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Materials characterization for stereolithography

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ABSTRACT: Stereolithography is an additive technology that allows the fabrication of three-dimensional macro and micro-parts for industrial and medical applications. By solidifying a liquid photo-sensitive monomer with a laser or UV-light source a polymeric part is built up layer by layer. The use of highly reinforced polymeric systems with metallic or ceramic particles also enables to transform this rapid prototyping technology into a rapid manufacturing one.

The quality and fabrication speed of stereolithographic parts strongly depends on the curing kinetics. Therefore it is crucial to optimize the polymeric mixture for a specific application. This research work investigates the curing kinetics of reinforced and non-reinforced unsaturated polyester resins with different photo-initiator concentrations. Two types of particles were considered: tungsten carbide and hydroxyapatite (concentrations of 30 wt%).

1 INTRODUCTION

Stereolithography is one of the most popular additive manufacturing processes to produce complex three-dimensional objects for industrial and medical applications (Melchels, 2012; Chan et al, 2012). It involves the curing or solidification of a liquid photosensitive polymer by using an appropriated light source, which supplies energy that induces a chemical reaction, bonding large numbers of small molecules and forming a highly cross-linked polymer (Bartolo, 2001, 2011; Bartolo and Mitchell, 2003; Bartolo et al, 2012).

The first step for the development of an intelligent system leading to the design, optimization and control of stereolithographic processes is to obtain adequate information about the reaction kinetics of the selected polymeric system.

This research work investigates the curing kinetics of reinforced and non-reinforced unsaturated polyester resins with different photo-initiator concentrations. Two types of particles were considered: tungsten carbide and hydroxyapatite.

The stereolithography of metallic or ceramic materials consists of a UV curable metallic or ceramic suspension prepared with a pre-polymer that will act as the binder material, a photo-initiator, powder and additives (Bartolo and Gaspar, 2008; Gaspar et al, 2008; Tian et al, 2012). Upon polymerization, the polymer bonds the metallic or ceramic particles conferring the necessary cohesion to the obtained metallic matrix. This matrix structure is then subjected to binder removal through an appropriate thermal treatment and sintering, which ensures the final properties of the model.

2 MATERIALS

2.1 *Pre-polymer*

An unsaturated polyester resin named Crystic 272 from Scott Bader was selected for this research work. This is an isophthalic resin with low viscosity resin that retains high streght in wet environments up to 60°C. The resin is styrene compatible and has the resistance required to this work.

2.2 *Photo-initiator*

The photo-initiator selected was the type I initiator 2,2-dimetoxi-2-phenilacetophenone, named Irgacure 651 (from Ciba-Geigy).

2.3 *Reinforcements*

Two types of reinforced particles were used in this research study: metallic and ceramic. The metallic particles used were tungsten carbide (average grain size of 6 μm), supplied by Durit – Metalurgia Portuguesa do Tungsténio (Portugal). The ceramic particles used were hydoxyapatite (average grain size of 70 nm), supplied by Fludinova, Engenharia de Fluidos (Portugal).

3 CURE MECHANISM

The curing reaction of unsaturated polyester resin is mainly a free radical chain growth co-polymerisation between the styrene monomer and the unsaturated polyester molecule. Polyester molecules form the backbone of the polymer network, while styrene

monomers serve as cross-linking agents to link the adjacent polyester molecules. The polymerisation process includes three major reactions: styrene-polyester vinyl, styrene-styrene and polyester vinyl-polyester vinyl. Previous reports on co-polymerisation of styrene and diethyl fumarate suggest that homo-polymerisation of styrene monomer is significant relative to the copolymerization between styrene and polyester vinyls. This is why the styrene monomer in unsaturated polyester resin is always present at a level stoichiometrically excess to the polyester vinyls. The reactivity of styrene homo-polymerisation is, however, much lower than that of styrene-polyester vinyl co-polymerisation. Homo-polymerisation of polyester vinyls is more difficult than the other two reactions because of the relative immobility of the long polyester chains. However, if the concentration of polyester vinyls becomes much higher than that of styrene monomer at a local site, the homo-polymerisation of polyester vinyls may be more favorable than the polyester-styrene co-polymerisation there.

For a mixture of polyester and styrene, we may picture the system as many coiled polyester chains swelled in styrene monomer. The coil size depends on molecular weight, chain stiffness, thermodynamic compatibility, and concentration of polyester chains. Chemical reaction may occur inside, outside and at the surface of the coils.

