

Oxygen diffusion in ceramic suspensions for stereolithography

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Received 19 February 2002; accepted 11 May 2002

Abstract

Optical profilometry and real-time infrared (RTIR) spectroscopy have been performed to determine the influence of oxygen diffusion in ceramics suspensions on stereolithography accuracy. As expected, oxygen tends to lower both polymerized depth and width by inhibiting the polymerization and scavenging the radicals. Researches concern the influence of process parameters (atmosphere composition and temperature) and dispersion formulation, through viscosity, its filler content or tertiary amine addition, on oxygen diffusion. Models, such as those of Wilke–Chang and Mackie and Meares, were used to fit the oxygen diffusivity in the piezoelectric ceramics suspensions. This study has led to the modification of the stereolithography process in order to allow piezocomposites fabrication with a higher accuracy. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Stereolithography; Oxygen inhibition; Diffusion; PZT; Suspensions

1. Introduction

Stereolithography is a rapid prototyping process for three-dimensional polymer parts fabrication (Fig. 1) [1]. In this technology, a computer-controlled laser beam (351–364 nm, ionized argon) induces polymerization of a liquid monomer into a solid polymer. The stacking of photopolymerized layers thanks to an elevator leads to the formation of a three-dimensional part. Recently, this process was modified to allow ceramic green parts fabrication from ceramic suspensions [2,3].

One of the main characteristic of the stereolithography process consists of a high polymerization depth in order to ensure the object cohesion, and also a low width of the polymerized voxel, which assured a high fabrication accuracy. Thus, the suspensions must be highly photosensitive, but the induced polymerization had to be well controlled in space.

In this technology, the photopolymerization takes place in a reactor in the presence of air. Numerous studies have already demonstrated the oxygen inhibition on resins photopolymerization, and especially of acrylates. However, if the influence of laser beam parameters and dispersion formulations on stereolithography accuracy have been well studied, the effect of oxygen on in situ reactions and on polymerization resolution is still misunderstood, especially for filled materials.

The objective of this work was to characterize the effect of oxygen diffusion on photopolymerization through the variation of parameters such as the suspension viscosity, its filler content, the temperature, the oxygen partial pressure and the addition of O₂ quenching agents. This research work will also lead to some modifications in the stereolithography process and dispersion formulation adjustments in order to take advantages of oxygen presence during the fabrication and to increase stereolithography accuracy.

2. Experimental procedure

This study was carried out with piezoelectric ceramic suspensions. Applications of this kind of ceramics are numerous: from microphones, strain gauges, to transducers and medical imaging [4–6]. Thus, for 2 years, our laboratory (DCPR) has been investigating the fabrication of piezocomposites thanks to the stereolithography process.

2.1. Raw materials

The piezoelectric ceramics are lead zirconate titanate Pb(Zr, Ti)O₃ (PZT) powders. They were provided with an average size of 5 μm, a density of 7.6 g/cm³ and a refractive index of 2.5.

Previous studies have shown that an optimal resin for the aforesaid application is an acrylate monomer, 1,6-hexanediol diacrylate (HDDA; UCB). However, some studies on

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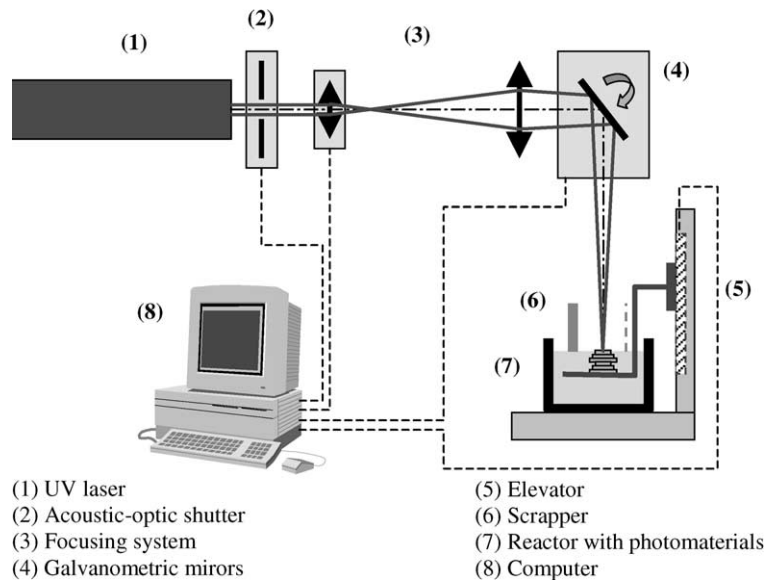


