Synthesis and Photopolymerization of Ethylene Glycol 3-Morpholine-propionate Methacrylate for Potential Dental Composite Application

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ABSTRACT: 2,2-Bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]-propane (bis-GMA), triethylene glycol dimethylacrylate (TEGDMA), camphorquinone (CQ), ethyl-4-dimethylaminobenzoate (EDMAB), or 2-(dimethylamine)ethyl methacrylate (DMEM) were composed of the modern dental composite system and acted as resin, diluent, photoinitiator, and coinitiator, respectively. In this study, ethylene glycol 3-morpholine-propionate methacrylate (EGMPM) was synthesized via Michael addition reaction to replace both the TEGDMA as a diluent and the nonpolymerizable amine EDMAB as a coinitiator. Mixtures of bis-GMA/TEGDMA/CQ/EGMPM and bis-GMA/TEGDMA/CQ/DMEM were found to have almost the same rate of polymerization and reach final double bond conversion at 58%, slightly lower than that of the bis-GMA/TEGDMA/CQ/EDMAB (63%) and bis-GMA/EGMPM/CQ (60%) under comparable visible light irradiation conditions.

In addition, the results of dynamic mechanical analysis showed that all of the four samples had approximately the same modulus and the glass transition temperature. The water sorption and solubility of bis-GMA/TEGDMA/CQ with different amines (EDMAB, DMEM, and EGMPM) had almost the same value except that the water sorption of bis-GMA/EGMPM/CQ was out of the range of the ISO 4049 (2000) standards. The results indicated that EGMPM was potentially a coinitiator for dental composite, because there are no significant differences in photopolymerization characteristic and physical properties when compared with traditional system (bis-GMA/TEGDMA/CQ/EDMAB). © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4589–4594, 2006

Key words: DMA; dental composite; FTIR; initiator; photopolymerization

INTRODUCTION

Since a resin mixture composed of 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)-phenyl]-propane (bis-GMA) was introduced by Bowen,[1] a great deal of work had been performed to improve the properties of the photocuring dental composite, both in academic research and industrial application. Those work focused on polymerization kinetic studies,[2–5] degree of conversion measurement and controlling,[6–11] toxicity of monomer and initiator,[12–14] mechanical properties,[15–17] water sorption and solubility,[18–21] color stability,[22,23] polymerization shrinkage,[24–26] and other aspects.[27–29]

The currently used commercial dental composite generally contained a mixture of various crosslinking dimethacrylates, glass- and/or silicon dioxide fillers and a photoinitiator system.[30] The initiator system of dental composite composed of a photoinitiator, which generally was camphorquinone (CQ) and tertiary amine derivative coinitiator. Upon irradiation, the photoinitiator system could produce free radical.[31,32] By free radical polymerization of dimethacrylates, a three-dimensional network was formed.

The tertiary amine derivative used as coinitiator was both toxic and mutagenic,[33] but it was a necessary component for the camphorqiunone visible light photoinitiator system. To decrease the toxicity and improve the polymerization process, much work had been done to replace the amine coinitiator. Some polymeric or macromolecular photoinitiators or coinitiators had been reported to have significant advantages over commercially available low molecular weight photoinitiators.[34–37] To further enhance the biocompatibility of the coinitiator, this study is done which involved the synthesis of a monomer containing a methacrylate group and a morpholine group that could be polymerized to form a more biocompatible polymer system.

In this study, ethylene glycol 3-morpholine-propionate methacrylate (EGMPM) was synthesized via Michael addition reaction. There were two different kinds of functional groups in this monomer. One group was the methacrylate, which could be polymerized by free radical chain growth process, link-

ing the EGMPM to the polymer network; and the other group was amine, which served as the coinitiators for hydrogen abstraction to form free radical. Because the EGMPM was incorporated into the polymer chain, it was difficult to leach out from the polymer matrix after being polymerized. The toxicity of this polymer should be low.

EXPERIMENTAL

Materials

Acrylic acid and thionyl chloride were distilled before used. Camphorquinone (CQ), ethyl-4-dimethylamino-benzoate (EDMAB), 2-(dimethylamine)ethyl methacrylate (DMEM), and bis-GMA (2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane) were used as received (Aldrich, USA). Triethylene glycol dimethylacrylate (TEGDMA, donated by Sartomer) was also used without further purification. Other chemicals were of analytical grade excepted as noted.

