



Macromolecular Nanotechnology

Photopolymerization of methacrylate monomers using polyhedral silsesquioxanes bearing side-chain amines as photoinitiator

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ARTICLE INFO

Article history:

Received 17 August 2011

Received in revised form 23 November 2011

Accepted 4 December 2011

Available online 11 December 2011

Keywords:

Silsesquioxanes

Nanocomposites

Methacrylates

Photopolymerization

ABSTRACT

Organotriethoxysilanes (APS-PGE2) were synthesized by reacting 1 mol of 3-(aminopropyl) triethoxysilane with 2 mol of 1,2-epoxy-3-phenoxypropane (PGE). Polyhedral oligomeric silsesquioxanes functionalized with bulky amino groups (ASSQO) were prepared by hydrolytic condensation of APS-PGE2 catalyzed by formic acid. Methacrylate resins were activated for visible light polymerization by the addition of 1 wt.% CQ in combination with the synthesized ASSQO at loadings between 0 and 30 wt.%. The progress of monomer conversion versus irradiation time showed that the CQ/ASSQO pair is an efficient photoinitiator system because a fast reaction and high conversion result from 60 s irradiation at 600 mW/cm². The lack of methacrylate groups in the ASSQO, able to polymerize with the methacrylate resin, results in the absence of chemical bond between the ASSQO cages and the matrix. Debonding of ASSQO cages from the polymer give rise to nanovoids; which allows the methacrylate matrix to yield and deform plastically. Consequently, the final effect is a decrease in the flexural modulus and compressive strength with increasing amounts of ASSQO. The present study highlights the surface effect on the overall properties in nanostructured materials.

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1. Introduction

Photopolymerization science has assumed in recent years an increasing relevance in many applications, ranging from the production of paper, coatings, in dentistry, imaging science, and printing. This technology is based on the use of photoreactive systems suited to absorb a light radiation of the appropriate wavelength and to produce primary radical species able to convert a multifunctional monomer into a crosslinked network. Photopolymerization of resins upon irradiation with visible light is commonly photoinitiated by the pair camphorquinone (CQ)/amine [1–3]. Generally, in free radical mediated polymerization, photogenerated radicals and the growing macroradicals are quenched by oxygen, which reduces the rate of polymerization. The presence of amine is useful in suppressing inhibition by the reaction of oxygen with the C-based rad-

icals through a radical chain transfer process which regenerates the initiation reaction [4].

Low-molecular-weight amines have intrinsic disadvantages such as odor, toxicity, and migration in UV-curing technology. An issue of primary concern in packaging systems is that the low molecular weight species may migrate from the coating into a packaged product. Similarly, in light-cured dental restorative resins, research has been directed towards the synthesis of amines with improved biocompatibility [5,6]. The toxicity of restorative materials containing amine co-initiator is connected to the mobility of the amine molecule if other components are essentially non-toxic. These complications may be avoided by the use of high molecular weight photoinitiators that reduce the tendency to migrate owing to their macromolecular nature. A way to reduce its leaching into tissue is by using polymerizable amines that are incorporated into the polymer chain [6] or to increase the size of the molecule by bulky substituent so that it does not diffuse out of the resin. In this regard, polyhedral oligomeric silsesquioxanes (SSQO) appear as an interesting approach to increase the size of the amine

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molecules. Polyhedral oligosilsesquioxanes are an interesting class of clusters derived from the hydrolytic condensation of trifunctional organosilicon monomers. SSQO molecules are cage-like organic–inorganic structures, which consist of a Si–O–Si inorganic cage surrounded by an organic substituent [7]. The inorganic cage may be a fully condensed closed structure of formula $(\text{RSiO}_{1.5})_n$, (R represents the organic substituent) or partially condensed open structure of generic formula $\text{T}_n(\text{OH})_m$, where $\text{T} = \text{RSiO}_{1.5-m/2m}$. The diameter of these structures ranges from 1 to 3 nm [7], depending on the number of silicon atoms in the central cage and the peripheral substitution groups surrounding this core. The SSQO unit can be viewed as a nanoparticle for both its size and filler function or a co-initiator for its ability to initiate photopolymerization. Interest in SSQO has grown rapidly over the past several years, particularly for polymer-related applications, where several families of SSQO monomers have been developed as precursors to hybrid inorganic–organic polymers [8–10]. The affinity of polyhedral oligosilsesquioxanes to various polymer materials can be easily controlled by the selection of the structure of the surrounding organic group [11]. Methacrylate [12,13], epoxy [14,15], amine [16], and (β -carboxyl) ester [17] are some examples of functional groups that have been incorporated into the organic part of oligosilsesquioxanes in order to optimize the molecular structure of cubic-oligosilsesquioxane according to different objectives [18].

The present study was carried out in order to explore the possibility of using silsesquioxanes bearing pendant tertiary amine groups as co-initiator of CQ. To our knowledge, the use of polyhedral oligomeric silsesquioxanes functionalized with bulky amino groups [ASSQO] as photoinitiators has not been previously reported in the scientific literature. The photopolymerization of methacrylate monomers using CQ in combination with amine functionalized polyhedral oligomeric silsesquioxanes (ASSQO) at loadings between 0 and 30 wt.% was investigated. Characterization of the polymerized materials was carried out by measuring flexural and compressive properties. The morphology of the photopolymerized materials was examined by means of Field Emission Scanning Electron Microscopy.

