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Cyclic acetal as coinitiator for bimolecular photoinitiating systems

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Abstract

Cyclic acetals were used to replace the conventional amines in bimolecular photoinitiating systems. The mixtures of benzophenone derivatives and cyclic acetals were used to initiate the UV photopolymerization of 1,6-hexanedioldiacrylate (HDDA). Camphorquinone (CQ)/1,3-benzodioxole (BDO) combinations were used to initiate the visible light photopolymerization of 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (BisGMA)/triethylene glycol dimethacrylate (TEGDMA) (70/30 wt%) for dental application. The kinetics was recorded by real-time infrared spectroscopy (RTIR). Ethyl 4-*N*,*N*-dimethylaminobenzoate (EDMAB) was used as control in the same photocuring condition. The results showed that the addition of cyclic acetals greatly increased the rate of polymerization (R_p) and final double bond (DC) of HDDA. Combination of *p*-chlorobenzophenone (CBP)/BDO had the highest initiating reactivity. BDO also showed an effective coinitiator for camphorquinone-based initiator system. Comparing with EDMAB, CBP/BDO and CQ/BDO indicated comparable initiating reactivity. Moreover, the natural component characteristics of BDO made it a promising alternative to commercial amine in biomolecular photoinitiating system.

Keywords: Bimolecular photoinitiating system; Coinitiator; Photopolymerization

1. Introduction

Photopolymerization of multifunctional monomers provides a method for production of highly cross-linked polymers [1–5], which is particularly useful for applications such as industry coatings and dental materials in which mechanical strength and durability are primary concerns.

Photoinitiated radical polymerizations are usually carried out in the presence of photoinitiators of the ''cleavage'' type or hydrogen abstraction type [4,6]. Among the most commonly used photoinitiators for free radical polymerization, bimolecular initiating systems are widely used in biomedical applications, especially in dental restorative fields, which undergo intermolecular hydrogen abstraction process from a coinitiator that contains labile hydrogen [2–4,7,8]. Tertiary amines are the most frequently employed co-initiators due to its higher reactivity. However, amines are known to mutagenicity and tend to induce substrate corrosion and cause yellow of the cured films. In particular, toxicity of the materials applied to the dental applications has caused public concern in the past years.

Comparing with the monomer system, the small-sized initiator molecules are more easily extractable [9,10], which cause the biocompatibility problems. Bowen and Argentar [11] had synthesized several tertiary aromatic amine coinitiators with molecular weight above 400 to reduce the toxicity. However, the solubility and color issues limit their use in biomedical and food industry. Thus, polymerizable amine emerges as required, which introduces the tertiary amine part to the polymer chains [12–14].

Although the commercial polymerizable amines have greatly improved the biocompatibility, seeking a more biocompatible coinitiator is still a great challenge. The acetal

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function is a well-known protecting group with unique reactivity [15,16]. It has ever been reported that the monoester radical generated by the photoirradiation onto cyclic acetal compounds could initiate the polymerization of vinyl compounds and methyl methacrylate [17,18]. More recently, photosensitized hydrogen abstraction from 2-alkyl-1,3-dioxolanes by triplet benzophenone provides a viable alternative for synthesis of 1,4-diketones [19]. Benzodioxole derivatives as another type of cyclic acetals are widely distributed in nature, and possess various biological activities [20–22]. It has been demonstrated that hydrogen abstraction process could also take place from the methylene-bridge carbon and form a methylenedioxybenzene radical [23]. In this study, cyclic acetals were used as hydrogen donors for bimolecular photoinitiating systems, and benzodioxole derivatives could be expected especially as a substitute for commercial aromatic tertiary amine in dental applications. The synergistic effect of cyclic acetals and BP derivatives or CQ was investigated by real-time near FTIR technique. The dynamic mechanical analysis was used to measure the glass transition (T_g) and modulus of the cured samples.

