Modeling and Simulation to Materials Development for Rapid Prototyping Process

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Many applications in the field of rapid prototyping require materials with specific characteristics in terms of weight and mechanical resistance which are difficult to obtain using simple polymeric, ceramic and metallic materials. In such situations, rather than developing a new material, which may or may not have the desired properties for a certain application, it is interesting to use the advantages of different materials to achieve the target. This can be done by incorporating another component in a given pre-existing material, thus obtaining a composite material. In this work, a novel rapid prototyping process, designed thermolithography is presented which needs to use materials with very well specified characteristics. The objective is to fabricate three-dimensional structures using the infrared (IR) laser beam from a carbon dioxide (CO₂) laser. The material to be cured is a sample composed of epoxy resin, diethylene triamine, and silica powder. Via infra-red radiation it is demonstrated the viability of a completely thermal localized curing process. Such resins typically cure, or solidify, when heated to moderately high temperatures and the obtained results show that it was possible to confine the heating in the required material region. This means that the cure process occurs in all three dimensions. A kinetic model was applied to study the curing kinetics and describe the main features of the process, namely diffusion-controlled effects after vitrification and fractional conversion, presenting an excellent agreement with experimental and predicted values. DSC (differential scanning calorimetry) data are also presented as a tool to take decisions in how to identify the material composition and operating conditions.

1. Introduction

Recently, Rapid Prototyping technology (RP) emerged as a step forward in the product cycle, reducing lead times for new products as well as improving design manufacturing and tooling costs (Jacob, 1995). Through Rapid Prototyping, a model is built up by adhering successive thin cross section of the object to be built until the model is complete. Rapid Prototyping consists on a process that starts with a 3D (three-dimension) design model through a CAD. The main objective is to reproduce this design which can be for instance a mechanical piece, an aerospace model or whatever objects useful and reproducible with this technology.
RP is an accuracy and fast method of building (Kodama, 1961). It can embrace great applications such as visible and micro structures. This last one has been developing in a satisfactory velocity and reached some good results. Further all of this, RP is a practical, useful, economical and ecological saver technique.

Presently, there are several Rapid Prototyping systems being used by companies and research centers, each employing a particular technology with its own materials and process. These systems, as shown in Figure 1, include:

- **Stereolithography Apparatus (SLA):** the basic concept is the layer manufacturing in which three dimensional polymer model is formed according to a model created on a CAD system, using an ultraviolet laser emitting radiation to cure a photosensitive resin to build a physical model.

- **Selective Laser Sintering (SLS):** in this process, a thin layer of powder is deposited over a platform to build a physical model, and a high power carbon dioxide (CO₂) laser sinters and traces the shape of each cross section of the model.

- **Fused Deposition Modeling (FDM):** by this technology, thermoplastic filaments are melted by heating and guided by a robotic device (extruder) controlled by a computer, to form the three dimensional object.

- **Laminated Object Manufacturing (LOM):** the laminated system builds three dimensional models by storing thin layers of material (usually paper coated on one side with polyethylene which acts as a heat sensitive adhesive) that are trimmed according to the desired shape, using a CO₂ laser beam operated in conjunction with an x y plotter.

![Figure 1. Rapid Prototyping Systems.](image)
2. Infrared Stereolithography Process

The main advantage of using a laser to cure (solidify) a resin is a highly localized curing. In this work, a different approach to the production of three dimensional models, which can be called Infrared Stereolithography, is presented. A CO₂ laser, emitting in infrared region at a wavelength of 10.6 µm, is used for the selective local heating of the thermosensitive material composed by epoxy resin, diethylenetriamine and silica powder. This process is important because it may provide novel means of manufacturing prototypes for industrial manufacturing (Jardini, 2001).

Figure 2 illustrates an Infrared Stereolithography process composed by a CO₂ laser with a laser beam focused and directed through an optoelectronic system, creating a cured layer. The sample was mounted on an elevator (Z motion) support, within a platform filled with the uncured resin. A computer system is used to carefully control the horizontal position of the sample surface to obtain precise localized cure.

The localized cure is the physical process characterized by a set of chemical reactions that provoke changes on the physical properties of the sample (normally from a liquid onto a solid material) by action of heat, catalyst and cure agents, isolated or in combination, with or without pressure. The localized cure consists on in the solidification, at the right proportion; only in the region of the material is irradiated by the laser beam. The present study is focused on the obtaining of the best values for each process variable, that is, to find out the more suitable process variable set for each operating condition, taking into account the process kinetic knowledge. Usually, this has been neglected and the procedure to find out the suitable operating conditions is based on try and error or operator experience. This is clearly a desired approach if less expensive, safe and quick developments are required.

The external temperature is one of the fundamental parameters in the resin cure process on the systems that operate with CO₂ laser. All these aspects have to be considered on the process analysis and bearing this in mind, is essential to have a representative process model with a suitable kinetic knowledge.