2. Experimental

2.1. Materials and general procedures

The resins were formulated from blends of 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (bis-GMA; Esstech, Essington, PA) and triethylene glycol dimethacrylate (TEGDMA; Aldrich) at mass fraction of 70:30. The 70:30 bis-GMA/TEGDMA blend is denoted BisTEG. 3-(aminopropyl)triethoxysilane (APS, Sigma, 98% purity), 1,2-epoxy-3-phenoxypropane (PGE, Aldrich, 99% purity), formic acid (85 wt.% Sigma), camphorquinone (Aldrich, 98% purity), and ethyl-4-dimethylaminobenzoate (EDMAB, Aldrich, 98% purity) were employed as received.

The resins were activated for visible light polymerization by the addition of 1 wt.% CQ in combination with the synthesized amine-functionalized silsesquioxanes.

The radiation source was a light-emitting diode (LED) unit (VALO, Ultradent, USA) with a wavelength range

410–530 nm and irradiance equal to 600 mW/cm². The intensity of the LED was measured with the chemical actinometer potassium ferrioxalate, which is recommended for the 253–577 nm wavelength range.

2.2. Characterization

2.2.1. Viscosity

The viscosity of the BisTEG resins modified with different proportions of silsesquioxanes was measured at 25 °C using a cone/plate viscometer Brookfield (HBTDV-IICP – Spindle CP 40)3.

2.2.2. Photolysis of CQ in the presence of ASSQO

The photodecomposition of CQ in the presence of ASSQO was followed using the changes in absorbance at the wavelength of its maximum absorption. The absorption spectra of CQ were measured with an UV–visible spectrophotometer (1601 PC, Shimadzu) at room temperature (ca 20 °C) in BisTEG resin. Bleaching experiments were carried out in 2.0 ± 0.2 mm thick samples sandwiched between two disposable 1 mm thick glass plates. The concentration of CQ in BisTEG resin was 1 wt.% and the ASSQO were used in different mass fractions ASSQO/CQ: 7.5, 15, and 30. The extinction coefficient of CQ in methacrylate resin was 42 l/mol cm⁻¹.

2.2.3. Measurement of double bond conversion

Fourier transform infrared (FTIR) spectra were acquired with a Nicolet 6700 Thermo Scientific. Near-infrared (NIR) spectra were acquired over the range 4500–7000 cm⁻¹ from 16 co-added scans at 2 cm⁻¹ resolution. The resins were sandwiched between two glass plates separated by a 2 mm rectangular rubber spacer and were tightly attached to the sample holder using small clamps. With the assembly in a vertical position, the radiation source was placed in contact with the glass surface. The specimens were irradiated at regular time intervals and spectra were collected immediately after each exposure interval. The background spectra were collected through an empty mold assembly fitted with only one glass slide to avoid internal reflectance patterns. The conversion profiles were calculated from the decay of the absorption band located at 6165 cm⁻¹.

2.2.4. Mechanical characterization

Flexural and compressive tests were carried out at room temperature (20 ± 2 °C) in an Instron testing machine (Model 4467) at a crosshead displacement rate of 2 mm/min. All test specimens were photopolymerized in ambient atmosphere at room temperature (20 ± 2 °C). Flexural and compressive specimens were irradiated for 20 and 40 s on each side respectively. Prior to mechanical testing, the specimens were stored at (20 ± 2 °C) for about 24 h. A set of test specimens was also post-cured at 120 °C for 2 h. The flexural modulus, E , and the flexural strength, σ_f were measured in three-point bending using sample dimensions recommended by the ISO 4049:2000(E): $(25 \pm 2) \times (2 \pm 0.1) \times (2 \pm 0.1)$ mm. Results were computed using the standard formula:

$$E = \frac{L^3 P}{4bd^3 y} \quad (1)$$

$$\sigma_f = \frac{3P}{2bd^2} \quad (2)$$

A minimum of four specimens were prepared for each system by photo curing the specimens at 600 mW/cm² for 1 min on each side.

Multifunctional methacrylates are brittle in nature. Like other brittle materials, they are weak in tension but quite strong in compression and capable of yielding under uni-axial compression. Therefore, the yield strength was determined in compression. Samples for compression testing were made by injecting the resins into polypropylene cylindrical disposable molds of 6 mm internal diameter. Samples were irradiated at 600 mW/cm² for 1 min on each side. The shrinkage during polymerization facilitated the removal of the specimens from the polypropylene mold. Prior to mechanical testing, the specimens were stored at room temperature for about 24 h. Cylindrical specimens having a length/diameter ratio of 1.5 were deformed between metallic plates lubricated with molybdenum disulfide. The deformation was calculated directly from the cross-head speed. True stress–deformation curves were obtained by dividing the load by the cross-sectional area. The compressive yield strength, σ_y , was determined at the maximum load.

2.2.5. Microscopy

Observations to examine the morphology of the composites by Field Emission Scanning Electron Microscopy (FESEM) were carried out with a Zeiss-Supra 40 instrument at 5 kV. The surfaces of the samples were coated with a thin Au–Pt layer.