2. Experimental

2.1. Materials

1,6-Hexanedioldiacrylate (HDDA) (donated by Sartomer Chemical Co.), 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (BisGMA, Aldrich) and triethylene glycol dimethacrylate (TEGDMA, Sartomer) were used as received. UV initiators (benzophenone derivatives) such as benzophenone (BP), *p*-chlorobenzophenone (CBP), and methyl-*o*-benzoylbenzoate (OMBB) were all donated by Runtech Chemical Co. Visible light initiator camphorquinone (CQ) was purchased from Aldrich. Cyclic acetals 1,3-benzodioxole (BDO, Acrōs Organics), 2-methyl-1,3-dioxolane (MDO, Aldrich), 2-phenyl-1,3-dioxolane (PDO, Aldrich), 2-methoxy-1,3-dioxolane (MODO, Acrōs Organics), acrolein ethylene acetal (AEA, Fluka Chemika), glycerol formal (mixtures of 40% 4-hydroxymethyl-1,3-dioxolane and 60% 5-hydroxy-1,3-dioxane) (GF, Fluka Chemika), and ethyl 4-*N*,*N*-dimethylaminobenzoate (EDMAB, Aldrich) were used without further purification. The chemical structures of photoinitiators and coinitiators are shown in Fig. 1.

2.2. Measurement

Real-time FTIR with a horizontal sample holder (Nicolet 5700, Thermo Electron, USA, equipped with an extended range KBr beam splitter and an MCT/A detector) was used to monitor the extent of polymerization. UV photopolymerization and visible light photopolymerization were triggered by EFOS Lite spot light source (5 mm crystal optical fiber, Canada) with 320–480 nm filter and with 400–500 nm filter, respectively. The UV light intensity was 42 mW/cm^2 (Honle UV meter, Germany) and the visible light intensity was 100 mW/cm^2 (400–1000 nm, Beijing Normal University, China). Photopolymerizations were carried out at room temperature in the mixture of monomer, initiator and coinitiator. All concentrations were with respect to the monomer, unless noted elsewhere. The solutions were injected into a mold made from glass slides and spacers with 15 ± 1 mm in diameter and 1.2 ± 0.1 mm in thickness. Real-time FTIR data were collected with resolution of 4 cm^{-1} and 0.3985 s sampling interval. The absorbance change of the =C–H peak area from 6100.70 to 6222.50 cm^{-1} was correlated to the extent of polymerization [24]. For each sample, the series RTIR runs were repeated three times.

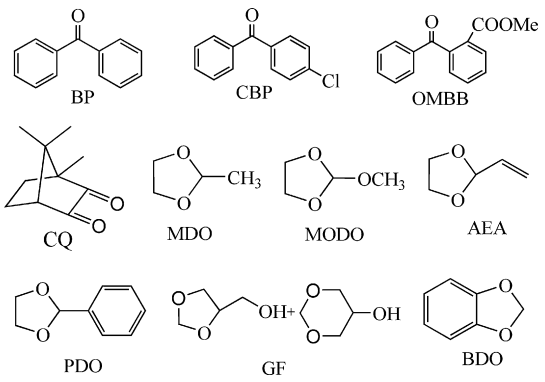

Fig. 1. Chemical structures of photoinitiators and coinitiators.

A dynamic mechanical analyzer (DMA) (Rheometyic, USA) was used to perform the mechanical properties measurement. The samples were photocured at room temperature with a visible light source (EFOS Lite with 400–500 nm filter, light intensity ≈ 500 mW/cm^2) for 15 min in a mold made from glass slides and spacers. The polymerized samples were kept at room temperature for 5 days after curing to ensure that post-polymerization process was completed. The samples used for DMA were thin rectangular films of approximately 1.2 mm thickness and dimensions of 7 mm × 35 mm. Dynamic mechanical analysis was performed over a temperature range from −50 to 200 °C with a ramping rate of 5 °C per minute using extension mode. The loss and storage modulus and the loss tangent (tan δ, ratio of loss to storage modulus) were recorded as a function of temperature, and the glass transition temperature (T_g) was taken to be the maximum of the loss tangent versus temperature curve.

