A FEASIBILITY STUDY OF A RAPID PROTOTYPING TECHNOLOGY BASED ON A PHOTOPOLYMER

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Abstract. Rapid Prototyping (RP) is a layer manufacturing process which is based on adding material in successive flat layers. In this process, a 3D CAD model is used directly to generate all information required for the part building. Among the various methods of adding layers, there are technologies that process photopolymeric materials, using an ultraviolet (UV) light to perform a photopolymerization or photocure process. Currently in Brazil, it is possible to find only RP processes developed by foreign companies and this motivates the development of national technologies. This work presents some initial studies carried out to allow a deposition and a photopolymerization of a polymer aiming the development of a RP technology. A photopolymer has been formulated and a RP apparatus has been assembled to test the main idea. With this prototype, some initial studies to analyze the functional viability of the process have been carried out. This work presents the development so far and some initial results. The first results are promising but they point to the requirement of further and deeper studies to analyze the process feasibility.

Keywords: Rapid Prototyping, photopolymerization, layer manufacturing

1. INTRODUCTION

Some manufacturing technologies have been developed with the objective to reduce the product development process. Rapid Prototyping (RP) is one of these manufacturing processes, which is also known as a layer manufacturing process (Beaman et al. 1997, Kai et al. 2003, Volpato, 2007). RP is based on manufacturing parts by adding material in flat layers. In this process, a 3D CAD model is used directly to generate all information for the part building. Among the various methods of adding material, there are technologies that use a photopolymerization or a photocure process to obtain a solid polymer, also known as photopolymer. Some examples of these commercial processes are Stereolithography (SL) and the InkJet Print (IJP), whose the main process parameters to be controlled, in both of cases, are related to the cure of polymeric material by ultraviolet (UV) light.

Currently in Brazil, it is possible to find only RP processes developed by foreign companies and this, by itself, motivates the development of national technologies (Volpato, 2007).

In order to work on that demand, the Prototyping and Tooling Group (NUFER), from UTFPR, has started a general research project in the area aiming the development of a RP technology. The project comprises basically two parts, involving software and hardware development. The project started with the development of a Rapid Prototyping Process Planning system, called RP3 (Volpato et al. 2005, Volpato et al. 2007, Volpato et al. 2008). This system is responsible for the first stage of the whole process, which is to slice the 3D CAD model, to obtain all 2D contours of the layers and to plan the material processing (scanning or depositing) strategies.

The purpose of this work is to present some initial studies carried out to implement the hardware part of the technology. The RP principle analyzed was the deposition of a photopolymer followed by a photopolymerization process. A photopolymer has been formulated and a RP apparatus has been assembled to test the main idea. The apparatus has a table with a Computer Numeric Control (CNC) for the X, Y and Z axes, a deposition head, which is able to produce a continuous filament of the material, and a UV light to activate the curing. With this apparatus, some initial studies with the objective to analyze the functional viability of the process have been carried out.

2. BACKGROUND

2.1. Photopolymerization process

Similar to other polymers, photopolymers are macromolecules built up by linking together large numbers of much smaller molecules. The difference is that the linking process is initiated by light absorption (Callister, 2003; Odian, 2004). This process is also named as photoinitiated polymerization.
Photocuring systems usually involve some basic compounds, each are: a) monomers (15-60Wt.%); b) photoinitiator (1-3Wt.%); c) co-initiator (1.6-3.2Wt.%); d) oligomers (25-90Wt.%) and e) additives (1-50Wt.%) (Rodrigues and Neumann, 2003; Sartomer, 2004). Each formulation of these compounds will yield material with different properties.

The photopolymerization is a type of reaction which is either classified as chain or addition polymerization. The chain polymerization is classified in three types, based on the reaction mechanism: a) Radical chain photopolymerization; b) Ionic chain photopolymerization and c) Ring-opening photopolymerization (Brandrup et al., 1999; Matyjaszewski and Davis, 2002; Fouassier, J.P. et al., 2003; Odian, 2004; Kricheldorf et al., 2005).

One important parameter in the process is the polymerization rate, i.e. how fast the polymerization occurs under UV exposure. This information is essential to select a suitable material to be applied in Rapid Prototyping. One experimental method to define polymerization rate involves separation and isolation of the polymer. It is called gravimetry and consists in finding the conversion degree, i.e. the amount of the monomer converted in polymer from an aliquot after exposition to UV (Mukherjee, 1978; Matyjaszewski and Davis, 2002; Odian, 2004; Sperling, 2006). After the irradiation of the aliquot during a specific time, the polymer is typically isolated by precipitation, which is achieved by the addition of a non-solvent into the system. The amount of polymer is found by weighting it after drying. Although this is one of the simplest methods, the technique is time-consuming and requires great care to obtain accurate results (Rodrigues and Neumann, 2003; Odian, 2004; Sperling, 2006).

