

DEVELOPPING OF NEW MATERIALS FOR RAPID PROTOTYPING APPLICATIONS

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Abstract. *In actually days, product developing time is progressively reduced. Therefore, application of rapid prototyping technologies are increasing its participation. In face of that, researching areas concerned is important to improve national industry. One of these areas is related to develop material for rapid prototyping applications, which is the main goal of this work, and it's also shown as the most important area concerned in rapid prototyping subjects. This paper presents a short review of photopolymerisation and its processes besides it exposes criteria that bound the use of materials in rapid prototyping applications. Another subject that is shown into this work is the research of suitable formulations of material which is based in acrylates. Whereas there is no national supplier of rapid prototyping material, the relevancy of this work was shown, by the fact that the response of this research presents two suitable formulations were found among four that were put on test.*

Keywords: *Rapid prototyping; Material Developping; Photopolymerization*

1 INTRODUCTION

As solution for market exigencies, the development product process (PDP), which is placed between the market and the enterprise, identifies opportunities, customer demands, technological possibilities, designing new products which take care of market expectations in less time. (ROZENFELD *et al.*, 2006) As consequence of the PDP changes, new manufacturing processes had to be developed to support these changes. (KOSHAL, 1993; LEONDES, 2001)

One of these new manufacturing processes is the rapid prototyping (RP) technology which aids the PDP to create prototypes (KOSHAL, 1993; LEONDES, 2001) reducing both product development time in the project phase and rework, consequently, releasing new reliable products earlier.(FOGGIATTO *et al.*, 2004)

Purpose

In front of a national demand (SOUZA *et al.*, 2004) the main goal of this research is to propose a new material for RP applications in order to help the development of a Brazilian Rapid Prototyping technology. Otherwise, the review contained in this work will provide essential informations to aide RP researches.

The informations this review describe are separated in five topics which relate both the essential characteristics of photopolymeric materials and the compounds involved in the polymerization of those materials, the photopolymerization processes, the controlling parameters, properties and application.

2 BACKGROUND

2.1 RAPID PROTOTYPING

These techniques basically consist of generating layers from 3D computer model by deposition of material layer-by-layer. These processes differ of other conventional processes which are based on removing of material. (SOUZA *et al.*, 2004; VANDRESEN, 2004)

In Figure 1 is represented the basic phases of RP, where the layers is computationally generated from 3D computer model to build layer-by-layer each layer upon which has previously done. (SOUZA *et al.*, 2004; VANDRESEN, 2004; GONÇALVES *et al.*, 2007)

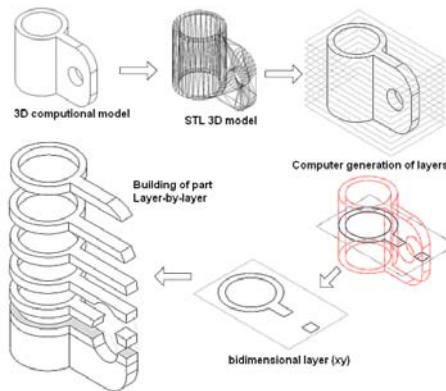


Figure 1 - Representation of phases of RP (VANDRESEN, 2004)

2.2 Stereolithography

Despite the variety of RP based on photopolymeric material, the main technology is stereolithography (SLA or SL) which build each layer by laser curing of resin (KIETZMAN, 1999; BARTON e FULTON, 2000; KARALEKAS, 2003; GONÇALVES *et al.*, 2007). In this technology there is a laser beam which moves in x and y axes to cure the material inside the machine, drawing the layer in according with the silhouette generated from computer. Forward finish each layer a platform move down to laser beam build the next layer until the finishing of part, as such as represented in Figure 2. (BEAL *et al.*, 2004; VANDRESEN, 2004; VOLPATO, 2007).

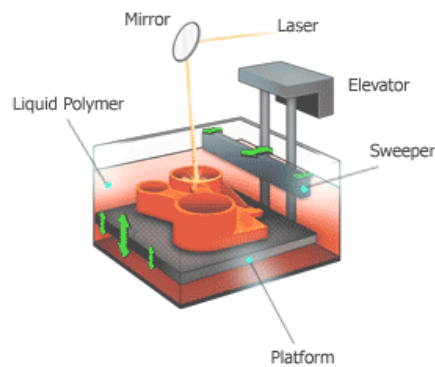


Figure 2 - Scheme of building part by SLA (KELYNIAM, 2008)

2.3 Inkjet Print

Another RP technology is the Inkjet print, which is commercially known either as *Polyjet*, a brand of the Israeli company *Objet Geometries Ltd.*, or *InVision*, brand of *3D Systems*.

