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Tris(trimethylsilyl)silane as a co-initiator for dental adhesive: Photo-polymerization kinetics and dynamic mechanical property

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Abstract

Objectives—The purpose of this study was to evaluate the polymerization behavior of a model dentin adhesive with tris(trimethylsilyl)silane (TTMSS) as a co-initiator, and to investigate the polymerization kinetics and mechanical properties of copolymers in dry and wet conditions.

Methods—A co-monomer mixture based on HEMA/BisGMA (45/55, w/w) was used as a model dentin adhesive. The photoinitiator system included camphorquinone (CQ) as the photosensitizer and the co-initiator was ethyl-4-(dimethylamino) benzoate (EDMAB) or TTMSS. Iodonium salt, diphenyliodonium hexafluorophosphate (DPIHP) serving as a catalyst, was selectively added into the adhesive formulations. The control and the experimental formulations were characterized with regard to the degree of conversion (DC) and dynamic mechanical properties under dry and wet conditions.

Results—In two-component photoinitiator system (CQ/TTMSS), with an increase of TTMSS concentration, the polymerization rate and DC of C═C double bond increased, and showed a dependence on the irradiation time and curing light intensity. The copolymers that contained the three-component photoinitiator system (CQ/TTMSS/DPIHP) showed similar dynamic mechanical properties, under both dry and wet conditions, to the EDMAB-containing system.

Significance—The DC of formulations using TTMSS as co-initiator showed a strong dependence on irradiation time. With the addition of TTMSS, the maximum polymerization rate can be adjusted and the network structure became more homogenous. The results indicated that the TTMSS could be used as a substitute for amine-type co-initiator in visible-light induced free radical polymerization of methacrylate-based dentin adhesives.

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Keywords

Dental adhesive; Silane; Co-initiator; Fourier transform infrared; Dynamic mechanical analysis; Polymerization kinetic

1. Introduction

Camphorquinone (CQ)/amine initiation system is the most widely employed system for visible-light curing of methacrylate-based dental restorative materials. CQ itself can photoinitiate polymerization, but at a low reaction rate. Aliphatic or aromatic amines, such as *N*,*N*-dimethylptoluidine, 2-ethyl-dimethylbenzoate, *N*-phenylglycine, ethyl-4-dimethylaminobenzoate (EDMAB), 2-(dimethylamino) ethyl methacrylate (DMAEMA), and many other amine-containing compounds, are widely used as co-initiators for CQ [1–9]. Among these compounds, EDMAB is a very popular co-initiator in dental restorative materials due to its low basicity and high efficiency.

The limitations of EDMAB include sensitivity to oxygen inhibition [10], unstable under acidic conditions [11] and in acidic dental resin formulations [12–14], and leached EDMAB is potentially cytotoxic [15]. Usually, an acid-base reaction occurs between electron donors and electron acceptors, which may result in a charge transfer complex (CTC). This charge transfer complex may interfere with polymerization. For example, the polymerizable co-initiator DMAEMA was ineffective for acidic monomers because of its strong basicity [6]. The search for new co-initiators remains an important issue in the development of durable dentin adhesives and composites.

Silyl radicals have widespread use in hydrosilylation and reduction reactions in organic chemistry. Tris(trimethylsilyl)silane (TTMSS) was synthesized by Gilman and co-workers in 1965 [16]. Nearly 20 years later, the Chat-gilialoglu laboratory discovered that TTMSS could serve as a radical-based agent [17,18]. Recently, the TTMSS radical has been characterized for applications in photoinitiation systems by Lalevee et al. [19–25]. Lalavee and colleagues reported that TTMSS had the following attributes: (1) a high inherent reactivity for the addition to double bonds, and (2) a low ionization potential which is associated with an oxidation process and the formation of silylium cations. Newly developed photoinitiator (PI) systems based on TTMSS exhibited a high reactivity both in free radical polymerization (FRP) [26] and free radical promoted cationic polymerization (FRPCP) [27]. The ability to efficiently consume oxygen is a particularly interesting feature of the PI systems based on TTMSS. Potentially the TTMSS-based PI systems can overcome the classical and well known oxygen inhibition of the FRP or FRPCR processes [22]. In addition, TTMSS did not exhibit a toxic response when tested in several biological test systems [28–30].

The efficacy of the PI systems depends on the H-atom donor ability of co-initiators and the compatibility of initiator components with resin. The hydrophobicity of CQ and EDMAB has limited their performance in the wet, oral environment. To address this limitation, a third component, iodonium salt, diphenyliodonium hexafluorophosphate (DPIHP), has been adopted into the two-component PI system [31,32]. DPIHP, with higher solubility in water, acts as an electron acceptor which offers dual roles, i.e., to regenerate the photosensitizer (CQ) and to generate additional active phenyl radicals [31]. Due to this unique ability, the iodonium salt is expected to promote the free radical polymerization within the CQ/TTMSS PI system.

It is well known that the structure and properties of polymeric materials are governed in part by the kinetics of the polymerization reaction. Polymerization kinetics determines the microgel structures, degree of conversion (DC), and many other characteristics [33–38]. Silanes in the presence of a PI such as benzophenone (BP), isopropylthioxanthone (ITX), or camphorquinone (CQ) are highly reactive and even better than a reference amine co-initiator such as EDMAB [22,24]. In spite of these advantages, there are no reports on the use of TTMSS as a co-initiator in methacrylate-based dental polymers.

In this work, HEMA/BisGMA (45/55, w/w) was used as a model resin. The polymerization behavior of this model resin when EDMAB or TTMSS was used as a co-initiator for photosensitizer CQ was studied in detail. The objective of this work was to evaluate the efficiency of TTMSS as co-initiator in neat methacrylate-based resin. The overall research hypotheses of this study were: (1) the polymerization behavior of neat resin formulated with TTMSS was comparable to neat resin formulated with EDMAB in the two-component PI system, (2) because of its ability to enhance radical efficacy, the addition of DPIHP will significantly increase the final degree of conversion and maximum polymerization rate, (3) the relative crosslink densities of the polymethacrylate network formulated using TTMSS was similar to EDMAB, and (4) the rate of polymerization with TTMSS will affect the mechanical properties of the neat methacrylate resin under dry and wet conditions.

