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Hybrid organic–inorganic macromolecular photoinitiator system for visible-light photopolymerization

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ABSTRACT

Hybrid organic–inorganic macrophotoinitiator bearing pendant tertiary amine groups (OI-AH) was prepared by hydrolytic condensation of a silane containing amino groups. The macromolecular amino-functionalized photoinitiator was used in combination with camphorquinone (CQ) for visible-light photo-polymerization. The OI-AH was incorporated into methacrylate resins at loadings between 1 and 10 wt.%. The photodecomposition of the CQ/OI-AH in methacrylate monomers under visible light irradiation ($\lambda = 470$ nm) was examined. The photolysis products of CQ/OI-AH were transparent at the irradiating wavelengths; consequently, the consumption of the CQ is accompanied by increased light intensity in the underlying lays. The clean and rapid photobleaching of CQ in combination with OI-AH makes this photoinitiator system very attractive for polymerization of thick sections. The evolution of monomer conversion versus irradiation time showed that the OI-AH is an efficient co-initiator of CQ because a fast reaction and high conversion of methacrylate groups result after 60 s irradiation with a LED source of 140 mW.

1. Introduction

Photoinitiated free radical polymerization finds extensive applications in the manufacture of coatings, printed circuits, encapsulation of electronic components, printing inks, and dental materials [1]. Photopolymerization of resins upon irradiation with visible light is commonly photoinitiated by the pair camphorquinone (CQ)/amine [2–4]. Low-molecular-weight amines have intrinsic disadvantages such as odor, toxicity, and migration in light-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. The toxicity of 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 migration is by using polymerizable amines that are incorporated into the polymer chain [3,5] or to increase the size of the molecule so that it does not diffuse out of the resin [6–10]. In this regard, the synthesis of hybrid organic–inorganic macrophotoinitiators appears as an interesting approach to increase the size of the amine molecules.

Hybrid polymers are composites containing inorganic and organic building blocks linked via stable covalent bonds [11]. A common method used for the preparation of such hybrid structures involves hydrolysis and polycondensation reactions of organically modified silicon alkoxides by sol–gel process. This leads to the formation of inorganic oxidic networks (Si–O–Si bonds) which contain terminal functional groups capable of specific chemical reactions [11]. In that way, amino-functionalized macrophotoinitiators can be synthesized by hydrolytic condensation of trifunctional organosilicon monomers containing amino groups [11]. It is worth mentioning that organic–inorganic hybrid coatings have attracted increasing interest over the last few years [12–18]. Hybrid coatings obtained by combining sol–gel process and photopolymerization showed improved thermal stability [13], flame retardancy [14], hardness and scratch-resistance [13,15–18] and exhibited excellent chemical and stain resistance properties [12].

The present study was carried out in order to study the reactivity of hybrid organic–inorganic macrophotoinitiators bearing pendant tertiary amine groups as co-initiator of CQ. The photopolymerization of methacrylate monomers using CQ in combination with

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amine functionalized hybrid organic–inorganic macrophotoinitiators at loadings between 0 and 10 wt.% was investigated.

2. Experimental

2.1. Materials

The resin formulation used for this study was 70:30 weight ratio of 2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane (commonly known as bisphenol-A diglycidyl ether dimethacrylate or bis-GMA) and triethylene glycol dimethacrylate (TEGDMA). bis-GMA (Esstech, Essington, PA) and TEGDMA (Aldrich) were used as received. The 70:30 bis-GMA/TEGDMA blend is denoted BisTEG. *N*-[3-(Trimethoxysilyl)propyl]aniline (TSPA, Sigma, 99% purity), 1,2-epoxy-3-phenoxypropane (PGE, Aldrich, 99% purity), formic acid (85 wt.% Sigma) and camphorquinone (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 hybrid organic–inorganic macro-photoinitiator (OI-AH).

