

Synthesis and Photo-Polymerization of Bio-Based Furanic Compounds Functionalized by 2-Hydroxypropyl Methacrylate Group(s)

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ABSTRACT: Bio-based compounds (FmHPM and FdHPM) with a furan backbone and photo-polymerizable 2-hydroxypropyl methacrylate (HPM) group(s) were synthesized from carbohydrate-derived furanyl alcohols (furan-2-methanol and furan-2,5-dimethanol) and their photo-polymerizing behaviors and mechanical properties after photo-polymerization were investigated. Half time values ($t_{1/2}$) of bio-based FmHPM and FdHPM were 10.4 s and 3.0 s and their shrinkage ratios were 3.0 and 6.1% during photo-polymerization, respectively. Tensile-shear strength of glass and polycarbonate joints bonded by bio-based furanic compounds appeared in range of 0.2–0.6 MPa and pencil hardness of film coated by bio-based furanic compounds after photo-polymerization showed 2H–3H. Newly synthesized bio-based furanic compounds allowed the feasibility to alternate petroleum-based Bis-GMA/TEGDMA, photo-polymerizable composition widely utilized in a variety of applications. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: lignocellulosic biomass; carbohydrate; bio-based; furanic; photo-polymerization

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INTRODUCTION

Unpredictably, fluctuating oil price in current market and possible huge cost of CO₂ emission in near future alerts petroleum-based chemical industry to change its paradigm. In this context, much attention is paid to bio-based chemicals derived from renewable and sustainable resources.^{1,2} Recently, standard method for determining bio-based content was developed, and a new certification and labeling program for bio-based products was launched by USDA.³ Therefore, many efforts were dedicated to develop bio-based polymers from bio-based chemicals,^{4–6} but no study has been tried yet on bio-based photo-polymerizable compounds to the best of our knowledge. Since 1960s, photo-polymerizable materials are extensively applied in adhesive, coatings, and printing inks.^{7,8} Among them, 2-hydroxypropyl methacrylate (HPM) (trivially called “epoxy methacrylate”) functionalized compounds with an aromatic backbone such as bisphenol A are often used as encapsulants of electronic devices and dental sealants.^{9,10} Lignocellulosic biomass is the most abundant and widely distributed feedstock on earth, and a number of studies are ongoing to transform lignocellulosic bio-

mass-based carbohydrate into useful chemicals.^{11–13} In particular, furanic compounds obtained by dehydration of carbohydrates are among most promising platform to apply various materials because they are considered as alternatives of petroleum-based aromatic compounds.¹⁴ In this article, we address the synthesis of HPM functionalized furanic compounds (FmHPM and FdHPM) using furan-2-methanol (FM) and furan-2,5-dimethanol (FDM) that could be obtained from major components of carbohydrates, hemicellulose, and cellulose. And we discuss their feasibility to alternate petroleum-based photo-polymerizable materials.

EXPERIMENTAL

Materials

FDM (98%) was supplied by Penn Specialty Chemicals, (Memphis) and recrystallized from ethyl acetate/hexane before use. FM (99%), epichlorohydrin (>99%), tetrabutylammonium bromide (TBABr, 99%), bisphenol A-glycerolate dimethacrylate (Bis-GMA) triethylene glycol dimethacrylate (TEGDMA, 95%) were purchased from Sigma-Aldrich and directly used without

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further purification. All other reagents including sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), hydrochloric acid (HCl), acetone and solvents including methanol, ethyl acetate, hexane, tetrahydrofuran (THF), dichloromethane were purchased from TCI (Japan), Duksan Pure Chemicals Co (Korea), Daejung Chemicals & Metals Co (Korea) and solvents were dried by generally known procedures when necessary. As photo initiators, Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) were obtained from Ciba Specialty Chemicals. Reactions were monitored by thin layer chromatography (TLC) using Silica gel Merck 60 F254 plate (thickness: 0.25 mm) and each spot was detected by UV at 254 nm and/or staining with KMnO₄ or anisaldehyde solution. Synthetic compounds were characterized by FT-NMR (400 MHz, INOVA-399, Varian and 400 MHz, JNM-AL400, Jeol) and tetramethylsilane (TMS) or residual solvent was used as internal standard. Chemical shift (δ) and coupling constant (J) were expressed in parts per million (ppm) and hertz (Hz), respectively. MS spectra were recorded on an Agilent Technologies GC-MS instrument equipped with a 7890 injector, 5975 mass selective detector and Thermo Finnigan LC-MS (Model No. LCQ). The mass spectrometer was operated in EI mode at 70 eV (m/z 50–650) and ESI mode (m/z <2000).