3. Results and discussion

3.1. Synthesis of amine-functionalized silsesquioxanes (ASSQO)

Organotriethoxysilanes containing amino groups were synthesized by reacting 1 mol of APS with 2 mol of PGE to give APS–PGE2, following a synthesis procedure described in previous reports [19,20]. The reaction was carried out in bulk, at 50 °C under vacuum, during 24 h. In these conditions the reaction attained complete conversion. The hydrolytic condensation of the organotriethoxysilanes containing amino groups (APS–PGE2) was performed by dissolving the silane in tetrahydrofuran (THF) in a ratio 1.5 ml THF/g APS–PGE2, and heating at 50 °C during 24 h, allowing continuous evaporation of volatiles. The hydrolytic condensation was catalyzed by formic acid 85 wt.% (molar ratios: [HCOOH]/Si = 3, [H₂O]/Si = 1.32). Formic acid acts both as a catalyst and as water source, promoting the condensation through the formation of siliiformates as intermediate species [21]. The characterization of the resulting amine-functionalized polyhedral oligomeric silsesquioxanes (ASSQO) has been reported in detail elsewhere [19,20] and is briefly described here. Matrix-assisted ultraviolet laser desorption/ionization

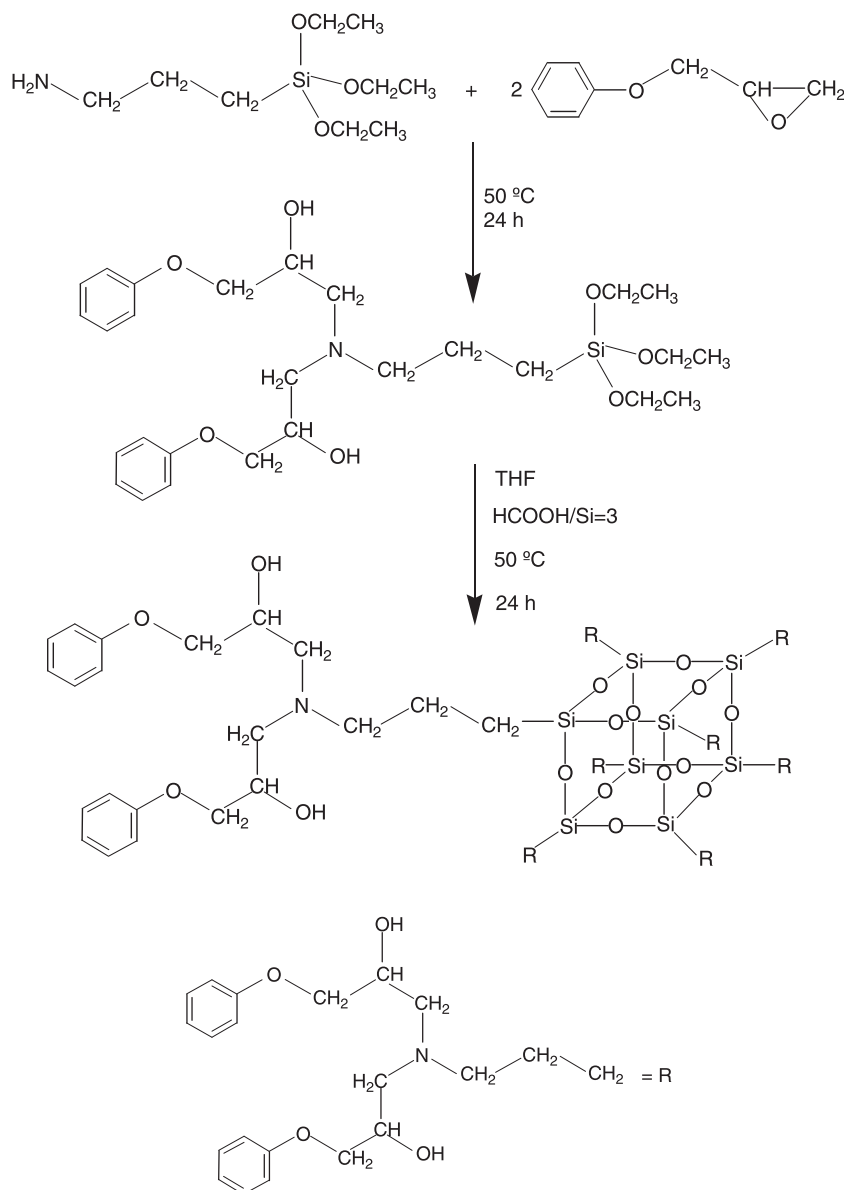
time-of-flight mass spectrometry (UV–MALDI–TOF MS) studies revealed that the ASSQO exhibit a relatively narrow distribution of polyhedral structures. The main species present in the ASSQO are polyhedral structures containing 8–11 Si atoms. According to the UV–MALDI–TOF MS spectra, the molar mass of the ASSQO are in the range 3163–4526 Da. Scheme 1 shows the structure of APS, PGE, and the reaction product corresponding to a completely condensed ASSQO with 8 Si atoms.

