Photopolymerization kinetics of a polyether acrylate in the presence of ceramic fillers used in stereolithography

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ABSTRACT

The photoinitiated polymerization of a commercial polyether acrylate oligomer with 2,2-dimethoxy-1,2-phenyl acetophenone (DMPA) as radical photoinitiator was studied by using real time infrared spectroscopy (RTIR). First, the effect of light intensity, photoinitiator concentration and reactive diluent (1,6-hexanediol diacrylate, HDDA) on reaction was investigated in homogeneous phase. The maximum conversion was obtained for 0.5 wt% of DMPA and 10–15 vol% of HDDA. Then, ceramic fillers (SiO_2, Al_2O_3, ZrO_2 and SiC) were added to the acrylate oligomer in order to be used later as reactive suspensions for stereolithography. The influence of the nature, size and concentration of these fillers on the kinetics and the final conversion was characterized. The index ratio between filler and organic matrix as well as the intergranular phase viscosity were found to be the main parameters governing the reaction in heterogeneous phase.

1. Introduction

Stereolithography (SL) is a rapid prototyping technique that allows the fabrication of complex three dimensional ceramic parts with final properties (mechanical, thermal, ...) close to those obtained by classical processing techniques [1]. This technology uses a UV laser beam that induces photopolymerization of a reactive system containing ceramic particles. The polymerization of cross-sectional patterns in stacked layers leads to the creation of complex 3D objects, as presented by Griffith and Halloran [2]. The data of the object to fabricate is transferred from a three dimensional CAD file to the automated equipment which physically builds the green part. The interest in this fabrication technique appeared in different domains of applications: microelectronics, with the elaboration of devices (filters, resonators) with high dimensional resolution and density, biomedical implants of hydroxyapatite with controlled porosities, structural complex alumina 3D parts, etc.

The reactive system consists of ceramic particles dispersed in a suitable photopolymerizable resin in which the photoinitiator is dissolved. Once polymerized, the photopolymer constitutes a rigid matrix around ceramic particles and confers the cohesion to the green body. This organic phase is subsequently removed by an appropriate thermal treatment at low temperature (debinding). Then the sintering of the green part at high temperature ensures the final properties of the ceramic piece. The volume fraction of powder in the reactive suspension must be larger than 0.5 to ensure good conditions for debinding and sintering [3,4]. Nevertheless, the viscosity of the suspension must be as low as possible to allow a good recoat of the liquid suspension on the polymerized underlayer [1]. Thus, a good homogeneity and a low viscosity of the suspension, which are in contradiction with a high ceramic loading, require the use of dispersant. Furthermore, the use of a diluent may also be beneficial to reduce the viscosity of the suspension.

In this paper, we report the use of suspensions of ceramic powders dispersed, with the help of a dispersant, in an organic matrix composed of an acrylic resin, a reactive diluent and a photoinitiator, as reported by Hinczewski and Chartier [5]. The aim of this work is to describe the influence of the different components of the ceramic suspension on the photochemical reaction. In a first time, the effects of light intensity, photoinitiator and reactive diluent concentration, on the photopolymerization kinetics of the unloaded, homogeneous, system were studied. In a second time, the influence of the size and concentration of the filler particles was investigated in terms of rheological behavior and reactivity of the suspension under UV radiation.

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Table 1
Physical properties of the reactants and fillers used.

Product	Density	η (mPa s) at 25 °C	Specific area (m² g⁻¹)	d_{50} (μm)	Refractive index n (365 nm)
PEAAM	1.15	70	–	–	1.488
HDDA	1.02	7	–	–	1.456
Al_2O_3	3.97	–	1.52	2.3	1.787
Al_2O_3	3.97	–	2.41	1.4	1.787
Al_2O_3	3.97	–	5.74	0.5	1.787
SiO_2	2.26	–	5.31	2.25	1.564
ZrO_2	5.92	–	4.48	0.65	2.249
SiC	3.38	–	0.60	12.25	2.553 (467 nm < λ < 691 nm)

d_{50} is the average particle size.