Synthesis of coinitiator

Synthesis of acryloyl chloride

Thionyl chloride (1 mol) was added into a three-necked bottle equipped with magnetic stirring, thermometer, dropping funnel, and condenser. Acrylic acid (AA) (1 mol) was added dropwise over 2-h period. The acid gas generated was absorbed by saturated NaOH solution. Then the mixture was raised to 70°C at the rate of 20°C per hour. The reaction was monitored with FTIR until the —COOH absorption peak at 1702 cm^{-1} turned into —COCl absorption peak at 1795 cm^{-1}. Subsequently, the mixture was distilled under reduced pressure (40°C/150 mmHg).

Synthesis of ethylene glycol acrylate methacrylate (EGAMA)[38]

A mixture of 83.81 g of 2-hydroxyl-ethyl methacrylate (HEMA) and 80 g of triethylamine in 220 g of

toluene was dissolved in a three-necked bottle equipped with stirrer, thermometer, and dropping funnel. Under cooling (0–5°C), 79.79 g of acryloyl chloride dissolved in 50 mL of toluene was added for 4 h. Then the mixture was allowed to stand overnight, the precipitate was filtered off and washed twice with 20 g of toluene. Then the reaction mixture was extracted twice with 75 g of water, 50 g of 1 mol/L hydrochloric acid, and 50 g of 1 mol/L sodium bi-carbonate solution and dried over night with anhydrous sodium sulfate. Subsequently, the toluene was removed by rotary evaporation. The yellow crude product was purified by silica gel (200–300 mesh) column chromatography using ethyl acetate as an eluent.

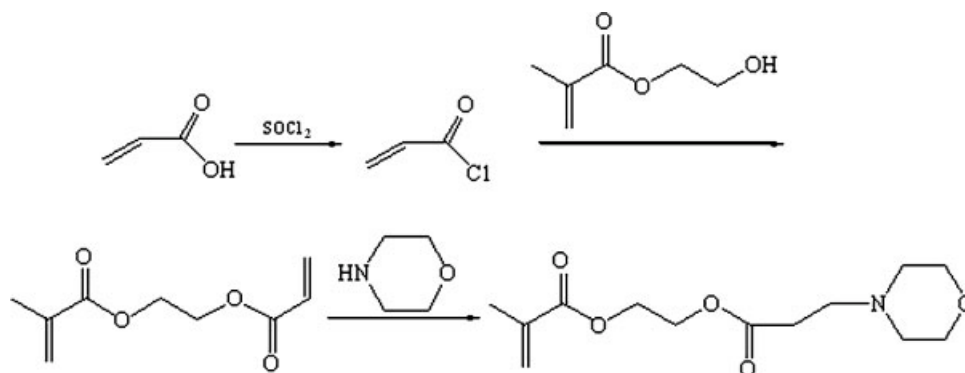#### Synthesis of ethylene glycol 3-morpholine-propionate methacrylate

A 9.20 g of EGAMA (0.05 mol) was dissolved in 25 mL of methanol. Mixture of 4.35 g of morpholine (0.05 mol) dissolved in 25 mL methanol was added dropwise at 0–5°C under magnetic stirring in N$_2$ atmosphere. FTIR was used to monitor the process of the reaction. When the N—H peak at 3315 cm^{-1} was disappeared, methanol was removed with rotary evaporation. Then the crude product was purified by silica gel (200–300 mesh) column chromatography using ethyl acetate: hexane = 50: 50(V/V) as an eluent. Figure 1 depicted all the synthesis process. The final product was identified by ^{1}H NMR.

^{1}H NMR (CDCl$_3$): δ6.02(1H), δ5.50(1H), δ4.25(4H), δ3.57–3.59(4H), δ2.58–2.60(2H), δ2.42–2.44(2H), δ2.36 (4H), δ1.85(3H).

Measurement

Instrumentation

^{1}H NMR spectrum was recorded on a Bruker AV600 unity spectrometer operated at 600 MHz, with CDCl$_3$ as the solvent. FTIR spectrum was recorded on a Nicolet 5700 instrument (Nicolet Instrument, Thermo

Figure 1   Synthetic rout of the ethylene glycol 3-morpholine-propionate methacrylate.

Company). The dynamic mechanical analyzer (DMA) (Rheometyic) was used to perform the mechanical properties measurement.

