

Experimental Study of Selective Laser Sintering of Parmax[®]

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Abstract

Selective Laser Sintering (SLS) has been used to successfully process crystalline polymers, ceramics and metals. However, wide range of materials available and their applications have acted as an impetus to expand the applications of SLS to different material systems. This paper presents one such experimental study undertaken to explore the application of SLS to process Parmax[®] polymers – a family of high performance amorphous poly p-phenylenes. As a part of the collaborative study, various process parameters and material formulations were tried out to ascertain the feasibility of the process and the initial results obtained look promising. This paper lists the material formulations tested and process parameters controlled. Also, analysis of the results of the experimental study and the outline of the next phase of research to be undertaken have been described. This study was motivated by the numerous applications of Parmax[®] in the electronics, defense and aerospace industries as well as the goal to expand the applications and utility of SLS.

Introduction

Rapid prototyping has become an essential tool in dealing with dramatically shortened manufacturing product life cycles. It replaces machine carved prototype models and patterns with machine-built components produced in a few hours, suitable for testing of form, fit and function. Functional testing often places the rapid prototyping part in an operating assembly, requiring high strength materials. Unfortunately, current polymeric rapid prototyping materials such as nylon and polycarbonate, do not offer sufficient mechanical properties for high strength components, restricting functional testing up to this point and thus limiting the overall utility of rapid prototyping.

To overcome this limitation, new materials with higher strength need to be processed through Selective Laser Sintering (SLS). One such material, developed at MPT is its novel, high strength class of rigid-rod Parmax[®] Self Reinforced Polymer (SRP) resins.

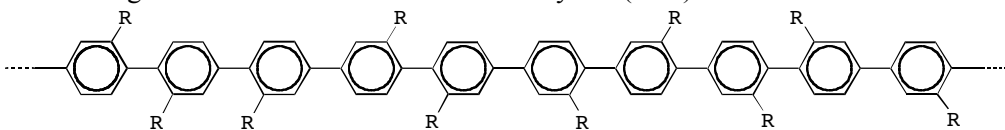


Figure 1. Generalized Structure of Rigid-Rod Parmax[®] SRPs

The extraordinary hardness, stiffness and strength of Parmax[®] SRPs make them attractive for a wide range of uses that include molded articles and extruded sheet, stock and profiles for aircraft interiors, electrical and electronic components, surgical instruments, bushings, gears etc.; films and coatings for fiberless printed wiring boards, abrasion resistant coatings etc.; foams for high strength, low moisture absorption core and structural components and in blends and additives in which Parmax[®] SRPs are used to improve the performance of other polymers. With its application extending into so many different areas, it becomes important to manufacture functional prototypes quickly and cheaply in order to demonstrate its capability and also arrive at optimized material formulations for each application. Thus being able to make Parmax[®] SRPs compatible to SLS is important from this point of view and this study aims at achieving the same.

The primary objectives of this research effort are to (1) develop sinterable powder formulations based on MPT's high-performance Parmax[®] SRP resins, (2) determine initial processing conditions for these powders via the Selective Laser Sintering (SLS) rapid-prototyping process, and (3) fabricate initial test coupons to demonstrate the high-integrity components that can result from this combination of material and processing. However, the ultimate goal of the research is to come up with optimized powder and process parameters to produce components with unprecedented mechanical properties, thus paving the way for the commercialization of Parmax[®] SRP-based SLS formulations.

The selection and development of powder formulations based on Parmax[®] SRP resins suitable for SLS processing were carried out at MPT under the aegis of an SBIR grant while determination of initial processing conditions and production of test coupons was conducted at the University of Texas.

The paper is organized in the following way. First, a brief description of mechanical and chemical properties of relevant Parmax[®] SRP resins developed, current resin processing methods as well as the Selective Laser Sintering process are stated. Following this, the process parameters considered, material formulations tested and the initial experimental trials are presented. The results of the experiments are then analyzed. The paper concludes with a section on the contributions of this effort and an outline for the next phase of the research.

Background

Powder Properties:

MPT's Parmax[®] SRPs, a new family of rigid-rod self-reinforcing polyphenylenes, possess a unique combination of high performance mechanical properties along with good processing capabilities. Research largely inspired and supported by the Air Force Materials Laboratory in the 1970's and 1980's has demonstrated that rigid-rod polymers possess exceptional mechanical properties[1], but most are either intractable or are soluble only in strong acid solvents. Parmax[®] SRPs have been designed to overcome the processing deficiencies of other rigid-rod polymers via the use of carefully chosen pendant side chains to impart solubility and thermal processability to the normally intractable rigid-rod polyparaphenylene backbone. Thus, Parmax[®] materials can be dissolved in a variety of common organic solvents (methylene chloride, N-methylpyrrolidinone, phenyl ethers and esters, etc.) and, perhaps most importantly, can be thermally fabricated (compression molded, extruded, injection molded, etc.).