2. Experimental

2.1. Materials

One amine modified polyether acrylate (PEAAM) was used as reactive oligomer. The photoinitiator is a 2,2-dimethoxy-1,2-phenylacetophenone (DMPA). 1,6-Hexanediol diacrylate (HDDA) was used as reactive diluent.

Six commercial ceramic powders were used as fillers. Their main physical properties are presented in Table 1. Three grades of alumina with different particle size were chosen. A 3 mol% Y_2O_3 stabilized zirconia, a silica and a silicon carbide were also used. A phosphate ester was used as an electrosteric dispersant for the fillers.

2.2. Preparation of the photocurable (un)loaded mixtures

For unloaded photocurable mixtures, the DMPA photoinitiator was mixed to the oligomer and/or the reactive diluent under stirring at room temperature and in the dark during 4 h. In the case of loaded photocurable suspensions, ceramic powders were first milled by attrition in order to breakdown agglomerates and to improve the filler dispersion and the stability of the suspensions. Attrition milling was performed in ethanol with the addition of phosphate ester. The three alumina powders as well as silica and zirconia powders were ball milled for 4 h, and the silicon carbide powder for 1 h. After milling, ceramic powders were dried at 40 °C for 12 h. The dispersant and the curable mixture were first blended, then the ceramic powder was progressively incorporated and the suspension was finally homogenized by ball milling. The powder concentration ranged from 10 to 40 vol% for Al_2O_3, SiO_2 and ZrO_2 powders and from 1 to 10 vol% for the SiC powder.

2.3. Real time infrared spectroscopy (RTIR)

Photochemical reactions were followed by real time infrared spectroscopy (Perkin Elmer FTIR 2000 spectrometer) in attenuated total reflection (ATR MK II Golden Gate, Specac, France). A drop of the reactive mixture was deposited and spread out over the ATR diamond crystal with a glass slide to ensure a uniformity of the surface analysis. UV radiation from a 200 W mercury–xenon lamp (LC8, Hamamatsu, Japan) was introduced into the FTIR spectrometer sample chamber by a flexible light guide so that it did not interfere with the IR beam. The radiation was monochromatic by means of the use of interferential filters centered on 365 nm. The light intensity was controlled by a UV radiometer (Intraspec II Oriel VLX-3W) at the sample surface taking into account the energy absorbed by the glass slide.

All the kinetic measurements were carried out at room temperature. The disappearance of acrylate double bond was followed at 1636 cm⁻¹. A reference band assigned to the carbonyl group was used at 1720 cm⁻¹ to calculate conversions. Conversion of the acrylate groups can be calculated by measuring the absorbance at each time of the reaction and determined as follows:

$$\chi_{(t)} = 100 \times \frac{(A_0^{1636}/A_0^{1720}) - (A_t^{1636}/A_t^{1720})}{A_0^{1636}/A_0^{1720}} \tag{1}$$

where $\chi_{(t)}$ is the conversion of the acrylate groups at t time, A_0 is the initial absorbance (before UV irradiation), A_t is the absorbance at t time.

2.4. Rheometric measurements

Rheological characterization of the suspensions was performed at room temperature with a controlled stress rheometer AR-G2 (TA Instruments) fitted with a cone with a diameter of 40 mm and an angle of 1.59°.