The synthesized ASSQO were liquid at room temperature. They were incorporated into the BisTEG methacrylate resin at mass fractions equal to 7.5, 15, and 30 wt.%. The optical clarity of the resins upon addition of the ASSQO indicates a good degree of dispersion of the nanofillers. Rheological studies showed that all the resins modified with ASSQO behaved as Newtonian liquids; i.e. the viscosity remained constant during the duration of the test. Table 1 shows the viscosity of resins containing different proportions of ASSQO. The relatively modest increase in viscosity in resins containing 30 wt.% SSQO (Table 1) is attributed to the absence of high molar mass oligomers.

3.2. Photolysis of CQ in combination with amine-functionalized silsesquioxanes

Camphorquinone acts in combination with hydrogen donors as tertiary amines, to generate radicals capable of initiating polymerization of methacrylate monomers. For related ketone/amine photoinitiation systems [1–5] it is generally considered that the amine radical is responsible for initiating the polymerization and that the radical formed from the ketone is not an efficient initiator due to a steric hindrance effect. The efficiency of a photoinitiator system is dictated, among other parameters by the degree of attenuation of the light intensity along the radiation path [22–26]. The effect of light attenuation caused by excessive levels of light absorbing compounds or thick sections is well known and has been termed the inner filter effect. This effect occurs when the light fails to reach the deeper layers of a sample because the absorbing species near the irradiated surface absorb most of it. Thus, when studying a photoinitiator system, it is relevant to assess changes in absorbance of the sample during irradiation. Depending on the nature of the photolysis products, the consumption of the photoinitiator can either lead to an increase in light intensity in the underlying layers (if the photolysis product is more transparent at the irradiating wavelengths) or a reduction in light intensity (if the photolysis product is strongly absorbing). Since the initiator decomposition can involve interaction with the chemistry of the matrix, the photodecomposition of CQ in combination with different proportions of amine-functionalized silsesquioxanes was studied in BisTEG resin by monitoring the decrease in absorbance at the wavelength of the maximum absorption of CQ.

Fig. 1 shows spectral changes during irradiation of CQ/ASSQO in BisTEG resin showing a continuous decrease in absorbance with irradiation time. By irradiating the sample for less than 60 s the absorbance of the CQ in the sample was reduced to 80% of the initial value. The photolysis of CQ started after an induction time, which is attributed to



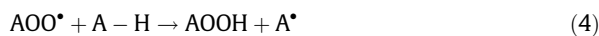
Scheme 1. Structures of APS, PGE, and the reaction product corresponding to a completely condensed ASSQO with eight Si atoms.

Table 1

Mass fraction of ASSQO in the BisTEG resin, r is the molar ratio [amine]/[CQ], t_{ind} is the induction time in the photobleaching of CQ studies, and $k = \Phi I_0$ is the rate constant for the photobleaching of CQ.

wt.% ASSQO	$r = [\text{amine}]/[\text{CQ}]$	Viscosity (cp)	t_{ind} (s)	$k = \Phi I_0$ (s^{-1})
0	0	780	–	–
7.5	3	1267	6	0.0778
15	6	1850	2	0.0781
30	12	4230	0	0.0782

the quenching of the triplet state of CQ by dissolved oxygen [2,4]. Amines suppress oxygen inhibition by the consumption of oxygen in a radical chain process [2,4]:



Thus formulations prepared with higher proportion of ASSQO resulted in the lower induction period because the inhibiting species were consumed faster (Table 1). Moreover, in resins photoactivated with 30 wt.% ASSQO an induction time is not observed. The rate of decomposition of CQ is related to the quantum yield and the radiation absorbed [27]:

$$-\frac{d\text{CQ}}{dt} = \frac{\Phi I_{\text{abs}}}{L} = \frac{\Phi I_0 (1 - e^{-\epsilon L \text{CQ}})}{L} \quad (5)$$

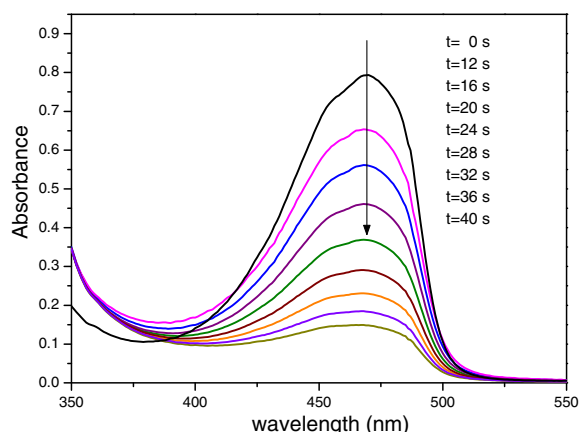


Fig. 1. Typical spectral changes during irradiation of a resin containing 1 wt.% CQ in combination with 15 wt.% ASSQO.