During the curing reaction two main phenomena occur: gelation and vitrification (Bartolo, 2011; Shibayama et al, 2005).

Gelation corresponds to the incipient formation of an infinite network. This phenomenon is characterized by the formation of an insoluble gel, which involves an abrupt change from a liquid-like to a solid-like behaviour, corresponding to a liquid to gel transition, and it is associated to a dramatic increase of viscosity (Pascault et al, 2002; Fouassier and Rabek, 1993).

There are two different types of gelation: chemical gelation, which result from the formation of chemical bonds and physical gelation, which result from the growth of physically connected aggregates. The principal distinction between chemical and physical gelation is the lifetime of the junctions. Chemical bonds are considered permanent while physical junctions due to intermolecular association are finite, constantly being formed and destroyed at such slow rates that the network appears to be permanently connected.

Vitrification involves a transformation from liquid or rubbery state to a glassy state and occurs when the increasing glass transition temperature, Tg, becomes equal to the reaction temperature (Pascault et al, 2002; Fouassier and Rabek 1993). 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 (Bártolo, 2001, 2011). Vitrification is associated to a decreased mobility of the polymeric chains (Lionetto et al, 2004; Bártolo, 2001, 2011). Unlike the gelation, vitrification is a reversible process.

4 CURE ANALYSIS

4.1 *Procedure*

Photo-initiated curing reactions were performed using a UV lamp (CAMAG UV), with 4 Watts of power and emitting radiation at a wavelength of 366 nm. The incident light intensity at the sample position (0.62 mW/cm^2) was measured using a Accu-Cal 30 UV radiometer (Intertronics), which corresponds to a distance of 154 mm between the sample and the lamp. All reactions were performed in the presence of air and at room temperature.

Photo-initiated cure reactions were performed to evaluate and model the effect of the following parameters:

- photo-initiator concentration (case I);
- type reinforcement particles (case II);

over the cure process.

A gel content method was used to evaluate the fractional conversion through the reaction.

5 RESULTS AND DISCUSSION

5.1 *Case I: The effect of photo-initiator*

Samples of unsaturated polyester resin CRYSTIC 272 (Scott Badder), with different amounts of photo-initiator Irgacure 651 (Ciba-Geigy) were used: 0.5, 1, 2, 3 wt%. These samples were cured at room temperature and the incident light intensity at the sample position, was measured to be 0.62 mW/cm^2. The initial resin system contains 37 wt% of styrene. Fractional conversions were evaluated using the gel content method, and the discrete experimental data obtained was fitted using a sigmoidal equation. Figure 1 shows the different cure profiles. The correlation between photo-initiator concentration, curing time and fractional conversion is shown in Figure 2.

5.2 *Case II: The effect of reinforcement particles*

5.2.1 *Tungsten carbide*

UP samples containing 1, 2 and 3 wt% of photo-initiator were reinforced with 30 wt% of tungsten carbide particles (particle size of 6 μm). The curing kinetic profiles are indicated in Figures 3 to 6.

5.2.2 *Hidroxyapatite*

UP samples containing 1, 2 and 3 wt% of photo-initiator were reinforced with 30 wt% of hydroxyapatite particles (particle size of 70 nm). The curing kinetic profiles are indicated in Figures 7 to 10.

5.3 *Discussion*

The cure profiles reveal that, after an induction period (due to both the inhibitor effect and oxygen dissolved in polymeric mixture), more evident for resin compositions with low concentration of photo-initiator, the