Real time infrared spectroscopy (RTIR)

Real-time infrared spectroscopy (RTIR) had become an important method for obtaining kinetics data. Conversion versus time profiles for all mixtures were determined by real-time near infrared (RTNIR) spectroscopy (Nicolet 5700).[8,9,39] Conversion data were obtained by monitoring the decay of the methacrylate double bond $=$C$-$H peak at 6165 cm^{-1}. Upon irradiation, the decrease of the $=$C$-$H absorption peak area from 6100.70 to 6222.50 cm^{-1} accurately reflects the extent of the polymerization, because the absorption of the peak area was directly proportional to the number of the methacrylate functionalities that had been polymerized. After baseline correction, conversion of the functional groups can be calculated by measuring the peak area at each time of the reaction and determined as following:

$$DC\ (\%)\ =\ (A_0\ -\ A_t)/A_0 \times 100 \qquad (1)$$

where DC was the conversion of methacrylate double bonds at t time, A_0 was the initial peak area before irradiation, and A_t was the peak area of the double bonds at t time.

Photocuring dental composite consisted of bis-GMA/TEGDMA/CQ/amine. A bis-GMA/TEGDMA (75:25 wt %) mixture was employed as the photopolymerizable resin, CQ (0.5% wt) was used as photoinitiator. Various concentration of the EGMPM (0.0–0.5 wt %) was used as the coinitiator. All samples were photocured in 1.2-mm thick plastic molds with a 6-mm diameter central opening connected by a 3-mm wide channel to one edge. The molds were clamped between the glass slides with spring loaded binder clips.[8] The mixtures were irradiated with a visible light source (Spectrum 800 Curing Light, Densply). The light intensity on the surface of samples was 50 mW/cm^2, which was detected by visible light radiometer (UV-A, 400–1000 nm, Beijing Normal University, China). Each spectrum was signal of one scan with the resolution of 4 cm^{-1} at room temperature. For each sample, the series RTIR runs were repeated three times.

Dynamic mechanical analysis (DMA)

The samples were photocured with a visible light source (Spectrum 800 Curing Light, intensity $\approx$ 800 mW/cm^2) for 5 min in a mold made from glass slides and spacers. The polymerized samples were put at room temperature for 5 days after curing to ensure that postpolymerization process was complete. The samples used for DMA were thin rectangular films and the dimension was 7 $\times$ 35 $\times$ 1.2 mm^3. 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.

Water sorption and solubility

Water sorption and solubility were measured according to ISO 4049 (2000) standards. Specimens, 15 $\pm$ 1 mm in diameter and 1.2 $\pm$ 0.1 mm in thickness, were stored in a desiccator that contained anhydrous calcium chloride. The samples were maintained at (37 $\pm$ 1)°C for 24 h. The temperature was then decreased to 23°C for 1 h, and the samples were subsequently weighed to an accuracy of $\pm$0.2 mg. This process was repeated until a constant mass m_1 was obtained.

The specimens were then immersed in water and maintained at 37°C for 7 days. After this time, the samples were taken out, washed with water, blotted to remove surface water, waved in air for 15 s, and weighed 1 min after being removed from water. This measurement was recorded as m_2. Following this weighing, the specimens were replaced into the desiccator, and the cycle described earlier was repeated until a final constant mass was obtained (m_3). The specimen volumes (V) were also measured. For every polymer system, the value was average of five specimens.

To calculate the water sorption (w_{sp}) and solubility (w_{sl}), the following equations were used:

$$w_{sp}\ =\ (m_2\ -\ m_3)/V \qquad (2)$$

$$w_{s1}\ =\ (m_1\ -\ m_3)/V \qquad (3)$$

All samples were cured with a visible light source (Spectrum 800 Curing Light, intensity $\approx$ 800 mW/cm^2) for 5 min.

RESULTS AND DISCUSSION

Synthesis of EGMPM

For the reaction of HEMA with acryloyl chloride, the acryloyl chloride had to be added slowly, and the reactant mixture had to be put in an ice water bath to keep the reaction going smoothly. A high reaction temperature would cause polymeriazation. An excess of triethylamine was added to remove the HCl produced during reaction. Otherwise, the HCl could add to acrylate double bond. The Michael addition

reaction of morpholine and EGAMA should be proceeding under ice water bath under nitrogen atmosphere. FTIR indicated that as soon as the morpholine added into EGAMA, the N—H peak at 3315 cm^{-1} began to disappear.

