

Photo-curing behaviors of bio-based isosorbide dimethacrylate by irradiation of light-emitting diodes and the physical properties of its photo-cured materials

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ABSTRACT: Bio-based isosorbide (1,4:3,6-dianhydroglucitol), which was obtained from biomass-derived carbohydrates, has recently attracted much attention as an alternative to bisphenol A (BPA) because of its rigidity and transparency. BPA is still widely used for a variety of chemical applications even though it is known to be an endocrine-disrupting chemical. BPA is a key precursor to most photo-curable materials ranging from encapsulants of electronic devices to dental sealants. In this study, photo-curable isosorbide dimethacrylate (ISDM) was synthesized from bio-based isosorbide as a substitute for BPA, and the photo-curing behaviors of ISDM by irradiation with light-emitting diode (LED) light were investigated. The photo-curing conversion and rates of ISDM formation were determined based on the change in the peak corresponding to the double bond within the methacrylate groups using attenuated total reflectance Fourier transform infrared (ATR–FTIR) spectroscopy. The effects of initiators and the wavelength of LED light on the photo-curing conversion and rates of ISDM formation were examined, and a comparative study was carried out with 2,2-bis[4(2-hydroxy-3-methacryloyloxy-propyloxy)phenylpropane] (Bis-GMA), which is a photo-curing material bearing a BPA moiety. In addition, the mechanical properties, such as surface hardness, adhesion strength, and transparency, after photo-curing of ISDM were evaluated. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42726.

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INTRODUCTION

To reduce the heavy dependence on petroleum, which has resulted in oil depletion and global warming, many efforts have recently been focused on replacing petroleum-based chemicals with bio-based ones derived from renewable and sustainable resources.¹ Among these chemicals, bio-based isosorbide (1,4:3,6-dianhydroglucitol), which is obtained by hydrogenation of glucose followed by dehydration of sorbitol, has attracted much attention as an alternative to bisphenol A (BPA) because of its rigidity and transparency.^{2,3} BPA is still widely used for a variety of chemical applications even though it is an endocrine-disrupting chemical (EDC).^{4,5} BPA is a key precursor of most photo-curable materials, ranging from encapsulants of electronic devices to dental sealants.^{6,7} Therefore, photo-curable materials should be derived from petroleum-independent and nontoxic chemicals instead of BPA. However, only a few examples of bio-based photo-curable materials bearing a rigid backbone have been reported.⁸

In the photo-curing process, a mercury-arc lamp, middle-pressure mercury-vapor, and metal halide lamp are typically used. However, these lamps consume a large amount of energy to generate the light, and the cooling and protection system should be equipped to treat the heat because of their broad spectrum. Since light-emitting diode (LED) were introduced, conventional light source devices have been replaced with LED because of its many advantages, such as good efficiency, long lifetime, low power consumption, lack of heat production, fast response, and small size.^{9,10} Therefore, LED light can lead to a safe and energy-efficient photo-curing process. In addition, photo-curing by irradiation with LED light can occur with heat-free operation and selective curing using a narrow range of wavelengths with an optical output controlled by adjusting an electric current and an instantaneous ON/OFF switch.^{11,12}

In this study, photo-curable isosorbide dimethacrylate (ISDM) was synthesized from bio-based isosorbide as a substitute for

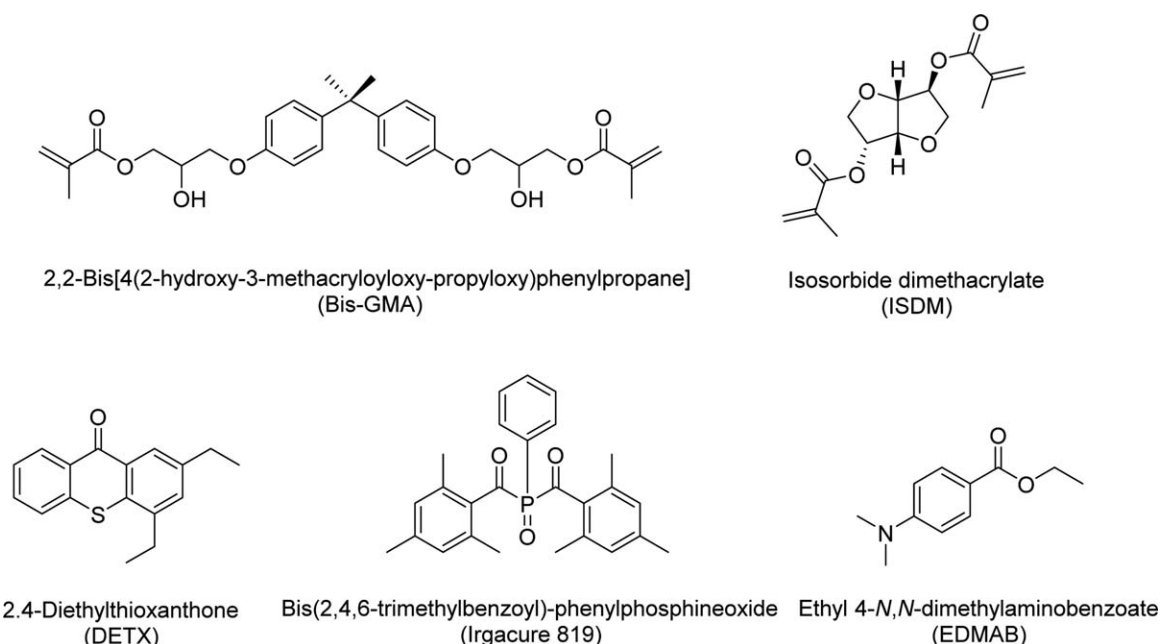


Figure 1. Chemical structures of compounds used in this study.