2.2. Some RP technologies

As mentioned before, there are many RP processes in the market. Amongst them, are related to this work: SL, IJP and Fused Deposition Modeling (FDM). The first two are based on the photopolymerization process. The latter deposits a continuous extruded thermoplastic filament. Many more important processes can be found in the literature and are not presented here for practical purposes (Beaman et al. 1997, Kai et al. 2003).

2.2.1. Stereolithography (SL)

The SL process is illustrated in Fig. 1. The process uses a liquid photopolymer and an UV laser to scan the top surface of the resin, which solidifies due to a curing process, known as photopolymerization process. The liquid resin is in a vat inside the equipment where there is a platform which will hold the part. The build platform lowers into the vat of resin after each layer has been processed. The resin is leveled by a blade which sweeps over the surface. The UV laser beam is controlled by a scanning system. The first solidified layer is comprised entirely of support structures, forming a bond with the build platform. Support structures are also required for undercuts and overhangs. The process is repeated until the part is completed.

The layer thickness varies from 0.025-0.5mm and the laser beam diameter can vary from 0.075 to 0.25mm. The commonly used materials are acrylic and epoxy based polymers (Volpato, 2007).

After removing the part from the equipment, it is necessary some post-processing stages in order to remover all support structures and to post-cure completely the resin in an oven. The post-cure is required because the polymer is 80 to 95% polymerized during processing (Kreith, 1999; Barton and Fulton, 2000; Volpato, 2007). No voids are observed inside the material, because any trapped resin will be post-cured.

![Figure 1. Schematic of SL process (Volpato, 2007)](image)

2.2.2. InkJet Print (IJP)

The IJP idea is depicted schematically in Fig. 2. The technologies based on this principle work with inkjet heads, which build the layers by depositing tiny drops of material. This material is then photo polymerized by a UV light,
instead of a laser. The materials available are similar to the SL process. Some of the commercial technologies available are the Polyjet, from Objet Geometries Ltd. (Israel), and the InVision, from 3D Systems (USA) (Kreith, 2005; Volpato, 2007, Kai et al. 2003).

These technologies also require support structures, but they use a different material (cheaper one) from the part model. The Polyjet technology uses a water jet to remove the support material after the part is removed from the machine. Because of the deposition method, layer thickness as thin as 16 µm is possible. No post-cure is required in this process and no voids are observed inside the material.

2.2.3. Fused Deposition Modeling (FDM)

The FDM technology was developed by Stratasys Inc. (USA). It uses two materials, one material for the part being built and one for the support structure. These two materials are supplied as filaments in coils or cartridges (Fig. 3). Each plastic filament is unwound from the coil and supplied to a specific extrusion nozzle. The two nozzles are heated to melt the plastics and are mounted in an extrusion head which moved in the X and Y directions. The part nozzle deposits a thin bead of extruded plastic to form each layer over a table. The table moves incrementally in the vertical direction (Z), allowing the addition of new layers. The plastic hardens immediately after being extruded from the nozzle (due to the temperature decreasing) and bonds to the layer below. The entire system is contained within a chamber which is held at a controlled temperature, much lower than the nozzles. The created support structures are later removed either by breaking them away from the object or, more recently, by using a water-soluble support material, being washed away. Amongst the materials available for the process are acrylonitrile butadiene styrene (ABS), and more recently polycarbonate (PC) and poly(phenylsulfone) (Kai et al. 2003; Volpato, 2007).

The material obtained in this process has some particular characteristics. It has internal voids which appear within a layer (between the deposited filaments) and between layers. The material has a high anisotropy, due to the layer additions principle and also due to filament orientation within the layers. Additionally, the surface roughness is much higher when compared to the SL and IJP technologies, due to the filament dimension.

Figure 2. Schematic of IJP process (Volpato, 2007)

Figure 3. Schematic of FDM process from Stratasys Inc. (Volpato, 2007)
3. PROPOSED RP TECHNOLOGY

As mentioned before, the proposed process is based on adding a photopolymer layer by layer and using a UV light to carry out the photopolymerization process. The photopolymer is laid by an extrusion head which is able to produce a continuous filament of the material. Figure 4 shows schematically the RP principle and the extrusion system. In contrast to current commercial technologies based on photopolymer, this process is not based on laser or inkjet technologies. The deposition principle is more similar to the FDM process. However, it differs from the FDM by using a liquid polymer instead of solid filament and a photopolymer instead of thermoplastic material.

To verify the feasibility of the proposed process, an apparatus has been assembled. In this apparatus, a CNC controls the step motors for the X, Y and Z axes of a table, and also the extrusion head. The extrusion head is basically a syringe with a step motor controlling the syringe knob. The fluid photopolymer is deposited through a metal nozzle (syringe needle). The internal diameter of the nozzle is 0.45mm.