EGMPM used as a coinitiator

Figure 2 graphically illustrated the double bond conversion versus visible light irradiation time of the bis-GMA/TEGDMA/CQ (75 : 25 : 0.5 wt%) with different concentration of the EGMPM. It clearly indicated that increasing the concentration of the EGMPM increased both the double bond conversion and the rate of polymerization. After ~ 250 s, the final double bond conversion of the mixture initiated by CQ alone was very low (~ 24%) and the rate of polymerization was almost constant. When the concentrations of EGMPM varied from 0.1 to 0.5 wt %, the double bond conversion increased from 27.3 to 46.4% after 50 s irradiation, respectively. And the final double bond conversion reached approximately from 52 to 58%.

Photoinitiated polymerization occurs by a chain reaction between the free radicals formed by the photoinitiating system and the monomer (MH). CQ was one of the photointiators involving hydrogen abstraction reaction. The hydrogen abstraction reaction could occur between CQ and the monomer, especially CQ and hydrogen donors. Tertiary amines were famous hydrogen donors of the bimolecular photoinitiator systems. Under the irradiation of visible light, CQ absorbed the photon energy and was excited. In the absence of hydrogen donor, CQ itself could photoinitiate the polymerization of TEGDMA. However, this reaction was not efficient.[31] This was the reason why photopolymerization initiated by CQ alone was slow.
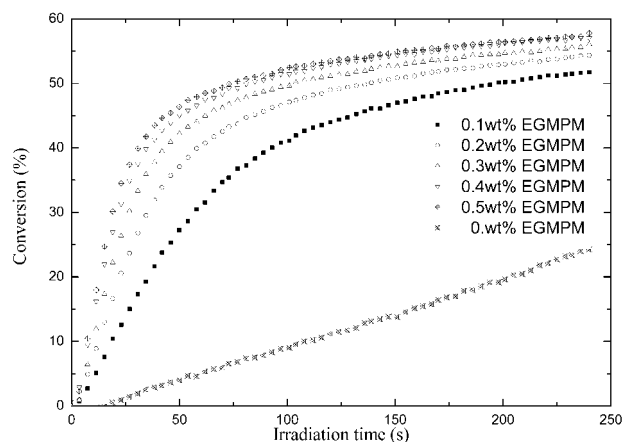
Figure 2 Double bond conversion as a function of irradiation time for bis-GMA/TEGDMA/CQ (75 : 25 : 0.5 wt %) with different concentration of the EGMPM.

Photoinduced electron transfer between the excited CQ and an amine by a mechanism that involved the formation of a charge transfer encounter complex, then followed by a proton transfer with the formation of a camphorquinone-kety radical (CQH$^•$) and an aminoalkyl radical (Am$^•$).[31,32] The CQH$^•$ were not reactive toward double bonds of methacrylate because of steric hindrance effect, whereas the Am$^•$ were an effective radical that initiated the polymerization through an addition reaction onto the double bond of methacrylate. EGMPM was one kind of polymerizable tertiary amine. When it was added into the mixture, it could act as the efficient hydrogen donor. It was obviously the concentration of the amine that had great effect on the rate of photopolymerization and final double bond conversion.

EGMPM served as a coinitiator and diluent

Bis-GMA had an extremely high viscosity. TEGDMA was usually incorporated into the resin system to improve the viscosity. In this study, the EGMPM was used both as a diluent to replace the TEGDMA, and as a coinitiator.

The effect of different coinitiator on the double bond conversion for bis-GMA/TEGDMA/CQ (75 : 25 : 0.5 wt %) showed in Figure 3(a). Figure 3(b) presented the compared profiles of EGMPM served as both a diluent and a coinitiator versus commercial TEGDMA diluent and amine coinitiator. The results indicated that when the concentration of the EGMPM was 25 wt %, the final double bond conversion was higher than that of 0.5 wt % EGMPM and reached 60%, which was slightly lower than that of the commercial aromatic amine coinitiator (0.5 wt % EDMAB), and the rate of photopolymerization could be comparable to that of EDMAB. But for the aliphatic amine coinitiator (0.5 wt % DMEM), it had almost the same rate of polymerization and final double bond conversion as that of the 0.5 wt % EGMPM. This could attribute to the concentration and structure of amines. It had been reported that the aromatic amines were more efficient coinitiators in methacrylate system than aliphatic amines.[2] It was reasonable that the double bond conversion and the rate of polymerization of EDMAB (aromatic amine) were higher than that of EGMPM and DMEM (aliphatic amine).