BPA, and the photo-curing behaviors of ISDM by irradiation with LED light have been investigated. The effects of initiators and the wavelength of LED light on the photo-conversion of ISDM were examined, and the mechanical properties, such as surface hardness, adhesion strength, and transparency, after photo-curing were evaluated.

EXPERIMENTAL

Materials

Isosorbide (1,4:3,6-dianhydro-D-sorbitol, 98%), methacrylate anhydride (94%), ethyl 4-*N,N*-dimethylaminobenzoate (EDMAB), tetrahydrofuran (THF, anhydrous, $\geq 99.9\%$), magnesium sulfate (MgSO_4 , $\geq 99.5\%$), and bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (Irgacure 819) were purchased by Sigma-Aldrich. Triethylamine (TEA) and DMAP (4,4-Dimethylaminopyridine) were purchased from Daejung, 2,4-Diethylthioxanthone (DETX), which was used as another initiator, and 2,2-bis[4(2-hydroxy-3-methacryloyloxy-propyloxy)phenylpropane] (Bis-GMA) were provided by Miwon Specialty Chemical (Figure 1). The solvents used for the work-up procedure included ethyl acetate, hexane, and dichloromethane (DCM), which were purchased from Samchun Chemicals (Korea). The PET films (Model name: H33R) were obtained from Kolon.

Synthesis of ISDM

Isosorbide (2.92 g, 20 mmol), TEA (44 mmol, 2.2 equiv), and DMAP (4.4 mmol, 0.22 equiv) were placed in a round-bottomed flask, and dry THF (60 mL) was added. Methacrylic anhydride (44 mmol, 2.2 equiv) in dry THF (30 mL) was added dropwise. Then, the reaction mixture was stirred under N_2 at room temperature for 15 h [Figure 2(a)]. THF was evaporated under reduced pressure after the reaction was complete. The resulting residue was diluted with DCM (50 mL), and the solution was sequentially washed with deionized water and brine. Next, the DCM layer was dried over magnesium sulfate, filtered,

and evaporated to dryness. Then, the crude product was purified by flash chromatography (hexane : ethyl acetate = 2 : 1) on silica to afford ISDM (4.12 g, 73%) as a transparent oil. Any other stereo isomers were not generated under this reaction condition. Synthetic ISDM was characterized with FT-NMR (Avance III, Bruker, Germany) and GC-MS (5975, Agilent, USA). Chemical shift (δ) and coupling constant (J) were expressed in parts per million (ppm) and hertz (Hz), respectively. The mass spectrometer was operated in ESI mode ($m/z < 2000$).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 6.14 (s, 1H, H_e), 6.09 (s, 1H, H_e), 5.60 (s, 1H, H_e), 5.58 (s, 1H, H_e), 5.24 (br, 1H, H_b), 5.19 (q, $J = 4$ Hz, 1H, H_b), 4.89 (t, $J = 4.0$ Hz, 1H, H_c), 4.52 (d, $J = 4.0$ Hz, 1H, H_c), 3.98 (br, 2H, H_d), 3.95 (dd, $J = 8.0$, 4.0 Hz, 1H, H_d), 3.87 (dd, $J = 8.0$, 4.0 Hz, 1H, H_d), 1.94 (s, 3H, H_e), 1.90 (s, 3H, H_e) [Figure 2(b)]. $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 166.9, 166.6, 135.9, 135.8, 126.7, 126.5, 86.2, 82.1, 78.4, 74.4, 73.6, 70.8, 18.5, 18.4. Mass spectrum (ESI) m/z calculated for $\text{C}_{14}\text{H}_{19}\text{O}_6$ [$\text{M} + \text{H}$] $^+$ 283.1, found 283.1.

Tensile-Shear Strength

Polycarbonate plates that were 0.3 cm thick were cut into flat coupons (i.e., 2.54 cm by 10.16 cm), and their surfaces were cleaned and dried. Then, the photo-polymerizable sample (20 $\mu\text{L} = 0.02 \text{ cm}^3$) containing an initiator was applied to the overlapped area ($2.54 \times 2.54 \text{ cm}^2$) between the plate pair, as shown in Figure 3. The resulting thickness of each adhesive material was $25 \pm 1.6 \mu\text{m}$. The prepared assemblies were photo-cured by irradiation using LED lamp. Based on a reported method,⁸ additional plates ($2.54 \times 5.08 \text{ cm}^2$) with the same thickness were attached on both ends of the specimens for grip. The tensile-shear strengths of the joints bonded by the photo-curing procedure were measured using universal testing machine (UTM) (5967, INSTRON, USA), and the loading rate was 1.27 cm/min.

