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Probing the Dual Function of a Novel Tertiary Amine Compound in Dentin Adhesive Formulations

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Abstract

Objectives—A novel tertiary amine compound containing three methacrylate-urethane groups was synthesized for application in dentin adhesives. The synthesis, photopolymerization kinetics, and leaching were examined in an earlier study using this novel compound as the co-initiator (0.5 and 1.75 wt% based on the total resin mass). The objective of this work was to investigate the potential of TUMA (8-(2-(((2-(methacryloyloxy)ethyl)carbamoyl)oxy)propyl)-6,10-dimethyl-4,12-dioxo-5,11-dioxo-3,8,13-triazapentadecane-1,15-diyl bis(2-methylacrylate)) to serve simultaneously as a co-initiator and co-monomer (15 to 45 wt% based on the total resin mass) in dentin adhesive formulations. The polymerization kinetics, water sorption and dynamic mechanical properties of these novel formulations were determined.

Materials and method—The monomer system contained Bisphenol A glycerolate dimethacrylate (BisGMA), 2-hydroxyethylmethacrylate (HEMA) and TUMA (synthesized in our lab) at the mass ratio of 45/55-x/x. Two photoinitiator (PI) systems were compared. One initiator system contains three components: camphorquinone (CQ), diphenyliodonium hexafluorophosphate (DPIHP) and ethyl-4-(dimethylamino) benzoate (EDMAB) and the second initiator system contains CQ and DPIHP. The control adhesive formulations are: C0-3: HEMA/BisGMA 45/55 w/w and 3-component PI and C0-2: HEMA/BisGMA 45/55 w/w and 2-component PI. These controls were used as a comparison to the experimental adhesive resins (Ex-3 or Ex-2), in which x represents the weight percentage of synthesized co-monomer (TUMA) to replace part of BisGMA. The control and experimental adhesive formulations were photopolymerized and compared with regard to the degree of conversion (DC), polymerization rate (Rp), water sorption and dynamic mechanical analysis (DMA) under both dry and wet conditions.

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Results—C0-3 and Ex-3 formulations had similar DC, while the DC of Ex-2 formulation was higher than C0-2. The DC was similar when comparing the two- component with the three- component photoinitiator system when TUMA was used at the same concentration. DMA under dry conditions shows higher rubbery storage modulus for all experimental formulations, while storage modulus at rubbery region under wet conditions was decreased as compared with control (C0-3). There was no statistically significant difference for the DMA results under both dry and wet conditions when comparing two- and three-component initiator systems with the same TUMA concentration.

Significance—The newly synthesized TUMA could serve simultaneously as a co-monomer and co-initiator in the absence of commercial co-initiator. This study provides information for the future development of new co-monomer/co-initiator for dentin adhesives and dental composites.

Keywords

Amine; Co-initiator; Co-monomer; Degree of conversion; Dynamic mechanical property; Photo polymerization

Introduction

Polymer-based composites have become the most common dental restorative material with a current use rate more than twice that of amalgam filling materials[1]. The durability of composite restorations does not, however, match that of dental amalgam[2–6]. The average clinical lifetime of posterior composite resin restorations is just 5.7 years due to secondary decay or fracture [7, 8]. The dominant reason for failure of composite restorations is secondary decay and clinically, the failure occurs most often at the composite/tooth interface [9, 10].

The composite is too viscous to bond directly to the tooth and thus, a low viscosity adhesive must be used to form a bond between the tooth and composite. The integrity of the adhesive and the adhesive/tooth bond is very important for the durability of resin-based dental restorations. The lack of durable and effective dentin adhesives is considered a major problem with the use of composites in restorative dentistry [9, 10]. The monomers used in dentin adhesives are particularly critical and monomer selection exerts considerable influence on the properties, durability and behavior of dentin adhesives in the wet, oral environment. Much attention and effort has been devoted to the development of new monomers. These new monomers are one approach in the research community's quest to develop dentin adhesives that provide durable bonding at the composite/tooth interface [11–14].