2. Materials & methods

2.1. Materials

2,2-Bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]propane (BisGMA, St. Louis, MO) and 2-hydroxyethyl methacrylate (HEMA, St. Louis, MO) were used as received without further purification as monomers in dentin adhesives. Camphoroquinone (CQ), ethyl-4-(dimethylamino) benzoate (EDMAB), tris(trimethylsilyl)silane (TTMSS) and diphenyliodonium hexafluorophosphate (DPIHP) were obtained from Sigma-Aldrich (St. Louis, MO). All other chemicals were reagent grade and used without further purification.

2.2. Preparation of adhesive formulations

The monomer mixtures were made with 45 wt% HEMA and 55 wt% BisGMA. The formulation containing CQ (0.5 wt%), EDMAB (0.5 wt%) and DPIHP (0.5 wt%) were used as controls [32,39]. The experimental formulations consisting of EDMAB, TTMSS and DPIHP are listed in Table 1. The mixtures of monomers/PIs are prepared in brown glass vials under amber light. The preparation of adhesive formulations and their polymer beams have been reported previously [40,41]. In brief, the solutions containing the monomers/PIs were mixed overnight at 23 ± 2 °C to promote complete dissolution and formation of a homogeneous solution. The prepared resins were injected into a glass-tubing mold (Wilmad, P 1m-1.2m-0-914m) and light-cured for 40 s at 23 ± 2 °C with a LED light curing unit (LED

Curebox, 100 mW/cm^2 irradiance, Proto-tech, Portland, OR). The polymerized samples were stored in the dark at 23 ± 2 °C for at least 48 h prior to testing. The resultant round beam specimens (L × D = 15 mm × 1.0 mm) were used to determine dynamic mechanical properties.

2.3. Real-time double bond conversion and maximal polymerization rate

The DC and polymerization behavior were determined by FTIR as described by our group [39,42]. Real-time in-situ monitoring of the photopolymerization behavior of the different adhesive formulations was performed using an infrared spectrometer (Spectrum 400 Fourier transform infrared spectrophotometer, Perkin-Elmer, Waltham, MA) at a resolution of 4 cm^{-1}. One drop of adhesive solution was placed on the zinc selenide (ZnSe) crystal top plate of an attenuated total reflectance (ATR) accessory (PIKE Technologies Gladi-ATR, Madison, WI) and covered with a mylar film to prevent oxygen inhibition of polymerization. A 40 or 120-s exposure to the commercial visible-light-polymerization unit (Spectrum® 800, Dentsply, Milford, DE) at an intensity of 550 mW/cm^2 was initiated after 50 infrared spectra had been recorded. Real-time IR spectra were continuously recorded for 600 s after light activation began. A time-based spectrum collector (Spectrum TimeBase, Perkin-Elmer) was used for continuous and automatic collection of spectra during polymerization. A minimum of three replicates were obtained for each adhesive formulation. The change of the band ratio profile-1637 cm^{-1} (C=C)/1608 cm^{-1} (phenyl) was monitored, and DC was calculated using the following equation based on the decrease in the absorption intensity band ratio before and after light curing.

$$\mathrm{DC}=\left(1-\frac{\mathrm{absorbance}^{\mathrm{sample}}_{1637\ \mathrm{cm}^{-1}}/\mathrm{absorbance}^{\mathrm{sample}}_{1608\ \mathrm{cm}^{-1}}}{\mathrm{absorbance}^{\mathrm{monomer}}_{1637\ \mathrm{cm}^{-1}}/\mathrm{absorbance}^{\mathrm{monomer}}_{1608\ \mathrm{cm}^{-1}}}\right)\times 100\% \quad (1)$$

The average of the last 50 values of the time-based spectra is reported as the DC value. The maximum polymerization rate ($R_{p(\mathrm{max})}/[M]$) was determined using the maximum slope of the linear region of the DC-time plots [32].

To determine the DC as a function of irradiation intensity, samples were irradiated with the commercial visible-light-polymerization unit (Spectrum® 800, Dentsply, Milford, DE) at intensities of 550, 300, or 50 mW/cm^2. Irradiation intensity was measured at the sample surface with a visible light curing meter (Cure Rite, Model 644726, Dentsply, Milford, DE).

2.4. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) is a thermal analysis technique that measures the properties of materials as they are deformed under periodic stress. This technique is particularly well suited for characterizing viscoelastic materials. Since the technique measures both elastic and viscous responses, it is considered a valuable tool for obtaining information regarding the crosslink density and structural heterogeneity of polymer networks [43,44].

In this study, DMA tests were performed using a TA instruments Q800 DMA (TA Instruments, New Castle, USA) with a three-point bending clamp. The dynamic mechanical properties of methacrylate-based dentin adhesives have been described by our group [41,42,45]. A sinusoidal stress is applied and the resultant strain is measured. The properties measured under this oscillating loading are storage modulus, loss modulus, and tan δ. The storage modulus (E') represents the stiffness of a viscoelastic material and is proportional to the energy stored during a loading cycle. The loss modulus (E'') is related to the amount of energy lost due to viscous flow. The ratio of loss (E''”) to storage modulus (E') is referred to as the mechanical damping, or tan δ. The frequency used to measure the storage modulus is 1 Hz with an amplitude of 15 μm and a preload of 0.01 N [41,45]. In the dry condition, the storage modulus is measured from 10 to 200 °C with a ramping rate of 3 °C/min. The glass transition temperature (T_g) is determined as the position of the maximum on the derivate storage modulus vs. temperature plots. Round beam specimens (1.0 mm × 15 mm) prepared as described previously are used for DMA measurements. A minimum of three specimens of each material are measured.

The inverse ratio (ζ) of the modulus in the rubbery region to the temperature was used to represent the relative crosslink density [46,47]. The full-width-at-half-maximum (FWHM) of the tan δ curves was used to represent the heterogeneity of the network.

Wet-condition DMA tests are operated using the three-point submersion clamp [46,48]. Round beam specimens (1.0 mm × 15 mm) are immersed in water at 23 °C for at least 5 days to be fully hydrated. The test temperature is varied from 10 to 80 °C with a ramping rate of 1.5 °C min^{-1}.

2.5. Statistical analysis

The results were analyzed statistically using one-way/two-way analysis of variance (ANOVA), together with Tukey’s test at $\alpha = 0.05$ (Microcal Origin Version 8.0, Microcal Software Inc., Northampton, MA) to identify significant differences in the means or interaction.