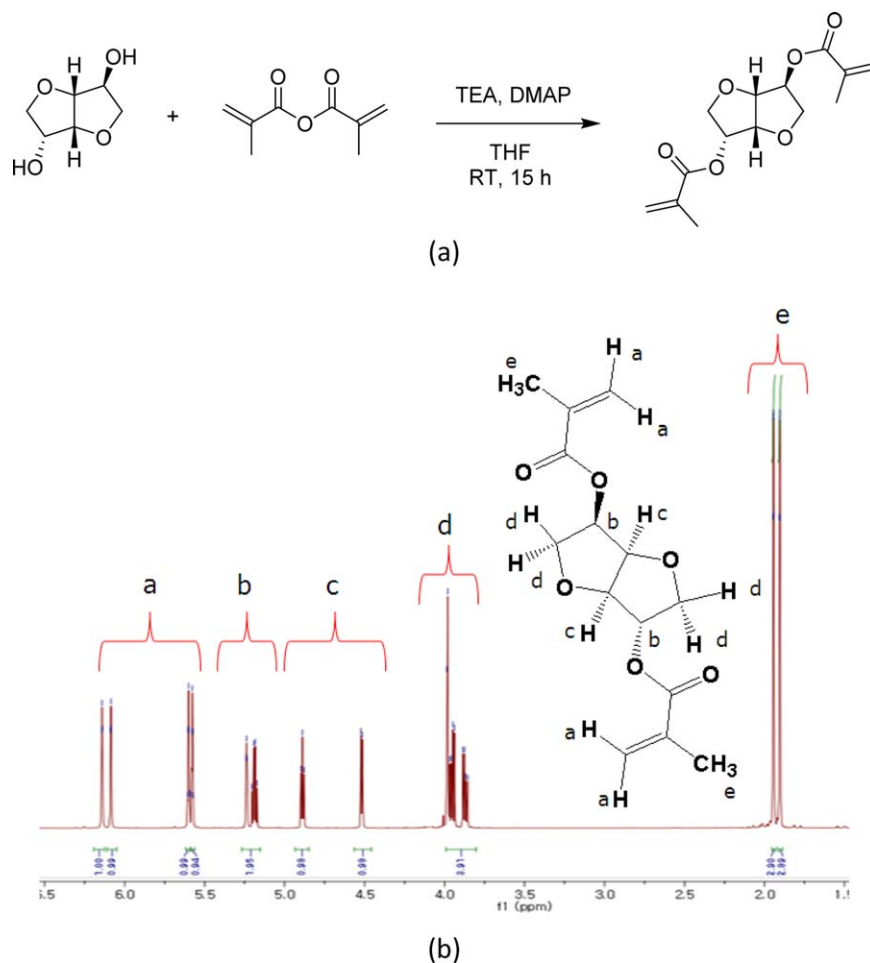


Figure 2. (a) Reaction scheme for ISDM from isosorbide and (b) ^1H NMR spectra of the synthesized ISDM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

LED Light Source

Two types of LED lamp devices (Lamp A & Lamp B) were manufactured, and they were used as the light source for photo-curing. Three types of LED bulbs emitting at three different wavelengths (i.e., 365, 375, 400 nm) were arrayed in Lamp A, as shown in Figure 4. In addition, Lamp B was constructed from the same bulbs emitting light corresponding to 400 nm. The light intensities of Lamps A and B were 95 and 120 mW/cm², respectively. Monochromatic Lamp B was used for the general experiments unless otherwise mentioned.

Photo-Curing Conversion and Rates

The photo-curing conversion and rates were determined based on the spectra recorded using a FTIR (FT/IR-6100, JASCO, Japan) equipped with an attenuated total reflectance (ATR) accessory.¹³ The ATR crystal was zinc selenide (ZnSe), and its refractive index at 1000 cm⁻¹ was 2.4 with a transmission range from 4000 to 400 cm⁻¹. The resolution of the recorded spectra was 4 cm⁻¹. The samples were cut into 5 × 0.5 cm² pieces and analyzed by observing the changes in the deformation of the C=C bond within the methacrylate group at 811 cm⁻¹.^{14,15}

The photo-curing conversion after a given irradiation time (t) was calculated using the following equation:

Photo-curing conversion (%)

$$= [1 - [(A_{811})_t / (A_{1722})_t] / [(A_{811})_0 / (A_{1722})_0]] \times 100$$

where $(A_{811})_0$ and $(A_{1722})_0$ are the absorbance (i.e., 811 and 1722 cm⁻¹, respectively) at the initial time and $(A_{811})_t$ and $(A_{1722})_t$ are the absorbance (i.e., 811 and 1722 cm⁻¹, respectively) at time t . In addition, all of the spectra were modified using baseline correction.

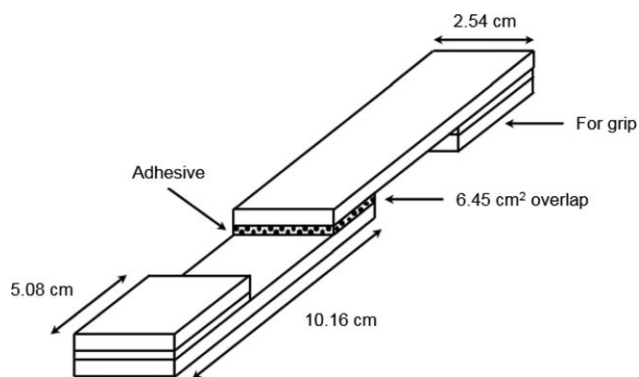


Figure 3. Dimension of the specimen used to measure the tensile-shear strength using UTM.

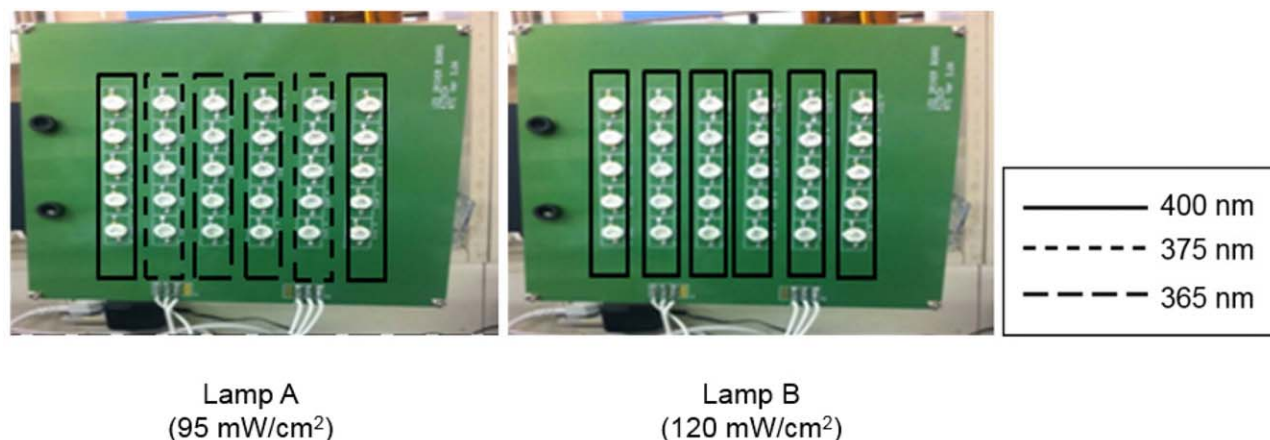


Figure 4. Appearance of LED lamp used in the photo-curing experiments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The photo-curing reaction constants (k) were approximately determined by curve fitting of the following equation assuming the deformation of the methacrylate group is the first order reaction.