DMA characteristics

The DMA results for several different resin mixtures were shown in Figure 4. The storage modulus of the bis-GMA/EGMPM/CQ and bis-GMA/TEGDMA/CQ/EGMPM samples were just between that of the bis-GMA/TEGDMA/CQ/EDMAB and bis-GMA/TEGDMA/CQ/DMEM samples, particularly at the range of body temperature (37°C). The glass transi-
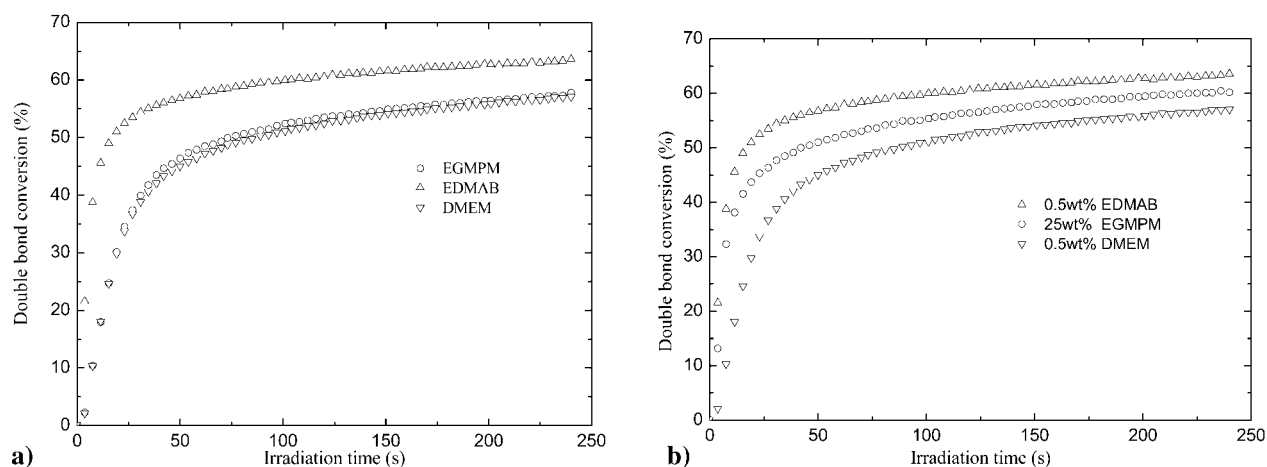
Figure 3 Conversion of double bond as a function of irradiation time for (a) Bis-GMA/TEGDMA/CQ (75 : 25 : 0.5 wt %)/ amine (EDMAB, DMEM, or EGMPM) with the concentration of 0.5 wt % and (b) Bis-GMA/EGMPM/CQ (75 : 25 : 0.5 wt %).

tion temperatures (T_g) of the four samples were nearly the same (86–91°C). These results were consistent with the results of its double bond conversion. But when 0.5 wt % EDMAB and 0.5 wt % EGMPM were used as a coinitiator, two peaks of tan δ versus temperature indicated that strong postcure occurred during heated. When 25 wt % EGMPM was used as both a coinitiator and diluent, and 0.5 wt % DMEM was used as conitiator, postcure was not very strong. Only a wide peak of tan δ versus temperature occurred, which meant a heterogeneous polymer network in the system.
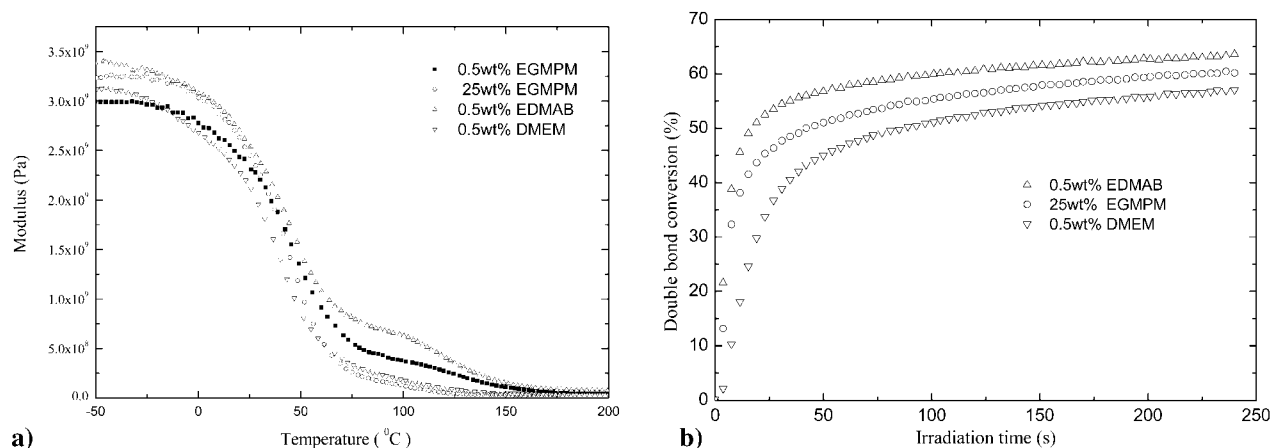
Water sorption and solubility