Parmax[®] SRPs are prepared by proprietary processes that assure the isomeric integrity of the structure. A variety of substituent groups (R) can be utilized, so Parmax[®] SRP resins comprise a

versatile class of polymers, like polyimides, polyesters, and polyamides, within which a wide range of structural variation is possible. We have surveyed many different derivatives including the thermoplastic rigid-rod Parmax[®]-1000 (benzoyl side chain structure) and Parmax[®]-2000 (4-phenoxybenzoyl side chain) homopolymers (Figure 2.) and the "tougher" and more processible Parmax[®]-1200 series of "kinked" copolymers. Currently it appears that the Parmax[®]-1000 and Parmax[®]-1200 derivatives will provide the first commercial Parmax[®] molding resin products.

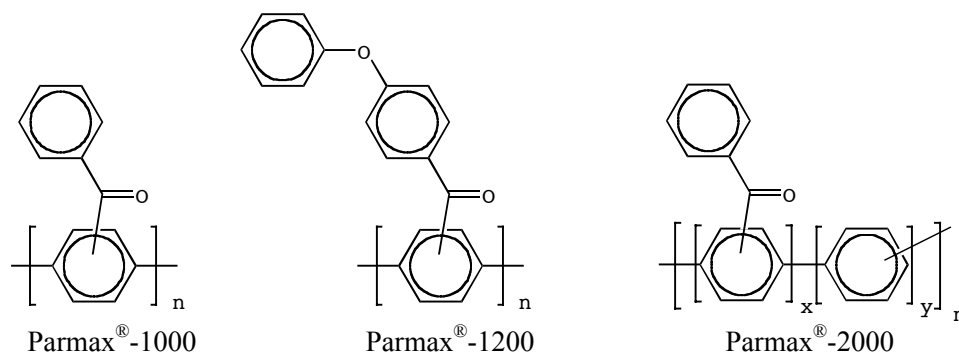


Figure 2. Chemical Structures of Some Thermoplastic Parmax[®] SRP Derivatives

Parmax[®] SRP resins demonstrate extraordinary strength, modulus, hardness, and other properties in a combination unrivaled by any other single material (Table 1). Metals are widely used for structural support but are heavy and subject to corrosion and fatigue. Common thermoplastics are inexpensive to fabricate into parts but currently cannot provide enough strength or stiffness for many applications. Fiber-reinforced composites have evolved to offer unprecedented strength-to-weight characteristics but are extremely difficult and expensive to process. As demonstrated in Figure 3, isotropic Parmax[®] resins possess unparalleled mechanical strength and modulus when compared to other engineering thermoplastics. In fact, on weight basis, Parmax[®] polymers are extremely competitive with structural metals such as aerospace grades of aluminum and titanium (Figure 4).

Table 1. Selected Properties of Thermoplastic Parmax[®] SRP Resins

	Parmax [®] -1000	Parmax [®] -2000	Parmax [®] -1200
Specific Gravity	1.21	1.23	1.23
Tensile Modulus (MSI)	1.5	1.2-1.4	1.2
Flexural Strength (KSI)	35-50	20-30	39-46
Rockwell Hardness	K98	K98	K90
Limiting Oxygen Index (1/8" thick)	41%	32%	42%