$$C_t = C_{\max}(1 - e^{-kt})$$

where C_t is photo-curing conversion at the time and C_{\max} is maximum photo-curing conversion.

The samples were coated onto PET films that were 15 μm in thickness using a bar coater (BC-VF0106, TQC, Netherlands). The distance between the sample and the LED lamp was fixed at 2 cm during irradiation.

RESULTS AND DISCUSSION

Effect of Initiator Concentration on the Photo-Curing Conversion and Rates

To confirm the feasibility of bio-based ISDM as a photo-curable material, its photo-curing behaviors such as photo-curing conversion and rate were examined and compared with commercially available Bis-GMA, which is one of the most popular BPA-based photo-curable materials. Understanding of the photo-curing behaviors is important for property control of the cured product and efficient curing process.

At first, the effect of the initiator concentration on the photo-curing conversion and rates were investigated. DETX was used as an initiator and three different concentrations were evaluated. EDMAB was used as a co-initiator and an equimolar amount of EDMAB was added to DETX and homogeneously mixed with DETX under dark conditions. The photo-curing conversion and rates were determined based on ATR-FTIR analysis. Bis-GMA was examined prior to ISDM. From the IR spectrum of Bis-GMA in the range of 780–850 cm^{-1} , the oop (out-of-plane) bending peaks of the para substituents on the aromatic rings and the C=C vibration stretching peak of the methacrylates appeared at 829 and 811 cm^{-1} , respectively. As the photo-curing progressed, the C=C vibration stretching peak of the methacrylates continued to decrease. The photo-curing conversion and rates were calculated based on the C=O vibration

stretching peak of the methacrylates at 1722 cm^{-1} as a reference peak (Figure 5).

Figure 6(a) shows the photo-curing conversion of Bis-GMA as a function of time. As the concentration of the initiators

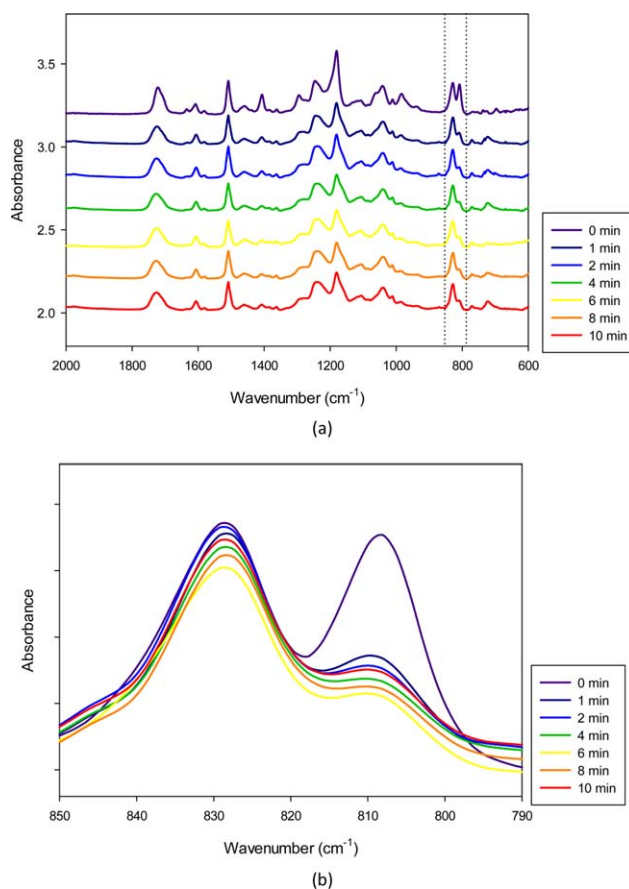


Figure 5. Change in the IR spectra during photo-curing of BisGMA initiated by 5 wt % DETX with equimolar EDMAB in the range of (a) 600–2000 cm^{-1} and (b) its magnified view (780–850 cm^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