3. Results and discussion

3.1. Cyclic acetals as coinitiator for BP derivatives

Real-time near FTIR technique is a convenient method to monitor the extent of polymerization for thick (1 mm) photocured samples [25,26]. Upon irradiation, the extent of polymerization as a function of time was accurately reflected by measuring the decrease of the =C–H absorbance peak area. And the rate of polymerization (R_p) could be calculated by the time derivative of the DC curve [24].

Benzophenone and its derivatives are the most prominent representatives of aromatic ketones used in bimolecular

initiating systems. Various factors had great influence on the rate of polymerization such as chemical structures of initiator systems, the wavelength of the incident light, the light intensity, etc. [27,28].

The effect of concentrations of MDO and BP on the UV photopolymerization of HDDA was performed (Figs. 2 and 3). Fig. 2 shows the kinetics of HDDA photoinitiated by mixture of 1.0 wt% BP and various concentrations of MDO. The obtained results showed that, in the absence of MDO, the monomer could serve as a hydrogen donor to produce radicals and initiated the polymerization, but developed a very low R_p and a long period of inhibition time. When MDO as a coinitiator was added to the formulation, it greatly improved the R_p and final DC of HDDA, which was agreed with the results reported by Ouchi et al. [17,18]. Increasing the concentration of MDO from 0 to 5.0 wt% caused the increase of the final DC and the maximum R_p (R_p^{max}, per second) from about 70–90% and 0.0088–0.0204 s^{-1}. It also led to the great decrease of inhibition time after 180 s exposure. This indicated that hydrogen abstraction from MDO occurred with the formation of initiating radicals to initiate the polymerization of HDDA. At the same time, the effective synergistic effect of MDO and BP

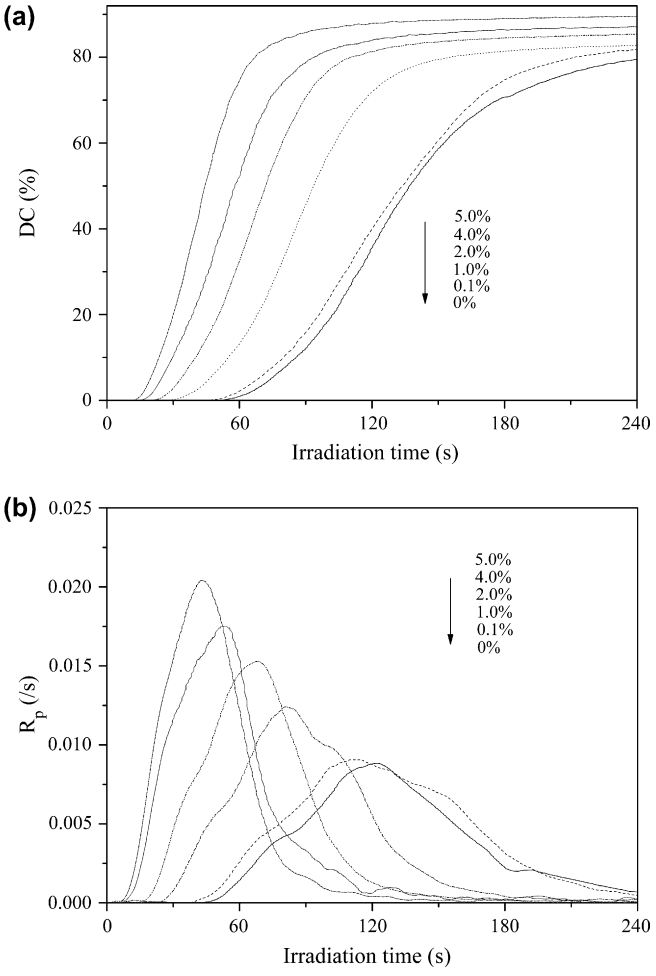

Fig. 2. UV photopolymerization of HDDA at a constant BP concentration (1.0 wt%) and different MDO concentrations (0, 0.1, 1.0, 2.0, 4.0 and 5.0 wt%).