3. Results

Fig. 1 shows the real-time polymerization kinetic profiles of the neat methacrylate formulation with two-component PI systems (CQ/EDMAB or CQ/TTMSS). When EDMAB was used as co-initiator, the double bond conversion and maximum polymerization rate varied slightly with an increase in EDMAB concentration from 0.5 to 1.0 wt%. These properties also showed a slight variation when the irradiation time was increased from 40 to 120s. The DC values were not significantly different ($p < 0.05$) after 10 min.

When TTMSS was used as co-initiator, an increase in concentration from 0.5, 1.0, and 3.0 wt% led to an increase in final DC (10 min) from 21.6 ± 0.2, 37.9 ± 0.4, to 54.3 ± 2.4%, respectively. When the irradiation time was increased from 40 to 120 s, the final DC was 30.3 ± 2.8, 51.4 ± 0.7, and 61.6 ± 0.7%, respectively. When TTMSS was used as the co-initiator, the DC at 120 s irradiation was significantly greater ($p < 0.05$) than the DC at 40 s. The maximum polymerization rates were not significantly different ($p < 0.05$). As the irradiation time is increased, the final DC also increased. The DC is affected by several factors including the PI system and the total dose of irradiation. From Fig. 1C, when EDMAB (0.5%) was used as the co-initiator, irradiation time had limited effect on the DC and 40 s irradiation was sufficient to achieve DC of about 60%. In contrast, irradiation time had a significant effect on DC when TTMSS was used as a co-initiator.

The DC of two-component PI formulations using EDMAB or TTMSS as co-initiator is shown in Table 2. With the increase of TTMSS concentration from 0.5 to 3.0 wt%, the DC (10 min) of CT-formulations increased from 21.6 ± 0.2 to 55.7 ± 0.6%, which was significantly lower than that of the control (CE-0.5, CQ/EDMAB = 0.5 wt%/0.5 wt%). However, increasing the irradiation time from 40 to 120 s, the DC of CT-3.0 (CQ/TTMSS = 0.5/3.0 wt%) was comparable with that of the control (CE-0.5, CQ/EDMAB = 0.5//0.5 wt %). Meanwhile, the DC of two-component formulations is observed to be a function of irradiation time, and is determined by the PI system. As the irradiation time is increased, the final DC also increased. With an increase in irradiation time from 40 to 120 s, the instantaneous DC showed about 4% increase using EDMAB as co-initiator, however, the instantaneous DC increased about 10% using TTMSS as co-initiator. An irradiation time of 40 s was sufficient to achieve final DC of 60.2 ± 0.1% and 64.6 ± 0.2% at 0.5 and 1.0 wt% EDMAB, respectively.

Fig. 2 shows the polymerization profiles of HEMA/BisGMA resin with binary co-initiators (combined EDMAB and TTMSS). In binary co-initiator formulations, the double bond DC was 61.0 ± 0.3 and 62.5 ± 0.6% with an increase of TTMSS concentration from 1 to 3 wt%. This DC was similar to the control (60.2 ± 0.2%). The $R_{p(\max)}/[M]$ was reduced from 0.043 ± 0.003 to 0.035 ± 0.003 s^{-1}, which was lower than the control (0.066 ± 0.004 s^{-1}). The DC decreased from 60.2 ± 0.2 to 52.4 ± 0.6% and the $R_{p(\max)}/[M]$ was reduced from 0.066 ± 0.004 to 0.038 ± 0.003 s^{-1} with a decrease in the concentration of EDMAB from 0.5 to 0.25 wt%.

Fig. 3 shows the polymerization behavior of the neat resin with three-component PI (CQ/EDMAB/DIPHP or CQ/TTMSS/DPIHP). The DC of the control with three-component PI was about 5% greater than that of two-component PI, and with the addition of iodonium salt, the $R_{p(\max)}/[M]$ was increased from 0.066 to 0.23 s^{-1}. When TTMSS was used as co-initiator and its concentration increased from 0.5 to 1.0 and even 3.0 wt%, the DC increased from 52.7 ± 0.5, 54.3 ± 0.2, and 61.5 ± 0.2%, respectively. The corresponding $R_{p(\max)}/[M]$ was 0.068 ± 0.002, 0.068 ± 0.011, and 0.044 ± 0.002 s^{-1}, respectively.

The DC values obtained from the real-time polymerization kinetics of the neat resin photocured by varying the light intensity are shown in Table 3. In two-component PI formulations (CQ/EDMAB or CQ/TTMSS), when EDMAB was used as the co-initiator, the irradiation intensity had minimal effect on the DC. When TTMSS was used to replace EDMAB, the DC was similar at about 55% except for the case when the light intensity was reduced to 50 mW/cm^2. In three-component PI systems (CQ/EDMAB/DPIHP or CQ/TTMSS/DPIHP), the decrease in light intensity did not have an effect on the final DC with either EDMAB or TTMSS. When plotting the DC vs. the total dose (irradiation intensity × irradiation time), the conversion values vary significantly as a function of the dose (Fig. 4).

The conversions were achieved rapidly at the lower light intensities. This result suggests that the conversion values were proportional to the light intensity at 40 s exposure.

Fig. 5 shows the storage modulus (A) and tan δ (B) as a function of temperature for the control and experimental adhesives with three-component PI. At 25 °C, the storage modulus values for both polymer networks are in the range of 4000–4500 MPa. The storage moduli decrease with increasing temperature, reaching the range of 28–34 MPa in the rubbery state. The rubbery storage modulus and T_g of the experimental formulation were slightly lower than that of control, and decreased with an increase in TTMSS concentration. When the TTMSS concentration was higher than 1 wt%, an obvious shoulder appeared at lower temperatures. The DMA results acquired under both dry and wet conditions are shown in Table 4 and Table 5. The relative crosslink density, which is calculated based on the inverse ratio (ξ) of modulus in the rubbery region to the absolute temperature, showed no significant difference ($p < 0.05$). The value of the full-width-at-half-maximum (FWHM) of the CTD-3.0 (CQ/TTMSS/DPIHP = 0.5/3.0/0.5 wt%) was significantly lower than that of the control ($p < 0.05$).