Photopolymerization using a visible light source is a popular and convenient means of curing dentin adhesives and composites [15]. The majority of commercial methacrylate-based dental resins contain camphorquinone (CQ)/amine pairs as visible light photoinitiating systems. CQ is a light absorbing photosensitizer and the amine compound is an electron donor serving as co-initiator. Recently, a third component (often a diaryliodonium or sulfonium salt) is applied into the CQ/amine photoinitiating system to improve the visible light induced photopolymerization [7, 16–20].

The co-initiator (amine compound) plays a critical role in the photoinitiation process [21]. The types of co-initiator as well as its ratio to the photosensitizer influence the quality of the polymerization. Many of the available amine co-initiators cannot be used in dental restorative materials because of cytotoxicity concerns [2, 22]. The release of co-initiators has been considered a source of adverse reactions [22], e.g. local and systemic toxicity, pulpal irritation, allergic and estrogenic effects.

A tertiary amine co-initiator (TUMA) containing three methacrylate-urethane groups was synthesized in our laboratory for application in dentin adhesives[23]. The results from an earlier study showed comparable degree of conversion with formulations containing 0.5% or 1.75% TUMA as compared to commercial amine co-initiators ethyl-4-(dimethylamino) benzoate (EDMAB) and 2-(dimethylamino) ethyl methacrylate (DMAEMA). Furthermore, there was no detectable leaching of the new co-initiator (TUMA), while 53.6% EDMAB and 11.2% DMAEMA were released. The results from this study suggest that TUMA is a promising co-initiator, which could prevent amine release from the final dentin adhesives.

The performance of adhesive formulations containing this new compound, (TUMA), as one of the major components (e.g., 15, 25, 35 and 45 wt%) was investigated in this study. The polymerization kinetics, water sorption and viscoelastic behavior of TUMA-containing formulations were compared with control formulations cured in the presence or absence of the amine co-initiator EDMAB. The purpose of this investigation was to determine the ability of TUMA to serve simultaneously as co-initiator and co-monomer in adhesive formulations. The hypothesis of this investigation is that there is no statistically significant difference in the viscoelastic properties of dentin adhesives with TUMA as the comonomer when formulated in the presence or absence of EDMAB.

1. Experimental

2.1 Materials

Bisphenol A glycerolate dimethacrylate (BisGMA, Polysciences, Warrington, PA) and 2-hydroxyethylmethacrylate (HEMA, Acros Organics, NJ) were used as received without further purification, as monomers. TUMA (8-(2-(((2-(methacryloyloxy)ethyl)carbamoyl)oxy)propyl)-6,10-dimethyl-4,12-dioxo-5,11-dioxo-3,8,13-triazapentadecane-1,15-diyl bis(2-methylacrylate)) was synthesized in our lab and used as the co-monomer with HEMA and BisGMA [23]. Based on our previous studies, [12, 15, 24–27] camphorquinone (CQ), ethyl-4-(dimethylamino) benzoate (EDMAB) and diphenyliodonium hexafluorophosphate (DPIHP) were used as a three-component-photoinitiator system. CQ, EDMAB, and DPIHP were obtained from Aldrich (Milwaukee, WI, USA) and used without further purification. Two-component-photoinitiator system containing only CQ and DPIHP was used for comparison. All other chemicals were purchased from Sigma-Aldrich at reagent grade and used without further purification. The chemical structures are shown in Table 1.

2.2 Preparation of resin formulations

The procedure for resin formulation preparation has been reported [28–30]. The control formulations consisted of HEMA and BisGMA with a mass ratio of 45/55, which is similar

to widely used commercial dentin adhesives. It should be noted that there are two control formulations: C0-3 is HEMA/BisGMA 45/55 and 3-component photoinitiator system; C0-2 is HEMA/BisGMA 45/55 and 2-component photoinitiator system. These controls were used as a comparison to the experimental adhesive resins (Ex-3 or Ex-2), in which x represents the weight percentage of synthesized co-monomer (TUMA) to replace part of BisGMA. CQ, EDMAB and DPIHP at concentrations 0.5, 0.5 and 1.0 wt% with respect to the total amount of monomers, were used as a three-component-photoinitiator system (C0-3 and Ex-3 groups). The two-component-photoinitiator system contains only CQ (0.5 wt%) and DPIHP (1.0 wt %) (C0-2 and Ex-2 groups). The resin mixtures were prepared in brown glass vials and stirred for 48 h on an orbital shaker to form a homogeneous solution.