Fig. 1. Stereolithography process.

polymerization kinetics have also been carried out on a triacrylate monomer, trimethylolpropane triacrylate (TMPTA). 2,2'-Dimethoxy-2-phenylacetophenone (DMPA; Irgacure 651, Aldrich) was used as UV photoinitiator. To ensure a good homogeneity and stability of the high-loaded suspension, the use of a dispersing agent, acting both by electrostatic and steric repulsion, was compulsory. PZT powder was coated with a phosphoric ester (Beycostat C213, CECA) [7,8]. Moreover, methyldiethanolamine (MDEA; Aldrich) was used in some experiments as an oxygen quenching agent.

2.2. Preparation of photocurable suspensions

Firstly, the powder was coated with 1.5 wt.% dispersant with respect to the ceramic in acetone thanks to ultrasonic probe (Sonic Dismembrator 550, Fischer Scientific). Then the solvent was evaporated at room temperature to allow the dispersant to remain absorbed onto particles surfaces. After drying, PZT was desagglomerated with a 80 μm sieve. Finally, piezoelectric ceramics were mixed with resin and 1 wt.% photoinitiator by weight of monomer during 40 min by ball milling (300 rpm) (Retsch PM400, Fischer Scientific).

2.3. Methods of characterization

The dispersion reactivity has been verified by cure depth (E_p) and width (L_p) measurements. The thickness of a polymerized voxel (E_p) has been determined thanks to an optical profilometer (UBM) whereas its width (L_p) was measured both by profilometry and optical microscopy.

The observation of photopolymerization kinetics was achieved by real-time infrared (RTIR) spectroscopy [9,10]. This technique allows to monitor in real time the

disappearance of acrylates double bonds during UV polymerization thanks to IR spectroscopy (Perkin-Elmer 1310). The absorbance of the carbon-carbon acrylate bond was observed at 810 cm^{-1} . A 40 μm thick film of the sample was placed on a NaCl disc and exposed to the radiation of two UV lamps (Mazda, 364 nm). The light intensity received by the sample is around 3 mW/cm^2 .

3. Results and discussion

3.1. Photopolymerization of the suspension in presence of air

3.1.1. Irradiation conditions

The density of energy (DE in J/cm^2) received by the suspension during a unit of time is represented by the following expression:

$$\text{DE} = A \frac{P_0}{w_0 v} \quad (1)$$

where P_0 is the power of irradiation (W), w_0 the laser beam radius (150 μm), v represents the scanning speed of the x - y galvanometer (m/s) and A the constant. For each experiment, these parameters (P_0 , w_0 and v) are kept constant in order to neglect the variation of polymerized width due to some evaluations of the density of energy.

According to Beer-Lambert's law and due to the Gaussian shape of the laser beam, the intensity absorbed by the suspension $I_a(r, z)$ at the width r and the depth z is represented as follows [2]:

$$I_a(r, z) = \alpha_A c_A \frac{2P_0}{\pi w_0^2} \exp\left(-\frac{2r^2}{w_0^2}\right) \exp(-\alpha_A c_A z) \quad (2)$$

where α_A is the molar extinction coefficient and c_A the photoinitiator concentration.