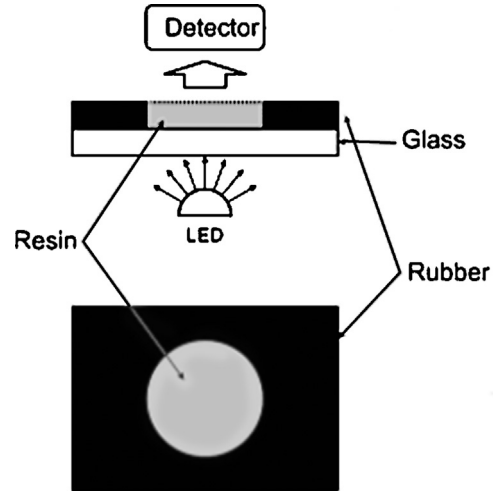
The light source employed was assembled from a LED with its emittance centered at 470 nm (Luxeon LED, Philips). The LED was selected in order to obtain an optimum overlap between the spectral irradiance of the curing unit and the absorption spectrum of CQ. The diameter of the irradiation area was 10 mm, which is equal to photocuring sample's diameter. The intensity of the LED was 140 mW and the irradiance at the surface of the specimen was 178 mW/cm^2.

2.2. Synthesis of hybrid organic–inorganic amine-functionalized photoinitiator (OI-AH)

A trialkoxysilane containing an aromatic tertiary amine group was prepared by reacting 1 mol of TSPA with 1 mol of PGE (a monofunctional epoxy compound). Reaction was carried out under vacuum, for 48 h at 90–95 °C. The product of this reaction is named TSPAP. Hybrid organic–inorganic photoinitiator functionalized with bulky amino groups (OI-AH) was prepared by dissolving TSPAP in THF (0.66 g TSPAP/1 ml THF), and then adding a 3 M HCOOH aqueous solution up to a molar relation $H_2O/Si = 3$. This solution was placed in an open tube at 50 °C for 24 h, allowing continuous evaporation of volatiles. Both silane TSPAP and OI-AH photoinitiator were characterized by size exclusion chromatography (SEC) with a Knauer K-501 device provided with three Phenomenex Phenogel columns (50 Å, 100 Å and M2) and RI detector Knauer K-2301. THF was used as a carrier at a rate of 1 ml min^{-1}. Fourier-transformed infrared spectra (FTIR) were recorded with a Genesis II-Mattson device, in the transmission mode, making coatings on NaCl (MIR) or glass (NIR) windows.

2.3. Photobleaching of CQ in the presence of OI-AH

The photodecomposition of CQ in the presence of the synthesized OI-AH was followed using the changes in absorbance at the wavelength of its maximum absorption. The absorption spectra of CQ were measured with an UV–vis 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 OI-AH were used in different mass fractions OI-AH/CQ: 1, 2, 5 and 10. The extinction coefficient of CQ in methacrylate resin was 42 l/mol cm.



Scheme 1. Measurement of transmitted light during irradiation of BisTEG resin photoactivated with CQ/OI-AH.

In addition to UV–vis experiments, the photobleaching of the CQ was assessed by monitoring the decrease in light absorption as a function of continuous irradiation time. The absorption changes were studied by recording the transmitted light that passed through samples of BisTEG containing CQ/OI-AH. The resin was contained in a 10 mm diameter well constructed from a rubber gasket material and with a glass slide (Scheme 1). The thickness of the samples was equal to 2 ± 0.2 mm. The photodetector of the transmitted light was an OPHIR device (OPHIR Optronics, Israel), PD 2000, range 2 lW–200 mW, precision ±3%. The light source was placed underneath the sample and in contact with the glass substrate. The detector (with a 10 mm diameter sensing area) was placed above and at the center of the sample at a distance <1 mm in order to collect and measure all of the transmitted light as a function of irradiation time. Measurements were also carried out in resins without photoinitiator to correct for the radiation scattered/reflected at the air/glass/resin/air interfaces. Three replicates of each test were performed.