3. Results and discussion

3.1. Photopolymerization of PEAAM in homogeneous phase

Photopolymerization kinetics and conversion are affected by different parameters: the concentration of reactants ([A] and [M]), the nature of the photoinitiator (Φ_a, ε), the incident radiation intensity (I_i), the sample thickness (ℓ) [6] and the medium viscosity [7]. In particular, the three last parameters are influent on the absorption phenomenon which is predicted by the Beer–Lambert's law for a non scattering medium.
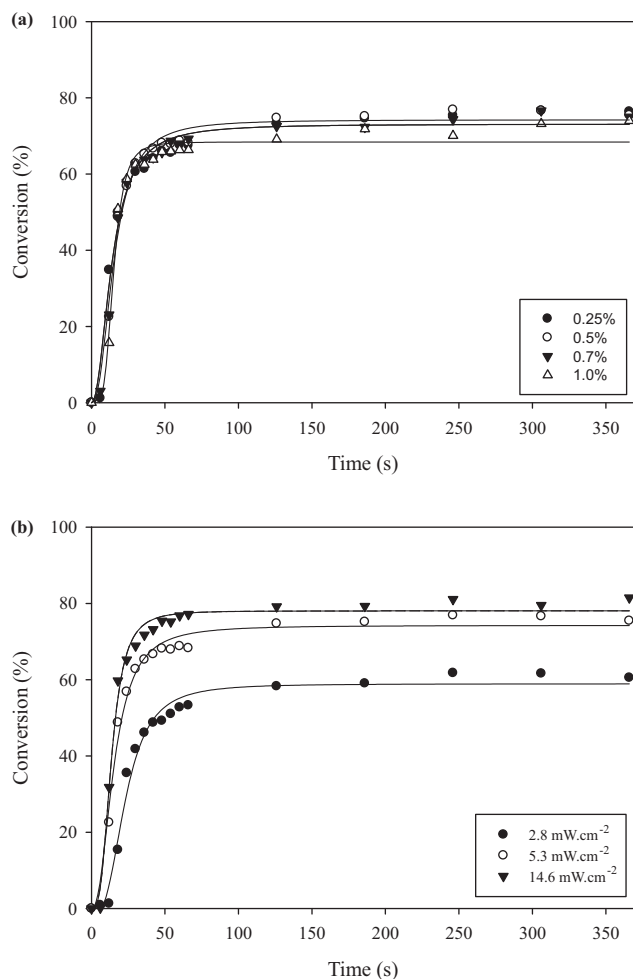
3.1.1. Influence of the sample thickness

PEAAM samples of various thicknesses containing 0.5 wt% of photoinitiator were irradiated with a light intensity of 5.3 mW cm⁻². For these unloaded systems, no variation of the kinetics was observed for thicknesses below 160 μm. This can be explained by the poor radiation light absorption by the reaction medium. In the two following paragraphs, the experiments were conducted on thin layers (~20 μm), so that the UV radiation intensity could be considered constant inside all the sample thickness.

3.1.2. Influence of the photoinitiator concentration and of the UV light intensity

The photopolymerization kinetics of PEAAM with different concentrations of DMPA, ranging from 0.25 to 1 wt%, was studied (Fig. 1a). A decrease in conversion was observed for photoinitiator concentrations larger than 0.7 wt%. This lowering can be attributed either to termination reactions of growing macroradicals with primary radicals coming from the photoinitiator photolysis, or to recombination of primary radicals [6,8,9].

Additionally, by fixing the DMPA concentration at 0.5 wt%, photopolymerization kinetics of PEAAM is increasing with light intensity, as shown in Fig. 1b. Indeed, primary radicals are produced in larger amount, increasing the initiation rate of macromolecu-

Fig. 2. Flow curves at 20 °C for different compositions of PEAAM/HDDA. The HDDA amount is given in vol%.

which was measured in the plateau region (i.e. when the conversion did not vary versus time), reached a maximum for 10–15 vol% HDDA (Fig. 3). This is likely due to two antagonistic effects induced by the introduction of HDDA. On the one hand, the addition of this monomer lowers the viscosity of the reaction medium, increasing the mobility of reactive functions and then the ultimate conversion [6,11,17], as observed for HDDA amounts lower than 10–15 vol%. On the other hand, the substitution of the trifunctional resin (PEAAM) by the difunctional HDDA reduces the overall functionality of the system and the network density. This results in a lower excess of free volume, which is not in favor of an increase in the polymerization yield. This second effect seems to be more important than the first one for HDDA amounts larger than 10–15 vol%.