2.3 Real-time conversion and maximal polymerization rate (Rp)

Real-time *in situ* monitoring of the visible-light-induced photopolymerization of the 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} [11, 13–15, 26, 27, 31]. One drop of adhesive solution was placed on the diamond crystal top-plate of an attenuated total reflectance (ATR) accessory (Pike, GladiATR, Pike Technology, Madison, WI) and covered with a mylar film. A 40-s exposure to the commercial visible-light-polymerization unit (Spectrum 800®, Dentsply, Milford, DE, ~480–490 nm[27]) at an intensity of 550 mW cm^{-2} was initiated after 50 spectra had been recorded. Real-time IR spectra were recorded continuously for 600 s after light curing began. A time-resolved spectrum collector (Spectrum TimeBase, Perkin-Elmer) was used for continuous and automatic collection of spectra during polymerization. Three replicates were obtained for each adhesive formulation.

The change of the band ratio profile ($1637 \text{ cm}^{-1}(\text{C}=\text{C})/1715 \text{ cm}^{-1}(\text{C}=\text{O})$) was monitored for calibrating the DC of the methacrylate groups. DC was calculated using the following equation, which is based on the decrease in the absorption intensity band ratios before and after light curing. The average of the last 50 values of time-based data points is reported as the DC value at 10 minutes.

$$DC = \left(1 - \frac{\text{Absorbance}_{1637 \text{ cm}^{-1}}^{\text{sample}} / \text{Absorbance}_{1715 \text{ cm}^{-1}}^{\text{sample}}}{\text{Absorbance}_{1637 \text{ cm}^{-1}}^{\text{monomer}} / \text{Absorbance}_{1715 \text{ cm}^{-1}}^{\text{monomer}}} \right) \times 100\%$$

The kinetic data were converted to $R_p/[M]_0$ by taking the first derivative of the time versus conversion curve[28, 32], where R_p and $[M]_0$ are the rate of polymerization and the initial monomer concentration, respectively.

2.4 Preparation of adhesive polymer specimens

The preparation of the polymer specimens has been reported[11–14, 25, 32–34]. In brief, round beams with a diameter of 1 mm and a length of at least 15 mm were prepared by injecting the adhesive formulations into glass-tubing molds (Fiber Optic Center, Inc., part

no.: ST8100, New Bedford, MA). Fifteen specimens were prepared for each formulation. The samples were light polymerized with an LED light-curing unit for 40 s (LED Curebox, 80 mW/cm² irradiance, Prototech, Portland, OR).

It is noted that in our experiments, the polymerization kinetics study is conducted at higher light intensity (550mW/cm², halogen light) than the beam specimen preparation conditions (LED curing box, 200 mW/cm²). The beam specimens were prepared using LED light, which has a higher efficiency to induce the photo polymerization. The light sources and the intensity settings have been adjusted so that the degree of conversion and polymerization rate are matched between the systems under these two conditions (unpublished data).

The polymerized samples were stored in the dark at room temperature for 48 h to allow for post-cure polymerization. The samples were extracted from the glass tubing and characterized using dynamic mechanical analysis.

2.5 Dynamic mechanical analysis (DMA)

The viscoelastic properties of the adhesives were characterized using DMA Q800 (TA Instruments, New Castle, USA) with a 3-point bending clamp[13, 14, 25, 32, 33]. The cylinder beam specimens (1 mm×15 mm) were divided into two groups. The first group consisted of dry samples. These specimens were tested using a standard 3-point bending clamp. The test temperature was varied from 10 to 220 °C with a ramping rate of 3°C/min, a frequency of 1 Hz, an amplitude of 15 μm, and a pre-load of 0.01 N. The second group consisted of wet samples, which were stored in distilled water at 37 °C for five days, as described under water sorption.

The wet samples were tested by 3-point bending, using a water submersion clamp. The test temperature was varied from 10 to 80 °C with a ramping rate of 1.5 °C/min at a frequency of 1 Hz. The properties measured under this oscillating loading were storage modulus (E') and $\tan \delta$. The ratio of the loss modulus (E'') to the storage modulus E' is referred to as the mechanical damping, or $\tan \delta$ (i.e., $\tan \delta = E''/E'$). Five specimens of each adhesive formulation were measured, and the results from the five specimens per each formulation were averaged.