2.4. Measurement of double bond conversion

Measurements of conversion versus time at room temperature (20 °C) in resins prepared with CQ/OI-AH were carried out in 2.0 ± 0.2 mm thick samples using near infrared spectroscopy (NIR) with a Genesis II Mattson FT-IR (Madison, WI). Because the present study has direct relevance to real-life photocuring situations, which occur in the presence of air, dissolved oxygen was not excluded from the resins. The NIR spectra were acquired over the range 4500–7000 cm^{-1} from 16 co-added scans at 2 cm^{-1} resolution. Unfilled resins were sandwiched between two 1 mm thick glass plates separated by a 2 mm thickness rubber spacer, which were tightly attached to the sample holder using small clamps. With the assembly positioned in a vertical position, the photoirradiation source was placed in contact with the glass surface. In order to obtain the double bond conversion as a function of the irradiation time, the samples were irradiated for specific time intervals and the spectra recorded. These spectra were corrected with the background spectrum 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} [3]. Two replicates were used in the measurement of conversion.

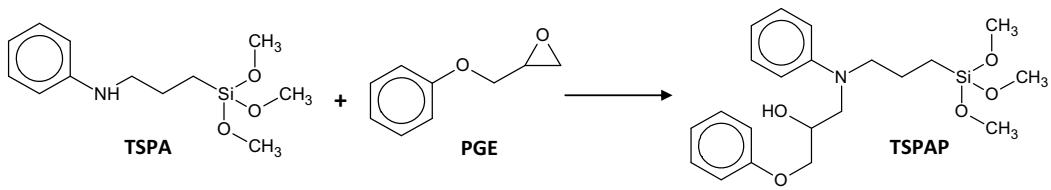


Fig. 1. Epoxy-amine reaction between TSPA and PGE to give the TSPAP silane.

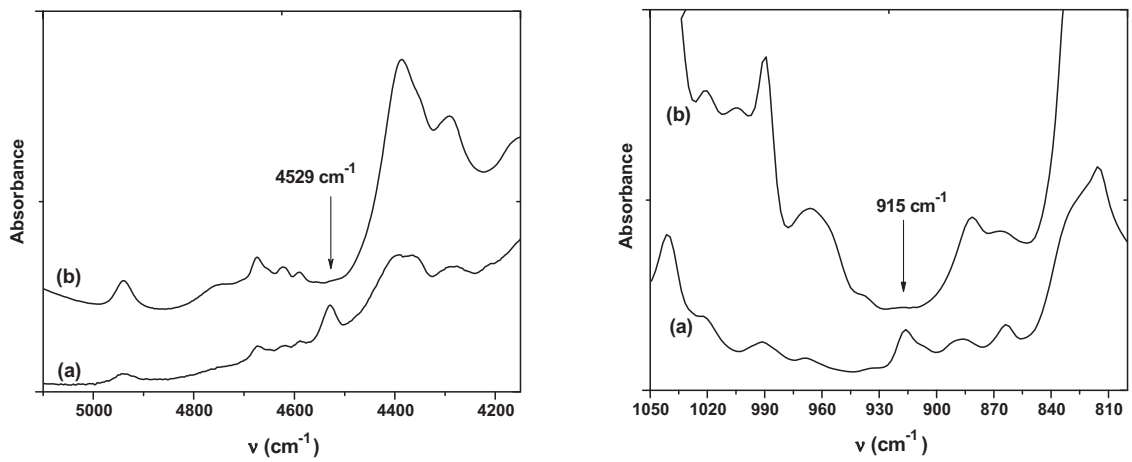


Fig. 2. FTIR spectra (NIR and MIR) of the reaction mixture TSPA + PGE (a) $t = 0$ and (b) $t = 48$ h.

3. Results and discussion

3.1. Synthesis of hybrid organic–inorganic amine-functionalized photoinitiator (OI-AH)

The reaction of the silane TSPA with the monofunctional epoxy compound PGE to give the TSPAP silane containing bulky amino functional group is shown in Fig. 1.

Reaction between PGE and an aliphatic amine is usually completed in 24 h at 50 °C [19]. However, in this case, because of the low reactivity of the aromatic amine longer reaction times and higher temperatures had to be employed in order to achieve complete conversion. Fig. 2 shows that after 48 h reaction, characteristic peaks of epoxy group (915 cm^{-1} and 4530 cm^{-1}) completely disappear.