Synthetic Procedure

Preparation of Furan Mono-epoxide (FmE). A mixture of 50% w/w aqueous NaOH (22.0 g, 275 mmol), epichlorohydrin (23.5 mL, 300 mmol), TBABr (644 mg, 2.0 mmol) was stirred vigorously at room temperature and placed in a water bath. To this stirred mixture was added FM (9.81 g, 100 mmol) in THF (30 mL) dropwise under argon. The progress of the reaction was monitored by TLC. After 2 h, the reaction was completed, and the reaction mixture was poured into ice/water (200 mL). The aqueous phase was then extracted with ethyl acetate (200 mL \times 2). The combined organic phase was washed with brine to neutrality, dried over magnesium sulfate, filtered, and evaporated to dryness. The crude product was then purified by flash chromatography (ethyl acetate:hexanes = 1:1 to 2:1) on silica to afford FmE (13.3 g, 86.3 mmol, 86%) as a clear oil. ¹H NMR (400 MHz, CDCl₃, δ): 7.42–7.40 (m, 1H), 6.35 (s, 2H), 4.58–4.48 (m, 2H), 3.76 (dd, J = 11.2, 2.8 Hz, 1H), 3.44 (dd, J = 11.2, 5.6 Hz, 1H), 3.20–3.12 (m, 1H), 2.28–2.77 (m, 1H), 2.64–2.59 (m, 1H); ¹³C NMR (100 MHz, CDCl₃, δ): 151.6, 143.2, 143.1, 110.5, 110.4, 109.9, 109.8, 70.8, 65.2, 50.9, 44.5. EIMS (m/z (%)): 154.1 (12) [M^+], 97.1 (62), 81.1 (100) (calcd mass of C₈H₁₀O₃: 154.06).

Preparation of Furan di-epoxide (FdE). A mixture of 50% w/w aqueous sodium hydroxide (19.2 g, 240 mmol), epichlorohydrin (21.9 mL, 280 mmol), TBABr (644 mg, 2.0 mmol) was stirred vigorously at room temperature and placed in a water bath. To this stirred mixture was added FDM (2.56 g, 20.0 mmol) in THF (20 mL) dropwise under argon. The progress of the reaction was monitored by TLC. After 2 h at 50 °C, the reaction was completed, and the reaction mixture was poured into ice/water (100 mL). The aqueous phase was then extracted with ethyl acetate (100 mL \times 2). The combined organic phase was washed with brine to neutrality, dried over magnesium sulfate, filtered, and evaporated to dryness. The crude product was

then purified by flash chromatography (ethyl acetate:hexane = 4 : 7) on silica to afford FdE (3.52 g, 14.7 mmol, 74 %) as a clear oil. ¹H NMR (400 MHz, CDCl₃, δ): 6.32–6.28 (m, 1H), 4.58–4.46 (m, 2H), 3.80–3.74 (m, 1H), 3.48–3.40 (m, 1H), 3.20–3.18 (m, 1H), 2.82–2.78 (m, 1H), 2.64–2.58 (m, 1H); ¹³C NMR (100 MHz, CDCl₃, δ): 152.0, 110.5, 110.4, 70.9, 65.3, 50.9, 44.4. EIMS (m/z (%)): 240.1 (1) [M^+], 166.1 (66), 125.1 (42), 109.1 (100), 94.1 (35) (calcd mass of C₁₂H₁₆O₅: 240.10).

Preparation of Furan Mono-2-hydroxypropyl methacrylate (FmHPM). Into prepared FmE (1 g, 6.48 mmol) were added methacrylic acid (6 mL), triethylamine (2-3 drops) and diphenyl picrylhydrazyl (20 mg). Then the temperature was elevated to 100 °C and the reaction mixture was vigorously stirred for 2 h. The resulting mixture was washed with aqueous NaHCO₃ solution (20%, wt/V) and deionized water (\times 3 each) and the organic phase was washed with brine, dried over magnesium sulfate, filtered, and evaporated to dryness. The crude product was then purified by flash chromatography (ethyl acetate:hexanes = 1 : 1) on silica to afford FmHPM (1.0 g, 4.42 mmol, 68%) as a clear oil. ¹H NMR (400 MHz, CDCl₃, δ): 7.31 (s, 1H), 6.14–6.27 (m, 3H), 5.48 (s, 1H), 3.87–4.29 (m, 5H), 3.40–3.50 (m, 2H), 2.0 (s, 1H), 1.94 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, δ): 167.1, 151.0, 142.7, 125.9, 109.4, 68.4, 68.1, 65.3, 65.1, 18.0. ESIMS (m/z (%)): 262.2 [$M + Na$]⁺, 240.2 [M^+] (calcd mass of C₁₂H₁₆O₆: 240.25).