2.6 Water sorption

The water sorption protocol has been reported [13, 14]. In brief, water sorption was measured using cylindrical beam specimens (1 mm×15 mm). Five specimens were used for each adhesive formulation. The specimens were immersed in deionized water and stored at 37 °C. The water was changed daily. After five days of prewash, the polymer specimens were allowed to dry in the vacuum chamber at 37 °C until a constant weight (m_{1dry}) was obtained. After prewash, the dry specimens were then immersed in deionized water and stored at room temperature. At fixed time intervals (3, 6, 24, 48, 72 and 168 h), the polymer specimens were retrieved, blotted dry to remove excess liquid, weighed (m_{2wet}), and re-immersed in the water. The value (%) for solubility and mass change (water sorption) were calculated as:

$$\text{Mass change (\%)} = 100 \frac{m_{2\text{wet}} - m_{1\text{dry}}}{m_{1\text{dry}}} = \text{Water sorption (\%)}$$

2.7 Statistical analysis

For all experimental groups, the differences were evaluated using one-way analysis of variance (ANOVA), together with Tukey's test at $\alpha = 0.05$ to identify significant differences (Microcal Origin Version 8.0, Microcal Software Inc., Northampton, MA).

2. Results

3.1 Degree of conversion and maximum polymerization rate

The degree of conversion (DC) for resin formulations with three-component-photoinitiator system are shown in Fig. 1A. The DC of control (C0-3) is 64.4%. When TUMA was used as the co-monomer, at concentrations of 15 (E15-3), 25 (E25-3), 35 (E35-3) and 45 (E45-3) wt %, the DC, after 600s, was 67.2%, 65.9%, 61.7% and 59.8%, respectively. The DC with two-component photoinitiator system is shown in Fig. 1B. The DC for control with two-component photoinitiator (C0-2) was 24.0%. In comparison, with TUMA as the co-monomer, DC was 66.2%, 64.8%, 60.6% and 59.2% when there were 15, 25, 35 and 45 wt% of TUMA, even with this two-component photoinitiator system.

The results of maximum polymerization rates are shown in Fig. 2. For control formulations, R_p with three-component-photoinitiator system (C0-3) is $2.01 \times 10^{-1} \text{ s}^{-1}$. However, when there is only two-component-photoinitiator present, R_p of control (C0-2) is $0.40 \times 10^{-1} \text{ s}^{-1}$. When TUMA was used as co-monomer, there is no significant difference ($p < 0.05$) in R_p between the three- and two-component-photoinitiator systems with the same content of TUMA. The R_p values for three- and two-component-photoinitiator systems are 1.86 (E15-3) and $1.71 \times 10^{-1} \text{ s}^{-1}$ (E15-2), 1.72 (E25-3) and $1.64 \times 10^{-1} \text{ s}^{-1}$ (E25-2), 1.61 (E35-3) and $1.56 \times 10^{-1} \text{ s}^{-1}$ (E35-2), 1.49 (E45-3) and $1.62 \times 10^{-1} \text{ s}^{-1}$ (E45-2), in the presence of 15, 25, 35 and 45 wt% of TUMA, respectively.

3.2 Dynamic mechanical analysis (DMA) under dry conditions

The results of DMA under dry conditions for all adhesives are shown in Fig. 3 and Table 2. From Fig. 3, it is apparent that the storage moduli of experimental adhesives at rubbery region ($>180^\circ\text{C}$, $\sim 40\text{--}50 \text{ MPa}$) for both three- and two-component-photoinitiator systems are higher than control (27.1 MPa). The storage moduli at the rubbery region increased with increasing TUMA content. Moreover, with the same content of TUMA, there is no statistically significant difference ($p < 0.05$) in the storage moduli at rubbery region between three- and two-component-photoinitiator systems.

As shown in Table 2, T_g of control (C0-3) is 151.5°C . When TUMA was used as the co-monomer, T_g was comparable with control for both three- ($\sim 149\text{--}150^\circ\text{C}$) and two- ($\sim 150\text{--}153^\circ\text{C}$) component initiator systems. There was no statistically significant difference ($p < 0.05$) for $\tan \delta$ (Table 2) for all formulations.