That technology works with a inkjet which builds the layer in X and Y axis with a SLA similar material. After finish each layer, the material is photopolymerized by a UV light, Figure 3.(VANDRESEN, 2004; KREITH, 2005; VOLPATO, 2007)

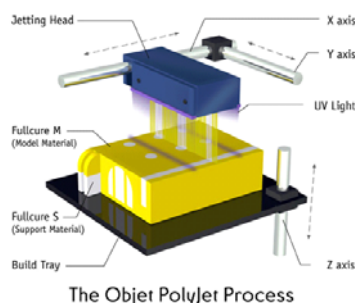


Figure 3 - Scheme of building part by Inkjet print (VOLPATO, 2007)

2.4 PHOTOPOLYMERIZATION

As such as another polymer, photopolymers are macromolecules built up by the linking together of large numbers of much smaller molecules, which linking is initiated by light absorption. (CALLISTER, 2003; ODIAN, 2004)

In this chapter is shown the characteristics of the photopolymeric materials, as such as the compound involved in their polymerization. Beyond of that description is cited some enterprises which manufacture those compounds.

Photocuring systems usually involve some basic compounds which will change the properties of material in each compounds formulation. These compounds are: a) monomers (15-60% on weight); b) photoinitiator (1-3% on weight); c) co-initiator (1.6-3.2%); d) oligomers (25-90% on weight); e) additives (1-50% on weight). (RODRIGUES e NEUMANN, 2003; SARTOMER, 2004)

2.4.1 Monomers

Monomer is a compound whose fundamental molecule which is called *mer* links with others *mers* to build a macromolecule. One monomer can have their *mers* linked by different sort of polymerizations. (BRANDRUP *et al.*, 1999; CALLISTER, 2003; ODIAN, 2004; SPERLING, 2006) For example, methyl methacrylate monomer (MMA) is known to be photopolymerized by: a) Radical chain photopolymerization; b) Ionic chain photopolymerization; (ANDRZEJEWSKA, 2001; FOUASSIER, J. P. *et al.*, 2003; ODIAN, 2004; KRICHELDORF *et al.*, 2005)

One monomer is basically suitable for being photopolymerized when this one has basically got either carbon-carbon or carbon-oxygen double-bond functional group within its composition. However, there is other functional groups that also are suitable for this application, as epoxies functional group which is widely used in stereolithography, an rapid prototyping technology. These three functional groups cited above are represented in Figure 4. (BARTON e FULTON, 2000; ODIAN, 2004)

As the monomer fundamental molecules have short carbon chain, the monomers have low viscosities which make their manipulation be easy. (SARTOMER, 2004)

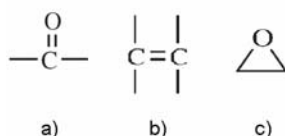


Figure 4 - Suitable functional groups for photocuring, a) carbon oxygen double-bond; b) carbon-carbon double-bond; c) ethylene oxide (epoxy) (ODIAN, 2004)

2.4.2 Oligomers

Following any polymerization process, the molecules length become bigger as well as the solution viscosity. (ODIAN, 2004; SARTOMER, 2004) As the solution cannot be known as monomer, at this process point, this one is called oligomer either whose units rate is placed between two and twenty *mers* or the molecular weight exceed 8000. (JASTY, 1999) (SARTOMER, 2004)

2.4.3 Photoinitiators

The growing of either the monomer or oligomer depends on the initiator referent to which specific polymerization, Section 2.4.5. When the polymerization is started by either ultraviolet light or visible light (250-400 nm) this initiator is called photoinitiator. (JASTY, 1999; MATYJASZEWSKI e DAVIS, 2002; CIBA, 2003; RODRIGUES e NEUMANN, 2003; ODIAN, 2004)

The photoinitiators based on radicals formation are usually classified as Type I and Type II initiators according to the mechanism by which primary radicals are generated. The Type I decompose via a direct unimolecular photofragmentation process, Figure 5, where the carbon-carbon bond is cloven. (JASTY, 1999; MATYJASZEWSKI e DAVIS, 2002; CIBA, 2003; RODRIGUES e NEUMANN, 2003; ODIAN, 2004; KRICHELDORF *et al.*, 2005)