The properties of water sorption and solubility were very important for dental composite. Materials with high water sorption and solubility were not suitable for use as dental composite. ISO 4049 (2000) standards for dental restorative resins were: water sorption

(< 40 µg/mm^3) and water solubility (< 7.5 µg/mm^3). Table I gave the results of water sorption and solubility for several mixture resins initiated by CQ and different tertiary amines system. The results indicated that bis-GMA/TEGDMA/CQ with different amines (EDMAB, DMEM, and EGMPM) at the concentration of 0.5 wt % had almost the same water sorption (less than 40 µg/mm^3) and solubility (less than 7.5 µg/mm^3). But bis-GMA/EGMPM/CQ (75 : 25 : 0.5 wt %) system had higher water sorption because of the hydrophilic amine group in EGMPM. The value was out of the range of ISO 4049 (2000) and so, EGMPM was not suitable for use as diluent of dental composite.

CONCLUSIONS

EGMPM could be synthesized by Michael addition reaction of amine and acrylate. As the concentration

Figure 4 (a) Storage modulus and (b) tan δ as a function of temperature for bis-GMA/EGMPM/CQ (75 : 25 : 0.5 wt %) and bis-GMA/TEGDMA/CQ(75 : 25 : 0.5 wt %) with different amines (EDMAB, DMEM, and EGMPM) at the concentration of 0.5 wt %.

TABLE I
Water Sorption and Solubility of Bis-GMA/TEGDMA/CQ (75 : 25 : 0.5 wt %)
with Different Amines (EDMAB, DMEM, and EGMPM) at the Concentration
of 0.5 wt % and Bis-GMA/EGMPM/CQ (75 : 25 : 0.5 wt %)

	Water sorption	Solubility
Bis-GMA/TEGDMA/CQ/EGMPM (0.5 wt %)	34.71 ± 1.18	2.36 ± 0.33
Bis-GMA/TEGDMA/CQ/EDMAB (0.5 wt %)	35.84 ± 1.39	2.12 ± 0.27
Bis-GMA/TEGDMA/CQ/DMEM (0.5 wt %)	37.73 ± 2.73	2.64 ± 0.63
Bis-GMA/EGMPM/CQ	42.16 ± 2.70	1.98 ± 0.52

Mean of five samples ± standard deviation ($\mu g/mm^3$).

of EGMPM increases, the double bond conversion and the rate of photopolymerization of resin mixtures increases. When the concentration of amine was 0.5 wt %, the rate of polymerization and the final double bond conversion were lower than that of aromatic amine EDMAB, but almost the same as that of aliphatic amine DMEM. When the concentration of EGMPM was 25 wt %, the EGMPM could serve as both the reactive diluent and the coinitiator, the rate of polymerization and the final double bond conversion were comparable to that of aromatic amine EDMAB, indicating that EGMPM was a potential diluent. The modulus and T_g of the four samples were very close. Water sorption and solubility of the samples were all in the ISO 4049 (2000) standards except that of EGMPM used as both diluent and coinitiator.

EGMPM could be used potentially as a coinitiator for dental composite, because the photopolymerisation characteristics and the physical properties of the polymer formed were comparable to commercial coinitiators.