3.3 Dynamic mechanical analysis (DMA) under wet conditions

The results of DMA under wet condition are shown in Fig. 4 and summarized in Table 3. The storage modulus values for the experimental formulations are lower than the control (C0-3) at 37 and 70 °C. Moreover, with the same content of TUMA, there is no statistically significant difference ($p < 0.05$) in storage moduli at rubbery region (70 °C under wet condition) between three- and two-component-photoinitiator systems. As shown in Table 3, under wet conditions T_g decreases with an increase in TUMA content. Meanwhile, the intensity of $\tan \delta$ peaks increased with increasing TUMA.

3.4 Water sorption

Results of water sorption are shown in Fig. 5. The water sorption value for the control formulation is 10.2%. Water sorption increased with increasing TUMA content to 10.7% (E15-3), 11.4% (E25-3), 12.4% (E35-3) and 12.9% (E45-3) with three-component initiator system. The water sorption values are 11.3% (E15-2), 12.1% (E25-2), 12.3% (E35-2) and 13.2% (E45-2) with the two-component initiator system.

3. Discussion

Our former investigation suggested that TUMA is a promising co-initiator[23], which offers comparable photopolymerization efficiency and prevents amine leaching from the adhesive polymers. Since there are three-methacrylate groups in each TUMA molecule, it is very likely that it could serve as a crosslinkable comonomer in dental resins. This investigation probed the potential of this newly synthesized compound to function simultaneously as a co-initiator and crosslinkable comonomer in dentin adhesive formulations.

Polymerization kinetics in regard to degree of conversion (DC) and polymerization rate (R_p) is the first concern with the elimination of the commercial tertiary amine, EDMAB. For control formulations, with and without co-initiator (EDMAB), there is a significant difference in DC and R_p . The DC and R_p were much lower with the two-component as compared to the three-component-photoinitiator system. When TUMA was used as the co-monomer, DC and R_p for experimental adhesives without EDMAB were similar to the formulations with EDMAB. The results indicate that when TUMA was used as a co-monomer, it was not necessary to add the co-initiator, EDMAB. The results support the ability of TUMA to serve simultaneously as a co-monomer and co-initiator.

Generally, dental polymeric materials formed by photo-polymerization of multifunctional methacrylates are highly crosslinked polymer networks. Crosslinking density is an important factor in the viscoelastic behavior as well as the structural heterogeneity of polymer networks[33]. Dynamic mechanical analysis (DMA) is sensitive to structure and variation in the stiffness of materials, and it can be used to provide information on the structure and properties of polymer networks.

When TUMA was used as the co-monomer, the storage moduli at rubbery region were higher than control when the specimens are tested under dry conditions. The results suggest that the crosslinking density was increased by introducing this new co-monomer that contains three methacrylate-urethane groups. With the same content of TUMA, the storage

moduli at the rubbery region were similar between three- and two-component-photoinitiator systems. These results suggest that the crosslinking density is not influenced by co-initiator (EDMAB) in the presence of TUMA. Under these conditions, EDMAB could be eliminated from the formulation without compromising the dynamic mechanical properties of the dentin adhesive.

Since water or saliva is always present in the oral environment, it is also important to understand the viscoelastic properties of polymers under wet conditions. The setup with three-point bending water-submersion clamp used in this work is expected to simulate the wet environment of the mouth. In the current study, the decreased mechanical properties noted with the experimental formulations, under wet conditions, could be associated with more water sorption. Water could act as a plasticizer in the crosslinked network [35–38]. Water is also known to facilitate the degradation of methacrylate adhesives[39, 40], which have numerous ester groups that are subject to both hydrolytic degradation and enzymatic hydrolysis. In addition, the broad glass transition curves for all the samples tested here indicate that the polymer networks are heterogeneous with glass transition occurring over a broad range of temperature. This could be attributed to the polymerization of multi-functional monomers which can produce very heterogeneous networks, i.e., networks that exhibit regions that are highly crosslinked and regions with limited crosslinking. In other words, highly increased crosslink density, as noted in the dry experimental samples, may be accompanied by a sacrifice in homogeneity of the polymer network structure and a significantly weaker structure in the loosely crosslinked regions potentially causing premature failure, especially with the increased water sorption. Under these conditions, the adhesive/dentin bond could have limited structural integrity and durability. Although it has been reported that monomers with urethane groups are resistant to hydrolytic degradation [41], the results with TUMA suggest that further optimization is required to provide a hydrophilic/hydrophobic balance that would lead to improved viscoelastic properties under wet conditions.