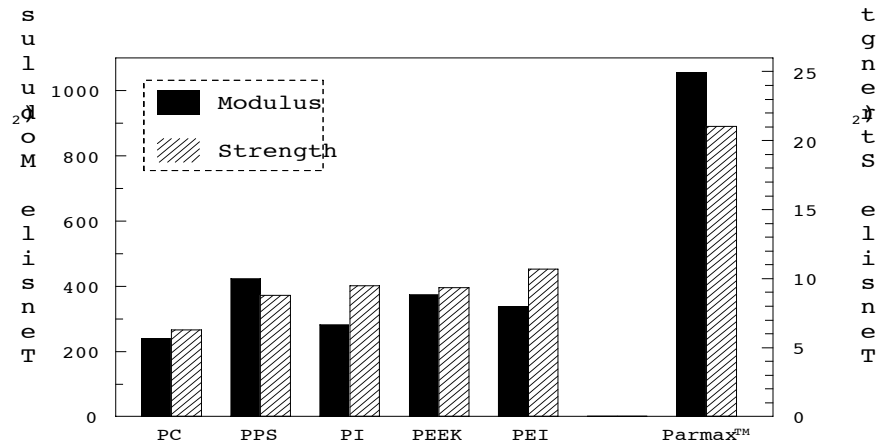


Figure 3. Mechanical Properties of Engineering Plastics and Parmax® SRPs

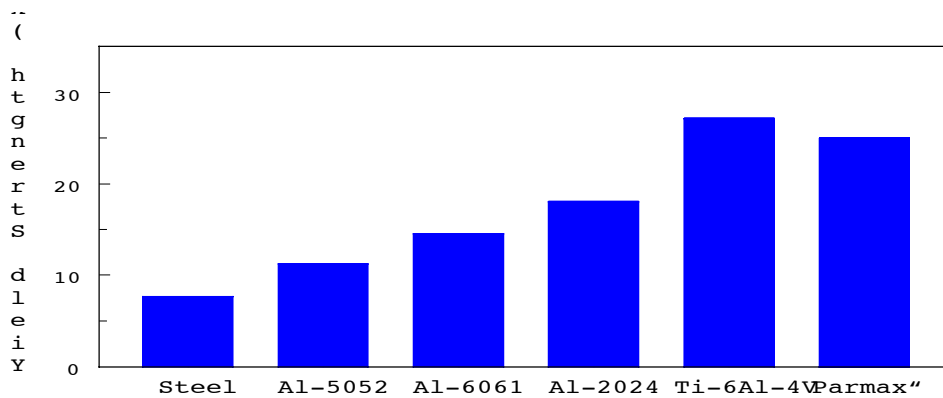


Figure 4. Specific Strength Comparison of Various Metals with Parmax® SRPs

Processing Techniques:

Ultra high performance, isotropic Parmax® SRP polymers are processed utilizing conventional polymer techniques. These include routine extrusion, thermoforming and compression molding operations. Injection molding grades are under development and their availability is anticipated for fourth quarter of 2001. Processing temperatures are in the range of 290 to 340 °C. Within this processing window, Parmax® SRP resins display remarkable stability and do not require any additional stabilizers to facilitate the processing. The excellent solubility of these materials in common organic solvents allow for the facile preparation of films and coatings from solution.

Selective Laser Sintering Process:

Selective Laser Sintering is a rapid prototyping process in which powdered material is melted into the desired shape through the repeated scanning of cross-sectional areas that will eventually form the 3D model[14]. The machine (figure 5) consists of one part piston which translates within the part cylinder; 1 or 2 feed pistons that move within the powder cartridge and act as the powder feeding/collection system; a roller mechanism for spreading powder; heating coils, sensors and controllers for heating and maintaining the powder at the correct temperature;

laser and its accompanying optics to focus the laser beam precisely; blower, sensors and controllers that maintain the process chamber inert(not shown in figure); a computer interface that serves as the communication link between the user and the machine(not shown in figure). The SLS process is accomplished with a CO₂ laser which scans a cross section of the part on the surface of the part bed. After one cross section is scanned, the part piston moves down and the feed pistons, carrying powder above them, move up. Then a roller sweeps across the bed, laying a fresh layer of powder and the whole process is repeated till the whole component is made. Uneven or large temperature gradients need to be minimized during the build so as to prevent excessive part curl. This is achieved by preheating the powder in the feed bins as well as the part piston to prescribed temperatures.

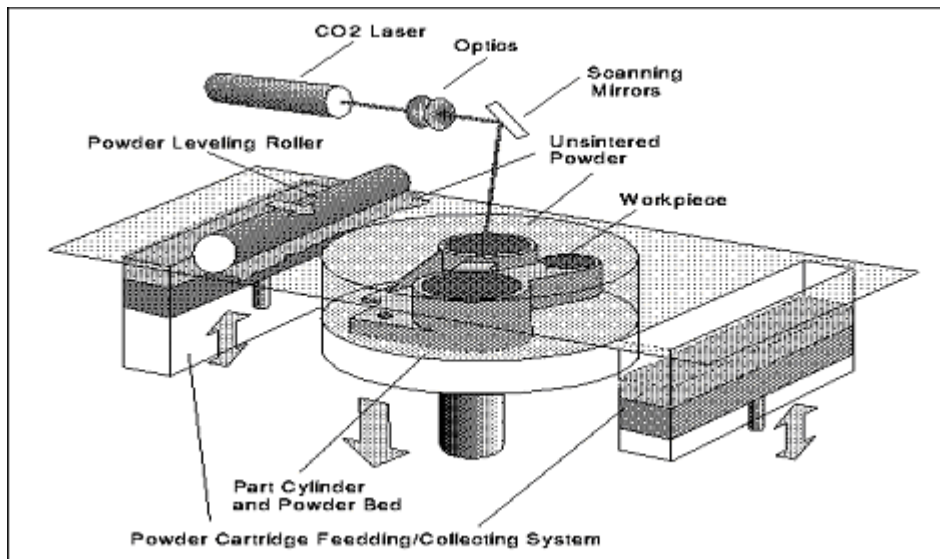


Figure 5: Schematic of the Selective Laser Sintering Process

Approach

The aim of the study, as stated before, is to process Parmax[®] SRPs using Selective Laser Sintering. There are many powder as well as process parameters that affect the quality of components produced. Hence, to manufacture functional prototypes, these parameters have to be optimized to achieve the desired values of performance variables(responses) such as strength, modulus and dimensional accuracy. Since the SLS process has not been mathematically modeled to the extent desired, a set of experiments need to be performed to identify important parameters and establish mathematical relationships between them that will help optimize the process.

The first step in the research process was to identify the parameters that could affect the process. An initial study revealed 12 SLS process parameters and 4 powder parameters that could be controlled. These are briefly discussed below.

SLS Process Parameters

The 12 SLS parameters are powder age, powder type, part bed temperature, feed piston temperature, part piston temperature, laser power, powder layer thickness, feed rate, chamber atmosphere, part orientation, roller speed and time between layers.