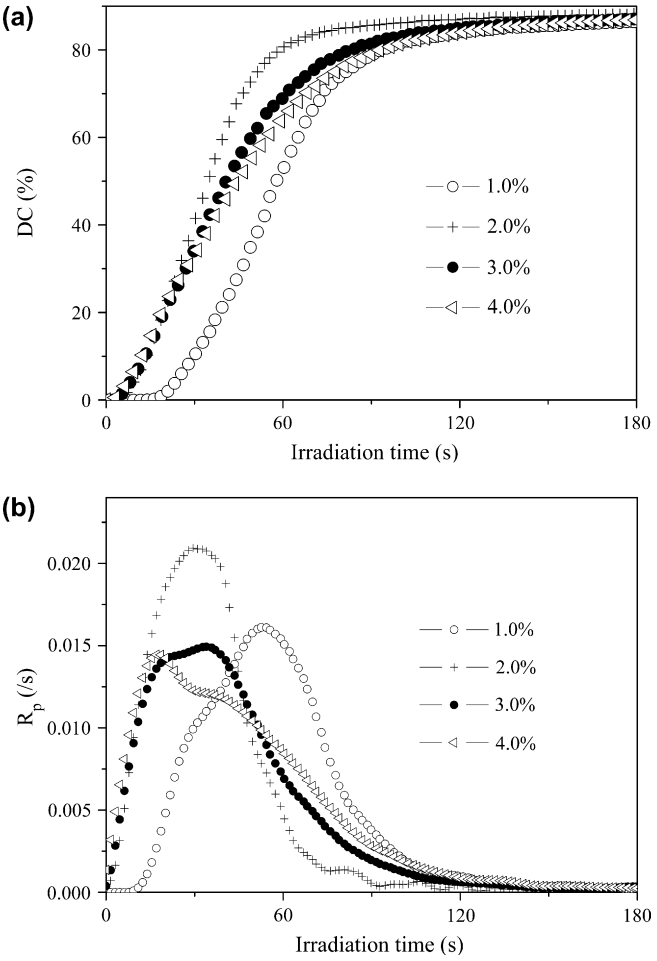

Fig. 3. Effect of [BP] on the photopolymerization of HDDA with 4.0 wt% MDO as coinitiator.

indicated that MDO had the potential to overcome the deficiency of the current BP/amine initiating systems in practical applications.

The photopolymerization kinetics of HDDA was also greatly affected by the concentrations of BP (Fig. 3). There was an optimum cure rate (0.0209 s^{-1}), which obtained at 2.0 wt% BP with a constant concentration of MDO (4.0 wt%). Further increase in concentration of BP did not produce corresponding increases in cure rate. This might attribute to the light absorption process with higher photoinitiator concentrations, which consisted of the light screening of the initiator itself and its photolysis products and the absorptivity of the photoinitiator [28].

Since the activity of most bimolecular photoinitiators for UV curing relied on the well-known photoreduction of aromatic ketones, the chemical structures of BP derivatives played a great role in the kinetics of photopolymerization [4,27]. Substituents on the aromatic ketones not only influenced the absorption characteristic and photochemical reactivity, but also greatly enhanced the solubility. This also improved the efficiency of the photoinitiator. Fouassier [28] had summarized the comparison of relative R_p and k_{DH}/kq of different *para*-substituted BP, and found that *para*-chloride

substituted BP had the higher relative R_p and k_{DH}/kq than that of non-substituted BP. As shown in Fig. 4, for three BP derivatives, CBP showed the highest R_p and the shortest inhibition time. When compared with the non-substituted BP, OMBB had much lower R_p. This result was similar to that of reported results.