By considering the intensity absorbed at the center of the beam ($r = 0$), the polymerization depth E_p ($z = E_p$) is defined by:

$$E_p = D_p \ln \left(\frac{DE}{DE_c} \right) \quad (3)$$

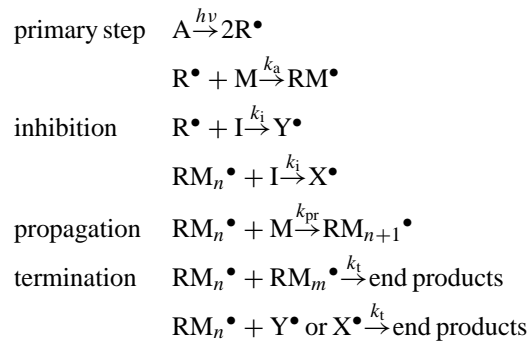
where DE_c is the minimum density of energy necessary to begin the polymerization and D_p the laser penetration depth. Similarly, the polymerization width L_p ($2r = L_p$) at the suspension surface ($z = 0$) could be represented as follows:

$$L_p = \sqrt{2}w_0 \sqrt{\ln \left(\frac{DE}{DE'_c} \right)} \quad (4)$$

Even if these equations will not be subsequently used for actual calculations, they contribute towards the understanding of oxygen influences on stereolithography resolution.

3.1.2. Polymerization kinetics

Acrylates polymerize by a free-radical mechanism. Thus, after irradiation at 364 nm with the laser, there is a cleavage of the aromatic ketone A in two radicals R^\bullet , which induces the polymerization of the monomer M. Two kinds of terminations have been considered: an homogeneous one (combination) and an heterogeneous one due to the presence of oxygen (or more generally inhibitors I), which leads to end products creation:



The rate constant of propagation k_{pr} is of approximately 10^4 mol/(l s) for such resins.

Oxygen is known to inhibit the polymerization reaction, especially the polymerization of acrylates, by scavenging the radicals in the suspension.

3.1.3. Coupling between diffusion and reaction

During the polymerization of a suspension, two types of molecules are diffusing: the radicals, which diffuse away from the irradiated area, and the inhibitors, which tend to limit the reaction zone.

To determine the influence of oxygen inhibition on photopolymerization and on stereolithography accuracy, two phenomena must be compared: kinetics of reaction and diffusion of oxygen. To evaluate that effect, the polymerization of a triacrylate in presence or in absence of air was observed by RTIR spectroscopy.

Fig. 2 clearly shows the inhibition of the polymerization by the oxygen dissolved in the dispersion or in the ambient air. Oxygen reacts with the radicals and then decreases the polymerization rate. It also leads to conversion rates much lower than in absence of O_2 (after gas removal and polymerization under a film of polyethylene). As a conclusion, even if the polymerization kinetics tends to be predominant, the influence of oxygen diffusion cannot be neglected.

Consequently, the oxygen diffusion within the ceramics suspensions has been characterized through the influences of both the operating conditions and the dispersion formulation.

3.2. Influence of the operating conditions

3.2.1. Effect of the partial pressure in oxygen

Experiments were carried out on suspensions, which have been first placed in an oven at room temperature and at different pressures ranging from 100 to 1000 hPa. After polymerization by the laser beam under a nitrogen flow, the polymerized width of the voxels was plotted as a function of air pressure (Fig. 3).