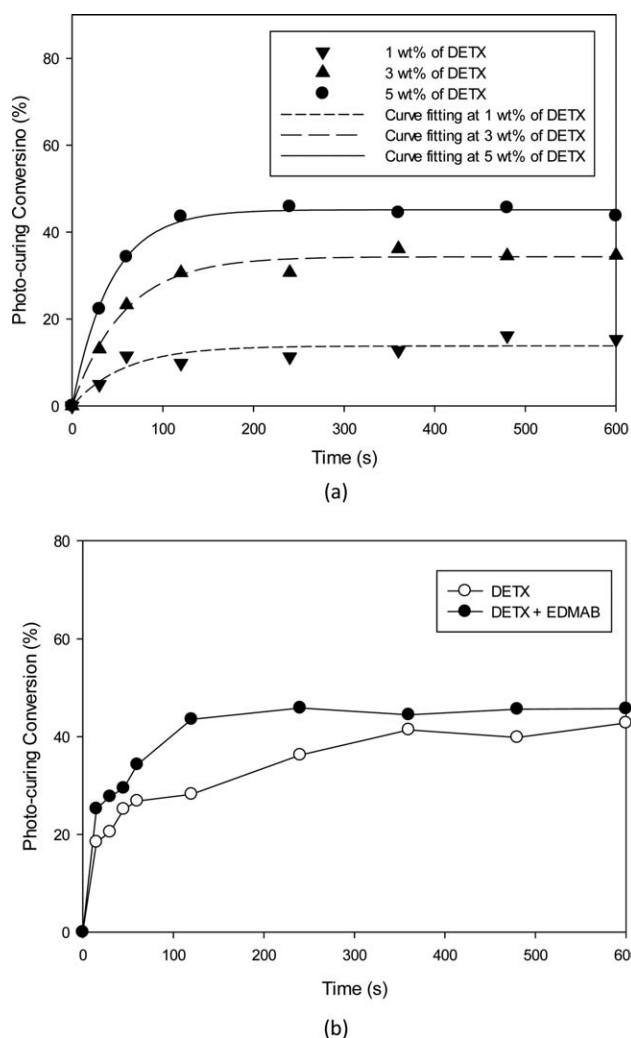


Figure 6. (a) Photo-curing profile of Bis-GMA as a function of the initiator (DETX with equimolar EDMAB) concentrations and (b) change of photo-curing profile without a co-initiator (EDMAB).

increased from 1 to 5 wt %, the photo-curing conversion was enhanced. The photo-curing conversion of Bis-GMA was only 17% using 1 wt % of the initiator. In addition, the conversion was increased to 47% when 5 wt % of the initiator was used. However, no further enhancement of the conversion was observed using 10 wt % of the initiator (data not shown). The maximum photo-curing conversion of Bis-GMA was less than 50% [Figure 6(a)]. Therefore, the LED light intensity was insufficient to photo-cure Bis-GMA. The Photo-curing rates according to the concentration of the initiator were compared with the reaction constant (k). When 1 and 3 wt % of the initiator was used, similar photo-curing rates ($17.5 \pm 5.7 \times 10^{-3} \text{ s}^{-1}$ and $17.5 \pm 1.8 \times 10^{-3} \text{ s}^{-1}$, respectively) were shown. Even though the photo-curing rate ($k = 23.6 \pm 1.1 \times 10^{-3} \text{ s}^{-1}$) was enhanced using 5 wt % of the initiator, no significant acceleration of photo-curing took place.

Tertiary amine compounds with electro-donating moiety are known as co-initiators to allow acceleration of curing rate.¹⁶ To determine the effect of such an amine co-initiator, the results from the sample with and without EDMAB were compared.

The final photo-curing conversion was increased from 41% to 46% by the addition of EDMAB and the photo-curing rate was also increased ($23.3 \pm 4.6 \times 10^{-3} \text{ s}^{-1}$ compared to $31.7 \pm 4.7 \times 10^{-3} \text{ s}^{-1}$). However, no noticeable increase in both the final photo-curing conversion and the photo-curing rate was observed [Figure 6(b)].

Next, the photo-curing conversion and rates of ISDM were investigated. Based on the IR spectrum of ISDM from 780 to 850 cm^{-1} , a C=C vibration stretching peak corresponding to the methacrylates appeared at 811 cm^{-1} , and this peak decreased in intensity as the photo-curing process progressed. The C=O vibration stretching peak of methacrylates at 1722 cm^{-1} was used as a reference peak (Figure 7).

Similar to Bis-GMA, an increase in the initiator concentration from 3 to 10 wt % led to enhancement of the photo-conversion. However, the final photo-conversion of ISDM increased to 80%, which is nearly two times higher than that of Bis-GMA. It is believed that this high conversion is because of low viscosity (48.6 cP at 25°C) of ISDM because ISDM unlike Bis-GMA can play a role as a diluent during the photo-curing.¹⁷ On the other hand, the photo-curing rates of ISDM were lower than those of Bis-GMA and the photo-curing reaction constant

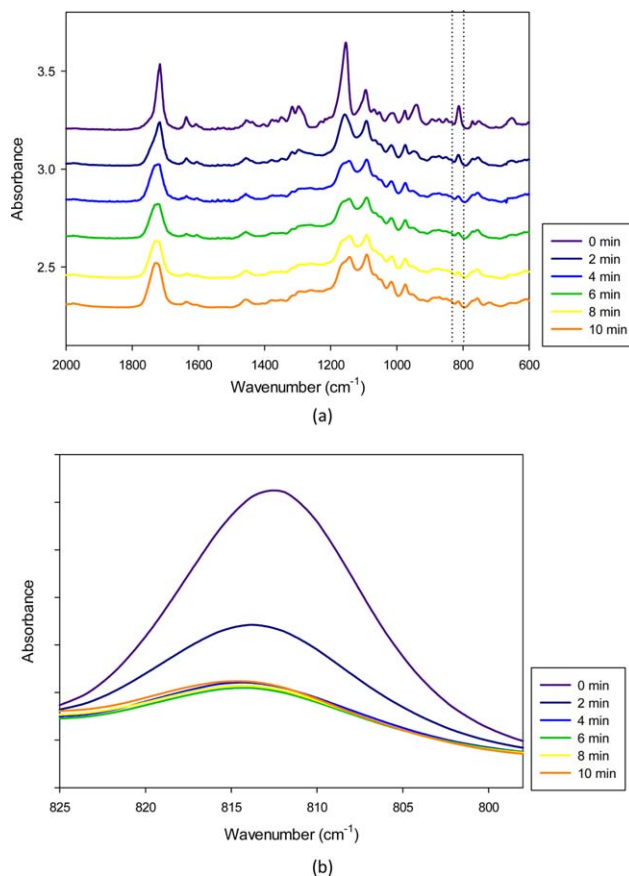


Figure 7. Change in the IR spectra during photo-curing of ISDM initiated by 3 wt % DETX with equimolar EDMAB in the range of (a) 600–2000 cm^{-1} and (b) its magnified view (800–825 cm^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