where CQ is the molar concentration of CQ, I_0 is the irradiance (in moles photons s^{-1}/cm^2) at the base of the sample, ε is the absorption coefficient of CQ equal to 2.302 times its extinction coefficient (42 ± 2 l/mol cm), L is the thickness of the sample, and Φ , which is usually termed the quantum yield of the photoinitiator consumption, is the fraction of photoinitiator reduced per absorbed photon. Integrating Eq. (5) yields:

$$\ln \left[\frac{10^{\varepsilon L CQ} - 1}{10^{\varepsilon L CQ_0} - 1} \right] = -\Phi \varepsilon I_0 t \quad (6)$$

where ($\Phi \varepsilon I_0$) is the CQ rate constant for the photobleaching of CQ, and CQ_0 is the initial concentration of CQ. A typical plot of Eq. (6) is presented in Fig. 2. A satisfactory fit of experimental measurements of absorbance to a first-order kinetics for the decomposition of CQ in combination with ASSQO is observed. Table 1 shows the rate constant for the photobleaching of CQ, calculated from the slope of the lines resulting from Eq. (6). It is seen that, for the range of amine concentration studied, the rate of photobleaching of the

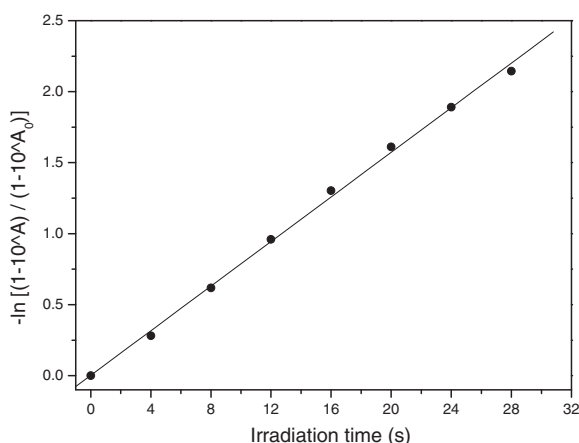


Fig. 2. Typical plot of Eq. (6) for a resin containing 1 wt.% CQ in combination with 15 wt.% ASSQO.

CQ was independent of the amine concentration. These results are in agreement with trends reported by Cook [28] for the photodecomposition of CQ/amine systems. The author found that if the intersystem crossing of the excited singlet to the triplet state is the rate determining step, then the consumption of CQ is independent of the amine concentration and only depends on the amine reactivity.

For a thick-section cure, it is advantageous to use photobleaching initiators in which light absorption by the initiator photoproducts is lower than that by the original photoinitiator molecule, thereby allowing more light to pass through the system [22–26]. Fig. 1 shows that the photolysis products of CQ/ASSQO are transparent at the irradiating wavelengths, consequently the consumption of the CQ leads to an increase in light intensity in the underlying lays. The clean and rapid photobleaching of CQ in combination with ASSQO makes this photoinitiator system very attractive for polymerization of thick sections.

3.3. Double bond conversion

The photoinitiation capability of CQ in combination with ASSQO was assessed. The photolysis of CQ, in the presence of hydrogen donors such as amines, leads to the formation of a radical produced from carbonyl compound (ketyl-type radical) and another radical derived from the hydrogen donor [1–4]. The photopolymerization of methacrylate monomers is usually initiated by the amine radicals, and the ketyl radicals are usually not reactive toward methacrylate monomers due to steric hindrance and delocalization of unpaired electron. Thus, the number and type of active amine radical determine the photopolymerization rate.

Fig. 3 shows the progress of monomer conversion versus irradiation time in BisTEG resin with different amount of ASSQO. In resins containing 7.5, 15, and 30 wt.% of ASSQO the molar ratio amine/CQ, calculated assuming complete reaction of the OH groups in the condensation reaction, is approximately 3, 6, and 12 respectively (Table 1). The evolution of the polymerization reaction photoinitiated by the pair CQ/ethyl-4-dimethylaminobenzoate (EDMAB), which showed an optimum polymerization rate [1], is shown for comparison in the same plot. Plots in Fig. 3 show that amine groups present in the ASSQO are efficient co-initiator for CQ because a fast reaction and high conversions are obtained after 60 s irradiation at 600 mW/cm². As expected, the polymerization reaction increases with increasing content of ASSQO because the number of amine radical increases. The influence of the mass fraction of ASSQO on the final monomer conversion is attributed to the temperature rise in the sample due to the exothermic reaction. A higher sample temperature increases the mobility of the reaction environment (i.e. monomer, radical, and polymer) and consequently increases the reaction rate parameters. In addition, once the photocuring temperature approaches the glass transition temperature the material vitrifies and the reaction is virtually stopped, thus limiting the maximum conversion. Therefore, the samples containing higher proportions of ASSQO attained a higher temperature and therefore reached a higher limiting conversion.

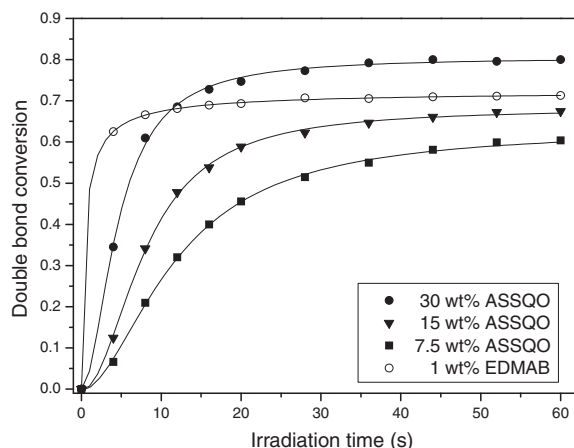


Fig. 3. Monomer conversion (measured using NIR spectra) versus irradiation time for a 2 mm thick BisTEG resin specimen containing 1 wt.% CQ in combination with different proportions of 7.5, 15, and 30 wt.% ASSQO. The conversion in a resin photoactivated with CQ/EDMAB is shown for comparison.