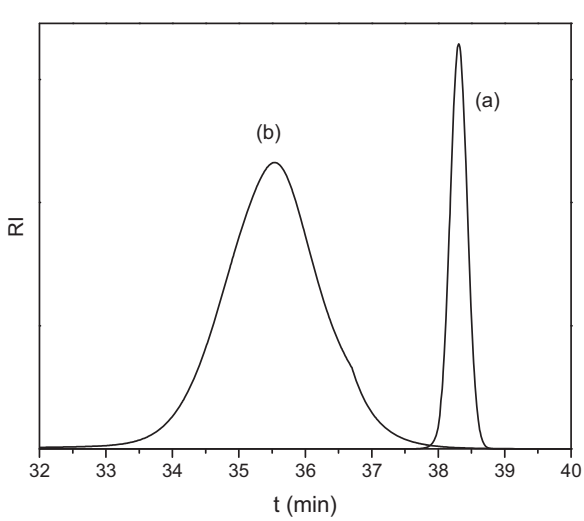


Fig. 3. SEC chromatograms of (a) silane TSPAP and (b) SSO obtained by hydrolytic condensation of TSPAP.

SEC characterization of the silane TSPAP (Fig. 3) showed a narrow peak in the region of low molecular masses (curve a, $t = 38.3$ min). For the resulting product of the hydrolytic condensation of TSPAP, the peak is broader and it is shifted to shorter elution times (curve b, $t = 35.5$ min), indicating the presence of higher molecular mass species.

According to results shown in Fig. 3 and previous characterization by Matrix-assisted ultraviolet laser desorption/ionization time-of-flight mass spectrometry (UV–MALDI-TOF MS) [20], the hydrolytic condensation of TSPAP resulted in a distribution of molecular masses between 2600 and 4700 g mol^{-1}, which can be assigned to species containing 8–14 silicon atoms [20]. Some of the most representative species of the SSO are depicted in Fig. 4.

It must be noticed that every group R that is bonded to the silicon atom in Fig. 4 has one tertiary amine group, thereby acting as a macromolecular co-initiator of CQ in the photopolymerization of double bonds. Fig. 4 shows that the hydrolytic condensation of the TSPAP monomer results in cage-like organic-inorganic structures, which consist of a Si–O–Si inorganic cage surrounded by an organic substituent [11]. The inorganic cage may be a fully condensed closed structure or partially condensed open structure. The diameter of these structures ranges from 1 to 3 nm [11], depending on the number of silicon atoms in the central cage and the peripheral substitution groups surrounding this core. Ideally, trifunctional monomers such as TSPAP would be expected to polymerize to highly-crosslinked networks analogous to silica gels. However, in many sol–gel processes, cyclization reactions play an important role giving rise to soluble species [11]. Under the reaction conditions used in this study, the polycondensation of TSPAP resulted in amino-functionalized clusters with a very large fraction of intramolecular cycles. The absence of higher molar mass oligomers is attributed to the absence of intermolecular reactions that lead to polymer growth. The synthesized OI-AH was liquid at room temperature. It was incorporated into the BisTEG methacrylate resin at mass fractions equal to 1, 2, 5 and 10 wt.%. The optical clarity of the resins upon addition of the OI-AH indicates a good degree of dispersion.