4. Discussion

In dental resins, the photopolymerization reaction is initiated by multicomponent photoinitiator systems, such as two-component CQ/amine or three-component CQ/amine/iodonium salt, which are activated by visible light. Indeed, the amine free radical, formed after the hydrogen abstraction from amine by activated photosensitizer CQ, starts and guides the polymerization of methacrylate at a high rate. It has been widely reported that the type of amine directly affected the polymerization behavior [49,50]. It has also been reported that the amine systems undergo an acid-base reaction with acidic monomers and this reaction can affect the initiation of the polymerization process [51].

Recently, the silyl radicals were reported as efficient species in FRP and FRPCP. The rate constants increase together with a decrease of the bond dissociation energy BDE(X–H). The BDE(X–H) of EDMAB and TTMSS are 92.8 and 79.8 kcal/mol, respectively [52]. Therefore, Si–H showed an efficient hydrogen transfer and high reactivity compared with C–H. It has been reported that the polymerization profiles in the presence of TTMSS for acrylate were better than that obtained in the presence of EDMAB. The profiles showed an increase of both the polymerization rates and final conversions [25]. Based on these results, TTMSS was selected as a co-initiator in the current investigation. The effect of TTMSS on the photopolymerization, and the relationship between polymerization kinetics and the mechanical performance of a model dental adhesive resin were determined.

One of the distinct clinical advantages of light-cured dental restorative materials is that light-curing offers the practitioner flexibility in terms of manipulating the material and initiating the polymerization reaction. Parameters that may negatively affect the conversion include insufficient light intensity and irradiation time that is too short. There is agreement in the literature that the source intensity should be over 400 mW/cm^2, that irradiation time should be no more than 60 s [53–56], usually less than 30–40 s [1]. The parameters are based on studies that directly or indirectly determined the conversion or conversion rate at a given time after light irradiation.

For the TTMSS silyl radical, a high reactivity with addition rate constant (k_{add}~2.2 × 10^7 M^{-1} s^{-1}) to methyl acrylate was noted [22]. For the EDMAB generated radical, the value is 5 × 10^5 M^{-1} s^{-1} [57]. These results demonstrate the high potential of the silyl radicals to act as a photoinitiating species. In the present study, the generation of silyl radical involves an interaction between excited CQ and TTMSS that leads to hydrogen abstraction. When TTMSS replaces EDMAB as co-initiator, a lower reactivity is clearly noted in Fig. 1. In the two-component PI system, the DC of the TTMSS-containing formulation was significantly lower ($p < 0.05$) than that of the control (CE-0.5, CQ/EDMAB = 0.5/0.5 wt%). The maximum polymerization rate with TTMSS is slower than that with EDMAB. It is reported that the hydrogen abstraction rate constants of PI/silane (k_H~10^6 – 10^8 M^{-1} s^{-1}) are much lower than that of PI/amines ($k'_H \sim 10^8 - 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$) [22]. This has been attributed primarily to a different mechanism, i.e., electron/proton transfer for amine vs. hydrogen atom transfer for silane [10]. The lower CQ/TTMSS interaction could limit the concentration of produced silyl free radical, which is the crucial step to determine the polymerization rate and the final conversion of methacrylate. It is observed that the DC of TTMSS-containing formulations increased significantly with an increase in TTMSS concentration from 0.5 to 3.0 wt% or irradiation time from 40 to 120 s (Table 2). Meanwhile, the maximum polymerization rates remained similar, which indicated that the maximum polymerization rate was not determined by the TTMSS concentration or irradiation time. Thus, based on these results the first hypothesis, which state that the polymerization behavior of neat resins formulated with TTMSS or EDMAB is comparable in the two-component PI system, is rejected.

Assuming that the termination of free radical photopolymerization occurs primarily through a bimolecular process, the rate of free radical photopolymerization R_p is expressed by Eq. (2) [58,59], where k_p is the propagation rate constant, k_t the termination rate constant, and R_i the initiation rate as defined in Eq. (3) [58]. In Eq. (3), ϕ_i represents the initiation quantum yield that corresponds to the number of starting polymer chains per photon absorbed, I_0 is the intensity of incident light, ε is the molar extinction coefficient of the PI, $[I]$ is the concentration of the PI, and d is the thickness of the sample.

$$R_P = k_p \left(\frac{R_i}{k_t}\right)^{1/2} [M] \qquad (2)$$

$$R_i = \phi_i I_{\mathrm{abs}} \phi_i I_0 \left(1 - 10^{-\varepsilon[I]d}\right) \qquad (3)$$

With an increase in irradiation time from 40 to 120 s, the I_{abs} was enhanced and the R_i increased accordingly with both EDMAB and TTMSS. All of the R_p are proportional to the irradiation time or the total dose. However, the hydrogen abstraction rates between CQ/

EDMAB and CQ/TTMSS were different, which led to different ϕ_i values. Due to the fast hydrogen abstraction rate of CQ/EDMAB, the DC increased slightly with an increase in irradiation time. When TTMSS was used as co-initiator, with an increase in irradiation time, the DC increased significantly (see Fig. 1B and C). It must be noted that the 120 s irradiation time, utilized in this work, is not necessarily applicable or appropriate for the clinical setting. The clinical recommendation is generally less than 60 s [53].

In the binary co-initiator formulations (mixture of EDMAB and TTMSS as co-initiator), with the increase of TTMSS concentration from 1.0 to 3.0 wt%, the concentration of the generated free radical was increased and the final DC was increased slightly. However, the maximum R_p was decreased accordingly. This result was attributed to a competition reaction between the generated amine radical with monomer or TTMSS (See Scheme 1). It was reported that some carbon-centered radicals can abstract a hydrogen atom from TTMSS, and the rate constants were about (1.4–3.8) × 10^5 M^{-1} s^{-1} [60]. Because the addition rate constant is very close to the hydrogen abstraction rate constant, part of the amine radicals can react with TTMSS and generate silyl radicals (Scheme 1), which then react with monomers and produce the macroradicals. At the same time, due to the lower bond dissociation energy of Si–H, the macroradical can react with TTMSS via "chain transfer" reaction. The polymer chain is terminated and generates a TTMSS radical, which can then begin a new polymer chain. Since the initiation stage of CQ/TTMSS is slower than CQ/EDMAB, it can be assumed that the EDMAB radicals will be formed first during the irradiation and initiate the poly-merization. Following the initiation, two reactions may occur: (1) EDMAB radical reacts with TTMSS, and (2) macroradicals react with TTMSS, which reduced the maximum polymerization rate.