To meet the requirement of practical applications such as rapid curing speed, excellent physical and mechanical properties, the coinitiator had to be sufficiently reactive and suitable for initiation. In Fig. 5, cyclic acetals with different chemical structures were employed as coinitiators for CBP. The obtained results showed that all cyclic acetals used in this study could be used as coinitiators to increase R_p and final DC of HDDA. However, the CBP initiating system with different cyclic acetals developed different kinetic parameters such as R_p, final DC and inhibition time.

The relative rate of hydrogen atom abstraction by photogenerated *tert*-butoxyl from a variety of cyclic ethers, acetals and orthoformates had been investigated using EPR spectroscopic technique [29,30]. There was a pronounced stereoelectronic effect, which produced high rates of abstraction from cyclic acetal carbon. Thus, methyl group attached to the acetal carbon atom exerted a significant activating effect on hydrogen abstraction. However, the activating effect of phenyl or vinyl group was proved to be smaller than that of methyl group, which probably because the delocalization of the unpaired electron on to the unsaturated group came at the expense of planarisation at acetal carbon [30]. In addition to the stereoelectronic factor, molecular conformation also affected the abstraction rate. For example, Malatesta et al. [29] found that the more mobile envelope conformation of five-numbered cyclic acetals had higher hydrogen abstract rate than that of six-numbered ones. Ouchi and Hamada [17] also reported the results that the strain of ring could affect the ability to promote the polymerization.

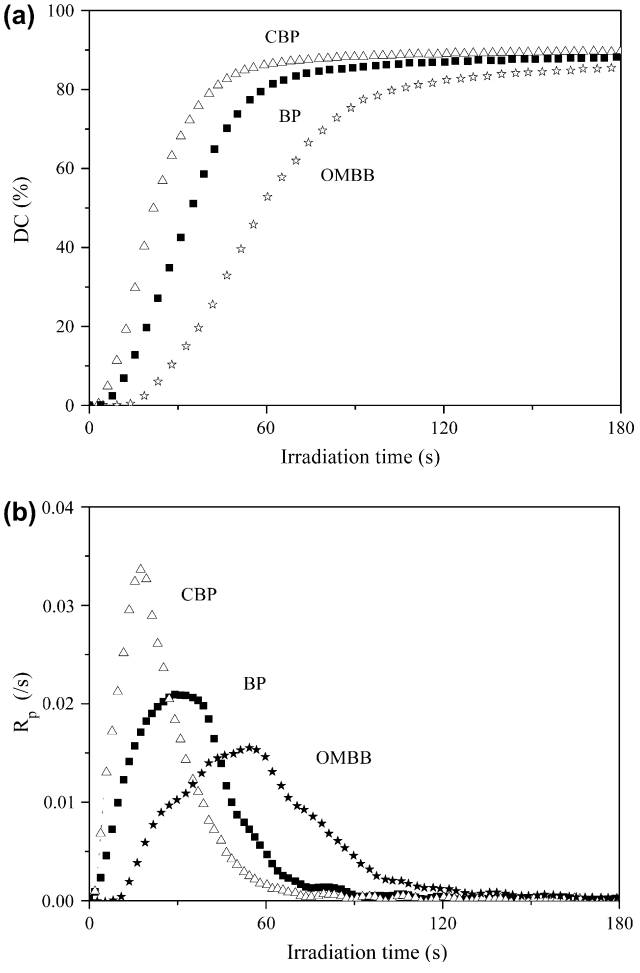

Fig. 4. Effect of BP derivatives on the polymerization of HDDA. [MDO] = 4.0 wt%; [BP derivatives] = 2.0 wt%.