The first parameter to consider in the process is the type of powder to be used. There are currently 12 commercially available powders that can be used with the SLS process. Each of these have different physical properties and chemical properties and produce different results. This study focuses on only Parmax – a family of high performance amorphous poly p-polyphenes.

The designer then has the choice of using either new powder or recycled powder. The powder in the machine is pre-heated very close to its melting or softening temperature causing partial melting. This might cause clumping and hence change the particle size. Therefore, every time the powder is used, different laser power and pre-heating temperatures might be needed. Temperatures of the part bed, part piston and feed pistons have been observed to have a great effect on the properties of the final part. Normally, the feed pistons and part pistons are kept at temperatures below the part bed temperatures. This is to minimize powder clumping that might occur due to prolonged exposure of powder very close to its melting or softening point. The feed piston temperature and the part bed temperature have an effect on part curl, strength of part and on the dimensional accuracy.

The laser power is another important parameter. The laser power can be controlled by varying the incident laser power, the scan speed of the laser and the scan spacing of the laser. However the machine allows the user to change only the incident power. The laser power like the piston and part bed temperatures has a profound effect on the part curl, strength and dimensional accuracy.

The orientation is an important factor in determining the quality of the part. Because the build proceeds in the z direction(upward), taller part take longer to build. Hence the build time can be minimized by orienting the longer dimension of the part in the X or Y direction(parallel to the bed of the machine). Orientation may also effect the part strength because in the Z direction, there is a potential problem with proper bonding between the layers. This is also expected to cause a decrease in strength along the Z direction. Surface roughness is also effected by the part orientation. The layered nature in which parts are produces causes a “stairstep” effect on the surfaces that are not parallel or perpendicular to the part bed surface[14].

Layer thickness is a controllable parameter that effects many part properties. Among these are build time, strength, density and accuracy. The layer thickness is controlled by the movement of the part piston. More the movement of the part piston downward, more is the layer thickness. Coupled with the layer thickness is the feed rate which is determined by the distance moved by the feed pistons upward. The convention used in the process to ensure a uniform layer to be spread across the part piston is to have a feed rate that is twice the layer thickness. However, the particle size may effect the feed rate setting that is needed.

The roller speed and the time between layers are parameters that have an effect on the build time and is suspected to have an impact on the part curl. This is because the roller speed determines the time in which the powder is spread across the part piston and also the force it applies on the sintered part while the time between layers determines the amount of time the freshly laid powder has to attain the part bed temperature. If enough time is not given for the freshly laid powder to attain the part bed temperature, large temperature gradients might occur leading to excessive part curl.

An inert atmosphere in the chamber is required during processing to prevent oxidation that might cause loose powder to solidify. This is achieved by supplying a steady flow of nitrogen to the build chamber. The percentage of oxygen present in the chamber effects post processing and accuracy of the part. Since it is known that a more inert atmosphere would

always be preferred, a steady nitrogen flow is maintained to limit the oxygen content below 5.5%(default machine parameter value).

Powder Parameters

The four important powder parameters are particle size, density, viscosity and chemical structure.

Powder particle size determines the time taken for the powder to melt when sintered. Also it is related to the minimum powder layer thickness and the feed rate. Large particle size causes an increase in the layer thickness and leads to poor consolidation and hence strength. Thus it is important to arrive at an optimum particle size.

The density of the powder is known to have a direct impact on the strength of the processed component and also on the degree of consolidation. Typical densities of powders that have been processed are between 0.4 gm/cm^3 to 0.6 gm/cm^3

Viscosity determines the ease with which the powder flows and it is desirable that the powder exhibits low viscosity at the processing temperatures. However, modification of viscosity often entails a change in the chemical structure.

Chemical Structure of the powder is one of the most important parameters but often its modification is difficult and restricted. The structure of the polymer determines its viscosity, crystallinity and melting temperature.

Performing an exhaustive set of experiments taking all of the 16 variables into account is time consuming and a waste of resources. In order to identify those variables that have a major effect on the response, an initial set of experiments were performed. The work progressed on dual tracks. One was formulation of Parmax[®] SRP resins suitable for SLS and the other was SLS process optimization.

Initial formulation selection

Research effort executed under the Phase I SBIR Contract initiated with assessment of the critical parameters of the successful SLS formulations and the fit that current Parmax[®] SRP resin offer. The first parameter examined closely was the effect of the powder particle size. The focus was on the identification of Parmax[®] SRP resins with a range of particle sizes to bracket the acceptable limits on this parameter. The initial two formulations represented materials with mean particle sizes varying from $8 \mu\text{m}$ (1200-341) to $60 \mu\text{m}$ (1200-367). Bulk densities for the two formulations were 0.02 gm/cm^3 for 1200-341 and 0.25 gm/cm^3 for 1200-367 Micrographs of these two formulations can be found in Figures 6 and 7, respectively.