Preparation of Furan di-2-hydroxypropyl Methacrylate (FdHPM). Into prepared FmE (1 g, 4.16 mmol) were added methacrylic acid (7 mL), triethylamine (2-3 drops) and diphenyl picrylhydrazyl (20 mg). Then the temperature was elevated to 100 °C, and the reaction mixture was vigorously stirred for 2 h. The resulting mixture was washed with aqueous NaHCO₃ solution (20%, wt/V) and deionized water (\times 3 each) and the organic phase was washed with brine, dried over magnesium sulfate, filtered, and evaporated to dryness. The crude product was then purified by flash chromatography (ethyl acetate:hexanes = 1 : 1) on silica to afford FdHPM (1.37 g, 3.57 mmol, 86%) as a clear oil. ¹H NMR (400 MHz, CDCl₃, δ): 6.16 (s, 2H), 6.0–5.96 (d, 2H), 5.46 (s, 2H), 4.41–4.38 (m, 6H), 4.11–4.0 (m, 4H), 3.47–3.37 (m, 4H), 2.0 (s, 2H), 1.91 (s, 6H); ¹³C NMR (100 MHz, CDCl₃, δ): 167.0, 151.5, 135.8, 125.7, 110.0, 70.69, 70.67, 68.3, 68.1, 18.0. ESIMS (m/z (%)): 435.2 [$M + Na$]⁺, 413.2 [$M + H$]⁺ (calcd mass of C₂₀H₂₈O₉: 412.17).

Photo-DSC

To evaluate photo-polymerizing patterns of synthesized bio-based furanic compounds (FmHPM and FdHPM), their kinetic profiles were investigated by means of heat flow integrals.^{15,16} The heat released from photo-polymerization as time progressed was measured using photo-DSC (TA Instruments Q-1000) equipped with a photocalorimetric accessory (Novacure 2100, EXFO Photonic Solutions, Canada), which used light from a 100 W middle-pressure mercury lamp under nitrogen atmosphere. The light intensity was determined by placing an empty DSC pan on the sample cell. The UV light intensity at the sample was 20 mW/cm² over the wavelength range of 300–545 nm. The weight of photo-polymerizable sample containing 1 wt% of TPO as photo-initiator was about 4 mg, and the sample was

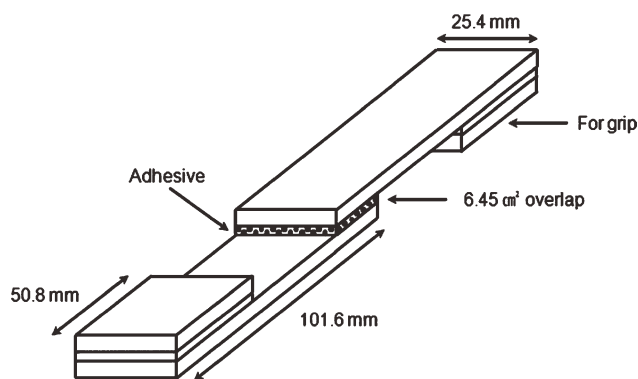


Figure 1. Dimension of the specimen and schematic diagram of the assembly for the lab shear test using UTM to measure adhesion strength.

placed in an open aluminum DSC pan with a diameter of about 8 mm. The measurements were carried out at 25 °C. The heat flow integrals were calculated with Universal Analysis 2000 software (TA Instruments) value. Photo-polymerizing rate of each compound was determined by its halftime value ($t_{1/2}$), i.e., the time to reach half of the heat flow integral.