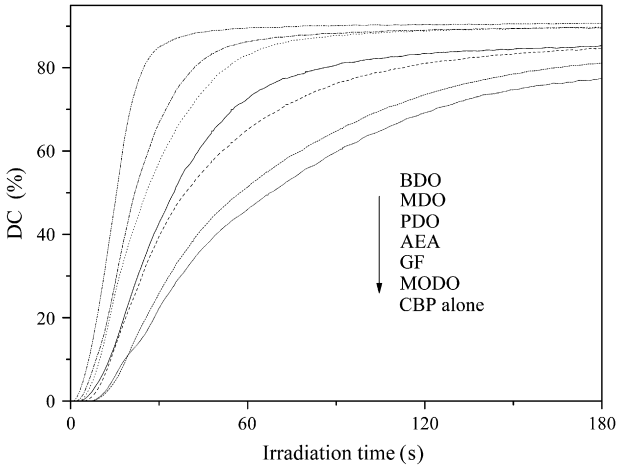

Fig. 5. Effect of chemical structure of cyclic acetals on the polymerization of HDDA. [acetals] = 4.0 wt%; [CBP] = 2.0 wt%.

In this study, MDO had relatively higher R_p than that of PDO and AEA, which was constant with the reported rate of hydrogen abstraction from cyclic acetals. GF with 60% six-numbered cyclic acetal, 5-hydroxy-1,3-dioxane, had lower reactivity. The abnormally lowest reactivity of MODO might be a consequence of the anomeric effect [29]. BDO indicated an effective coinitiator for CBP. It showed the highest R_p and final DC (91%) as well as the shortest inhibition period (about 5 s). It was promising that BDO had comparable R_p and final DC to that of commercial coinitiator EDMAB (Fig. 6). Moreover, BDO could lead to the complete cure with acceptable curing speed within 30 s, which was significant for practical applications, especially for dental restoration.

3.2. 1,3-Benzodioxole as coinitiator for CQ

CQ/tertiary amine initiating system as an essential component of the dental formulations is usually employed to initiate the visible light photopolymerization of dental resins [2,3,7–9]. It plays a great role in the kinetics and mechanical properties of the cured samples. The efficiency of this system depends on the concentrations of CQ and amine, as well as on the nature of the coinitiator and the intensity of the curing light, which directly affect clinically parameters such as curing speed and degree of conversion [8].

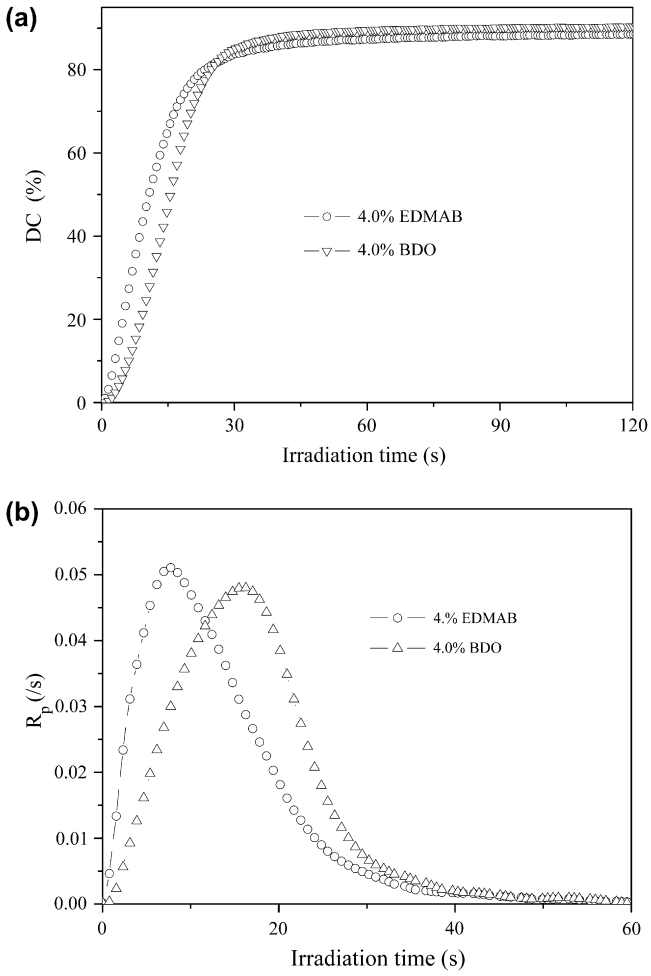

Fig. 6. Comparison of BDO and EDMAB for UV photopolymerization of HDDA at a constant concentration of CBP (2.0 wt%).