References

1. Bowen, R. L. U.S. Pat. 3,066,112 (1962).
2. Cook, W. D. Polymer 1992, 33, 600.
3. Lovell, L. G.; Stansbury, J. W.; Syrps, D. C.; Bowman, C. N. Macromolecules 1999, 32, 3913.
4. Anseth, K. S.; Decker, C.; Bowman, C. N. Macromolecules 1994, 27, 650.
5. Kucybala, Z.; Pietrzak, M.; Paczkowski, J.; Rabek, J. F. Polymer 1996, 37, 4585.
6. Ferracane, J. L.; Creener, E. H. J Dent Res 1984, 63, 1093.
7. Pianelli, C.; Devaux, J.; Bebelman, S.; Leloup, G. J Biomed Mater Res 1999, 48, 675.
8. Stansbury, J. W.; Dickens, S. H. Dent Mater 2001, 17, 71.
9. Kerbouc'h, P.; Lebaudy, P.; Lecamp, P.; Bunel, C. Thermochim Acta 2004, 410, 73.
10. Falk, B.; Vallinas, S. M.; Crivello, J. V. J Polym Sci Part A: Polym Chem 2003, 41, 579.
11. Rueggeberg, F.; Tamareselvy, K. Dent Mater 1995, 11, 265.
12. Stanley, H. R. Toxicity Testing of Dental Materials; CRC: Boca Raton, FL, 1985.
13. Pelka, M.; Danzl, C.; Distler, W.; Petschelt, A. J Dent 2000, 28, 341.
14. Haley, T. J.; Berndt, W. O. Handbook of Toxicology; Hemisphere: New York, 1987.
15. Yong, J. S.; Kannurpatti, A. R.; Bowman, C. N. Macromol Chem Phys 1998, 199, 1043.
16. Atai, M.; Nekoomanesh, M.; Hasnemi, S. A.; Amani, S. Dent Mater 2004, 20, 663.
17. Lovell, L. G.; Lu, H.; Elliott, J. E.; Stansbury, J. W.; Bowman, C. N. Dent Mater 2001, 17, 504.
18. Martin, N.; Jcdynakicwicz, N. Biomaterials 1998, 19, 77.
19. Toledano, M.; Osorio, R.; Osorio, E.; Fuentes, V.; Prati, C.; Garcia-Godoy, F. J Dent 2003, 31, 43.
20. Sideridou, I.; Tserki, V.; Papanastasiou, G. Biomaterials 2003, 24, 655.
21. Sideridou, I.; Achilias, D.; Spyroudi, C.; Karabela, M. Biomaterials 2004, 25, 367.
22. Schulze, K. N.; Marshall, S. J.; Gansky, S. A.; Marshall, G. W. Dent Mater 2003, 19, 612.
23. Power, J. M.; Fan, P. L.; Raptis, C. N. J Dent Res 1980, 59, 2071.
24. Stansbury, J. W. J Dent Res 1992, 71, 434.
25. Cook, W. D.; Forrest, M.; Goodwin, A. A. Dent Mater 1999, 15, 447.
26. Fogleman, E. A.; Kelly, M. T.; Grubbs, W. T. Dent Mater 2002, 18, 324.
27. Draughn, R. A. J Biomed Mater Res 1981, 15, 489.
28. Peutzfeldt, A.; Asumssen, E. J Dent Res 1992, 71, 1847.
29. Nie, J.; Lovell, L. G.; Bowman, C. N. Biomaterials 2001, 22, 535.
30. Moszner, N.; Salz, U. Prog Polym Sci 2001, 26, 535.
31. Jakubiak, J.; Allonas, X.; Fouassier, J. P.; Sionkowska, A.; Andrzejewska, E.; Linden, L. A., Rabek, J. F. Polymer 2003, 44, 5219.
32. Rabek, J. F.; Fouassier, J. P.; Nie, J.; Audrzewska, E.; Jakubiak, J.; Paczkowski, J.; Wryszcynski, A.; Sionkowska, A. Trends Photochem Photobiol 1999, 5, 51.
33. Albrecht, W. N.; Stephenson, R. L. Scand J Work Environ Health 1988, 14, 209.
34. Nie, J.; Bowman, C. N. Biomaterials 2002, 23, 1221.
35. Ahn, K. D.; Han, D. K.; Lee, S. K.; Lee, C. W. Macromol Chem Phys 2003, 204, 1628.
36. Angiolini, L.; Caretti, D.; Salatelli, E. Macromol Chem Phys 2000, 201, 2646.
37. Ullrich, G.; Herzog, D.; Liska, R.; Burtscher, P.; Moszner, N. J Polym Sci Part A: Polym Chem 2004, 42, 4948.
38. Muh, K.; Marquardt, J.; Klee, J. E.; Frey, H.; Mulhaupt, R. Macromolecules 2001, 34, 5778.
39. Decker, C.; Moussa, K. Macromolecules 1989, 22, 4455.