3.2. Photopolymerization of PEAAM in heterogeneous phase

The kinetic behavior of PEAAM loaded with different ceramic powders was studied on layers of identical thickness ($150 \pm 10 \, \mu m$) under a light intensity of $5.3 \, mW \, cm^{-2}$. In a general way, the introduction of filler in the organic matrix modifies the photocurable system in terms of medium viscosity and optical properties, which magnitude depends on the nature, concentration and particle size and shape.

Fig. 3. Ultimate double bond conversion of homogeneous PEAAM/HDDA mixtures in the presence of 0.5 wt% DMPA at $I_0 = 5.3 \, mW \, cm^{-2}$.

Fig. 1. Change of acrylate double bond conversion versus: (a) photoinitiator concentration at $I_0 = 5.3 \, mW \, cm^{-2}$ and (b) incident UV light intensity in the presence of 0.5 wt% DMPA.

lar chains. This leads to a boost of the polymerization rate and, therefore, to a raise of the ultimate conversion [6,10–16].

In the following experiments, the concentration of DMPA was fixed to 0.5 wt% with regard to the acrylate reagents and a UV light intensity of $5.3 \, mW \, cm^{-2}$ was chosen.
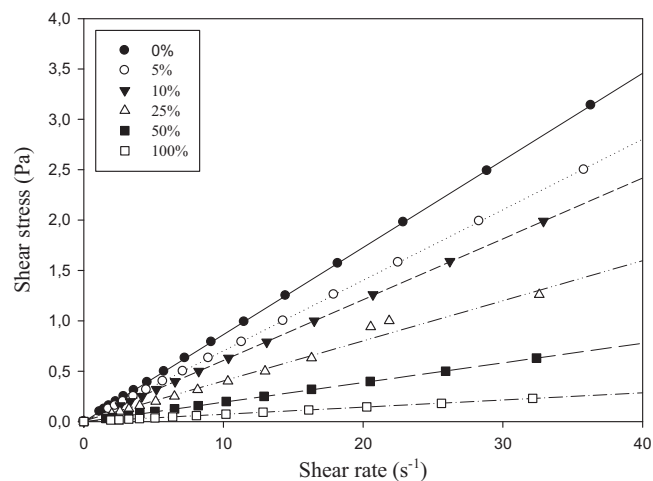
3.1.3. Influence of the reactive diluent

The use of a reactive diluent allows decreasing the viscosity of a loaded medium, therefore permitting the increase of the ceramic filler concentration. The choice of reactive diluent must meet the following criteria: good wetting of the ceramic particles, good miscibility with the main monomer/oligomer and high reactivity to UV light in order to provide higher conversions.

1,6-Hexanediol diacrylate (HDDA) was chosen to carry out this study. This compound is a classic monomer used in photocurable systems. Its reactive functions are similar to those of the PEAAM oligomer and its viscosity is 10 times lower. The photopolymerization of pure HDDA and pure PEAAM presents the same kinetic profiles with a final conversion of 80%.

Different mixing ratios of PEAAM/HDDA varying from 5 to 50 vol% HDDA were studied. As shown in Fig. 2, the rheological behavior of all the mixtures is Newtonian and the viscosity is decreasing with increasing HDDA concentration.