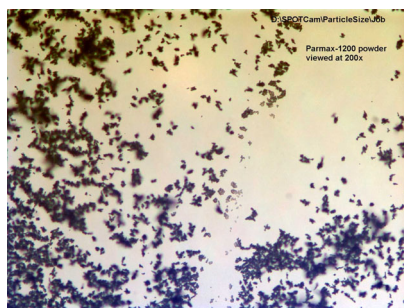


Figure 6. 1200-341 powder structure and size

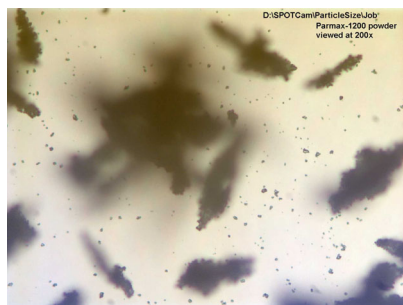


Figure 7. 1200-367 powder structure and size

Both of the formulations utilized in this first SLS iteration are the Parmax[®] 1200 derivative, the chemical structure of which can be found in Figure 8.

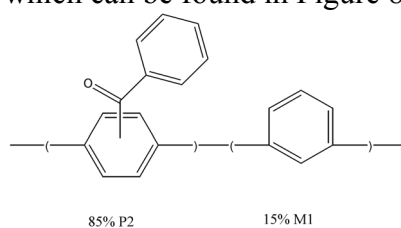


Figure 8. Structure of Parmax[®] 1200

Parmax[®] 1200 is a copolymer with about 15% of the flexible meta-phenylene linkages present. This intentional kink introduces a degree of flexibility to the otherwise rigid para-phenylene backbone. This limited flexibility is translated into improved processability and molecular flow above glass transition temperature (T_g), when compared to the completely rigid Parmax[®] 1000.

Initially, three materials were planned for the first iteration, with the remaining formulation being Parmax[®] 1200-367 with its particle size further reduced. This was attempted through the use of jet milling at Fluid Energy in Hatfield, PA. This vendor, however, failed to induce any particle size reduction. This was particularly puzzling, since the same vendor previously ground Parmax[®] 1200 to the 10-20 μm particle size specification. As a result of this failure, only 2 Parmax[®] SRP formulations were tested during the first iteration of this effort.

Initial sintering trials

Initial experiments were conducted using Parmax[®] 1200-367 to ascertain the feasibility of the process, reduce the number of process parameters by eliminating variables that had little effect on consolidation and to get the outer bounds on the important parameters. These experiments were driven by intuition and the insights obtained during experimentation and not by following formal experimentation methodologies. This was mainly because an exhaustive set of experiments could not be run with the powder available and the goals of the experiment did not warrant a large set of experiments to be run.

DSC curves of Parmax[®] 1200 indicated the onset of softening temperature (T_g) as 152 °C. With knowledge gained from processing parts using DuraForm (nylon-based SLS material), the part heater temperature was initially set at 132 °C, the left and right feed pistons were at 60 °C and a laser power of 5.5 watts (default power setting for DuraForm) was used. With these settings the powder did not consolidate. Hence the laser power was increased to 6 watts (at z

(measure of part thickness) = 0.012”). This did not alter the result and subsequently (at $z = 0.016$) it was increased to 9 watts. This sintered the powder to a greater extent but the sintered powder was turning brown (which at this point was thought undesirable). To minimize the discoloration the part heater temperature was increased to 132 °C (at $z=0.02$ ”) and various laser powers were tried out. Also, part heater temperature was ramped up by 2 °C and at $z = -.524$ ” it was increased further by 4 °C to 142 °C. However, these changes brought about little change in the result. One main reason for not increasing the part heater temperature appreciably was to avoid solidification of all the powder in the part piston leading to wastage of large amounts of expensive powder. An interesting phenomenon that was noticed during the experiment was that at around 0.028”, the sintered powder started warping and at 0.056” it was high enough to lead to movement of the part under the roller. Warping could occur due to the following reasons:(1) localized expansion due to uneven temperature gradients while scanning by the laser. (2) Excessive force applied by the movement of roller over the sintered part (3) uneven expansion due to a large difference in temperatures between the feed pistons and part pistons.

Green parts obtained in these first iterations can be seen in Figure 9. Following this stage, the parts were sent to Bodycote IMT for an additional HIP-ing step.

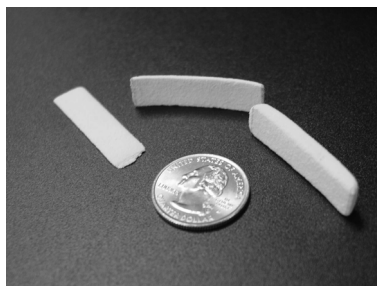


Figure 9. First Parmax[®] SRP parts produced via SLS

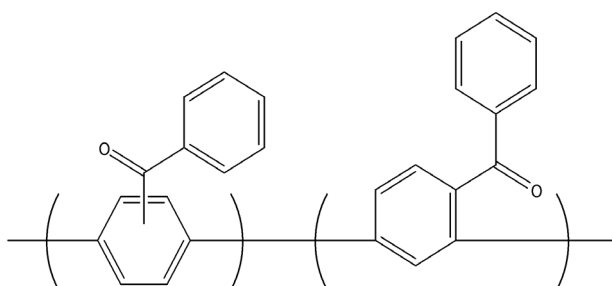
Through this experiment it was established that the grain size of the 1200-367 powder formulation was suitable for the SLS process, at least for the initial levels of consolidation. The roller was able to spread the powder evenly and bulk density variability was minimized. Based on the results of this run, overall powder bulk density and viscosity of the powder at these temperatures might have to be varied to optimize the consolidation. From the point of view of the process parameters, the operating temperatures could be increased, other parameters like roller speed, power layer thickness and feed distance need to be controlled so as to determine their impact on warping and powder consolidation.