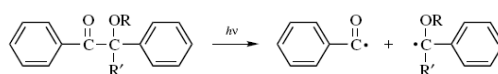


Figure 5 - Example of Type I photoinitiator decomposing (MATYJASZEWSKI e DAVIS, 2002)

The Type II undergo a bimolecular reaction where a coinitiator interacts with the initiator, Figure 6, which normally generates radicals by: a) hydrogen abstraction (redox); b) electron transfer. An other molecule that can interact with the initiator is the photosensitizer. However, it keeps itself unmodified. (JASTY, 1999; MATYJASZEWSKI e DAVIS, 2002; YURTERI *et al.*, 2002; RODRIGUES e NEUMANN, 2003; ODIAN, 2004; KRICHELDORF *et al.*, 2005)

There is another type of photoinitiator that is neither Type I nor Type II, it is classified ionic photoinitiator by the sort of polymerization, Ionic chain polymerization. Normally the ionic initiation concerns inorganic compounds as consequence of an electrodonating substituent. In this case the ArI or ArS ArI or ArS bond yields a radical-cation which reacts with HY to yield an initiator-coinitiator complex that acts as a proton donor to initiate the cationic polymerization.(ANDRZEJEWSKA, 2001; ARCHER, 2001; RODRIGUES e NEUMANN, 2003; ODIAN, 2004; KABATC e PACZKOWSKI, 2006)

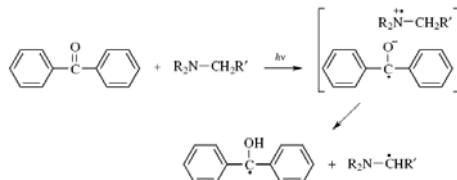


Figure 6 - Example of Type II photoinitiator radicalsgeneration by Hydrogen abstraction (MATYJASZEWSKI e DAVIS, 2002)

2.4.4 Co-Initiators

Coinitiator is a compound which interacts with a Type II photoinitiator. As the aromatic ketones are the photoinitiators more useful in commercial practice, the coinitiators most commonly employed for are amines. These amines are shown to be the rate of polymerization that increases in order primary < secondary < tertiary. Those amines can also be located on the aromatic ketone themselves, Figure 7.(JASTY, 1999; ANDRZEJEWSKA, 2001; MATYJASZEWSKI e DAVIS, 2002; ODIAN, 2004; KRICHELDORF *et al.*, 2005)

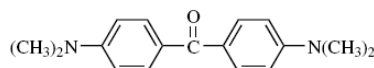


Figure 7 - Representation of a tertiary amine located in aromatic ketones, coinitiator Benzophenone/N,N-dimethyl aniline (MATYJASZEWSKI e DAVIS, 2002)

Others coinitiators that also support Type II photoinitiator activation are alcohols, amides, amino acids and ethers. (ODIAN, 2004)

For ionic photoinitiator, there is also a fundamental compound to cite, electric-donor, as onium salt. (MALMSTRÖM *et al.*, 1995; YURTERI *et al.*, 2002; KABATC e PACZKOWSKI, 2006) This compound makes conditions to the ionic photoinitiator build their ions(cation or anion). (JASTY, 1999; CIBA, 2003; ODIAN, 2004)

In spite of thermal-curing and photo-curing processing similarities, the specific advantages are known to be: a) very fast polymerization; b) high molecular weight; c) almost 100% conversion; d) solvent-free formulation; e) room temperature treatment; f) low energy requirements. However, photo-curing is limited to low penetration of light energy through a thickness of material.(BRANDRUP *et al.*, 1999; MATYJASZEWSKI e DAVIS, 2002; RODRIGUES e NEUMANN, 2003; ODIAN, 2004)

2.4.5 Phases and Sorts of Cure

The photopolymerization is a type of polymerization which is either classified as chain or addition polymerization. This polymerization is divided in three types of polymerization which are detailed in this Chapter. These types are classified by their polymerization mechanism as: a) Radical chain photopolymerization; b) Ionic chain photopolymerization.(BRANDRUP *et al.*, 1999; JASTY, 1999; MATYJASZEWSKI e DAVIS, 2002; FOUASSIER, J.P. *et al.*, 2003; ODIAN, 2004; KRICHELDORF *et al.*, 2005)