4. Conclusion

A newly synthesized tertiary amine, TUMA, could be used both as a co-initiator and co-monomer. In the absence of EDMAB (two-component photoinitiator system), the DC and Rp of the TUMA-containing formulations were similar with three-component photoinitiator system (with EDMAB). The hypothesis is supported, e.g., the DMA results suggest that it is not necessary to add EDMAB into the TUMA-containing formulation. Dynamic mechanical properties were enhanced for TUMA-containing formulations under dry conditions, while decreased under wet conditions.

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Fig. 1.

Real-time conversion of adhesive resins with three- (A) and two-component (B) photoinitiator systems. The adhesives were light-cured for 40 sec at room temperature using a commercial visible-light-curing unit (Spectrum® 800, Dentsply, Milford, DE. Intensity is 550 mW/cm⁻²). Real-time IR spectra were continuously recorded for 600 s after light activation began. N= 3 ± SD. ^a Significantly (p <0.05) different from the control formulation (C0-3) with three-component photoinitiator system. ^b Significantly (p <0.05) different from the control formulation (C0-2) with two-component photoinitiator system. The symbols of Ex-3 and Ex-2 indicate three- and two-component photoinitiator systems, respectively.

Fig. 2.

The maximum polymerization rate of adhesive resins with three- and two-component photoinitiator systems. ^a Significantly ($p < 0.05$) different from the control formulation (C0-3) with three-component photoinitiator system. ^b Significantly ($p < 0.05$) different from the control formulation (C0-2) with two-component photoinitiator system. The symbols of Ex-3 and Ex-2 indicate three- and two-component photoinitiator systems, respectively.

Fig. 3.

DMA under dry condition: Comparison of the storage modulus versus temperature curves for adhesives with three- and two- component photoinitiator systems. C0-3 is the control formulation with three-component photoinitiator system. DMA (TA instruments, Q800) with a three-point bending clamp was conducted over a temperature range of 0 to 220 °C with a ramping rate of 3 °C/min at a frequency of 1 Hz. The symbols of Ex-3 and Ex-2 mean three- and two-component photoinitiator systems, respectively. There are 15 (A), 25 (B), 35 (C) and 45 (D) wt% of TUMA co-monomer replacing BisGMA.

Fig. 4.

DMA under wet condition: Comparison of the storage modulus versus temperature curves for adhesives with three- and two- component photoinitiator systems. C0-3 is the control formulation with three-component photoinitiator system. The symbols of Ex-3 and Ex-2 mean three- and two-component photoinitiator systems, respectively. There are 15 (A), 25 (B), 35 (C) and 45 (D) wt% of TUMA co-monomer replacing BisGMA.

Fig. 5.

Water sorption of resin polymers cured with different weight contents of TUMA. A) Ex-3 formulations are three-component photoinitiator system; B) Ex-2 formulations are two-component photoinitiator system. C0-3 is the control formulation with three-component photoinitiator system. Symbols: E15, E25, E35 and E45 represent 15, 25, 35, and 45 wt % of TUMA.

Table 1

Chemical structures used in the dentin adhesives

Initiator system		Monomer system
Photosensitizer	CQ	HEMA
Electron donor	EDMAB (with or without)	BisGMA
Iodonium salt	DPIHP	TUMA