The second material formulated for this iteration, Parmax[®] 1200-341, could not be adequately processed owing to the extremely low bulk density of this powder. Even though it appeared that the small particle size would be beneficial from the standpoint of better surface finish as well as larger particle surface area for laser to operate on, the flocculent nature of this material did not allow the Sinterstation 2000 roller to distribute the powder evenly.

Formulations aimed at viscosity reduction

Based on results obtained during the first half of the effort, a second iteration of materials was formulated for the laser sintering trials. The stated goal during this phase of the effort was an improvement of the molecular flow of Parmax[®] SRP resins at the Sinterstation operating temperatures. Formulations were as follows:

- Plasticized Parmax[®] SRP formulation (1200-366), containing 15% of di-octyl phthalate (DOP), an esteric plasticizer commonly used in PVC industry. DOP and Parmax[®] SRP resin were compounded using a 1” Davis Standard Killion Single Screw Extruder (SSE). Approximately 6 lbs of this formulation was produced and pelletized. Pellets were then sent to Particle Reduction Corp of Elk Grove Village, IL for another attempt at particle reduction. The two processes used were hammer milling and jet milling. Hammer milling successfully ground Parmax[®] SRP pellets to approximately 500 μm particle size (consistency of beach sand). Unfortunately, further milling, utilizing the jet milling facilities, was again unsuccessful.
- Formulation utilizing a different copolymer of Parmax[®] SRP materials, Parmax[®] 1215K (Formulation designation 1215-373), structure of which can be found in Figure 10. This chemical structure modification had a goal of reducing the viscosity of the resulting material at Sinterstation processing temperatures, and also to examine the suitability of chemistry modification as means for optimizing sinterable Parmax[®] SRP derivatives. Viscosity reduction is achieved through an addition of benzoxy-substituted meta-phenylene linkage. This hinders efficient packing of the rigid rod backbone chains, resulting in increased disorder within the polymer lattice. Resulting free volume increase translates into lower viscosity at processing temperatures of interest. 1215-373 had particle size of approximately 70 μm with bulk density of 0.23 gm/cm³.



Parmax-1215

Figure 10. Chemical structure of Parmax[®] 1215K

Sintering studies of 1200-366 and 1215-373

As a baseline for this round of sintering trials, conditions that led to the consolidation of parts in the first iteration were replicated. It became immediately obvious that 1200-366’s sand-like powder consistency was unsuitable for laser sintering process, owing to the inability of the Sinterstation roller to distribute the material evenly across the sintering surface. The second formulation, labeled 1215-373 was successfully consolidated using the same parameters utilized in previous successful consolidation, 1200-367. Following the baseline establishment, the remainder of the machine time was devoted to the sintering parameter optimization, utilizing 1200-367 and 1215-373 materials.

Effect of the powder layer thickness on part consolidation and warping

Localized expansion arising from uneven temperature gradients while scanning by the laser might be affected by process parameters such as powder layer thickness, time between layers, feed distance, part heater temperature, laser power used and the left and right feed temperature. The third experiment concentrated on studying the effect of powder layer thickness, feed distance and part heater temperature.

Left and right feed distances were set initially at 0.014" and the powder layer thickness was increased to 0.006". The left and right feed heaters were set at 120°C during the warm up stage and at 145°C during the sintering stage. However, owing to the technical difficulties with Sinterstation 2000, the powder could not be heated beyond 115°C. The part heater was set at 154°C and laser power used was 6 watts. The increase in the powder layer thickness and the feed distance did not seem to have an impact on the warping and so the powder layer thickness and feed distance were decreased to 0.005" and 0.012" respectively (at $z=0.18$ ") while the part heater temperature was ramped up to 165°C to aid consolidation of powder. To prevent discoloration of the powder, the laser power was not increased beyond 7.5 watts.

Based on these results, we suspect that powder layer thickness and feed distance were not the primary reasons for uneven temperature gradients and localized expansion leading to warpage. Also, we conclude that the temperature reached by the powder on preheating to 165°C and application of laser power of 7.5 watts is not high enough to sinter it completely.

Impact of roller motion

The next experiment focused on studying the effects of the roller motion over the sintered part and also the time elapsed between laying of fresh powder by the roller and the start of the sintering process. The movement of the roller carrying powder might apply a force on the sintered part that is enough to cause yielding. So in this experiment the roller speed, and the amount of powder it carries, which is directly related to the feed distance, are varied, as is the time between which layers of powder are laid down.