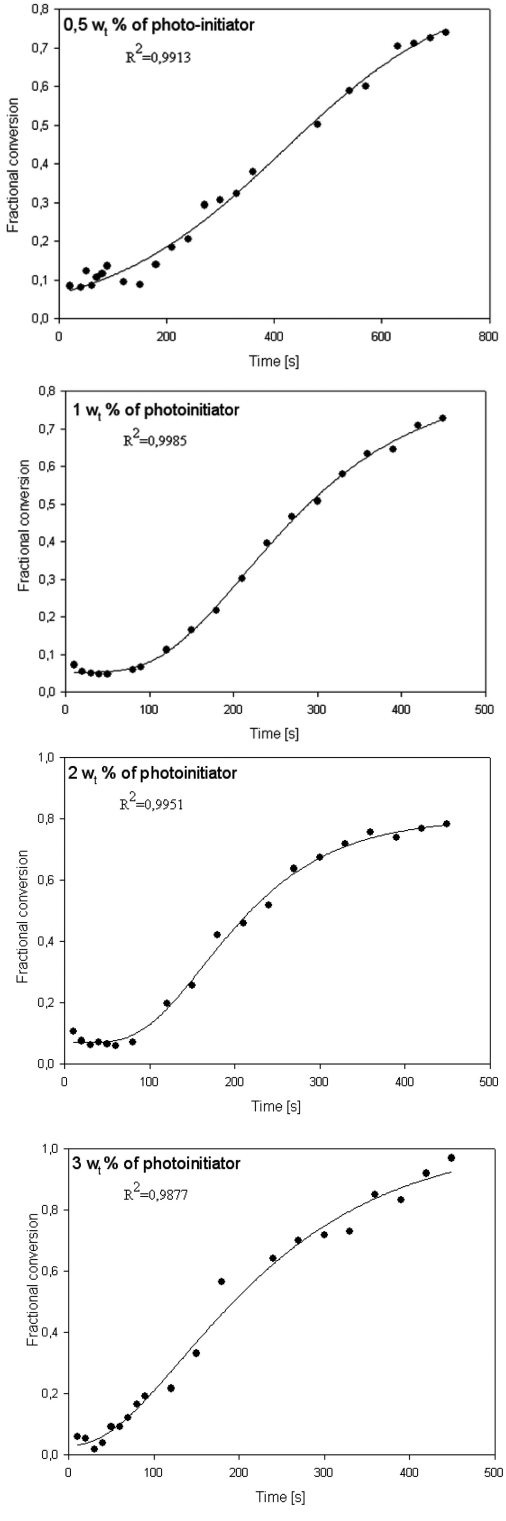

Figure 1. Case I: variation of the fractional conversion vs. irradiation time for the different photo-initiator (PI) concentrations investigated. The lines correspond to the continuous experimental values obtained by fitting the discrete data (●).

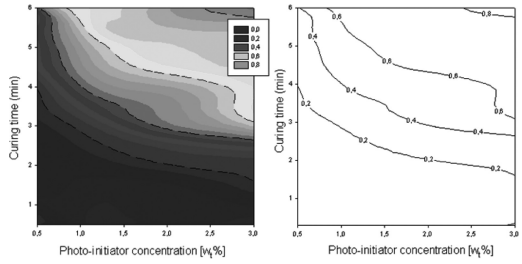

Figure 2. Case I: contour plot that shows the effect of the photo-initiator concentration and the curing time on the cured material fraction.

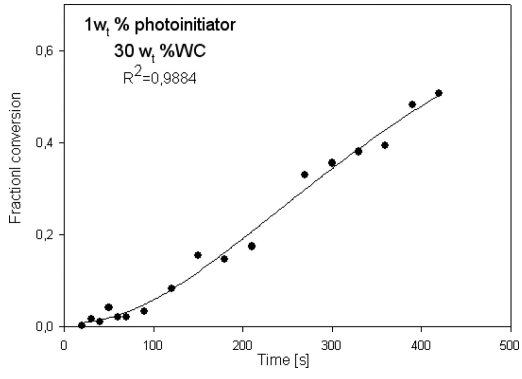

Figure 3. Case II: curing of unsaturated polyester resin with 30 wt% of Tungsten Carbide particles and 1 wt% of photo-initiator. The lines correspond to the continuous experimental values obtained by fitting the discrete data (●).

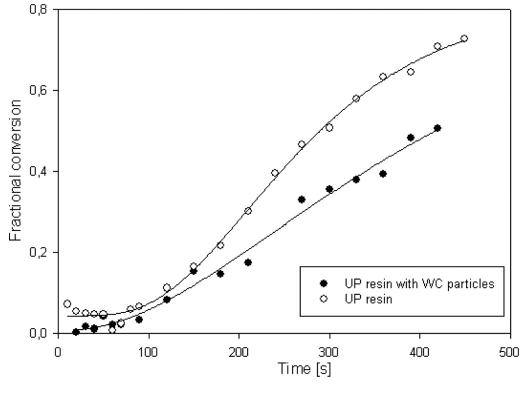

Figure 4. Case II: comparison between the curing kinetics profile of unsaturated polyester resins containing 1 wt% of photo-initiator and unsaturated polyester resin with 30 wt% of tungsten carbide particles and 1 wt% of photo-initiator.