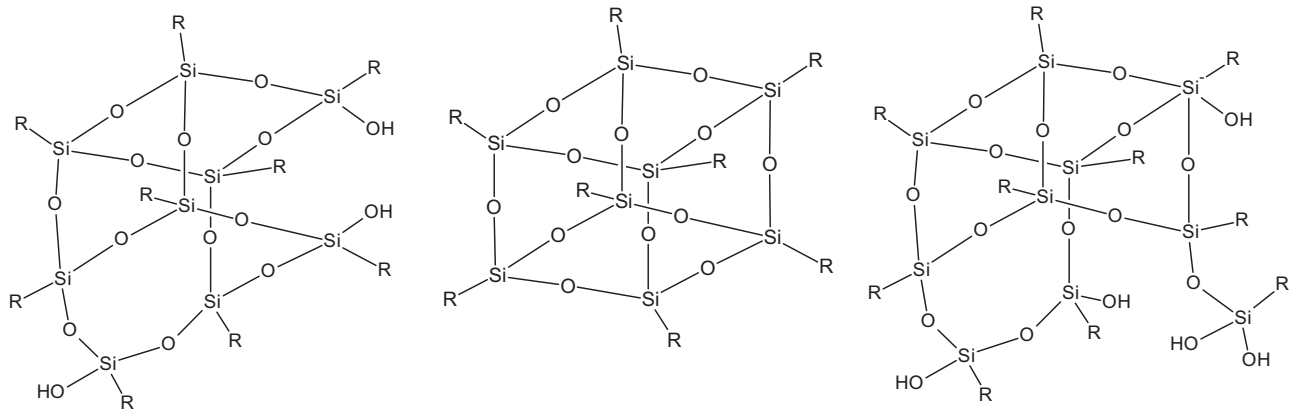


Fig. 4. Representative structures resulting from the hydrolytic condensation of TSPAP.

3.2. Photolysis of CQ in combination with hybrid organic–inorganic photoinitiator

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 [2–5] 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 [21,22]. 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 lays (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 OI-AH was studied in BisTEG resin by monitoring the decrease in absorbance at the wavelength of the maximum absorption of CQ. Fig. 5 shows spectral changes during irradiation of CQ/OI-AH in BisTEG resin showing a continuous decrease in absorbance with irradiation time. CQ displays an intense dark yellow color due to the presence of the conjugated diketone chromophore that absorbs at 470 nm. During irradiation of CQ and reduction of one of the carbonyl groups, the conjugation is destroyed, causing loss of the yellow color. By irradiating the sample for less than 120 s the absorbance of the CQ in the sample was reduced to 80% of the initial value.

In addition to UV–vis studies, the photobleaching of CQ in polymerizing resins was assessed by monitoring the transmitted light intensity under continuous irradiation. Fig. 6 shows a typical plot of the recorded transmitted light (I_T) and the absorbed light (I_A) by the CQ as a function of irradiation time corrected by subtraction of the light lost by scattering at the sample interfaces or absorbed by the resin alone.

As was mentioned previously, an important characteristic of photopolymerization reactions is the spatial non-uniformity of the reaction rate, due to the variation of local light intensity throughout the specimen [21,22]. Initially, the initiator concentration is uniform, and the light intensity will decrease with depth according to

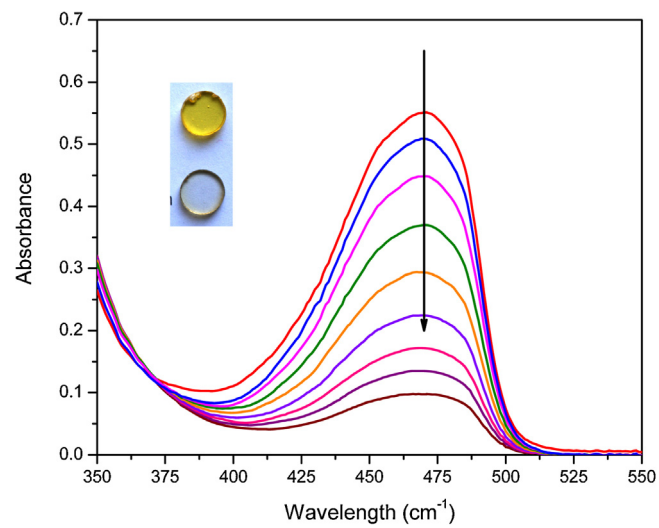


Fig. 5. Typical spectral changes during irradiation of BisTEG resin containing 1 wt.% CQ in combination with 5 wt.% OI-AH. The irradiation times were 0, 8, 16, 32, 48, 64, 80, 92 and 120 s. CQ displays an intense dark yellow color due to the presence of the conjugated diketone chromophore that absorbs at 470 nm. During irradiation of CQ the conjugation is destroyed, causing loss of the yellow color. (For interpretation of the reference to color in the text citation of this figure, the reader is referred to the web version of this article.)