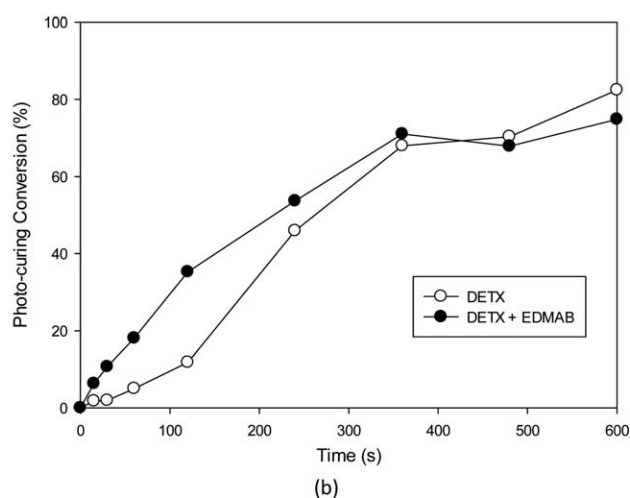
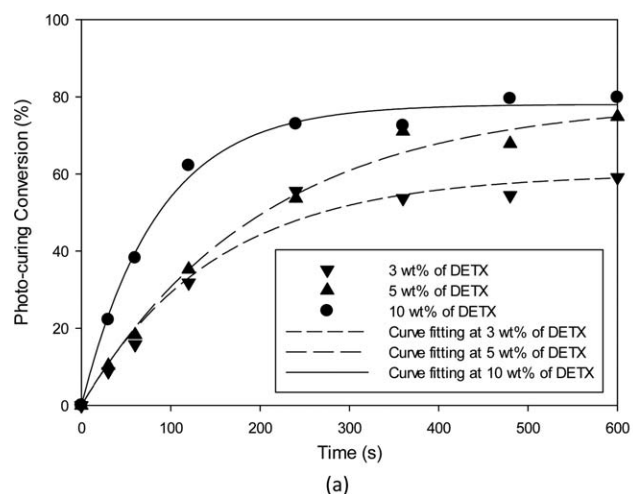


Figure 8. (a) Photo-curing profile of ISDM as a function of the initiator (DET X with equimolar EDMAB) concentrations and (b) change of photo-curing profile without a co-initiator (EDMAB).

of Iso-GMA with 10 wt % of initiator was only $11.0 \pm 0.8 \times 10^{-3} \text{ s}^{-1}$ [Figure 8(a)]. Unlike Bis-GMA, the photo-curing rates of ISDM were conspicuously accelerated by addition of EDMAB as an amine co-initiator. When 5 wt % of the initiator was used, only 10% of ISDM was photo-converted without EDMAB after 120 s. Meanwhile, nearly 40% of the photo-conversion was accomplished with EDMAB [Figure 8(b)]. Even photo-curing of ISDM tended to be retarded in the absence of EDMAB in the initial stage. It was considered that EDMAB may assist the formation of radicals in a Norrish type II reaction.^{18–20}

Surface Hardness

To evaluate the surface hardness of isosorbide-based materials photo-cured by LED light, the pencil hardness was investigated. The samples were coated in a 10 μm thick layer onto a PET film using a bar coater (K Bar, AK Print Coat Instruments), and then, the coated sample was irradiated with LED light (distance: 2 cm). The surface hardness was measured using the pencil hardness tester (CKH-112D, CK Trade, Korea) based on ASTM D3363 and all experiments were repeated five times. First, Bis-GMA was photo-cured with 1 wt % of the initiator

(i.e., DET X with equimolar EDMAB). The pencil hardness of the photo-cured coatings exhibited B and HB after irradiation for 1 and 10 min, respectively. On the other hand, no proper photo-cured coatings were formed without EDMAB. When the concentration of the initiators was increased to 3 wt %, the pencil hardness was enhanced to 2H after irradiation for 1 min. However, no additional change was observed using a longer irradiation time (10 min) or an initiator concentration of more than 3 wt %. Based on these results, the maximum pencil hardness of the photo-cured coatings from Bis-GMA was determined to be 2H. The irradiation time to achieve the maximum pencil hardness (2H) could be reduced to 0.5 min using a high concentration of the initiator (i.e., 5 wt %). The co-initiator (EDMAB) had little effect on the pencil hardness [Figure 9(a)]. Unlike Bis-GMA, ISDM did not form photo-cured coatings with soft pencil hardnesses, such as H, HB, and, B, because the uncured ISDM has a low viscosity, which prevented solidification of the coatings. The pencil hardness of the coatings photo-cured from ISDM was measured after sufficient photo-curing conversion. The coatings photo-cured using ISDM and 1 wt %