The standard sample used in this work is composed by a mixture of epoxy resin, diethylenetriamine and silica. The amount of silica in the sample is essential for the success of resin confinement (cure) under laser action.
3. Material Development

The thermosensitive material studied in this work is composed of epoxy resin denominated diglicidil ether of bisfenol A (DGEBA), diethylenetriamine (DETA) as curing agent and silica powder. Thermosensitive materials are usually low molecular weight, semi-liquid substances. The localized cure becomes critical when the mixture of sample components is not appropriate. If the sample composition is not well established, the curing will be incomplete, hindering the formation of a structure of high molecular weight and high density of cross linking (May, 1988).

The material developed for the Infrared Stereolithography process must comply with essential criteria:

- Success in confining reaction to a localized region is heavily dependent on the exact ratio of reactants.
- Silica plays an important role controlling the localized cure. If the amount of silica in the process is not sufficient, the curing is not localized. If the amount is too large, the contact between the reagents is blocked up, the cure is not complete.

4. The Curing Reaction: Mechanism and Modeling

A kinetic model has been applied to describe the major events occurring during the curing reaction of thermosensitive materials. The curing reaction of DGEBA and DETA involves the formation of a three-dimensional network through of curing reaction. This reaction is characterized by two main events: gelation and vitrification (Li, 2000). Gelation corresponds to the incipient formation of an infinite molecular network, which is associated to an increase in viscosity and a decrease in processability. After gelation, as the reaction further progress, the amount of solid material increases and the polymer becomes more cross-linked. Vitrification corresponds to the formation of a glassy solid material, due to an increase in both the cross-linking density and molecular weight of the polymer being cured. The rate of the reaction will undergo a significant decrease after vitrification and the reaction becomes very slow as it is controlled by the diffusion of the reactive species. The diffusion-controlled effect will also determine the final degree of conversion. Many kinetic models assume that only one reaction can represent the whole cure process, and can be expressed by equation (Prime, 1997):

$$\frac{\partial \alpha}{\partial t} = k_c(T) \cdot f(\alpha)$$  \hspace{1cm} (1)

where $\frac{\partial \alpha}{\partial t}$ is the reaction rate, $f(\alpha) = (1 - \alpha)^n$ is a function of conversion and $k_c(T)$, the chemical controlled rate constant, is as function of the temperature.

The rate constant is supposed to observe an Arrhenius law, and therefore can be expressed by:

$$k_c(T) = k_0 \exp\left(\frac{-E_A}{R(\Delta + T)}\right)$$  \hspace{1cm} (2)

where $k_0$ is the pre-exponential factor of the rate constant, $E_A$ is the activation energy, $R$ is the gas constant, $\Delta + T$ is the absolute temperature.
Considering the rate constant expression, equation (1):

$$\frac{d\alpha}{dt} = k_0 \exp \left( \frac{-E_A}{R(\Delta + T)} \right)(1 - \alpha)^n$$

(3)

However, kinetic models do not explicitly include the effects of resin composition on the rate of cure and, consequently, the kinetic parameters must be recalculated after each change in the resin formulation. Moreover, these models cannot predict the diffusion control effects after vitrification (Bártolo, 2001).

5. Experimental Results

Differential scanning calorimetry (DSC) was employed for the study of thermosensitive cure reaction. DSC was to determine the isothermal cure for the different isothermal cure temperatures investigated. Thermosensitive resin was composed by DGEBA (10 parts) and DETA (1.4 parts). The isothermal curing profiles measured by DSC is shown in Figure 3, where the variation of the fractional conversion is given by vs. time, for different isothermal cure temperatures.

![Figure 3. DSC isothermal curing profiles.](image)

6. Curing Simulation

Different isothermal cure profiles were obtained using kinetic model of eq. 3. The cure profiles indicated above reveal that, after an induced period, the conversion rate increases rapidly, followed by a progressive slowing down until the cure profile reaches a plateau corresponding to the maximum value of the fractional conversion. The Figure 4 indicates of the fractional conversion.

![Figure 4. Simulated isothermal curing profiles.](image)
Figures 5 compare the fractional conversion values predict by the kinetic model with those obtained experimentally as a function of heating time. As observed, a good agreement is obtained during the final stages of the curing.

![Graphs showing conversion vs. time for 100ºC and 110ºC](image)

*Figure 5. Variation of the conversion vs. time. The symbol (Δ) correspond to the experimental values and symbol (●) results by kinetic model.*

6. Conclusions

The aim of this work is to describe, in detail, factors concerning to the complex physical, chemical and mathematical theory associated with Infrared Stereolithographic process. The research described here was undertaken by using a thermosensitive resin. A kinetic model is proposed to describe the major events occurring during the reaction process, including a diffusion factor, showing an excellent agreement with experimental and predicted values.

7. Acknowledgements

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8. References

Bártolo, P.J., 2001. Optical approaches to macroscopic and microscopic engineering, Thesis (PhD), University of Reading, UK.