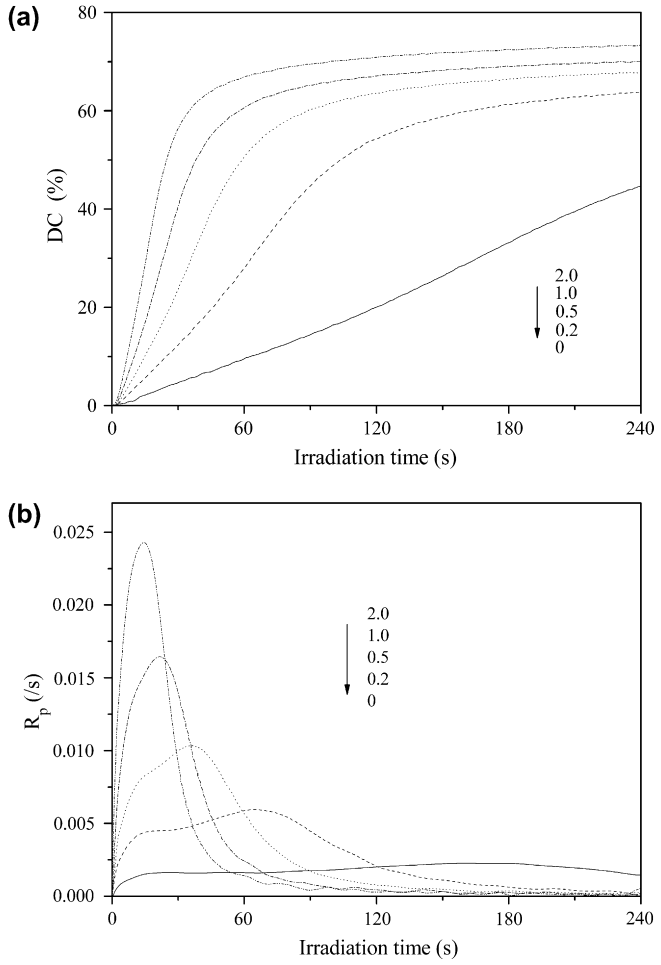

Fig. 7. Visible light photopolymerization of BisGMA/TEGDMA (70/30 wt%) with 0.5 wt% CQ and different BDO concentrations (0, 0.2, 0.5, 1.0, 2.0 wt%).

BDO could be used as a promising alternative coinitiator to EDMAB in UV curing fields. Unlike the amines, BDO, as a new kind of effective synergist, was a natural component from dietary plant [21]. The natural benzodioxole derivatives such as safrole, isosafrole, and myristicin were found in a wide variety of human food, essential oils, and flavors. They were extracted from plants, such as sassafras, nutmeg, parsnips, carrots, parsley, pepper, and sesame seeds [21,22]. Especially, the very low mammalian toxicity of BDO [31] made it more promising as a synergist for CQ in biomedical applications.

Fig. 7 shows the kinetics of dental resin, BisGMA/TEGDMA (70/30 wt%), at the same CQ concentration (0.5 wt%) and different BDO concentrations. The obtained results showed that the excited CQ could abstract hydrogen atom from TEGDMA but led to very low R_p, which could not meet the requirement in clinical applications. The increase of the concentration of BDO led to the increases of the maximum R_p (R_p^{max}, per second) and the final DC, but the decrease of the time in which R_p^{max} appeared (t_{max}, s), which indicated that BDO showed an effective coinitiator for CQ initiating system in dental applications as well.