It is well known that the reasonable intensity of the irradiation light has a dramatic effect on the polymerization rate [61]. When EDMAB was used as co-initiator, whether in the two-component or three-component PI system, the DC and the polymerization rate were similar even with a decrease in the light intensity from 550 to 50 mW/cm^2. The results indicated that EDMAB was an efficient co-initiator at these light intensities. When TTMSS was used as a co-initiator, without the addition of iodoium salt (DPIHP), the DC and polymerization rates increased with an increase in the light intensity. With the increase in irradiation intensity, the amount of light absorbed (I_{abs}) increased and the R_i was promoted, which showed a positive effect on the R_p. At the same time, with the addition of DIPHP, there was no significant difference in DC or polymerization rate with an increase in irradiation intensity. Although, the reaction mechanism using a three-component PI system is more complex, it was postulated that these results can be attributed to the generation of higher activity phenyl free radical [62] (see Scheme 1).

It has been reported that the polymerization rate and final conversion could be dramatically improved with the addition of iodonium salt, DPIHP, into the two-component initiator system [32]. The improvement in these properties was due to generation of the higher reactive phenyl radical between the amine or silyl radical and the DPIHP. Our results showed the same trend whether in CQ/EDMAB/DPIHP or CQ/TTMSS/DPIHP system. Meanwhile, the maximum polymerization rates of TTMSS-containing formulations were still significantly lower than that of the control (CED, CQ/EDMAB/DPIHP = 0.5/0.5/0.5 wt

%). Therefore, in the three-component PI system, with the addition of TTMSS, the maximum polymerization rate was reduced due to the slower initiation stage. However, the conversion (after irradiated 10 min) showed no significant difference ($p < 0.05$) when compared to the system with EDMAB as co-initiator. Thus, the results support acceptance of the second hypothesis, i.e., the addition of DPIHP will significantly increase the final conversion and maximum polymerization rate.

The copolymer specimens prepared with CQ/TTMSS system were relatively soft and could not be retrieved for dynamic mechanical analysis. Therefore, only the specimens prepared with three-component PI system were used to determine the mechanical properties shown in Fig. 5. At low temperature, both the control and experimental specimens showed a gradual decrease in storage moduli with increasing temperature. With the increase of TTMSS concentration from 0.5 to 3 wt%, the slope became more distinct. Near the glass transition temperature, storage moduli decreased drastically. As heating continues the storage moduli reached the rubbery plateau. During the visible-light irradiation, microgel formation at initiation sites and cyclization reactions have created a heterogeneous cross-linked network structure [63]. The loosely cross-linked regions, highly cross-linked regions and the unreacted monomers or initiators could give a network with a broad distribution of mobility [63]. When the TTMSS content was 0.5 wt%, the tan δ curve was similar with the control. With an increase of the TTMSS content to 3 wt%, rubbery moduli were slightly lower than that of the control and the shoulder peak of tan δ curve became more obvious. The shoulder peak was attributed to the side chains and unreacted ends in the polymer network [45].

In the present work, TTMSS may act as plasticizer, which facilitates the movement of the side chains. The rubbery modulus has been related to the crosslink density of the polymeric materials. The inverse ratio (ζ) of the modulus in rubbery region to the temperature has been used to represent the relative crosslink density [46]. The value of ζ suggested comparable relative crosslink density when TTMSS was used to replace EDMAB. The maximum polymerization rates were depressed with the addition of TTMSS, but the crosslink densities were not significantly different. Therefore, based on these results, the third hypothesis is accepted.

In Table 4 and Fig. 5, it is noted that the full-width-at-half-maximum (FWHM) values for the tan δ curves decreased with an increase in the TTMSS concentration. With the exception of the experimental specimen that contained 3 wt% TTMSS, the heights of tan δ peak for the experimental specimens were not significantly different from the control ($p < 0.05$). Previous investigators have reported decreased polymerization rate and more homogenous network structure with the addition of TTMSS [64]. The current investigation shows similar results, i.e., the heterogeneity of the copolymer was decreased by the slower polymerization rate associated with an increase in the TTMSS concentration.

Traditionally, HEMA/BisGMA dental resins initiated with three-component PI system form polymers with a heterogeneous network structure, because of the unequal reactivity of the functional groups in the co-monomers. The formation of microgels can be determined by many factors, such as the monomer structure, initiation rate, viscosity, and so forth [63,65]. It has been shown that the propagating radicals can react with pendant double bond by primary cyclization, or secondary cyclization. The crosslinking mechanism associated with the primary cyclization causes reduction in the effective crosslink density [34]. In the present study, the slower R_p with the addition of TTMSS promoted the primary cyclization; meanwhile, due to the lower bond dissociation energy of Si–H, the macroradical can react with TTMSS via “chain transfer” reaction. Therefore, the effective crosslink density could be decreased. In this manner, the copolymer of HEMA/BisGMA was expected to increase the homogeneity. Although the heterogeneity of copolymer was decreased by the slower polymerization rate, under dry conditions, the mean storage modulus for the experimental specimens (Table 4) was not significantly different from the control ($p < 0.05$).

When adhesive formulations are photopolymerized in the mouth, the copolymer can become saturated with water and this can lead to plasticization of the polymer. The three-point bending water-submersion clamp method is used to study the polymer under conditions that simulate the wet, oral environment. The moduli of the control and experimental specimens were significantly lower than that of the dry samples. These differences could be due to the plasticizing effect of water. When TTMSS was 1 wt%, the storage modulus at 25 or 37 °C was not significantly different from that of the control (Table 5). However, the moduli of the experimental specimens at 70 °C were significantly lower than that of the control ($p < 0.05$). These findings suggest that the effective crosslink density of network structure of the HEMA/BisGMA copolymer system was affected by changes in polymerization behavior and the structure was affected negatively by the wet environment. Two-away ANOVA has been used to analyze the effect of environment conditions (dry vs. wet). Based on the results from the mechanical property measurements under dry and wet conditions, the fourth hypothesis is accepted. The fourth hypothesis states that the polymerization rates will affect the mechanical properties of the polymethacrylate in dry and wet conditions.