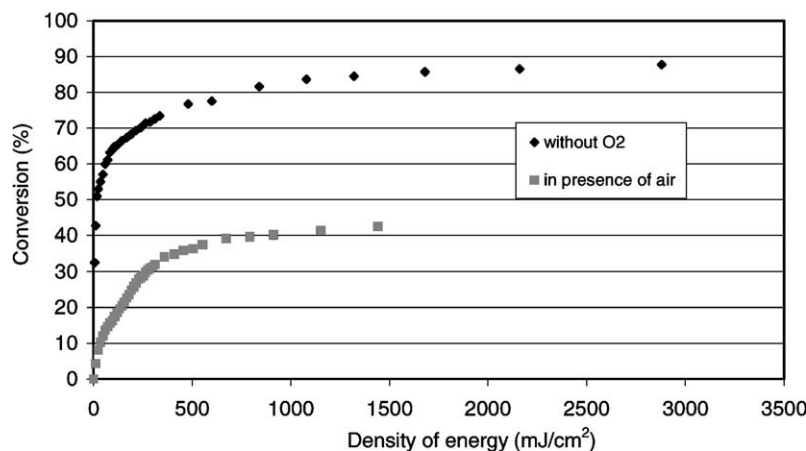


Fig. 2. Influence of oxygen on acrylates conversion (TMPTA): $I = 3$ mW/cm²; layer thickness = 40 μ m; mass concentration of DMPA = 0.35 wt.%.

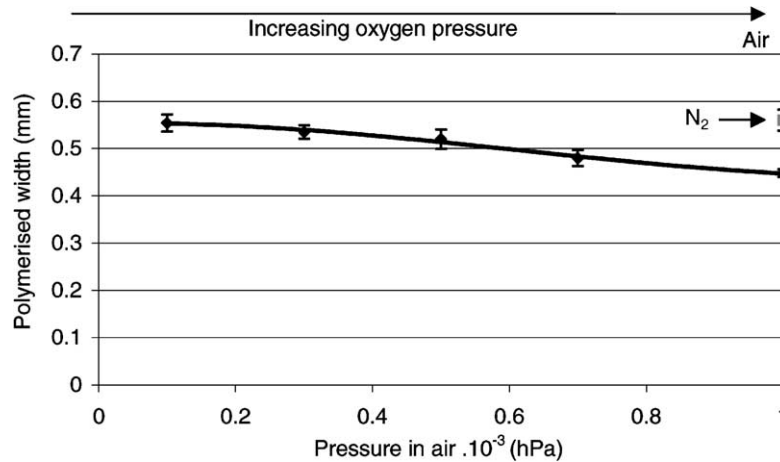


Fig. 3. Influence of air pressure on polymerized width. The filled square corresponds to the same experiment carried out with a sample polymerized under a continuous flow of nitrogen: $P = 40$ mW; scanning speed = 0.01 m/s; suspension = 80 wt.% PZT, 20 wt.% HDDA.

According to Henry's law, the concentration of the solute oxygen in the solution is directly proportional to the partial pressure of the gas above the dispersion. Thus, it could be noticed that the polymerized width tends to decrease for suspensions which a priori contain more oxygen.

A similar test was carried out with an 80 wt.% PZT suspension polymerized by stereolithography at ambient atmosphere or under a continuous flow of nitrogen. In the latter case, the polymerization width increases of approximately 25% towards the same sample used under standard conditions (Fig. 3). Thus, the use of a new system of ceramic suspensions deposition with nitrogen injection will lead to an increase of the polymerized depth but also to a loss of lateral resolution.

3.2.2. Influence of the temperature

The effect of an increase of the suspension temperature on the stereolithography accuracy was also observed. As

shown in Fig. 4, the polymerized width increases as the temperature increases. This phenomenon is consistent with the evolution of the effective diffusion coefficient of oxygen as a function of the temperature: a rise of this parameter leads to an augmentation of Brownian motion and so, of molecules mobility.

Moreover, the temperature dependence of oxygen solubility in a diacrylate monomer was studied by Scherzer and Langguth [11]. As an example, they have observed that an increase of temperature from 20 to 100 °C brings a decrease of oxygen solubility in the solution from 1.15 to 0.15 mmol/l. Thus, the increase of the polymerized width shown on Fig. 4 is consistent with these observations.

However, it should be noticed that if the diffusivity of the oxygen increases, it is also the case of the diffusivity of the radicals, which leads to crossed influences of parameters such as the temperature and the viscosity.