Only the model material extrusion head has been implemented so far. A support system will be developed in the future.

A 9W UV lamp is used to activate the curing (model PL-S 9W 10/2P UNP). The wave length of this lamp is within the UVA spectrum, i.e. from 350 to 400nm, which is not harmful (Philips, 2008). This lamp was defined based on the experimental results with the formulated photopolymer (section 4.1). The lamp is kept on during the extrusion of the material.

![Figure 4. Schematic representation of the RP technology proposed (a) and the extrusion system (b)](image)

4. EXPERIMENTAL STUDIES

In order to develop the process, checking its functional feasibility, first it was necessary to formulate a photopolymer adequate to the proposed RP process and then the filament behavior was analyzed. This section presents these studies.

4.1. Material studies

One of the main areas which support the RP technology is related to material development. For the desired application, a new material with conversion rate higher than 50% in 3s is required (Barton and Fulton, 2000).

In order to develop this new material, it was tested several formulations (Cunico, 2009). However, in this study, only two formulations tested are presented. The first one, named formulation 1, was composed of: methyl methacrylate (MMA: monomer) - 1ml; CN501 9 (oligomer) - 1ml and Irgacure 651 (photoinitiator) 4Wt.%. The second one, named formulation 2, was composed of: MMA - 0.5ml; CN501 - 1ml; Irgacure 184 (photoinitiator) 4Wt.% and benzophenone (co–initiator) 4Wt.%. More details about these materials can be found in Cunico (2009).

The polymerization rate was determined by the gravimetry method. To perform a polymerization analysis close to the RP process condition, a glass mould shown in Fig. 5 was used. In this mould, a thin layer of 0.12mm of the material to be tested was obtained. It is then exposed to the UV light for a specific amount of time (1, 2, 3, 5, 10s and so on). After the irradiation, the polymer was precipitated by the addition of a non-solvent ethanol (5ml). An electronic scale of 10mg accuracy was used to measure the compounds and the polymer amount after UV irradiation. In this study it was used the lamp PL-S 9W 10/2P UNP as source of UV light, which provides a wave length between 350 and 400nm, with
9W power. This wavelength is suitable for the photoinitiator processes used in the compounds (Irgacure 184 and 651) (Cunico, 2009). The distance between the source of UV light and glass mould which was 20mm.

### Figure 5. Glass mould scheme used to define material polymerization rate

#### 4.2. Process studies

The preliminary study carried out so far aimed to analyze the filament appearance and behavior, either individually and its interaction in a raster deposition strategy. The material used in the following experiments was the formulation 2. The RP apparatus was used for the following tests.

#### 4.2.1. Filament characterization

The main process parameters are: layer thickness (distance between the table surface and the nozzle tip), filament diameter, deposition head speed (X and Y) and extrusion speed (Z). Many combinations of these parameters have been analyzed by Cunico (2009). In this work, it is reported only the study of the variation of bead width according to the deposition head speed. Figure 6 shows the deposition trajectory planned to identify the bead width. The bead width was measured in three different positions (1, 2 and 3) with the aid of an optical microscopic, using a 50x scale.

The following parameters were used as constant: layer thickness: 0.15 mm; nozzle diameter: 0.45 mm and extrusion speed: 0.00075 mm/s. The deposition head speed was set to 40, 60 and 90 mm/min. Three specimens were then produced, one for each deposition head speed.

#### Figure 6. Scheme of the deposition trajectory for the filament study

#### 4.2.2. Filament interaction (interface)

This experiment was designed to identify interaction between consecutive filaments in a raster deposition strategy as shown in Fig. 7. The distance between the beads centre was set to 1.33, 1.40, 1.47 and 1.54 mm. The idea is to investigate what happens when a filament is deposited close to or touching a previously deposited one. This behavior is important when filling an area in a layer.

With the intention of highlight the interaction between the beads, it was used higher values of the deposition head speed and the extrusion speed. The following parameters were used in the test: layer thickness: 0.15 mm; nozzle
diameter: 0.45 mm, extrusion speed: 0.00126 mm/s and deposition head speed: 120 mm/min. Two specimens were produced with the same set of parameters and the results were analyzed by visual inspection.

5. EXPERIMENTAL RESULTS

The following sections present the results obtained.

5.1. Material studies – conversion rate

As an example of the material obtained during this study, Fig. 8 shows a polymerized sample of the formulation 1 (91% conversion) after 15s UV exposure and after the addition of the non-solvent ethanol (5ml).