In the literature, the TTMSS-based radicals were reported to possess outstanding reactivity and new photoinitiating systems have been proposed based on TTMSS [19–25]. In the present work, the maximum polymerization rates of methacrylate-based dentin adhesive were reduced dramatically by TTMSS. Compared with EDMAB, a decrease of both the polymerization rates and the final conversion were contradictory with Lalevee’s result [66]. These differences are attributed primarily to the use of acrylate monomers in Lalevee’s work while methacrylate monomers were used in the current study. In the present study, with the exception of the slow polymerization rates, comparable DC of C=C bond and mechanical properties, under dry condition, were observed with the addition of TTMSS. Placement of resin composite over the uncured adhesive surface layer will potentially produce further polymerization of the bonding agent by diffusion of reactive components from the composite into the adhesive. It has also been theorized that the placement of the resin composite will displace the uncured adhesive and generate a mixed layer of the two compounds at the interface. The diffusion of unfilled resin into the overlying resin composite was reported by Rueggeberg and Margeson [67], and they concluded that this diffusion allowed more opportunities for the migration of free radicals into the composite material. It is unclear whether the uncured adhesive layer is required for the coupling of a resin composite. Some studies have suggested a positive correlation between the oxygen-inhibition layer, which characteristically exhibits low conversion, and composite bonding

[68–70]. Investigation of the oxygen-inhibited layer and its impact on the interfacial composite/adhesive bond are ongoing.

5. Conclusions

The polymerization behavior and the mechanical properties of methacrylate formulations using TTMSS as a co-initiator have been determined. The DC varied as a function of the total irradiation dose and the PI system. In the two (CQ/TTMSS) or three (CQ/TTMSS/DPIHP)-component PI system, the R_p and DC were depressed compared with the control. Without the addition of iodonium salt, the R_p and DC showed an obvious dependence on the irradiation time and light intensity. Our results indicated that the two-component PI system based on the TTMSS exhibited a low reactivity in free radical polymerization, which was attributed to the decrease of the hydrogen abstraction yield between TTMSS and excited CQ. In three-component PI systems, when the co-initiator TTMSS was used at a concentration of 3 wt%, the degree of conversion was close to that of EDMAB at 0.5 wt%. In dry conditions, the storage modulus was insensitive to the polymerization rate. The relative crosslink densities of the experimental formulations showed no significant difference ($p < 0.05$) when compared to the control. The decrease of FWHM value with an increase of TTMSS concentration indicated that a more homogeneous structure can be obtained by slowing the polymerization rate. Further study is needed to provide a thorough understanding of the behavior of TTMSS when used under conditions representative of the wet, oral environment.

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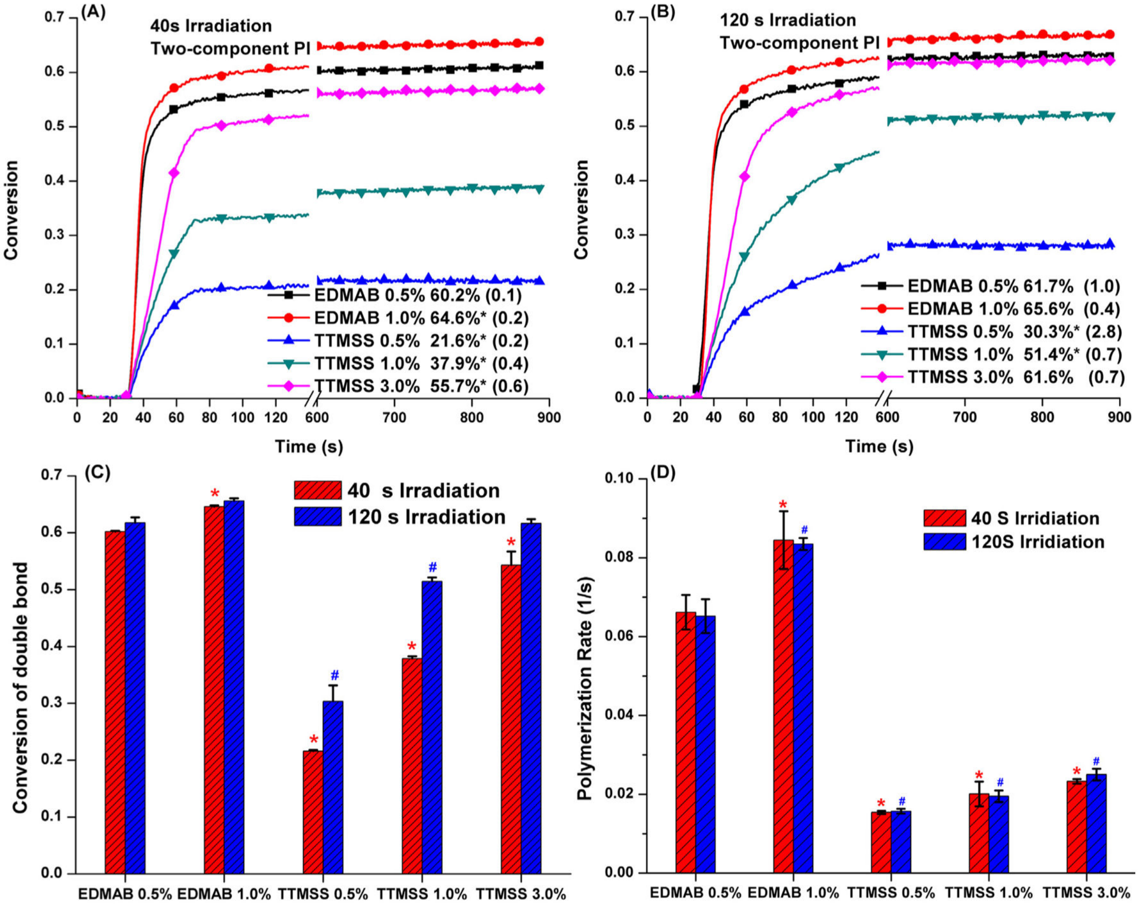


Fig. 1.