As far as the reactivity of the PEAAM/HDDA mixtures under UV irradiation is concerned, different behaviors can be distinguished in function of the HDDA concentration. Indeed, final conversion,
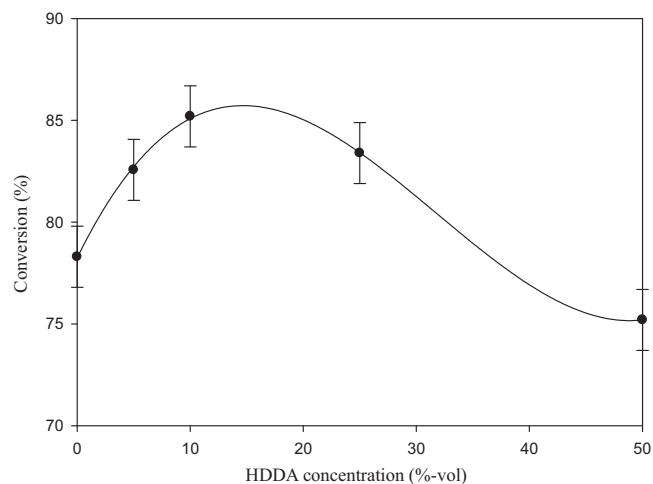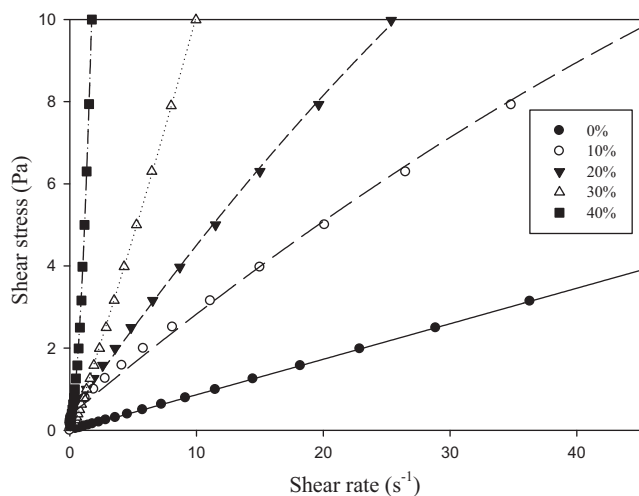
Fig. 4. Flow curves at 20 °C for PEAAM suspensions versus weight percent of SiO$_2$.

Fig. 6. Flow curves at 20 °C for PEAAM suspensions loaded with 40 vol% SiO$_2$ as a function of the weight percent of dispersant (with respect to the powder).

3.2.1. Influence of the rheology of the photocurable medium

Fig. 4 shows the rheological changes of PEAAM when loaded by 10–40 vol% SiO$_2$, whereas Fig. 5 presents the final conversion of PEAAM versus the concentration and the nature of the ceramic filler.

As expected, the viscosity of the loaded mixtures is increasing with the filler concentration. On the other hand, it is noteworthy that, despite the higher viscosity of the reaction medium in the presence of 10 vol% silica, the end conversion of the loaded system is identical to that of the resin itself. This suggests that the bulk rheology of the suspension did not affect the diffusion process of reactive functions during photopolymerization.

In order to confirm this assumption, a phosphate ester was added to the 40 vol% SiO$_2$/PEAAM suspension. This dispersant will act on the interaction between silica particles inside the organic matrix [18]. As shown In Fig. 6, the rheology of the suspension was affected by the addition of the phosphate ester. Whatever the amount of phosphate ester, the suspensions present a shear-thickening behavior which is exacerbated with the concentration of dispersant. The optimum state of dispersion was reached for a concentration of phosphate ester lower than 1 wt%. For larger amounts of dispersant, the apparent viscosity is increasing due to interaction between chains of dispersant adsorbed onto ceramic particles, as already observed in a previous work [19]. The similitude between
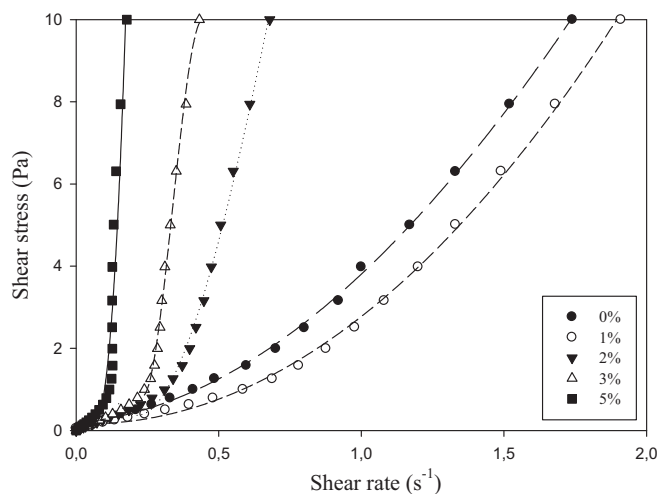
the different conversion curves presented In Fig. 7 confirms that the global suspension rheology did not significantly influence the photopolymerization kinetics. These results were also observed with alumina, SiC, and zirconia.