The modelization of such evolution of polymerized width due to oxygen diffusion was attempted thanks to

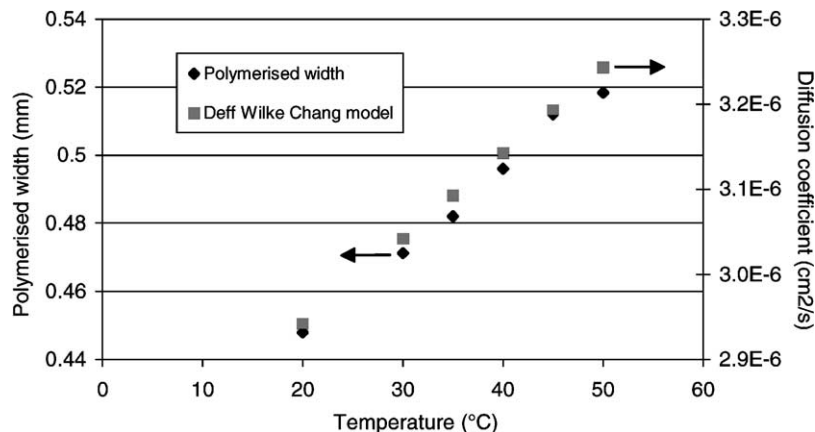


Fig. 4. Influence of the temperature on polymerized width. Comparison with the diffusion coefficient obtained by Wilke–Chang model: $P = 40$ mW; scanning speed = 0.01 m/s; suspension = 80 wt.% PZT, 20 wt.% HDDA.

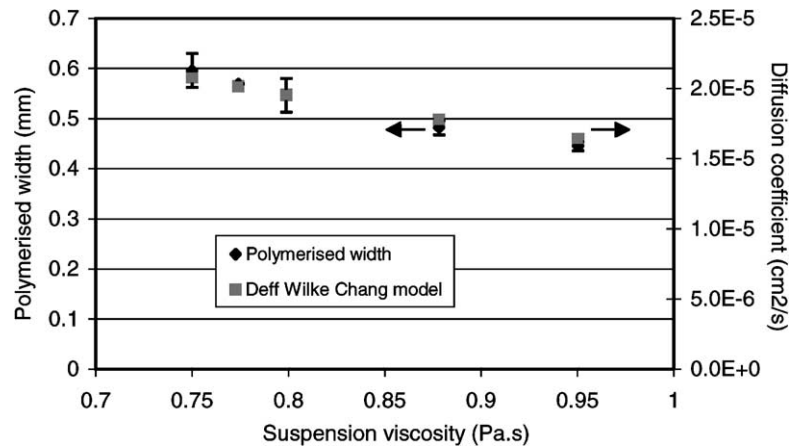


Fig. 5. Influence of the suspension viscosity on polymerized width. Comparison with the diffusion coefficient obtained by Wilke–Chang model: $P = 40$ mW; scanning speed = 0.01 m/s; suspension = 40 wt.% PZT, 80 wt.% HDDA.

Wilke–Chang relation [12]:

$$D^{\text{eff}} = 7.4 \times 10^{-8} \frac{T\sqrt{MX}}{\eta V^{0.6}} \quad (5)$$

where T is the temperature in Kelvin, M the molecular weight of the “solvent”, η the apparent viscosity, V the molal volume of the “solute”, and X a dimensionless “solvent” association factor, equal to 1 for non-hydrogen bonded solvents such as organic liquids (here $X = 1.2$). Even if, Wilke–Chang formula is dedicated to binary liquids calculations, it could be seen on Fig. 4 that the evolution of the polymerized width follows perfectly this law. The diffusion coefficients of oxygen in such suspensions are of about 3×10^{-10} m²/s, which is approximately 10 times higher than the diffusivity of O₂ in water at 20 °C (2×10^{-9} m²/s).