Polymerization profiles of HEMA/BisGMA (45 wt%/55 wt%) under visible-light irradiation (I_0 = 550 mW/cm^2) in the presence of two-component PI (CQ/EDMAB or CQ/TTMSS): conversion vs. time curves with 40 s (A) and 120 s (B) irradiation, conversion (C) and maximum polymerization rate (D) vs. co-initiator concentration. '*', '#' significantly ($p <$ 0.05) different from the control (CE-0.5, CQ/EDMAB = 0.5/0.5 wt%). The value in the () is the standard deviation.

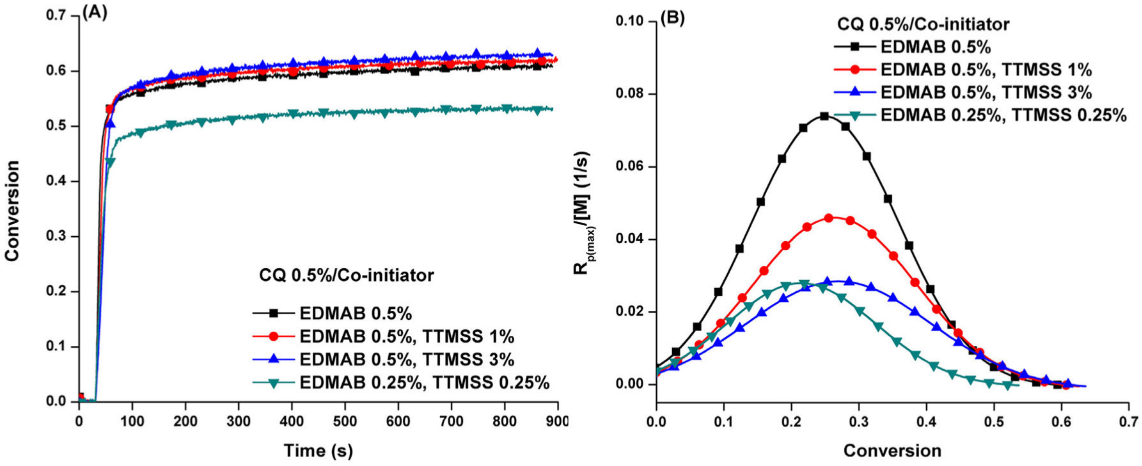


Fig. 2.

Polymerization profiles of HEMA/BisGMA (45 wt%/55 wt%) under visible light (I_0 = 550 mW/cm^2) in the presence of binary co-initiators (EDMAB and TTMSS).

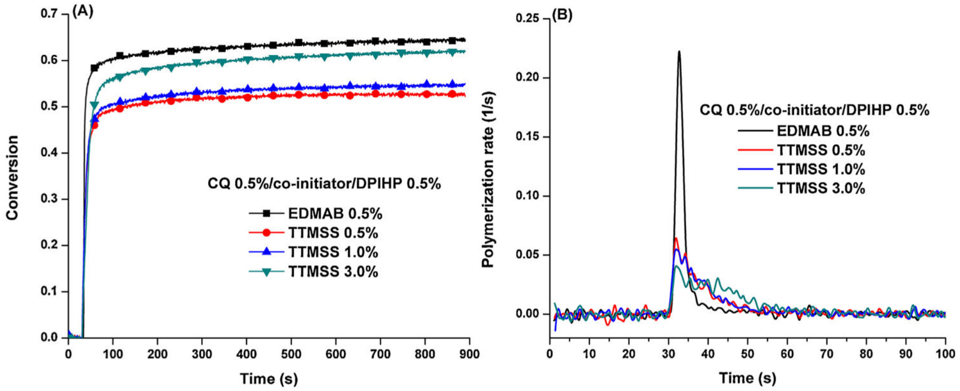


Fig. 3.

Photopolymerization profiles of HEMA/BisGMA (45 wt%/55 wt%) under visible light (I_0 = 550 mW/cm^2) in the presence of three-component PI. (CQ 0.5 wt%, DPIHP 0.5 wt%, and EDMAB or TTMSS).

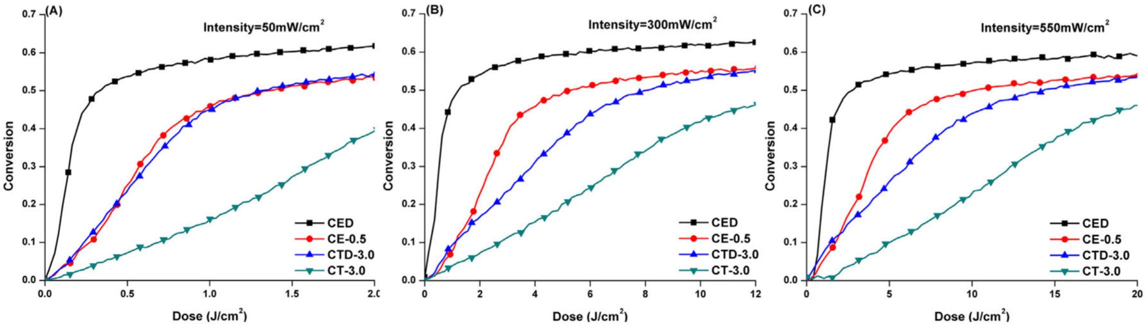


Fig. 4.

Conversion vs. dose (irradiation intensity × 40 s) for HEMA/BisGMA (45/55, w/w) resin at irradiation intensities of (A) 50, (B) 300, and (C) 550 mW/cm^2.