This Chapter will also contemplate another kind of polymerization called *Ring opening polymerization*, the epoxies functional group polymerization that can be photoinitiated as such as any other photopolymeric material.(MATYJASZEWSKI e DAVIS, 2002; ODIAN, 2004)

Radical Polymerization

This sort of chain polymerization is based on reactive species produced either by Type I or Type II photoinitiation processing which will progressively break the carbon carbon double-bond of each molecule to link each one with other, how Figure 8 is shown in. This processing is divided in four kinetic phases: 1) initiation, where the reactive species are created; 2) propagation, where the *mers* link each with other; 3) transfer chain, where the *mers are added to a chain*(above 2 *mers linked*) ; 4) termination, where the reactive species are inhibited.(BRANDRUP *et al.*, 1999; ANDRZEJEWSKA, 2001; MATYJASZEWSKI e DAVIS, 2002; FOUASSIER, J.P. *et al.*, 2003; ODIAN, 2004; KRICHELDORF *et al.*, 2005)

Both of these sorts of photoinitiation processing were described previously, where cleavage processing case, the photoinitiator (PI) interacts with one molecule to generate reactive species (R_1 and R_2), whereas hydrogen abstraction the photoinitiator interact with two molecules, co-initiator(AH or S) and photoinitiator (PI). However, only Electron transfer is an Ionic chain photopolymerization processing. (BRANDRUP et al., 1999; ANDRZEJEWSKA, 2001; MATYJASZEWSKI e DAVIS, 2002; FOUASSIER, J.P. et al., 2003; ODIAN, 2004; KRICHELDORF et al., 2005)

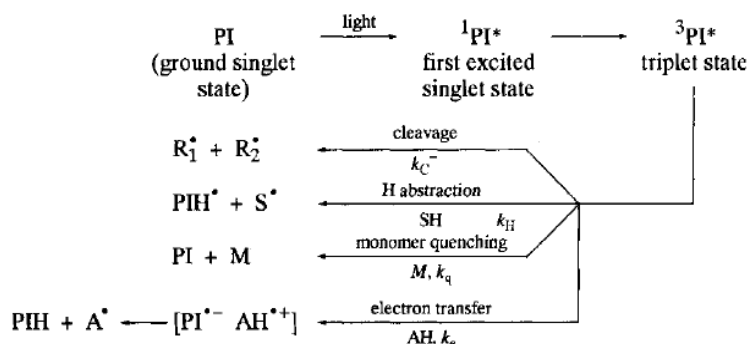


Figure 8 - Diagram of photoinitiation phase, where PI means photoinitiator; R, radicals; M, monomers; AH, an amine. (BRANDRUP et al., 1999)

2.4.6 Method of measuring polymerization rate

One of the experimental determination of polymerization rate is gravimetry which consists in finding the rate of the monomer converted in polymer from a aliquot after polymerization initiation, which is determined in this paper by exposition of monomer in UV. After the aliquot be irradiated during an specific time, the polymer is typically isolated by precipitation by addition of a non-solvent into the system. The rate of polymer is found after drying by weighting. Although this method is one of the most simple methods of determination of polymerization rate the technique is very time-consuming and requires great care to obtain accurate results. (MUKHERJEE, 1978; MATYJASZEWSKI e DAVIS, 2002; RODRIGUES e NEUMANN, 2003; ODIAN, 2004; SPERLING, 2006)

3 METHODS AND MATERIAL

In order to identify a suitable material for rapid prototyping applications, it was studied three photopolymeric materials, which are based on acrylate and have specific formulation.

Intending to measure polymerization rate, it was used the method gravimetry. In addition to that, it was built a mould in order to control layer thin and material volume. This mould is shown in Figure 9, where the dimensions of this one can be seen.

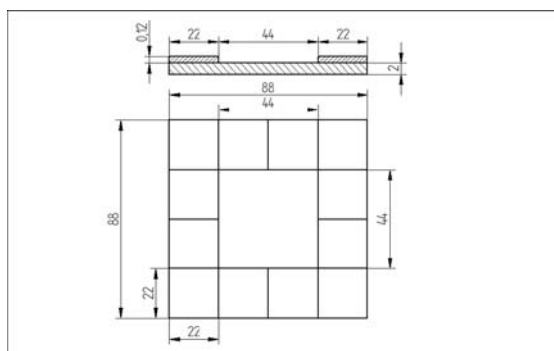


Figure 9 - Mould used to control material volume and layer thin

As source of UV radiation it was used the lamp PL-S 9W 10/2P UNP which provides λ between 350 and 400 nm with power of 9 W.