3.3. Influence of the formulation

3.3.1. Effect of the viscosity

Glycerin was added in small proportions to the PZT suspension in order to increase the viscosity (up to 10 wt.%). It should be noticed that in this range of glycerin concentrations, the reactivity of the dispersion is not modified.

As shown in Fig. 5, an increase of the viscosity seems to lower significantly the width of polymerization. This phenomenon could be explained by a drop of the radicals mobility combined with the inhibitive action of oxygen adsorbed and dissolved within the suspension. Moreover, the effective diffusivity of the radicals was modeled by Wilke–Chang relation (4). The evolution of the polymerized width as a function of the viscosity is well represented by this approach.

3.3.2. Influence of the filler content

In order to determine the influence of filler content on the diffusion of oxygen, two dispersions loaded at 40 and 80 wt.%, respectively, were tested. It should be stressed here that the piezoelectric ceramics greatly absorb the light at

364 nm. Thus, the width increase of the polymerized voxel due to the light diffraction on the particles could be neglected. Mackie and Meares relation, which is valid for highly-loaded suspensions, was used to model the decrease of the diffusivity due to the augmentation of the diffusional path because of the tortuosity [13,14]:

$$D^{\text{eff}} = D^0 \frac{(1 - \phi)^3}{(1 - \phi)^2} = D^0 f(\phi) \quad (6)$$

where ϕ is the volume fraction of fillers in the dispersion and D^0 the diffusion coefficient of the unloaded medium.

The ratio of the diffusivities of the two dispersions was calculated thanks to this formula:

$$\frac{D^{\text{eff}}(\phi = 37.5\%)}{D^{\text{eff}}(\phi = 12\%)} = 0.71 \quad (7)$$

whereas the ratio of the correspondent experimental polymerized widths is 0.75. This little difference of approximately 5% between the experimental and theoretical ratios justifies the use of this model for oxygen diffusion in highly-loaded PZT suspensions.

3.3.3. Addition of oxygen scavengers

Alkyl amines, for example, MDEA, are well-known oxygen quenching agents. Alkyl amines radicals react preferentially on oxygen in order to create peroxy radicals, which react on an other amine. The surfactant effect of some amines lead to the migration of some of these molecules at the interface between air and suspension, which protects the sample against further introduction of oxygen.

The addition of MDEA implies the consumption of the dissolved molecules of oxygen, then, the combination between oxygen and the radicals created by initiation step is lower, the lateral progression of the radicals is less disturb, which induces an increase of the polymerized width (Fig. 6).

This evolution is confirmed by the polymerization kinetics observed by RTIR spectroscopy (Fig. 7). Firstly, there is no

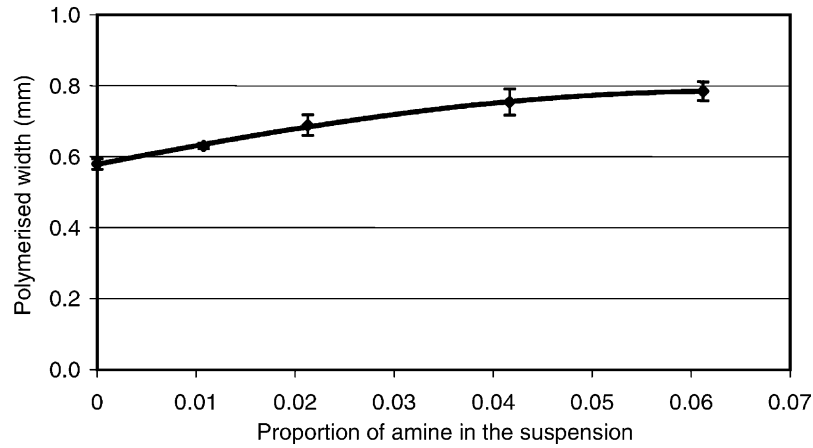


Fig. 6. Influence of the addition of MDEA on polymerized width: $P = 40$ mW; scanning speed = 0.01 m/s; suspension = 80 wt.% PZT, 20 wt.% HDDA.