The final DC was one of the very important parameters for dental composite, which had direct relationship with the mechanical properties and biocompatibility [2,3,32]. The comparison of kinetics initiated by BDO and EDMAB in Fig. 8 showed that BDO and EDMAB resulted in the comparable

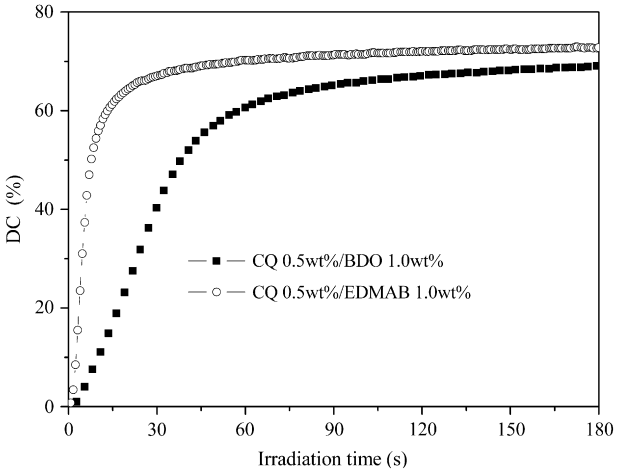

Fig. 8. Comparison of CQ/BDO (■) with CQ/EDMAB (○).

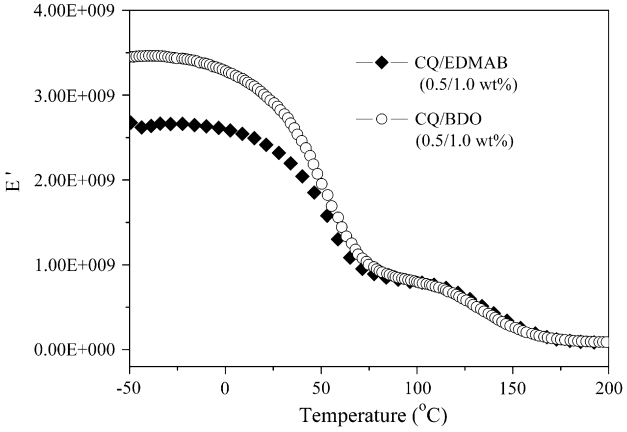

Fig. 9. Storage modulus for CQ/BDO (○) with CQ/EDMAB (◆) as measured by DMA.

final DC (around 70%), though developed different R_p. The different R_p for CQ/EDMAB and CQ/BDO might attribute to the difference in the nature between amine and BDO. For CQ/amine initiating system, amine acted as an effective coinitiator providing a source of abstractable hydrogen, and at the same time, scavenged peroxy intermediates that were formed by the reaction of oxygen with radical sites [27]. Thus, the high curing rate was obtained. Unlike the amine, the cyclic acetal radicals generated by the photoirradiation onto cyclic acetals might be rearranged rapidly by β-scission to the corresponding ester radicals [17,30]. However, the resulting ester end radicals were partially converted to inactive inner radicals by hydrogen migration [17], which might attribute to the lower R_p of CQ/BDO system. Although the initiating reactivity of CQ/BDO was lower than that of CQ/EDMAB, BDO as a natural component still made it have great potential to be used for dental resin composite.

The storage modulus for two samples is shown in Fig. 9. The storage modulus of BisGMA/TEGDMA initiated by CQ/BDO (0.5/1.0 wt%) was slightly higher than that initiated by CQ/EDMAB (0.5/1.0 wt%) around human body temperature (37 °C), which suggested that CQ/BDO initiator system could be used for dental composite with promising mechanical properties.

4. Conclusions

Cyclic acetals showed the potential as coinitiators for bimolecular photoinitiating systems. For UV photopolymerization of HDDA, the kinetics was related to the chemical structure of BP derivatives and cyclic acetals. Combination of CBP/BDO suggested the highest initiating reactivity. BDO was also an potential coinitiator for camphorquinone-based initiator system when it was used to initiate the polymerization of BisGMA/TEGDMA (70/30 wt%). Comparing with EDMAB, although CQ/BDO showed lower comparable reactivity, the natural component characteristics of BDO still made it a promising alternative to commercial amine in biomolecular initiating system.

Acknowledgments

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