During this run, the left and right feed distances were set at 0.012"; the feed heaters were at 120 °C while the part heater was set at 175 °C (10 degrees more than the previous experiment). The laser power was maintained at 6.5 watts through out the experiment. The roller speed was at the default value of 5 in/sec but the time between layers was set at 50 sec (default value 15sec). At various points in the experiment, the roller speed was varied from a minimum of 3 in/sec to 7 in/sec and the feed distance between 0.012" to 0.035". The effect on warping seemed minimal. The part heater temperature was increased to 180 °C and then to 190 °C. At these high temperatures, the powder in the part piston had started clumping and hence the roller was unable to spread the powder evenly. The clumping might have occurred because the temperature was too high or because of prolonged heating (the powder was at these temperatures for around 3 hours and being amorphous in nature might have started softening and coagulating gradually).

Laser power optimization

Through this experiment we aimed at obtaining the outer bounds for the laser power. The part heater, piston heater and feed heater temperatures were set at 165°C, 130°C and 100°C respectively. Laser power was varied from 6 watts to 30 watts. At values beyond 15 watts, the laser power was high enough to totally degenerate the powder. The powder was getting

completely charred at these high values, establishing the upper bound for the laser power application to Parmax[®] SRP resins.

From the above experiments, we conclude that the most important parameters that seem to impact sintering as well as warping are the feed piston temperatures, part heater temperature and laser power. Overall, these experiments were successful in eliminating 3 parameters (time between layers, roller speed and piston heater temperature). Also, it helped us obtain the outer bounds of part heater temperature and laser power. This information is going to be crucial in reducing the number of variables to be examined during the next phase of research, therefore speeding up the screening process and allowing us to concentrate on mission critical parameters.

Results

During the first phase of study, we have demonstrated successful processing of Parmax[®] SRP resins using Selective Laser Sintering (SLS) techniques, offering the prospect of rapid prototyping of components with unprecedented mechanical properties. This phase also elucidated the requirements for development of commercially practical Parmax[®] SRP SLS materials.

The research performed thus far consisted of these distinct phases:

Materials Formulation: The initial phase involved selection and development of sinterable powder formulations based on Parmax[®] SRP resins that would be suitable for processing by Selective Laser Sintering (SLS) rapid-prototyping process. Four candidate powder formulations were screened for sintering. Decisions to focus on these four candidate formulations were based on a number of properties of interest, most importantly powder particle size, viscosity, chemical structure and bulk density.

SLS Trials: Following the identification of the candidate formulations by MPT, initial processing studies at The University of Texas at Austin were performed. Following the initial parameter determination, a set of conditions were selected and the initial fabrication of the parts was undertaken. This formulation iteration consisted of 2 formulations, one of which failed due to the low bulk density and tackiness of the powder (Parmax[®] 1200-341). Using the second formulation, Parmax[®] 1200-367, with a bulk density an order of magnitude higher than the first attempt, initial test coupons were successfully fabricated. Both of these formulations are based on Parmax[®] 1200, structure of which is illustrated in Figure 8. Dimensions of the first parts were approximately 30 mm × 7 mm × 1-3 mm. Following a successful consolidation phase, green parts were subjected to Hot Isostatic Pressing (HIP) at Bodycote IMT of London, OH.

Mechanical Properties Assessment: Following this densification step, initial mechanical properties were measured (by standard 3 point bend test) and are reported in Table 2, along with typical properties of nylon and polycarbonate prepared by the SLS process. This data confirms the hypothesis that the intrinsically higher modulus and strength properties of Parmax[®] SRP resins would translate into higher mechanical properties of the SLS processed components when compared to the current materials in use. This is even more remarkable when considering that the bulk density of Parmax[®] SRP resin utilized in these experiments is less than 50% of the conventional SLS materials.

Material	Powder Bulk Density	SLS Properties	
		Tensile Strength	Flexural Modulus
Nylon	0.5-0.6 gm/cm ³	5,200 psi	0.13 Msi
Polycarbonate	0.6 gm/cm ³	3,400 psi	0.15 Msi
Parmax^{®+} 1200	0.25 gm/cm³	~10,000 psi	0.40 Msi

Table 2. Comparison of mechanical properties of Parmax[®] 1200 and other SLS materials

Based on the knowledge base acquired during the first effort iteration, a second set of formulations was produced in an attempt to improve on the sintering characteristics observed during the initial trials. These included a structurally modified component, Parmax[®] 1215-373 (Figure 10), and a plasticized formulation to reduce the viscosity (Parmax[®] SRP 1200-366). One of the formulations, Parmax[®] 1200-366, underwent particle reduction via a hammer mill in order to obtain the powder necessary to attempt laser sintering. The second iteration of the sintering trials succeeded in fabricating parts of comparable quality to 1200-367 using Parmax[®] 1215-373, while the plasticized Parmax[®] 1200-366 proved very difficult to feed, owing to the very coarse grain structure resulting from the particle reduction operation. Optimization of the laser sintering conditions was relatively limited owing to the small supply of candidate resins, as well as some machine limitations with Sinterstation 2000 at University of Texas. However, preliminary sintering condition optimization successfully eliminated several variables, thus rendering the next phase optimization effort a much less time intensive task.