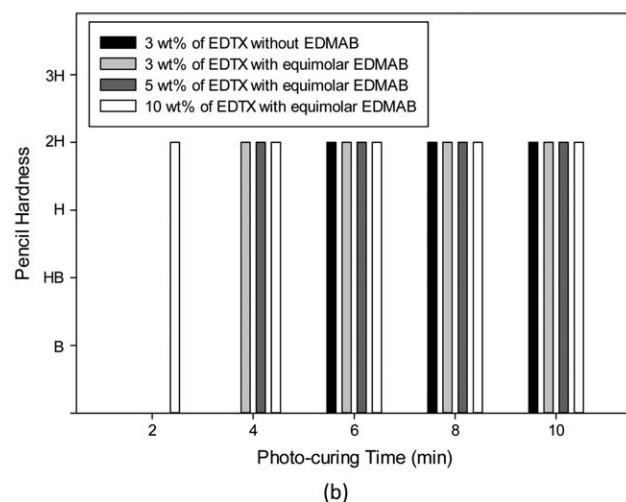
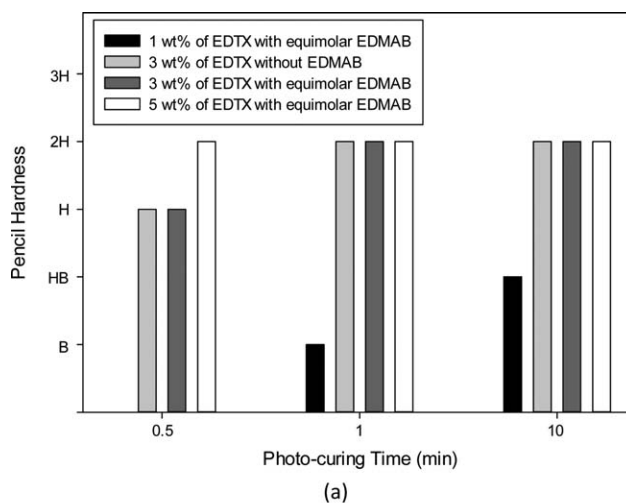


Figure 9. Pencil hardness of the photo-cured materials obtained from (a) Bis-GMA and (b) ISDM after LED irradiation as a function of the photo-curing time and initiator concentrations.

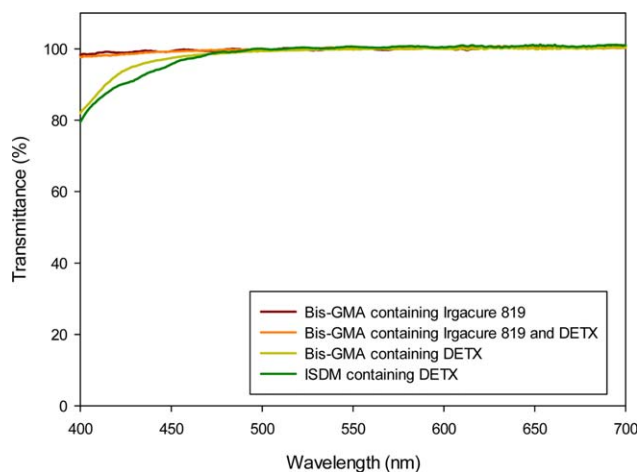


Figure 10. Transmittance of the coatings photo-cured from Bis-GMA and ISDM using LED light. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the initiator failed to exhibit a measurable pencil hardness. The preparation of photo-cured coatings with a measurable pencil hardness required at least 3 wt % of the initiator (EDTX) and an irradiation time of 6 min. When an equimolar amount of the co-initiator (EDMAB) was added, the irradiation time as reduced to 4 min. A higher concentration of initiator (10 wt %) allowed ISDM to be sufficiently cured in a shorter irradiation time (2 min). Once ISDM was photo-cured in a measurable range, the pencil hardness was determined to be 2H [Figure 9(b)].

Transmittance

The transmittance of the coatings photo-cured with LED light was measured in the range of 400–700 nm by a UV-Vis spectrometer. Each sample coating was 10 μm thick on a PET film followed by irradiation with LED light for 4 min using Lamp A. The distance between the sample and the light source was 20 cm. When DETX (5 wt %) was used as the initiator, the photo-cured coatings obtained from both Bis-GMA and ISDM were transparent from 470 to 700 nm (transmittance efficiency: $\sim 100\%$), which was decreased below 470 nm because of the strong absorbance of the DETX moiety (Figure 10). For Bis-GMA, this problem could be resolved by replacing DETX with Irgacure 819. Even with the use of both DETX and Irgacure 819, no decreased in the transmittance was observed below 470 nm. However, Irgacure 819 failed to initiate ISDM, and no photo-cured coatings were properly formed. Further studies to resolve this issue are currently ongoing.

Tensile-Shear Strength

To evaluate the adhesion strength of the isosorbide-based materials photo-cured with LED light, the tensile-shear strength of the polycarbonate plate pair bonded by the photo-cured ISDM was examined and compared to that of Bis-GMA. ISDM and Bis-GMA (20 μL) were loaded between polycarbonate plates and photo-cured by irradiation with LED light for 0.5, 1, and 2 min. All experiments were repeated five times. For Bis-GMA, when 3 wt % DETX was used as the only initiator, the

tensile-shear strength of the bonded polycarbonate plate pair was less than 1 MPa after irradiation for 30 s, and this strength was three times higher (3 MPa) after adding EDMAB as a co-initiator. When the photo-curing time was extended to 1 min, the tensile-shear strength increased to more than 4 MPa. However, a longer photo-curing time (2 min) resulted in lower adhesion (3.3 MPa). Therefore, higher conversion may lead to cohesion of Bis-GMA itself, decreasing the adhesion to the adherend (i.e., polycarbonate plate) [Figure 11(a)]. ISDM exhibited better performance than Bis-GMA for bonding with the polycarbonate plate pair. The tensile-shear strength of the polycarbonate plate pair bonded by the photo-cured ISDM was as high as 8 MPa [Figure 11(b)]. The photo-curing conversion of ISDM was higher than that of Bis-GMA. In addition, the oxygen-containing isosorbide ring has a higher polarity compared to the phenyl ring, which can enhance compatibility with the polar polycarbonate surface.²¹ Similar to Bis-GMA, the EDMAB co-initiator was essential for increasing the adhesion strength.