The compounds of materials formulation studied in this work can be regarded in Table 1, which shows proportion of monomer, oligomer and initiation used in each formulation.

Table 1 - Relation of compounds of material formulation

Formulation	Monomer/ oligomer	Initiator
1	Methyl Methacrylate (1ml) / CN501 (1ml)	Irgacure 184 (2 % weight)
2	Methyl Methacrylate (1ml) / CN501 (1ml)	Irgacure 651 (4 % weight)
3	Methyl Methacrylate (0.5ml) / CN501 (1ml)	Irgacure 184 (4 % weight)/ Darocur BP (4% weight)

4 DISCUSSION AND RESULTS

As result of the studies of the materials developed, it was found conversion curves for each material formulation. In these curves, it is possible to identify the polymerisation rate, defining a parameter for selecting a suitable material for rapid prototyping applications.

In according with Barton (2000), a material will be suitable to be used in rapid prototyping applications if it have at least 50% its volume polymerized in 4 seconds from the initiation of the polymerization.

Figure 10 shows a photo of two phases of material after exposed in UV and gravimetric proceeds carbon tetrachloride.

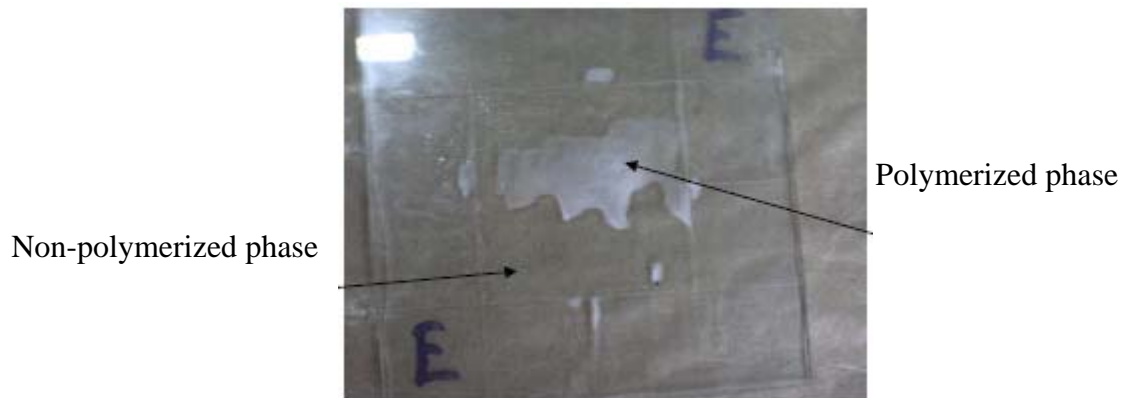


Figure 10 - Photo of two phases of material after UV exposition and gravimetric proceeds

In first formulation, as it was shown in Figure 11, it was obtained a polymerization of 91% in 14 seconds. Whereas 53% of this material has been polymerized in 5 seconds, this one was not found suitable for RP even though its results have been goods in comparison with traditional process.

The curve shown in this figure has a behavior exponential, decreasing the polymerization velocity in high values of conversion. However, this is typical a characteristic of photopolymers.