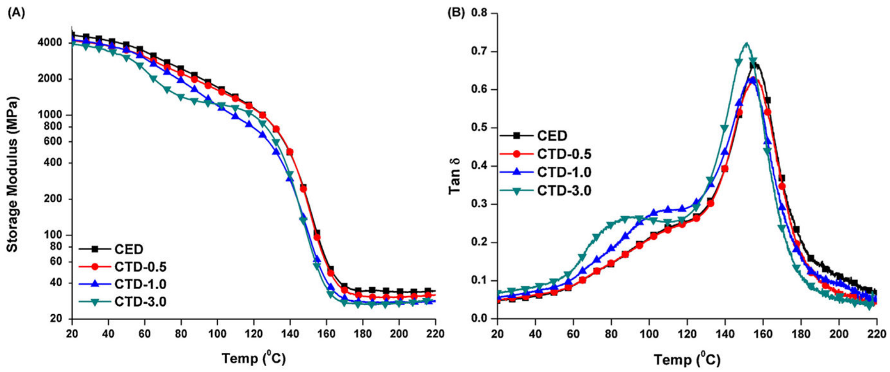
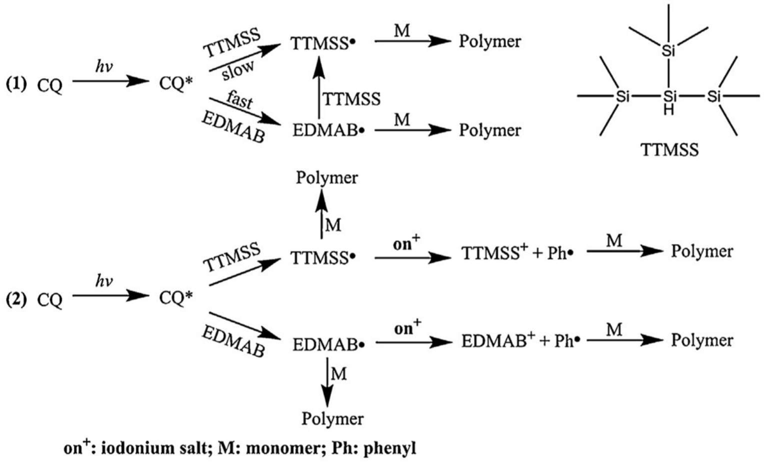


Fig. 5.

The Storage modulus (A) and tan δ (B) versus temperature curves for the control and experimental adhesives with three-component PI in dry condition. (CED: EDMAB 0.5 wt%, CTD-0.5: TTMSS 0.5 wt%, CTD-1.0: TTMSS 1.0 wt%, and CTD-3.0: TTMSS 3.0 wt%. Other components in the formulation were HEMA/BisGMA = 45/55, CQ 0.5 wt%, DPIHP 0.5 wt%).



Scheme 1.

The illustration for the generation of free radicals in two-component and three-component PI systems.

Table 1

Formulations of the control and experimental adhesive speciments with different PI.

Type	Run[a]	CQ	EDMAB	TTMSS	DPIHP
Two-component PI	CE-0.5[b]	0.5	0.5	/	/
	CE-1.0	0.5	1.0	/	/
	CT-0.5	0.5	/	0.5	/
	CT-1.0	0.5	/	1.0	/
	CT-3.0	0.5	/	3.0	/
Three-component PI	CED[c]	0.5	0.5	/	0.5
	CTD-0.5	0.5	/	0.5	0.5
	CTD-1.0	0.5	/	1.0	0.5
	CTD-3.0	0.5	/	3.0	0.5
Binary co-initiator	CET-1.0	0.5	0.5	1.0	/
	CET-3.0	0.5	0.5	3.0	/
	CET-0.25	0.5	0.25	0.25	/

[a] The resin was mixed HEMA/BisGMA in the ratio of 45/55 (w/w).

[b] The formulation was used as the control in two-component or combined co-initiator PI systems.

[c] The formulation was used as the control in three-component PI system.

Table 2

Instantaneous DC of two-component PI formulations with varied irradiation time.

Run[a]	CQ	EDMAB	TTMSS	DC of 40 s irradiation (%)		DC of 120 s irradiation (%)	
				40 s[b]	600 s[c]	120 s[b]	600 s[c]
CE-0.5	0.5	0.5	/	54.6 (0.2)	60.2 (0.1)	58.2 (1.2)	61.8 (1.0)
CE-1.0	0.5	1.0	/	58.7[*] (0.3)	64.6[*] (0.2)	62.6[*] (0.1)	65.6 (0.4)
CT-0.5	0.5	/	0.5	19.5[*] (0.6)	21.6[*] (0.2)	29.7[*] (3.0)	30.3[*] (2.8)
CT-1.0	0.5	/	1.0	32.7[*] (0.5)	37.9[*] (0.4)	46.2[*] (0.1)	51.4[*] (0.7)
CT-3.0	0.5	/	3.0	48.1[*] (0.1)	55.7[*] (0.6)	57.8 (0.7)	61.6 (0.7)

[a] The resin was mixture of HEMA/BisGMA (45/55, w/w) and the irradiation intensity is 550 mW/cm^2.

[b] Instantaneous DC after 40 or 120 s light irradiation turn off.

[c] DC after light irradiation turn off for 600 s.

[*] Significantly (p < 0.05) different from the control (CE-0.5).

Table 3

DC of the two/three-component PI formulations at varied irradiation intensity[a].

Run	Irradiation intensity (mW/cm^2)	DC[b] (%)
CED	50	68.3 (0.2)
	300	68.0 (0.1)
	550	63.9 (0.2)
CE-0.5	50	59.5 (0.9)
	300	61.9 (0.3)
	550	60.2 (0.2)
CTD-3.0	50	59.4 (0.5)
	300	62.0 (1.7)
	550	61.5 (0.2)
CT-3.0	50	49.0 (1.0)
	300	55.6 (1.7)
	550	54.3 (2.4)

[a] The irradiation time is 40 s.

[b] DC after light irradiation turn off for 600 s.

Table 4

DMA results of the control and experimental samples containing three-component PI in dry condition.

Run	Storage Modulus (MPa)			T_g (°C)	tan δ	ζ (K/MPa)	FWHM of tan δ (°C)
	25 °C	37 °C	>160 °C				
CED	4450 (159)	4199 (124)	33.9 (0.5)	155.1 (1.4)	0.66 (0.01)	13.5 (0.2)	37.9 (2.6)
CTD-0.5	4086[a] (33)	3843[a] (30)	29.8 (1.6)	156.3 (0.2)	0.64 (0.02)	15.3 (0.8)	39.4 (0.4)
CTD-1.0	4245 (111)	3967 (123)	29.7 (1.6)	152.5 (2.1)	0.63 (0.01)	15.3 (0.9)	37.6 (1.2)
CTD-3.0	4434 (99)	4130 (99)	28.9 (1.0)	152.3 (0.5)	0.71[a] (0.02)	15.5 (0.5)	31.6[a] (1.0)

[a] Significantly ($p < 0.05$) different from the control (CED, CQ/EDMAB/DPIHP = 0.5/0.5/0.5 wt%).

The value in the () is the standard deviation.