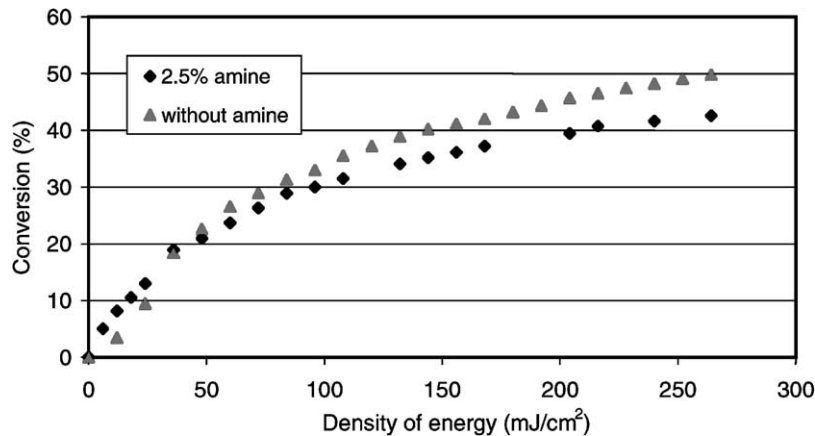


Fig. 7. Influence of amine addition on acrylates conversion (pure HDDA): $I = 3$ mW/cm²; film thickness = 40 μ m; in presence of air; mass concentration of DMPA = 0.35 wt.%.

inhibition time due to the presence of dissolved oxygen when 2.5 wt.% MDEA is introduced. Secondly, the polymerization rate R_p is greater in the early seconds with MDEA than in the standard conditions. However, this leads to a limitation of the polymerization extension due to gel effect: the penetration depth of the laser beam is then reduced, which induces a low conversion rate for the whole sample.

4. Applications to green parts fabrications

As demonstrated in previous studies, the penetration thickness of the laser is low in the case of PZT powders, which implies a difficult processing of piezoelectric ceramics by stereolithography [15,16] (Fig. 8). The linear representations of the polymerized depth and width of Fig. 8 have been deduced from Eqs. (3) and (4). They show the good agreement between the models and experimental data.

As a consequence, it was necessary to transform the stereolithography process by lowering the deposited layers

thickness to 20 or 10 μ m to ensure a good cohesion between the layers. It is also necessary to have the highest lateral accuracy for fine-scale fabrications (Fig. 8).

In this purpose, a new system of thin layer deposition was adapted to the stereolithography process: it consists of a nozzle, which injects nitrogen in order to spread the ceramics suspension. Considering the influence of oxygen partial pressure on the polymerized width, it would probably be useful to change the nitrogen by air when a high lateral resolution is required.

The temperature of the suspensions has been increased during the process and the resins were chosen on account of their low viscosity in order to lower the deposition thickness and to improve layers cohesion. However, these modifications have the drawback to decrease lateral accuracy.

It is worth noting that, if an increase of the filler content is often compulsory to obtain parts with good mechanical or piezoelectric properties and to make the sintering easier, it leads also to a better lateral accuracy.

Then, for some three-dimensional parts which need the fabrication of wide and thin films (for example, for