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. This progressive slowing down is due to diffusion limitations on the mobility of the reacting species as the cross-link density increases.

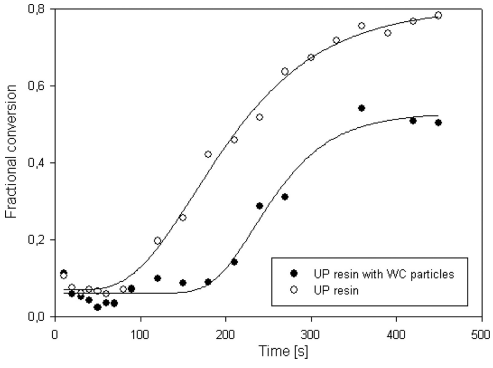

Figure 5. Case II: comparison between the curing kinetics profile of unsaturated polyester resins containing 2 wt% of photo-initiator and unsaturated polyester resin with 30 wt% of tungsten carbide particles and 2 wt% of photo-initiator. The lines correspond to the continuous experimental values obtained by fitting the discrete data (●).

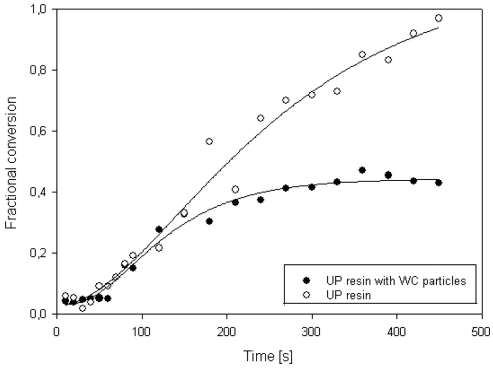

Figure 6. Case II: comparison between the curing kinetics profile of unsaturated polyester resins containing 3 wt% of photo-initiator and unsaturated polyester resin with 30 wt% of tungsten carbide particles and 3 wt% of photo-initiator. The lines correspond to the continuous experimental values obtained by fitting the discrete data (●).

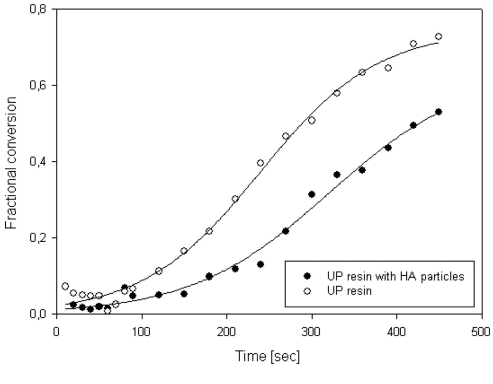

Figure 7. Case II: comparison between the curing kinetics profile of unsaturated polyester resins containing 1 wt% of photo-initiator and unsaturated polyester resin with 30 wt% of hydroxyapatite particles and 1 wt% of photo-initiator. The lines correspond to the continuous experimental values obtained by fitting the discrete data (●).

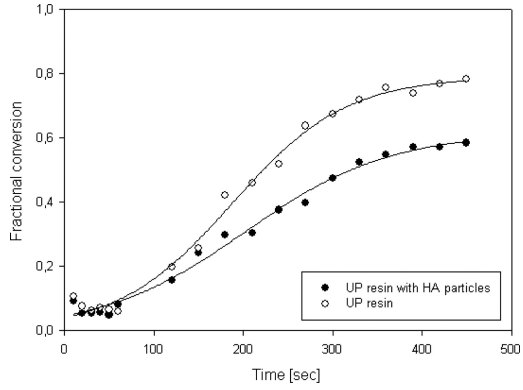

Figure 8. Case II: comparison between the curing kinetics profile of unsaturated polyester resins containing 2 wt% of photo-initiator and unsaturated polyester resin with 30 wt% of hydroxyapatite particles and 2 wt% of photo-initiator. The lines correspond to the continuous experimental values obtained by fitting the discrete data (●).