In a second time, the effect of increasing the mobility of the reactive functions in the loaded medium was investigated by adding the reactive diluent HDDA to the previous suspension. A series of mixtures of PEAAM and HDDA with HDDA volume ratio varying from 5 to 25 vol% with regard to PEAAM was then prepared. The powder concentration was set at 40 vol% and was calculated from the total volume of reactive medium.

Fig. 8 shows the rheological behavior of suspensions containing 40 vol% SiO2 prepared with different amounts of HDDA. In a surprising way according to Fig. 2, the addition of 5 vol% HDDA led to an increase in the global viscosity of the silica suspension. This behavior is not explained but is likely due to interactions between the various constituents of the suspension (PEAAM, HDDA, silica). For larger amounts of HDDA, up to 25 vol%, the viscosity is logically decreasing. As observed in case of the homogeneous system (Fig. 3), the final double bond conversion followed the same behavior, i.e. a maximum conversion was reached for a dilution ratio of 10–15 vol% of HDDA/PEAAM (Fig. 9). This ultimate result shows that
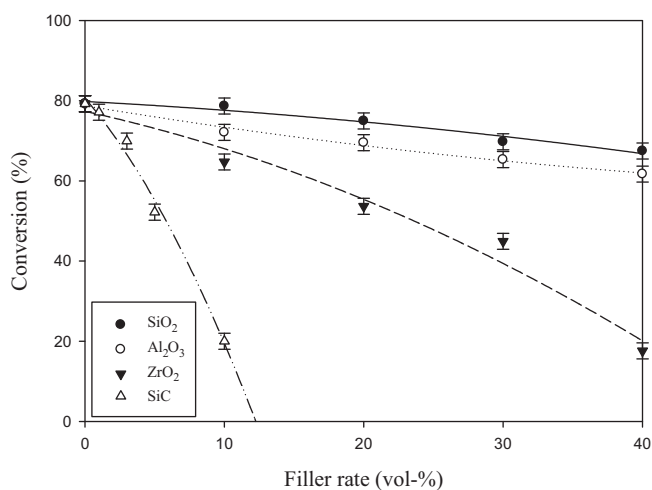