From Fig. 3 it is seen that the polymerization rate of CQ in combination with ASSQO was slower than that of the CQ/EDMAB pair. The different photoinitiation efficiencies of formulation containing CQ/EDMAB or CQ/ASSQO may be attributed to structural effects on the recombination rate of radicals and on the radical reactivity toward the monomer double bond [2]. In this regard, EDMAB has two methyl groups attached to nitrogen atom, whereas ASSQO has only methylene groups shielded additionally by the rest of the substituent. In addition, the mobility of EDMAB is expected to be higher than that of ASSQO structures due to the comparatively lower molecular weight of the former. The polymerization rate of the resin containing 30 wt.% ASSQO was slower than that of CQ/EDMAB at early stage. However, at 12 s irradiation the reversed trend was observed and the conversion of BisTEG photoactivated with CQ/ASSQO was slightly greater than that of BisTEG containing CQ/EDMAB. Again, the trend observed at early stage is explained by a comparatively lower mobility of the ASSQO in the reaction medium and to a dilution effect after addition of 30 wt.% of ASSQO; which acts as an unreactive diluent. As the polymerization time goes on, the number of low molecular-weight radicals is less than that of ASSQO because of both its higher termination rate and lower concentration. Moreover, at higher conversion, the intermolecular H-abstraction between amino groups in ASSQO and CQ is less affected by vitrification of the resin than that in the CQ/EDMAB because of the higher local amino concentration in ASSQO, which makes CQ/ASSQO photoinitiator systems yield more active species.

3.4. Mechanical properties

Mechanical characterization of the BisTEG resin containing ASSQO was carried out by measuring flexural and compressive properties. The applied load versus strain curves in flexural tests exhibited a linear relationship over the whole range of strain and all specimens fractured

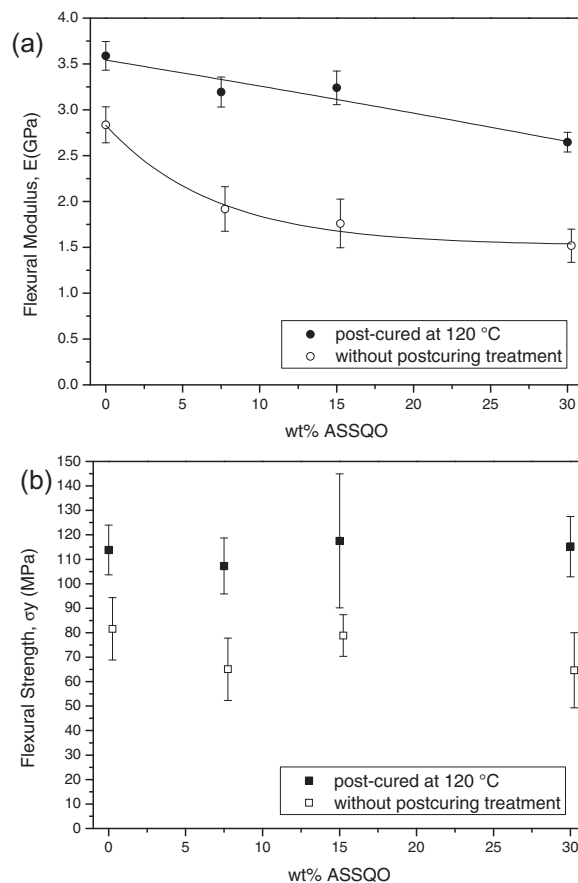


Fig. 4. Flexural modulus and flexural strength in resins containing 1 wt.% CQ in combination with different proportion of ASSQO.

catastrophically in the linear regime. Fig. 4(a) and (b) show the flexural modulus (E) and the flexural strength (σ_f) of materials prepared from BisTEG resin containing different proportions of ASSQO. A good degree of dispersion of the ASSQO was indicated by the optical clarity of the resins upon addition of the nanofillers. As shown in Fig. 3, the polymerization of dimethacrylates in the absence of external heating leads to glassy resins in which only some of the available double bonds have reacted. Before the completion of conversion, the vitrification phenomenon decelerates the reaction to a hardly perceptible rate [29]. The presence of non-reacted monomer can have a plasticizing effect on the polymer, thereby altering the overall properties of the hardened material. Thus, the mechanical behavior of methacrylate polymers containing ASSQO is influenced in a complex way by the presence of the ASSQO and the residual monomer. The flexural test results presented in Fig. 4 show that the presence of ASSQO resulted in a significant decrease in the flexural modulus. By the addition of 30 wt.% of ASSQO, the flexural modulus decreased by approximately 25% and 37% in samples with and without post-curing treatment respectively, compared with the unmodified resin. Conversely, the addition of ASSQO produced no apparent change in the flexural strength. The post-curing treatment at 120 °C increases

monomer conversion and reduces the plasticizing effect of the non-reacted monomer on the mechanical behavior of the nanocomposites. Thus, the higher values of flexural modulus and flexural strength of samples subjected to a post-curing treatment are attributed to a reduced amount of non-reacted monomer. The high data scatter observed in flexural strength values is associated to a brittle rupture of the test specimens [30,31]. Brittle fracture occurs due to the propagation of a crack in the material. Flaws of variable sizes, shapes and orientations with respect to the applied load are possible. Hence, variable crack sizes and their orientations with respect to the applied load can account for the observed scatter of fracture strengths, when nominally identical specimens are tested under nominally identical loading conditions [30,31].