Conclusion and Future Work

In summary, this research effort was successful in demonstrating that Parmax[®] SRP resins can be consolidated utilizing the SLS process. Sintered components were tested for mechanical properties and, as expected, far exceed mechanical properties obtainable with conventional SLS polymeric materials, even in their current un-optimized state, thus fulfilling all three of the objectives. Work performed on a structurally modified Parmax[®] 1215-373 also opens up new and exciting possibilities for optimizing the sinterability of Parmax[®] SRP resin even further through judicious chemistry and structure manipulation. This reinforces the promise that these materials hold for Rapid Prototyping applications following the optimization during the next phase of research. Commercial potential of this development will be especially significant in laser sintering of a wide variety of low-volume, high integrity components for many possible commercial and industrial prototype needs, as well as prototyping needs in aerospace, military and tooling areas. The ultimate goal of this project is to produce materials strong enough to be utilized as fully functional prototypes, not only visual design aides, and thus fulfill one of the most vexing needs of the laser sintering community. Parmax[®] SRP materials appear ready to be the materials the rapid prototyping community relies on to achieve these ambitious goals.

⁺ Properties measured after Hot Isostatic Pressing

Recommendations for further work involves continuing focus on optimization of Parmax[®] SRP materials that were initially processed by laser sintering techniques during the current study as well as the optimization of the Laser Sintering processing parameters. Therefore, a dual track approach is recommended:

Optimization of resin molecular architecture and composition (e.g., molecular weight and distribution, melt rheology, additives, co-monomer selection, degree of crystallinity etc.) and powder characteristics (e.g., particle size and distribution, bulk density, etc.) to enable effective sintering with high retention of mechanical properties. This work will be performed under a rigorously designed experimental matrix in order to maximize the efficiency of the research effort.

An optimal set of laser sintering conditions will be established. This will draw on the preparation of initial test coupons fabricated at the University of Texas at Austin during the Phase I effort, and will be performed on statistically based Design-Of-Experiments (DOE) principles. This work will be performed at University of Texas' Laboratory for Free Forming (where the technique was invented) to insure successful Laser Sintering parameter establishment.

References

1. Adams, W.W.; Eby, R.K.; McLemore, D.E.; Editors "The Materials Science and Engineering of Rigid-Rod Polymers," *Mat. Res. Soc. Symp. Proc.* **1989**, Volume 134.
2. Beaman J. J.; Barlow J. W.; Bourell, D. L.; Crawford R. H.; Marcus, H. L.; McAlea, K. P.; *Solid Freeform Fabrication: A new direction in Manufacturing: With research and applications in Thermal Laser Processing.* Kluwer Academic Publishers, **1997**.
3. Konstandakopoulou, F. D.; Gravalos, K. G.; Kallitsis, J. K. *Macromolecules* **1998**, 31, 5264-5271.
4. Nieuwhof, RP; Marelis, A. T. M.; Sudhoter, E. J. R.; Picen, S.J.; de Jeu, W. H. *Macromolecules* **1999**, 32, 1398-1406.
5. Puciarello, R.; Angioletti, C. *J. Polym. Sci.Part B: Polym. Phys.***1999**, 37, 679-689.
6. Kodaira, T.; Endo, M.; Kurachi, M. *Macromol. Chem. Phys.* **1998**, 10, 2329-2339.
7. Kricheldorf, H. R.; Domschke A. *Macromolecules*, **1996**, 29, 1337-1344.
8. Grob, M. C.; Feiring, A. E.; Auman, B. C. *Macromolecules*, **1996**, 29, 7284-7293.
9. Ge, J. J.; Guo, M.; Zhang, A.; Honigfort, P. S.; Mann, I. K.; Wang, S.; Harris, F. W.; Cheng, S. *Macromolecules* **2000**, 33, 3983-3992
10. Lindsay Smith, J. R.; McKeer, L. C.; Taylor, J. M. *J. Chem. Soc.; Perk. Trans. 2* **1989**, 1529-1537.
11. Oberhauser, T. *J. Org. Chem.* **1997**, 62, 4504.
12. Grob, M. C.; Feiring, A. E.; Auman, B. C. *Macromolecules*, **1996**, 29, 7284-7293.
13. Percec, V., Zhao, M., Bae, J. Hill, D. *Macromolecules*, **1996**, 29, 3727-3735.
14. Watson, D.A., *Process Optimization for Selective Laser Sintering Through the Use of Design Rules and Constraints*, Master's Thesis, The University of Texas at Austin, **1999**
15. Sutherland, J.W., DeVor, R.E., Chang, T., *Statistical Quality Design and Control*, Prentice-Hall, Inc, **1992**
16. Montgomery, D.C., *Design and Analysis of Experiments*, John Wiley and Sons, **1991**