls fabricated at (a) 20 mW and (b) 30 mW

height is more than that of pure polymeric wall. This shows the dependence of height on concentration of nanoparticles.

This trend is followed for any change in concentration of photo-initiator at the higher power (30 mW) level. But at the lower power (20 mW) level and lower concentrations of photo-initiator (3.34%, 4.99%), the height of the nanocomposite walls are smaller than the wall as fabricated without nanoparticles. This variation in the height can be attributed to the laser interaction with the presence of nanoparticles in the resin possibly causing the laser beam to scattered. Similar behavior was observed and discussed when using UV laser light [11, 23].

The laser interaction with the nanoparticle is an important phenomenon to be considered here. The refractive index of the monomer is 1.46 whereas that of the PLGA nanoparticle is 1.479. When the laser beam enters the polymer resin mixture, it comes across the uniformly distributed nanoparticles. This interaction between laser and nanoparticles causes scattering of light due to the change in the refractive index of the media [11, 34]. The nanoparticles scatter the incoming photons and the photons travel in the lateral direction rather than the longitudinal direction (responsible for depth) [11]. Thus, the final structure fabricated has a higher width and smaller height as compared to the structure fabricated without nanocomposite. This phenomenon is schematically shown in figure 3.9.

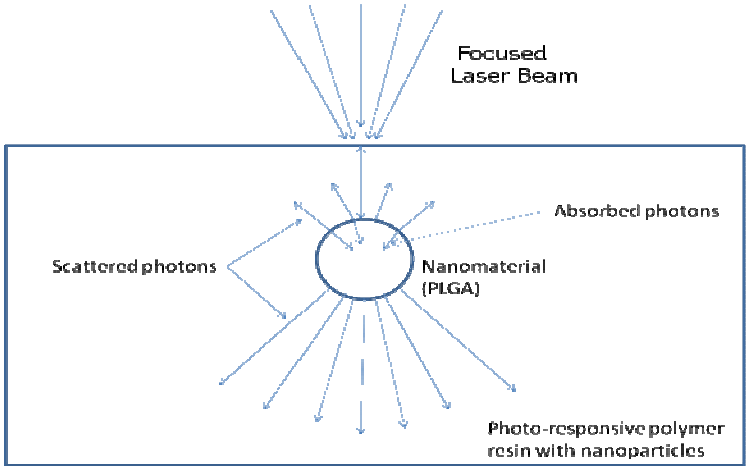


Fig. 3.9 scattering of light in presence of nanoparticle

The ratio of width to height of a structure gives its aspect ratio. The width and height of the fabricated walls are mentioned in the table 3.2 and 3.3. This information allows the calculation of the aspect ratio of the structures as shown in table 3.5. At the lower power (20 mW), the aspect ratio of the structure reduces as the concentration of the nanoparticles increases at constant concentration of photo-initiator. The lowest aspect ratio of 1:16.26 for the nanocomposite experiments was obtained at the highest concentration of nanoparticles (0.5%), lowest concentration of photo-initiator (3.34%) and lower power level (20 mW). The aspect ratio of the structures fabricated at high power increases as the concentration of the nanoparticle increases. The aspect ratio of the walls fabricated without the nanomaterials is larger than the aspect ratio of the walls fabricated with the nanoparticles when the concentration of the photo-initiator is kept constant.

Table 3.5 Aspect ratio (width/height) of structures fabricated by 2PP

		Power (mW)	
		20	30
% PLGA (by weight)	% PI (by weight)	Aspect Ratio	
0	3.34	1/30.98039	1/37.89474
	4.99	1/32.01439	1/47.09677
	6.56	1/38.88889	1/48.98551
0.01	3.34	1/28.75	1/21.62162
	4.99	1/28	1/30.76923
	6.56	1/31.47541	1/37.85714
0.1	3.34	1/16.9863	1/25.89744
	4.99	1/21.79487	1/31.70732
	6.56	1/34.41176	1/40.4878
0.5	3.34	1/16.26667	1/27.74194
	4.99	1/22.625	1/39.87179
	6.56	1/31.76471	1/34.69388

The presented results from the aspect ratio analysis show that the dimensions of the nanocomposite structure depends on the concentration of nanoparticles and photo-initiator and the power level used for fabrication. With proper selection of the parameters, the desired size of nanocomposite structure can be fabricated.

A 3D nanocomposite structure consisting of PLGA nanoparticles made of a number of walls next to each other was fabricated using 2PP in our laboratory and shown in figure 3.10. The process parameters used for this structure were power of 25 mW or 0.3125 nJ/pulse energy, 3.34% of photo-initiator (by weight) concentration, and 0.2% concentration of PLGA nanoparticles. A constant laser scanning speed of 3 mm/min was used and a focusing lens of 0.4 NA. In this fabricated structure, the PLGA nanoparticles are seen on the surface of the structure.