Table 2

DMA results under dry conditions

Sample	Storage modulus at 25 °C (MPa) × 10 ³	Storage modulus at 37 °C (MPa) × 10 ³	Storage modulus at 180 °C (MPa)	Tg (°C) ^a	Height of tan δ peak
C0-3 ^d	4.16±0.22	3.96±0.21	27.1±1.0	151.5±1.1	0.63±0.02
E15-3 ^e	4.65±0.04 ^b	4.39±0.05 ^b	40.5±2.3 ^b	150.3±0.2	0.63±0.02
E25-3	4.59±0.09 ^b	4.31±0.09 ^b	43.9±1.8 ^b	148.8±0.4 ^b	0.64±0.03
E35-3	4.58±0.11 ^b	4.29±0.10 ^b	47.9±3.5 ^b	148.2±0.7 ^b	0.63±0.03
E45-3	4.57±0.07 ^b	4.28±0.70 ^b	50.7±1.4 ^b	149.4±0.5 ^b	0.64±0.02
E15-2 ^f	4.54±0.11 ^b	4.26±0.09	38.4±1.5 ^b	152.0±1.1	0.61±0.02
E25-2	4.54±0.03 ^b	4.26±0.03 ^b	42.3±1.5 ^b	152.5±0.9 ^c	0.65±0.02
E35-2	4.50±0.11 ^b	4.21±0.10	47.4±2.0 ^b	150.4±0.5 ^c	0.64±0.02
E45-2	4.43±0.19	4.15±0.21	48.9±1.7 ^b	151.4±0.8 ^c	0.63±0.02

Values are mean (± standard deviation) for n = 5 in each group.

^aThe glass transition temperatures (Tg) values of the polymer networks were taken to be the maximum of the tan δ versus temperature curve, which was determined by using a dynamic mechanical analyzer.

^bSignificant (p<0.05) difference from C0-3.

^cSignificant (p<0.05) difference from Ex-3 with the same content of TUMA.

^{d,e}Formulations of C0-3 and Ex-3 group were prepared with three-component photoinitiator system, containing 0.5 wt% of EDMAB.

^fFormulations of Ex-2 group were prepared with two-component photoinitiator system, containing only 0.5 wt% of CQ and 1.0 wt% of DPIHP (No EDMAB).

Table 3

DMA results under wet conditions

Sample	Storage modulus at 25 °C (MPa) × 10 ³	Storage modulus at 37 °C (MPa) × 10 ³	Storage modulus at 70 °C (MPa) × 10 ²	Tg (°C) ^a	Intensity of tan δ at 70 °C
C0-3 ^d	2.38±0.05	1.98±0.05	3.39±0.35	58.9±0.4	0.40±0.02
E15-3 ^e	2.35±0.07	1.87±0.05 ^b	2.13±0.15 ^b	57.8±0.2 ^b	0.47±0.01 ^b
E25-3	2.27±0.06	1.79±0.04 ^b	2.15±0.16 ^b	57.8±0.1 ^b	0.48±0.01 ^b
E35-3	2.22±0.08 ^b	1.74±0.06 ^b	1.86±0.14 ^b	57.5±0.3 ^b	0.50±0.01 ^b
E45-3	2.21±0.03 ^b	1.66±0.03 ^b	1.42±0.12 ^b	55.9±0.1 ^b	0.53±0.01 ^b
E15-2 ^f	2.29±0.05	1.85±0.04 ^b	2.39±0.22 ^b	58.0±0.3 ^b	0.46±0.01 ^b
E25-2	2.33±0.04	1.85±0.04 ^b	2.05±0.16 ^b	57.9±0.1 ^b	0.49±0.01 ^b
E35-2	2.19±0.08 ^b	1.70±0.06 ^b	1.68±0.17 ^b	57.2±0.4 ^b	0.51±0.01 ^b
E45-2	2.21±0.04 ^b	1.69±0.01 ^b	1.63±0.11 ^b	56.2±0.3 ^b	0.52±0.01 ^b

Values are mean (± standard deviation) for n = 5 in each group.

^aThe glass transition temperatures (Tg) values of the polymer networks were taken to be the minimum of the Deriv. storage modulus versus temperature curve determined using a dynamic mechanical analyzer.

^bSignificant (p<0.05) difference from C0-3.

^cSignificant (p<0.05) difference from Ex-3 with the same content of TUMA.

^{d,e}Formulations of C0-3 and Ex-3 group were prepared with three-component photoinitiator system, containing 0.5 wt% of EDMAB.

^fFormulations of Ex-2 group were prepared with two-component photoinitiator system, containing only 0.5 wt% of CQ and 1.0 wt% of DPIHP (No EDMAB).