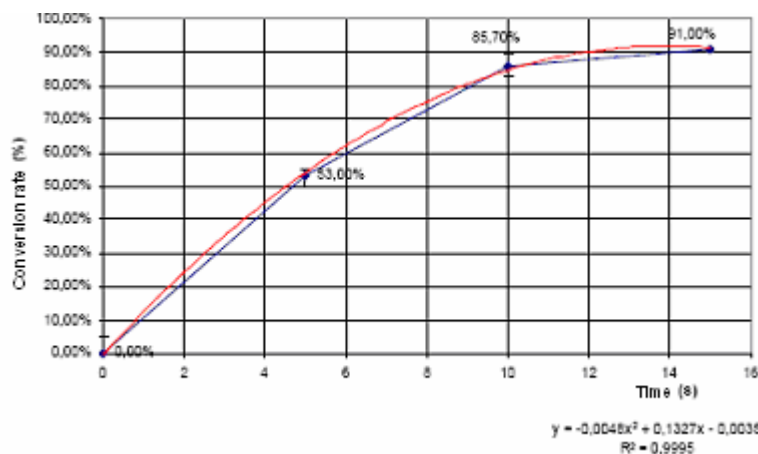


Figure 11 - Conversion curve of material formulation 1

In Figure 12, it was shown the conversion curve of the second material formulation. Despite the changing of both the type and proportion of photoinitiator in formulation, the final value of conversion curve was lower than the first

formulation. In addition to that, its behavior was regular, having an exponential conversion curve. Nevertheless, this second formulation has reacted faster than the first one, having a polymerization rate higher than 50% in 4 seconds. It makes this one suitable to RP applications.

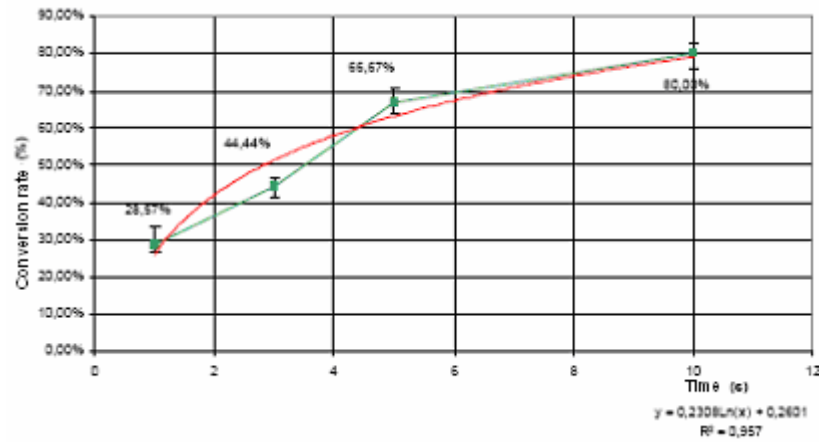


Figure 12 - Conversion curve of material formulation 2

In the last material studied, have been added another photoinitiator with the purpose of accelerate the process. In fact, it can be seen in Figure 13, where the conversion rate in 2 seconds was 75%. As consequence of this process acceleration, this material was found to be more suitable than the others studied.

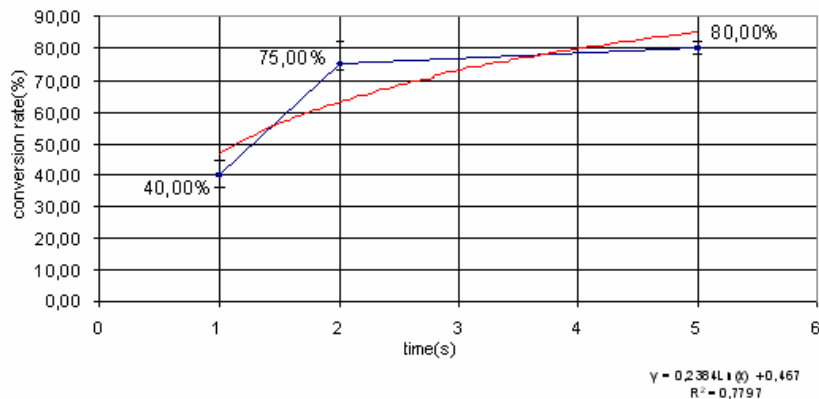


Figure 13 - Conversion curve of material formulation 3

As the development of material had already found a suitable one, which had 75% of polymerization rate in 2 seconds, it is needed to create an adequate equipment to follow the development of national RP.

5 Conclusions

In face of the result of experiment related to photopolymeric materials, the viability of this application was found. Its was possible to identify two suitable material for applying in RP, where the better one has had conversion rate of 75% in 2 seconds.

Through this work, it has been able to verify a positive indicative related to the development of a rapid prototyping national technology. However, there are yet lots of barrier to overcome, such as the continually research of material, development of electronic control and software interface and process characterization, which have to follow together to complete the development of this new rapid prototyping technology.

Otherwise, this paper could also compile the main information related to radical photopolymerization and its mechanism, being able to be used as database for another research related to either this work subject or any other one.

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