Fig. 5. End conversion of PEAAM + 0.5 wt% DMPA under a 5.3 mW cm^{-2} light intensity versus powder concentration for four different ceramic fillers.
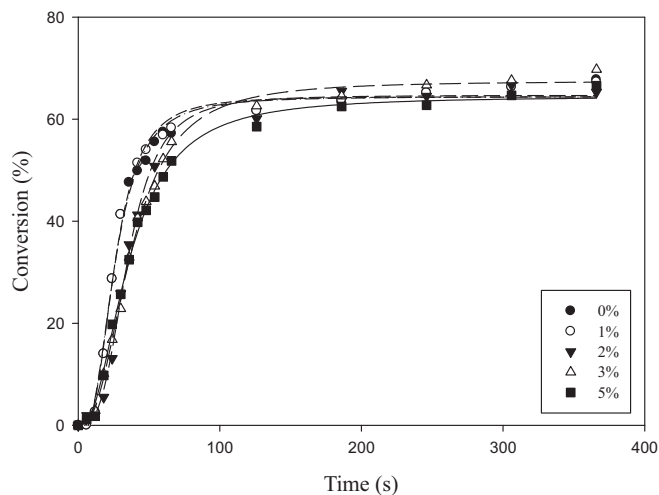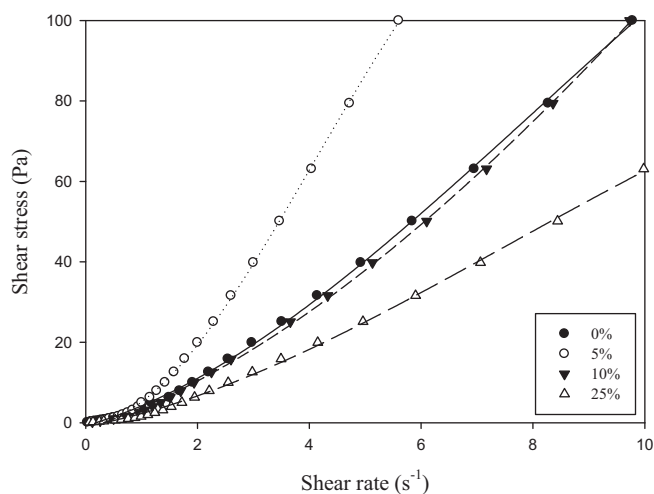

Fig. 7. Conversion profiles of PEAAM + 0.5 wt% DMPA suspensions loaded with 40 vol% SiO$_2$ versus time under a light intensity of 5.3 mW cm^{-2} for different weight percent of dispersant.
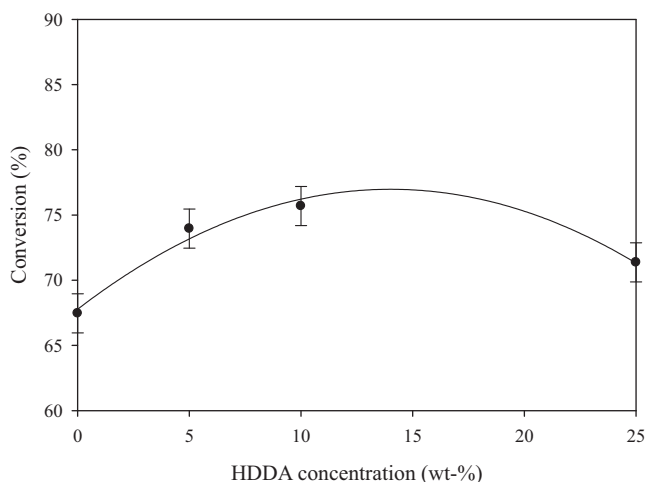
Fig. 8. Flow curves at 20 °C for different suspensions 40 vol% SiO2 and different PEAAM/HDDA ratios. The HDDA amount is given in vol% with respect to PEAAM.

Fig. 10. Variation of the end conversion of PEAAM + 0.5 wt% DMPA versus powder concentration for the three granulometries of alumina.
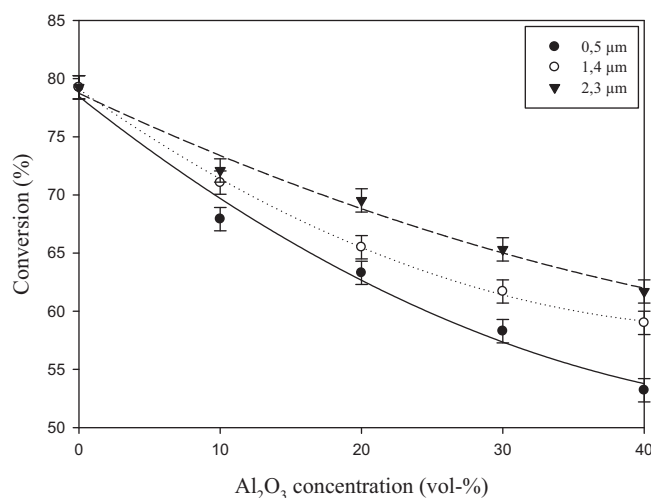
the viscosity of the intergranular phase, i.e. the medium where the polymerization took place, was unchanged by the addition of particles. Hence, the viscosity of the intergranular phase is the only parameter which influences the photopolymerization kinetics and not the global viscosity of the loaded suspension.