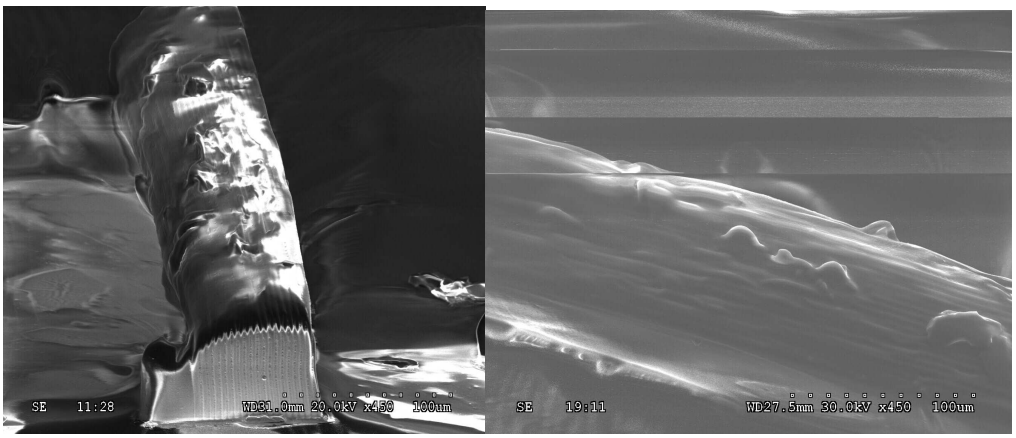


Fig 3.10 Nanocomposite structure fabricated using PLGA nanoparticles
by 2PP process in our laboratory

CHAPTER 4

CONCLUSIONS AND FUTURE WORK

Two Photon Polymerization is a novel and effective manufacturing method for fabrication of nanoparticle embedded micro/nano structures and devices for various applications. This method has been used for manufacturing of 2½D and 3D polymeric structures with minimum number of pre/post processing steps and good dimensional accuracy. This research focused on using two photon polymerization process for the fabrication of nanocomposites. Two-photon polymerization is studied as a novel technique for rapid prototyping of simple planar to complex 2½ D and 3D nanocomposite structures and devices.

Micro/nano composite 2½D structures were successfully fabricated from a monomer and photoinitiator resin doped with PLGA nanoparticles**.** The two photon absorption of photo-initiator molecules produces active radicals which successfully initiate the polymerization chain reaction. During this process of chain reaction, the uniformly distributed nanomaterials present in the resin mixture get trapped in between the reacting monomer molecules resulting in the formation of nanocomposites. This successful step makes 2PP a viable candidate for the fabrication of controlled three-dimensional (3D) micro/nano composite structures using direct laser writing.

The dimensions of the nanocomposite structure depend on several factors such as the concentration of the photo-initiator, concentration of nanoparticles and energy per pulse. In order to understand the effects of different parameters on dimensional changes experiments were performed. Two levels of power (20 mW, 30 mW), three (3) concentrations of photoinitiator (3.34%, 4.99% and 6.56%) by weight, and three (3) concentrations of nanoparticles (0.01%, 0.1% and 0.5%) by weight were selected for experimentation in order to assess their effects on the dimensions of fabricated nanocomposite structures/walls. The change in the dimensions

such as height and width of the fabricated walls with and without presence of nanoparticles and the various process parameter combinations were analyzed. It is concluded from the experimental analysis that the width of walls fabricated with nanoparticles is larger than width of the walls fabricated without the nanoparticles. The width of a nanocomposite structure is a function of concentration of nanoparticle and photo-initiator and energy/pulse. The width of nanocomposite increases with an increase in concentration of nanoparticle and energy/pulse. The height of the nanocomposite structure is a function of concentration of nanomaterial, concentration of photo-initiator and power level. Thus, by controlling these process parameters, desired size of the nanocomposite structure can be fabricated.

The results show that the range of the aspect ratio of the walls made with nanoparticles is 1:16 to 1:40 and that of pure polymeric structure is 1:30 to 1:50. This is due to the interaction of laser with the nanoparticles present in the polymer resin mixture. The scattering of the photons in lateral direction causes increase in the width of the nanocomposite structure and reduces the height of the structure resulting in lower aspect ratio as compared to the pure polymeric structure. The lowest aspect ratio of the nanocomposite fabricated in out laboratory is 1:16.22 for lower power level of 20 mW and concentration of photo-initiator as 3.34% with higher concentration of 0.5% nanoparticles. The results conclude that aspect ratio of nanocomposite structure is a function of concentration of nanoparticle and power level required for fabrication. It can be concluded that nanocomposite structures have lower aspect ratio than the pure polymeric structures and this is attributed to the scattering phenomenon discussed.

This study was performed to analyze the effect of the presence of PLGA nanoparticles in the polymer resin on the size of a fabricated structure. A further study can be performed to examine different polymeric, metallic, non-metallic and biodegradable nanomaterials and their effect on the size of the voxel. This study will be helpful for research in identifying various new applications of nanocomposites.

It is recommended that a study is performed to evaluate the changes in the physical, chemical or mechanical properties due to the presence of nanoparticles in the structure. The choice of materials could have a significant effect on the properties of the structures. The nanocomposites fabricated using various types of nanoparticles can be tested for physical properties such as mechanical strength, rigidity, refractive index change or any chemical changes due to the presence of nanoparticles.

It is recommended that a mathematical model is developed with the capability of analyzing and predicting the size of voxel for any given combination of process parameters and material characteristics.

This research has presented an approach to manufacture micro/nano composite structures with better understanding of various process parameters and materials using 2PP process. It is believed that 2PP will evolve as a unique and versatile method of nanocomposite fabrication of true 2½D and 3D micro/ nano devices on a commercial level.

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