The most striking behavior displayed by BisTEG resins modified with ASSQO is seen in the stress strain curves from compression tests. Multifunctional methacrylates are brittle in nature. Like other brittle materials, they are weak in tension but quite strong in compression and capable of yielding under uniaxial compression. Fig. 5 shows typical curves corresponding to the compression tests of the BisTEG resin containing different proportions of ASSQO. The compressive yield strength (σ_y) was determined from the maximum in the load versus deformation curve (Fig. 5). In Fig. 6, unmodified BisTEG resin is compared with resins containing different mass fractions of ASSQO. It is observed a significant decrease in the compressive strength (σ_y) with increasing content of ASSQO. This observation is in agreement with results reported by previous research on methacrylate-based nanocomposites [32–34]. Cohen et al. [32] found a noticeable decrease in the modulus and yield stress in poly(methylmethacrylate) (PMMA) containing polyhedral oligomeric silsesquioxane for loadings between 0 and 15 wt.%. Similarly, Ash et al. [33] reported that in nanocomposites prepared from PMMA loaded with 17 nm alumina nanoparticles the yield strength of the nanocomposite lies some 20 MPa below that of the neat PMMA. As shown in Fig. 3 the conversion of methacrylate monomer increases with the content of ASSQO. Consequently, the

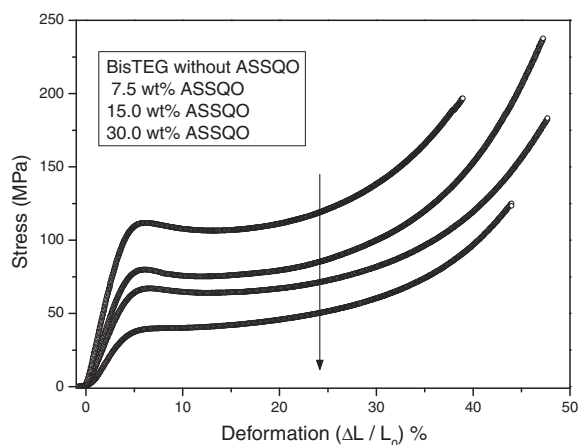


Fig. 5. Typical plots of the compression tests of resins containing 1 wt.% CQ in combination with different proportion of ASSQO.

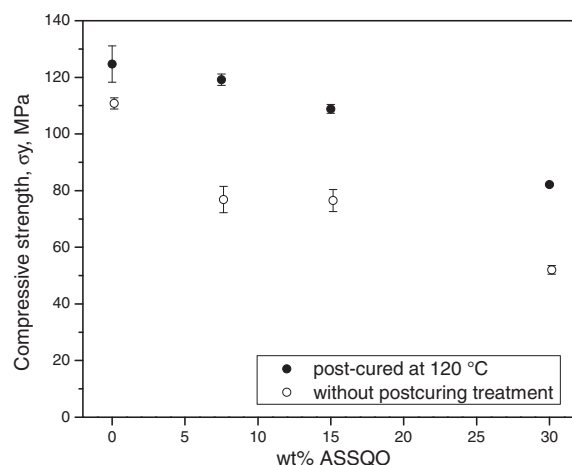


Fig. 6. Compressive yield strength in resins containing 1 wt.% CQ in combination with different proportion of ASSQO.

marked reduction in the yield stress with increasing ASSQO content (Figs. 5 and 6) can not be associated to the plasticization caused by the unreacted monomer.

Different from traditional micro-reinforced composites, in nanostructured materials the surface effect becomes significant and might have a substantial influence on the overall properties. The lack of methacrylate groups in the ASSQO able to polymerize with the BisTEG resin results in the absence of chemical bond between the ASSQO cages and the matrix. It is conceivable that debonding of ASSQO cages from the polymer give rise to nanovoids. These nanovoids would allow the methacrylate matrix to yield and deform plastically thereby reducing the yield stress values. As it was shown in Fig. 3, the lower residual monomer content in samples containing a higher proportion of ASSQO should be accompanied by a higher number of nanovoids. Consequently, the final effect is a decrease in σ_y with increasing amounts of ASSQO.