Linear Shrinkage Ratio

Based on reported method,¹⁷ linear shrinkage ratio was firstly measured by linometer (RB Model 308, R&B, South Korea). The photo-polymerizable sample (30 μ L) containing photo-initiator (1 wt% of TPO) was loaded onto circle-shaped stainless steel plate (20 mm in diameter) and covered with slide glass (75 \times 25 \times 1.1 mm³). Then they were placed on linear variable differential transformer (LVDT) transducer, and the slide glass on the top was fixed [Figure 1(a)]. UV light was irradiated on the assembly using spot curing equipment (SP-7, Ushio, Japan). The average UV light intensity at the sample was \sim 4.5 mW/cm² over the wavelength range of 300–545 nm. The displacement of the adhesive sample during photo-polymerization was recorded by software. Finally, this linear shrinkage in vertical direction was transformed to volume data, and shrinkage ratio was calculated.

Tensile-Shear Strength

Glass and polycarbonate plates in thickness of 0.1 and 0.3 cm, respectively were cut into flat coupons 2.54 cm by 10.16 cm, and their surfaces were cleaned and dried. Afterward, the photo-polymerizable sample (20 μ L) containing photo-initiator (1 wt% of TPO) were applied to overlapped area (2.54 \times 2.54 cm²) between plate pair as shown in Figure 1(b). The resulting thickness of each adhesive compound was about 25 μ m on average. The prepared assemblies were photo-polymerized by UV irradiation using UV-curing equipment with 100 W high-pressure mercury lamp (main wave length: 340 nm). The UV light intensity at the sample was about 190 mW/cm² in UV-A range, which was measured with an IL 390C Light Bug UV radiometer (International Light Technologies, MA). Based on reported method,¹⁸ additional plates (2.54 \times 5.08 cm²) with the same thickness as used for bonding were attached on both ends of the specimens. For tensile-shear test, the specimen loading rate is 1.27 cm/min.

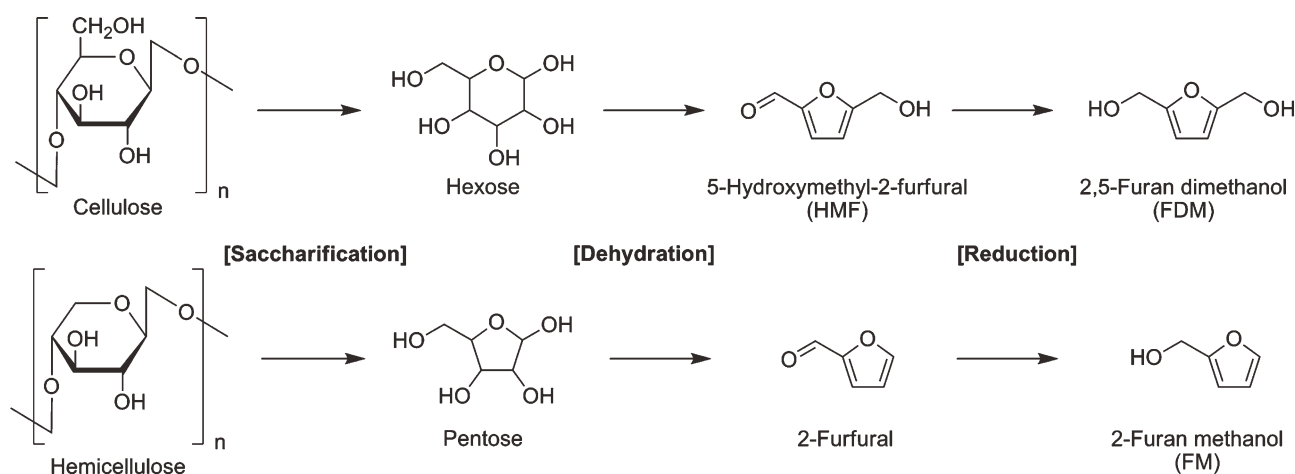
Pencil Hardness

The photo-polymerizable samples containing photo-initiator (1 wt% of TPO) were coated on PET film in 4 μ m of thickness by bar coater and they were photo-polymerized for 300 s in conveyer belt type UV curing device (UV light intensity at the sample: 185 mW/cm² in UV-A range). Then surface hardness was measured using pencil hardness tester (CKH-112D, CK Trade, South Korea) based on regulation of ASTM D3363.