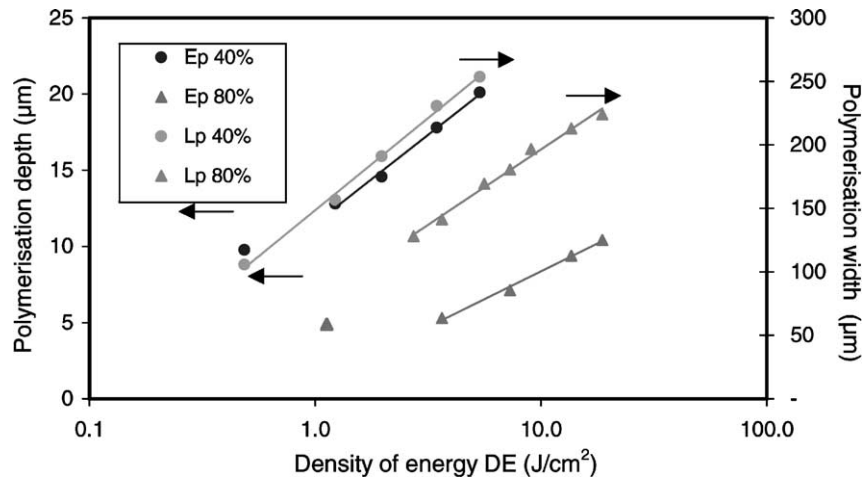


Fig. 8. Depth and width of polymerization for 40 and 80 wt.% PZT suspensions in HDDA: in presence of air; mass concentration of DMPA = 0.35 wt.%.

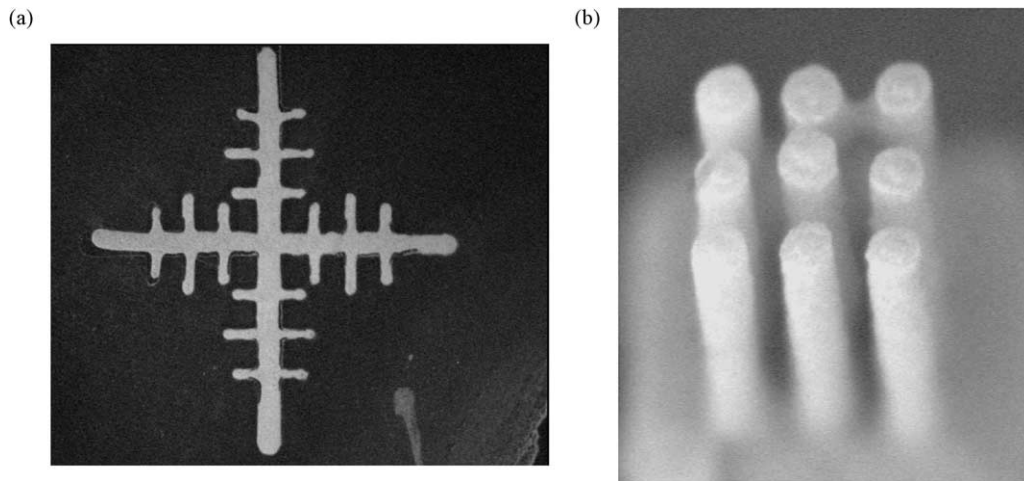


Fig. 9. (a) The 80 wt.% PZT flake on glass, lateral accuracy = 70 µm; (b) 50 wt.% PZT rods.

piezoelectric applications), the introduction of a few percent of MDEA could be conceivable.

These improvements have led to the design and fabrication of simple green parts with 80 wt.% of PZT and more elaborated transducers loaded at 50 wt.%, similar in shape to those typically obtain with standard methods as “dice and fill” or “pick and place” (Fig. 9). The piezoelectric properties of these objects are studied at present in other laboratories (LPMO, CNRS, Besançon, France and LGEF, Lyon, France).

5. Conclusions

The need of accuracy improvement of the stereolithography process makes it necessary to take into account the specific role of oxygen in this technology.

Through this study, the coupling between oxygen diffusion and lateral accuracy has been revealed. The influences of operating conditions and of suspensions formulation on

the polymerized width have been discussed. On one hand, it emerges from this research that an increase in temperature or the oxygen scavenger concentration leads to a drop of lateral accuracy. On the other hand, the pressure in oxygen and the suspension viscosity limit the polymerization extend by quenching the radicals, and the filler content increases the tortuosity; which could be an advantage for stereolithography accuracy.

As a consequence, the stereolithography process was modified by a new system of thin layer deposition and the dispersion formulation optimized, in order to obtained a good lateral accuracy and a satisfactory vertical layer cohesion in the demonstrated parts.

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