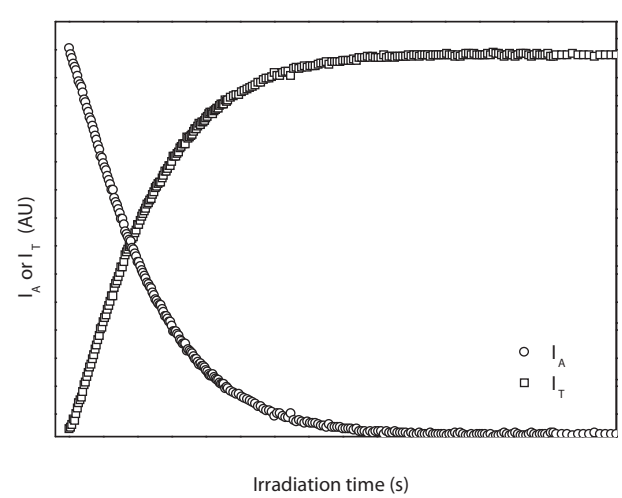


Fig. 6. Typical registers of transmitted and absorbed light intensity vs. irradiation time for BisTEG resin photoactivated with CQ/OI-AH. The ordinate is in arbitrary units.

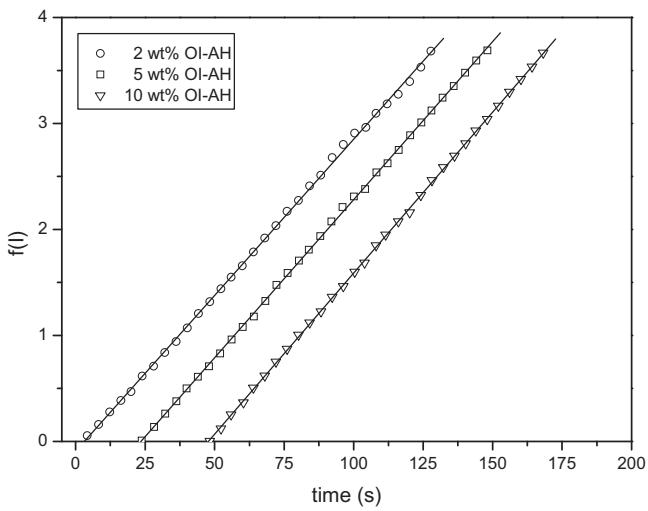


Fig. 7. Plots of Eq. (4) for BisTEG resins containing 1 wt.% CQ in combination with 2, 5 and 10 wt.% OI-AH. The plots are shifted for clarity. The regression coefficients were >0.99.

the Beer–Lambert law. In addition, with photobleaching initiators, as the initiator is consumed, the light penetrates more deeply into the sample. This results in a spatiotemporal variation of the local concentration of photoinitiator (and thus photoinitiation rate), which can be assessed from the photobleaching rate constant of the photoinitiator [21]. The rate of photoconsumption of CQ is related to the volumetric rate of absorption of photons by the following expression [21]:

$$-\frac{dCQ}{dt} = \frac{\Phi I_A}{V} = \frac{\Phi I_0^*(1 - e^{-2.302\varepsilon CQL})}{AL} \quad (1)$$

where Φ is the quantum yield for the photoinitiator consumption (defined as the number of CQ molecules decomposed per photon absorbed), I_A is the number of photons per unit times absorbed by the sample in unit volume V, I_0^* is the incident light intensity (in terms of the number of photons irradiating the surface per unit time), ε is the decadic wavelength dependent extinction coefficient of CQ (42 ± 2 l/mol cm) [3], CQ is the molar concentration of CQ averaged over the sample thickness, A and L are the area and thickness of the sample respectively and t is the irradiation time. Eq. (1) can be integrated provided that the CQ concentration represents the depth (or volume) averaged concentration [21]. Thus, the decomposition rate constant can be assessed in a thick sample by integrating Eq. (1) [21]:

$$-\ln\left[\frac{1 - e^{2.302\varepsilon CQL}}{1 - e^{2.302\varepsilon CQ_0 L}}\right] = 2.302\Phi\varepsilon I_0 t = kt \quad (2)$$

where CQ_o is the initial concentration of CQ, I_0 is the incident light irradiance (calculated as the incident light intensity divided by the sample area A) and k is the pseudo first order decomposition rate constant of the CQ consumption. According to the Beer–Lambert law, the absorbance of the sample (ABS) is given by:

$$\mathrm{ABS} = \varepsilon LCQ = -\log\frac{I_T}{I_0} \quad \text{and} \quad CQ = -\frac{1}{2.303\varepsilon L}\ln\left(\frac{I_T}{I_0}\right) \quad (3)$$

Combination of Eqs. (2) and (3) yields:

$$f(I) = -\ln\left[\frac{I_{T0}}{I_T}\frac{(I_0 - I_T)}{(I_0 - I_{T0})}\right] = 2.303\Phi\varepsilon I_0 t \quad (4)$$

From the evolution of the transmitted light during irradiation, the rate constants for the CQ consumption were calculated using Eq. (4). Plots of $f(I)$ against time, give straight lines with a slope equal to the rate constants for the CQ consumption. Fig. 7 shows plots of Eq. (4) from measurements of transmitted light versus time during irradiation of BisTEG resin. The photobleaching of CQ in combination with OI-AH in BisTEG resin resulted in linear plots with regression coefficients greater than 0.995 during the total period of irradiation (Fig. 7). Since the polymerizing BisTEG resin changes from relatively viscous material to glassy networks during the irradiation period, the linearity of the plots in Fig. 7 shows that the rate of photobleaching of CQ in is not sensitive to the mobility of the medium.

Generally, in free radical mediated polymerization, photogenerated radicals and the growing macroradicals are quenched by oxygen, which reduces the rate of polymerization [23]. The presence of amine is useful in suppressing inhibition by the reaction of oxygen with the C-based radicals through a radical chain transfer process, which regenerates the initiation reaction [23]. The photolysis of CQ started after an induction time ranging between 4 and 8 s, which is attributed to the quenching of the triplet state of CQ by dissolved oxygen [23,24]. Formulations prepared with higher proportion of OI-AH resulted in lower induction periods because the inhibiting species were consumed faster. It is seen that, for the range of amine concentration studied, the rate of photobleaching of the CQ was independent of the amine concentration. These results are in agreement with trends reported by Cook [24] 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 [21,22]. Fig. 5 shows that the photolysis products of CQ/OI-AH 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 OI-AH makes this photoinitiator system very attractive for polymerization of thick sections.

3.3. Conversion of methacrylate resin photoactivated with CQ/OI-AH

The photoinitiation capability of CQ in combination with OI-AH 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 [2,24]. 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. 8 shows the progress of monomer conversion versus irradiation time in BisTEG resin with different amount of OI-AH. As expected, the polymerization reaction increases with increasing content of OI-AH because the number of amine radical increases. Plots in Fig. 8 show that amine groups present in the OI-AH are efficient co-initiator for CQ because a fast reaction and high conversions are obtained after 60 s irradiation. The evolution of the polymerization reaction photoinitiated by the pair CQ/ethyl-4-dimethylaminobenzoate (EDMAB), which showed an optimum polymerization rate [3], is shown for comparison in the same plot. From Fig. 8 it is seen that the polymerization rate of CQ in combination with OI-AH was slower than that of the CQ/EDMAB pair. The different photoinitiation efficiencies of formulation containing CQ/EDMAB or CQ/OI-AH may be attributed to structural effects on the recombination rate of radicals and on the radical reactivity toward the monomer