3.2.2. Influence of the optical index of the ceramic filler and of its concentration

Fig. 5 also shows the final double bond conversion versus filler concentration for four powders with different optical index. In all cases, end conversion (and polymerization rate) is decreasing when powder concentration is raised. This decrease is not related to the freezing of the reaction by gelation since all the samples are at the same temperature. Nevertheless, the only varying parameter is the UV light intensity, which decreases within the sample thickness because of a light scattering phenomenon by the loaded medium [20]. Moreover, for the different transparent materials (silica, alumina and zirconia), the values of conversion are larger when the optical index is close to that of the resin [21,22]. In this respect, in the case of silica with an index ratio of 1.05, the polymerization kinetic profile of the 10 vol% SiO_2 suspension was identical to the one of the organic matrix. But, for larger concentrations,

the existence of a greater scattering phenomenon was responsible of a decrease of the polymerization rate and final conversion. In the case of alumina, the index ratio is 1.20. Here, the scattering phenomenon appears for low powder concentrations (10 vol%). The ultimate conversion is lower than the one for silica. Lastly, the scattering phenomenon is far more marked for zirconia based suspensions with an index ratio of 1.51. At last, the photopolymerization of absorbent silicon carbide loaded resin is very influenced by the powder concentration. Indeed, only small concentrations (<10 vol%) allowed conversion of acrylate groups, with a smaller polymerization efficiency than the one obtained for transparent materials. Nonetheless, most of the light is absorbed by SiC particles and, consequently, the final conversion is very low [23].

All these results show that the refractive index ratio between the ceramic filler and the organic matrix is the main parameter governing the light scattering phenomenon. This is in agreement with the works of Griffith and Halloran [24].

3.2.3. Influence of the particle size

The effect of the filler particle size on the final conversion of PEAAM was investigated for three different alumina powders (d_{50} = 0.5, 1.4 and 2.3 μm). These powders exhibit a close chemical composition and narrow particle distributions after attrition milling [25].

The changes observed on final conversion (Fig. 10) mark the influence of the particle size on photopolymerization kinetics. Indeed, for suspensions filled with the 0.5 μm mean particle size powder, the lowering of the final conversion is 15% when the powder loading varies from 10 to 40 vol%, compared to the one for suspensions filled with the 2.3 μm mean particle size powder which is 10%. The deterioration of the final conversion with the lowering of the particle size could be allocated to an increase in scattering centers for a given volume concentration [20].

4. Conclusion

The first part of this paper dealt with the photopolymerization kinetic study of an acrylate oligomer in the presence of DMPA as photoinitiator and HDDA as co-monomer. HDDA was found to play the rule of reactive diluent for concentrations around 10–15 vol%. In the second part, the kinetic study was performed in heterogeneous medium by adding different ceramic fillers. The study of the rheological behavior of the loaded suspensions showed that the

Fig. 9. Ultimate double bond conversion of heterogeneous PEAAM/HDDA/SiO2 suspensions in the presence of 0.5 wt% DMPA at I_0 = 5.3 mW cm^{-2}.

overall rheology did not affect the kinetics of photopolymerization, which was only governed by the intergranular phase viscosity. The influence of the optical properties of the medium, and more particularly, of the refractive index ratio between ceramic filler and organic matrix, was also demonstrated. Indeed, the speed and yield of polymerization decreased all the more than the index ratio was high. In addition, the decrease in the final double bond conversion versus the filler concentration and particle size could also be attributed to a light scattering phenomenon.

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