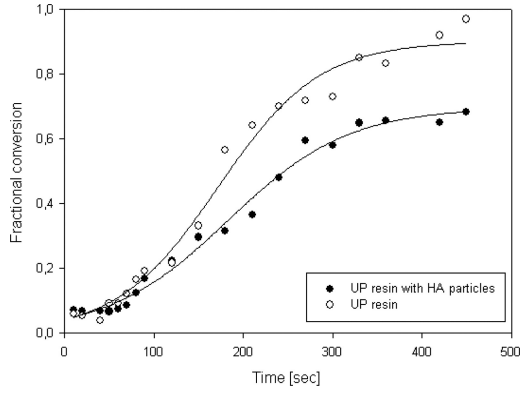

Figure 9. Case II: comparison between the curing kinetics profile of unsaturated polyester resins containing 2 wt% of photo-initiator and unsaturated polyester resin with 30 wt% of hydroxyapatite particles and 3 wt% of photo-initiator. The lines correspond to the continuous experimental values obtained by fitting the discrete data (●).

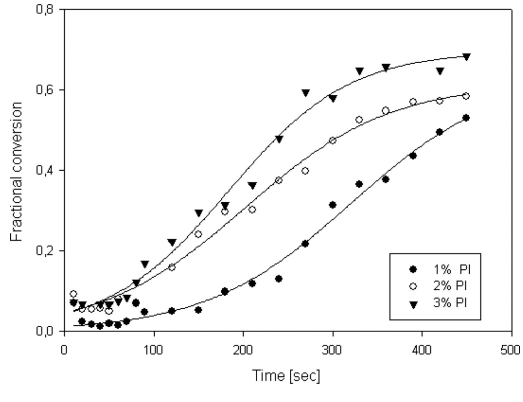

Figure 10. Case II: comparison between the curing kinetics profile of unsaturated polyester resins containing different amounts of photo-initiator and 30 wt% of hydroxyapatite.

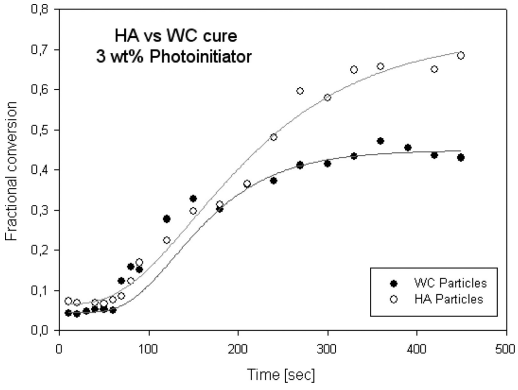

Figure 11. Case II: comparison between the curing kinetics profile of unsaturated polyester resins containing different amounts of photo-initiator and 30 wt% of hydroxyapatite and 30 wt% of tungsten carbide.

As the cure progresses, free volume is consumed by chemical reactions, decreasing the movement of the chains participating in network formation. After vitrification the reaction is very slow as it becomes diffusion-controlled (the diffusivity of the reactive groups is seriously reduced). If the photo-initiator concentration is too high the cure process will only be obtained at the surface of the resin, as the radiation does not penetrate deeply in the polymeric layer.

For polymeric systems reinforced with metallic and ceramic particles results show that the curing kinetics is lower than for non-reinforced systems due to the diffraction effects of the reinforced particles. It was expected that the high packing effect, more significant for lower particles size, the curing profiles were lower. However, as illustrated in Figure 11 this was not observed mainly due to the high reflectivity of the tungsten carbide. The tungsten carbide mixture also produces a more viscous mixture that reduces the light penetration depth.

6 CONCLUSIONS

The curing process suggests:

(i) the resin, initiator and reinforcements are initially mixed together and a homogeneous mixture obtained;
(ii) by exposing a resin sample to UV radiation, radicals are produced by fragmentation of the initiator;
(iii) at the beginning of the reaction, most of the free radicals formed from the initiators are immediately consumed by the inhibitors and oxygen dissolved in the sample. Some radicals can also disappear through combination reactions. However, continued irradiation will ensure the production of new radicals;
(iv) the induction period can be reduced by increasing of the initiator concentration;
(v) after this stage, the initiator molecules continuously fragment, creating free radicals that start the polymerisation process;
(vi) this reaction is mainly a free radical chain growth co-polymerisation between the styrene monomer and the unsaturated polyester molecule. Polyester molecules form the backbone of the polymer network, while styrene monomers link adjacent polyester molecules;
(vii) as the reaction proceeds, long polymer chains are formed, increasing the viscosity of the medium and reducing mobility of the polymeric chains being formed. As a consequence the polymerisation rate starts to decrease;
(viii) vitrification causes incomplete conversion;
(ix) by reinforcement particles to polymeric system, keeping the same layer thickness, the fractional conversion decreases due to scattering effects and a decrease on the light penetration depth.

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