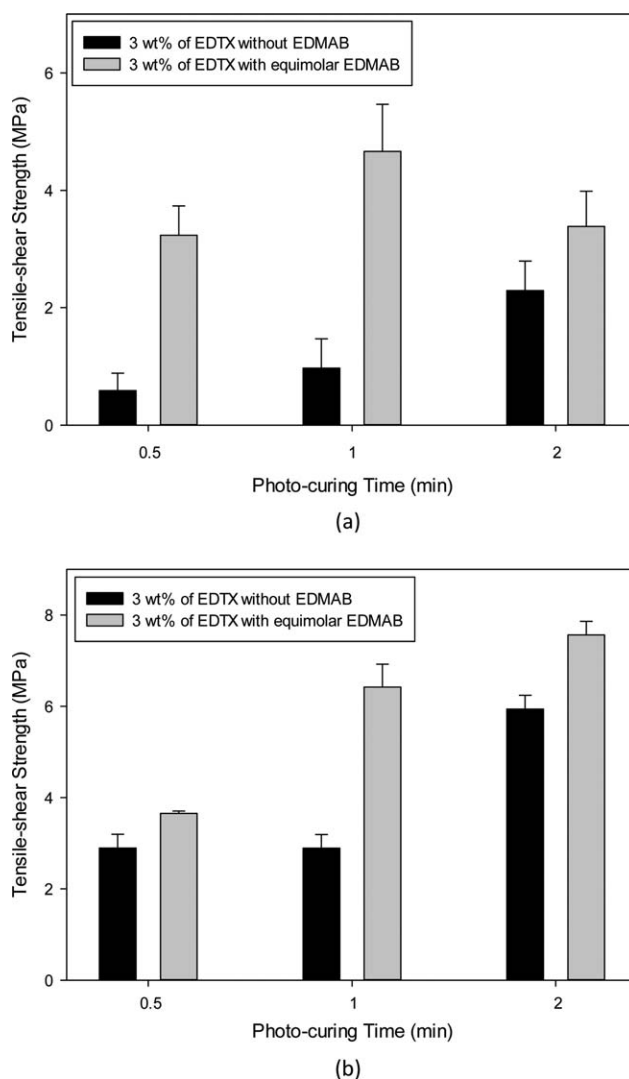


Figure 11. Tensile-shear strength of polycarbonate plate pair bonded by (a) Bis-GMA and (b) ISDM after irradiation with LED light.

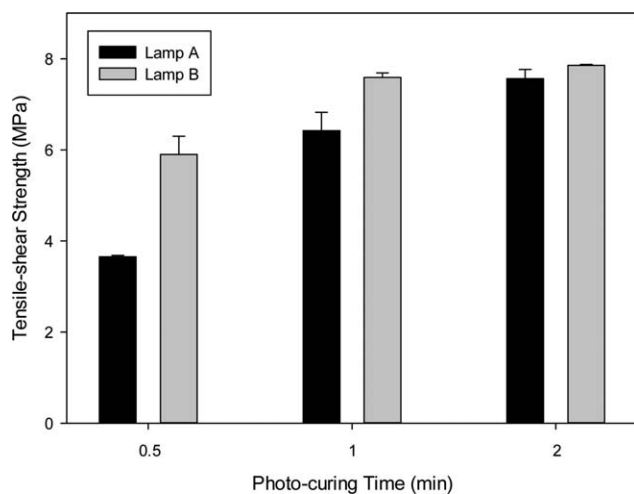


Figure 12. Tensile-shear strength of a polycarbonate plate pair bonded by ISDM as a function of the LED light source.

To examine the effect of the LED light source on the photo-curing procedure, ISDM was photo-cured by irradiation with two different lamps to prepare bonding polycarbonate plate pairs, and the tensile-shear strengths of the resulting joints were compared (Figure 12). One lamp was designed to emit light at three different wavelengths (i.e., 365, 375, and 400 nm) (Lamp A, intensity: 95 mW/cm²), and the other lamp was designed to emit light at a single wavelength of 400 nm (Lamp B, intensity: 120 mW/cm²). Based on the results, Lamp B, which has a higher intensity, exhibited better performance than Lamp A. Although Lamp A is able to emit a higher energy light (i.e., 365 and 375 nm) than Lamp B, it was not beneficial because 400 nm is preferable when EDTX is used as an initiator.

CONCLUSIONS

Photo-curable bio-based ISDM was synthesized from a biomass-derived isosorbide, and the photo-curing behaviors of ISDM using irradiation by LEDs and the mechanical properties of the photo-cured ISDM were investigated. ISDM was readily synthesized from biomass-derived isosorbide using methacrylic anhydride in the presence of triethylamine in an isolated yield of 73%. ISDM exhibited a nearly two times higher photo-curing conversion using the LED light source than Bis-GMA, which is one of the most widely used photo-curable materials. When 5 wt % of an initiator (DETX) was used, the photo-conversion increased to 80%. In addition, the photo-curing rates were enhanced using an amine co-initiator (EDMAB), especially during the initial stage. In the surface hardness test, the coatings photo-cured from ISDM exhibited a 2H maximum pencil hardness, and this value was similar to that of Bis-GMA. The photo-cured ISDM was transparent at 470–700 nm, but its transmittance decreased below 470 nm because of the use of DETX as an initiator. Interestingly, ISDM exhibited better adhesion performance than Bis-GMA. When ISDM with 3 wt % of the initiator was bonded in a polycarbonate plate pair after LED irradiation for 2 min, the tensile-shear strength of the joints was approximately 8 MPa. In addition, the tensile

strength of the polycarbonate plate pair bonded by Bis-GMA was slightly less than 5 MPa. As a result, it was confirmed that bio-based ISDM could be a candidate to alternate petroleum-based Bis-GMA as a photo-curable material.

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