Figure 7. Scheme of the deposition trajectory with 4 different distances between filaments

Figure 8. Example of the formulation 1 with 91% polymer conversion after 15s UV exposure and after the addition of the non-solvent ethanol (5ml)

Figure 9 and 10 show the polymerization curves (conversion rate) for the tested materials. As can be seen, for the formulation 1, after 3s the material reaches 44.44% of polymerization and after 5s, 66.67%. However, for the formulation 2, after 2s the material already reached 75% of polymerization and after 5s, 80%. Then, the formulation 2 had a better response in terms of conversion rate for the experimental used conditions. This result can be considered suitable for a RP technology because the process is fast. Additionally, as it does not reach 100% polymerization in a relative short time, it can allow a good interaction (merging) of the filament with its neighbors before the process is complete. This would contribute to reduce the incidence of voids inside the layer and the part. However, because of that, a post-cure of the part might be necessary after the process.
Figure 9. Polymer conversion rate curve for the formulation 1: MMA (1ml), CN501 (1ml) and Irgacure 651 4Wt.%

Figure 10. Polymer conversion rate curve for the formulation 2: MMA (0.5ml); CN501 (1ml); Irgacure 184 4Wt.% and Benzophenone 4Wt.%

5.2. Filament characterization results

Figure 11 shows a picture of the material deposited to study the filament characterization. The material was deposited as planned and it kept well the filament shape from the start to the end. In Fig. 12 it is possible to observe the top view of the shape of some filaments obtained by optical microscope images.

Figure 11. Example of the deposited trajectory (60mm/min)
The result for the bead widths according to the deposition head speed is presented in Fig. 13. The curve shows that, as expected, as the speed increases the bead width decreases. For the deposition head speed of 90mm/min, the bead width was close to the nozzle diameter. The thinner the bead width the better for the RP technology, because it would be more adequate to produce small features and corners.

One point to be observed in this chart is that, as the deposition head speed increases the standard deviation also increases. This can be explained by the decreasing of the extruding system control sensitivity, as the deposition head speed increases. This shows that this control system needs to be improved in order to improve process productivity.

5.3. Filament interaction results

The two specimen’s pictures of this experiment are presented in Fig. 14. In these images, it is possible to identify points where the filament is separated, at the beginning of the raster, points of indetermination, at the middle, and points of complete union between them, at the end of the raster. For the distance between centres lower than 0.40mm there was filament union. For values higher than 0.52mm there was filament separation and for values between 0.52 and 0.4mm, it was identified indetermination in the filament interaction. It was observed that, when there was union between filaments, the results show a complete integration between them. No division line was noticeable in the optical microscope (50x zoom).

As can be seen in the pictures, the bead widths varied from the beginning to the end of the raster. This behavior is thought to be associated with the higher deposition speeds used for this experiment, considering what was observed in the previous experiment (increasing in the standard deviation). Another point is that, it is clear in the two pictures an over deposition (excess) of the material at the beginning of the raster. In addition, it is possible to note an increasing in the bead width during the changing in the raster direction. As these problems were not noticeable at lower deposition head speed and extrusion speed, it seems that the apparatus dynamic response needs to be improved.
6. DISCUSSION AND CONCLUSIONS

As the RP technologies are only provided by foreign companies, it was highlighted the need to develop a national technology. This work presents some initial results of a research in this area, which is in its early stage.

The formulated material used in this work was adequate for this initial intended application. It was observed that after 2s it reached 75% of polymerization degree, therefore, responding quickly to the UV light exposure. It is important to mention though that this formulated material was not extensively studied and consequently it was not optimized to the RP application. Further studies, specifically about the material properties, are necessary and will be done in the near future.

From the filament behavior study, it was observed that it is possible to obtain a well behaved filament with the proposed material and manufacturing method. It was also identified a complete union (integration) between successive filaments when the centre distance was lower than 0.4mm.

The proposed technology tends to be cheaper than the SL one, as it applies UV lamp, instead of an UV laser. Because a complete filaments fusion is possible, it is expected that no voids will be produced in the part, as observed in the FDM process. Therefore, there will be a tendency of building parts with higher homogeneity than the FDM process. However, the process speed seems not very high, similar to the FDM process. In addition, when it was tried to speed up it, by using higher deposition rates, the apparatus response was not appropriated, i.e. some deposition problems appeared (ex. higher standard deviation for the bead width, over deposition of material at the beginning of the process and changing in the bead width when changing the direction of deposition).

In general, some positive signs related to the development of a national RP technology have been verified. It is possible to infer that the process can be feasible. However, there are still a lot of barriers to be overcome. Further studies are required, mainly related to material development, a better process understanding (process parameters interaction), and a better machine control. All these components need to progress together in order to complete the development of this new technology.

7. REFERENCES

8. RESPONSIBILITY NOTICE

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