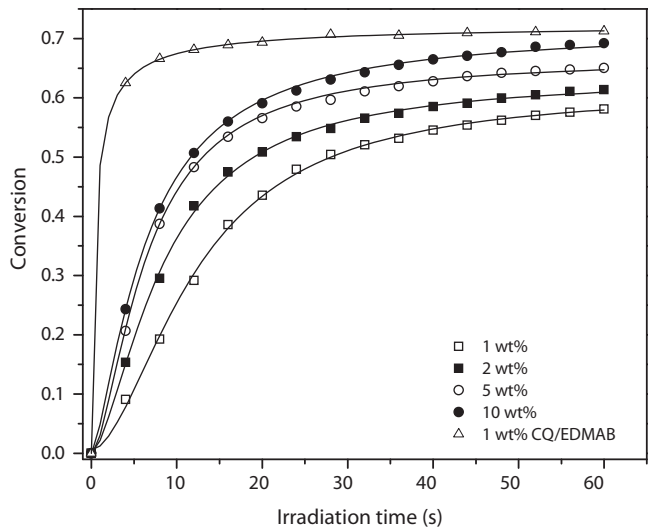


Fig. 8. Monomer conversion versus irradiation time for a 2 mm thick Bis-TEG resin specimen containing 1 wt.% CQ in combination with 1, 2, 5 and 10 wt.% OI-AH. The polymerization reaction photoinitiated by the pair CQ/ethyl-4-dimethylaminobenzoate (EDMAB) is shown for comparison.

double bond [2]. In addition, the mobility of EDMAB is expected to be higher than that of OI-AH structures due to the comparatively lower molecular weight of the former.

In previous studies, different organic–inorganic oligomeric silsesquioxanes functionalized with bulky amino groups were prepared and used as coinitiator of CQ in the photopolmerization of methacrylate resins. In a first stage, organotriethoxysilanes were synthesized by reacting 1 mol of 3-(aminopropyl) triethoxysilane with 2 mol of 1,2-epoxy-3-phenoxypropane [25] or 1 mol of *N*-(β-aminoethyl)-γ-aminopropyltrimethoxy silane with 3 mol of 1,2-epoxy-3-phenoxypropane [26]. The amino-functionalized organic–inorganic oligomeric silsesquioxanes were obtained in a second stage by the hydrolytic condensation of the modified silanes catalyzed by formic acid. In comparison with those previous studies, the present OI-AH showed a higher reactivity for the photopolymerization of methacrylate resins. Resins containing 10 wt.% of the OI-AH reached 70% conversion after 60 s irradiation (Fig. 8) while in the previous studies, the amount of organic–inorganic oligomers needed to reach 70% conversion was 20 wt.% [25] or 30 wt.% [26]. The amino groups of the OI-AH synthesized in this study contain nitrogen atoms bonded to an aromatic ring. In analogy with EDMAB, this feature is considered responsible of its higher reactivity compared with the organic–inorganic oligomeric silsesquioxanes studied previously. The comparatively lower amount of OI-AH needed to reach the same value of monomer conversion has a direct impact on the mechanical properties of the cured materials. 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 chemical bonds between the OI-AH and the methacrylate matrix give rise to nanovoids which allow the methacrylate matrix to yield and deform plastically under load. Resins containing a higher proportion of OI-AH should be accompanied by a higher number of nanovoids. As reported previously [25,26], the final effect is a decrease in flexural modulus and compressive strength with increasing amounts of OI-AH.

4. Conclusions

Hybrid organic–inorganic macrophotoinitiatos functionalized with amino groups (OI-AH) were prepared by hydrolytic condensation of a silane containing bulky amino groups. OI-AH were incorporated into methacrylate resins at loadings between 1 and 10 wt.% for visible light polymerization.

The photolysis products of CQ/OI-AH 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 OI-AH makes this photoinitiator system very attractive for polymerization of thick sections.

The evolution of monomer conversion versus irradiation time showed that the OI-AH are efficient co-initiator of CQ because a fast reaction and high conversion result after 60 s irradiation with a LED source of 600 mW/cm^2.

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