The surfaces of the specimens used in the flexural tests were analyzed by FESEM and the micrographs are presented in Fig. 7(a)–(c). Micrographs of the neat resin (not shown here) showed a very smooth “mirror-like” fracture surface which is associated with brittle fracture. The addition of ASSQO produced a significant change in the fracture surface aspect compared with the neat resin. Fig. 7(a)–(c) show the drastically different feature of the BisTEG resin containing 7.5 or 30 wt.% ASSQO. The fracture surface is very rough which is indicative of considerable crack branching. Again, the rough surface revealed by the micrographs may be attributed to the plastic deformation of the methacrylate matrix via a nanovoid growth mechanism promoted by debonding of the ASSQO nanocages from the matrix. The presence of voids is highlighted in Fig. 7(c). This confirms that plastic void growth and coalescence in the methacrylate matrix, initiated by debonding of the ASSQO nanocages, has occurred. Although these voids were observed in the fracture surfaces of samples containing 7.5, 15, and 30 wt.% ASSQO they could not be seen on a coated fracture surface of the pure methacrylate polymer. Kinloch et al. [34] reported the presence of

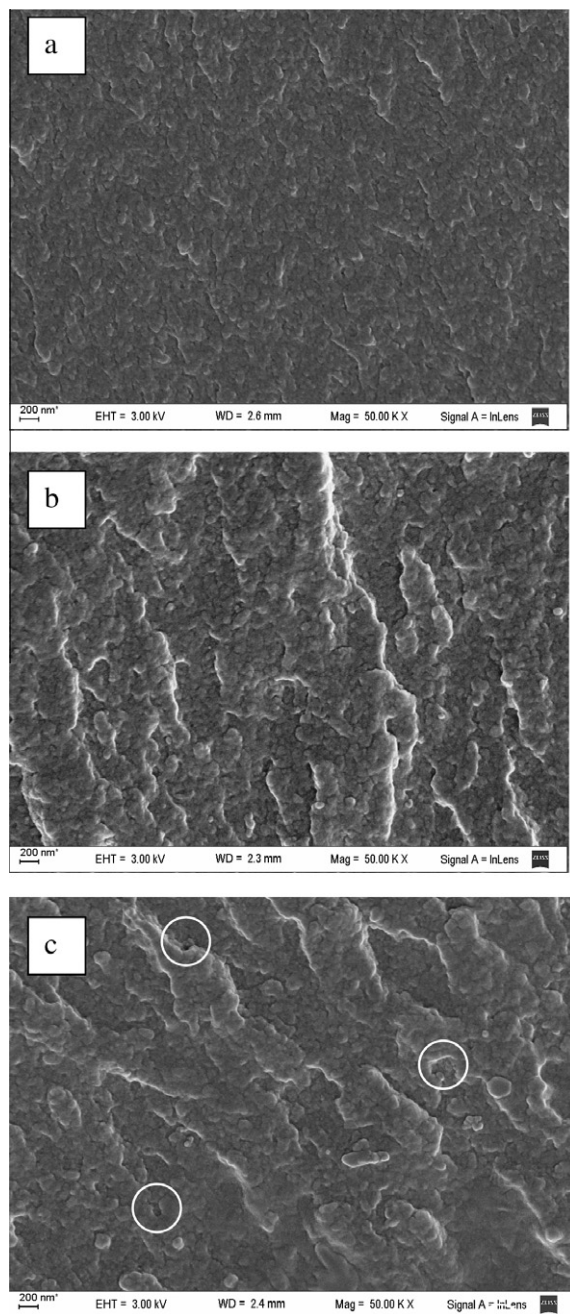


Fig. 7. FESEM images of the fracture surfaces of BisTEG polymer containing (a) 7.5 wt.% ASSQO, (b) 30 wt.% ASSQO, (c) voids that increased its size after deformation of the matrix are highlighted.

nanovoids in an epoxy-anhydride network modified by the addition of silica nanoparticles of 20 nm in diameter. Debonding of the silica nanoparticles and subsequent plastic void growth was demonstrated by the authors from FESEM micrographs; which revealed the presence of nanoparticles surrounded by voids.

From results obtained in this study it emerges that the photoinitiator system CQ/ASSQO exhibits properties that make it attractive as photoinitiator of methacrylate mono-

mers in thick sections (~ 2 mm). Unfortunately, the high photobleaching and polymerization rates of the CQ/ASSQO pair are accompanied by a reduction in the compressive properties. Modification the molecular structure of the ASSQO through the incorporation of polymerizable methacrylate groups is certainly necessary in order to achieve an optimal adhesion between the nanocages and the surrounding methacrylate monomer.

4. Conclusions

Polyhedral oligomeric silsesquioxanes functionalized with amino groups (ASSQO) were prepared by hydrolytic condensation of APS-PGE2 catalyzed by formic acid.

ASSQO were incorporated into methacrylate resins at loadings between 0 and 30 wt.% for visible light polymerization. The optical clarity of the resins upon addition of the ASSQO indicates a good degree of dispersion of the nanofillers. The evolution of monomer conversion versus irradiation time showed that the ASSQO are efficient co-initiator of CQ because a fast reaction and high conversion result after 60 s irradiation at 600 mW/cm².

The high polymerization rates is accompanied by a reduction in the overall mechanical properties. Debonding of ASSQO cages from the polymer give rise to nanovoids; which allows the methacrylate matrix to yield and deform plastically. Consequently, the final effect is a decrease in the flexural and compressive properties with increasing amounts of ASSQO. Modification the molecular structure of the ASSQO through the incorporation of polymerizable methacrylate groups is certainly necessary in order to achieve an optimal adhesion between the nanocages and the surrounding methacrylate monomer.

Acknowledgements

The financial support provided by the CONICET and the ANPCyT is gratefully acknowledged. The authors are grateful to Esstech for the generous donation of the Bis-GMA monomer used in this study.

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