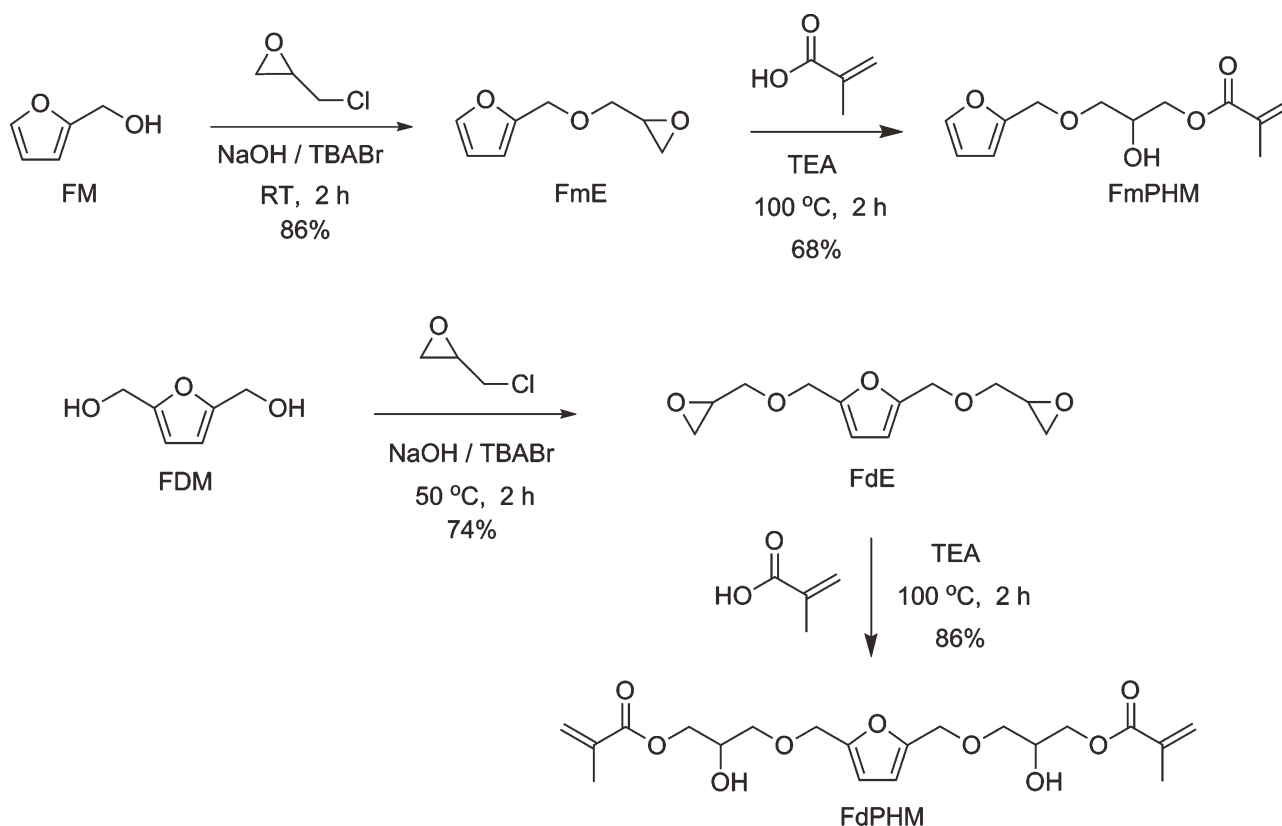
RESULTS AND DISCUSSION

Synthesis

Carbohydrates obtained from lignocellulosic biomass are hemicellulose and cellulose and they can be depolymerized to afford monosaccharides corresponding to hexose^{19,20} and pentose^{21–23} (representatively glucose and xylose). Following catalytic dehydration reaction, monosaccharides can be transformed into furfural intermediates (5-hydroxymethyl-2-furfural, so called HMF from hexose,^{24–26} and 2-furfural from pentose)^{27–29} and subsequent reduction produces hydroxymethylated furanic compounds, 2,5-furan dimethanol (FDM)^{30–32} and 2-furan



Scheme 1. Synthetic routes of furanic platform compounds (2,5-furan dimethanol, FDM and 2-furan methanol, FM) from lignocellulosic biomass-based carbohydrates (cellulose and hemicellulose).



Scheme 2. Synthetic routes for preparation of FmHPM and FdHPM from carbohydrate-derived FM and FDM, respectively.

methanol (FM)^{33,34} (Scheme 1). For preparation of bio-based photo-polymerizable compounds, we used bio-based FDM and FM as starting materials and introduced photo-polymerizable HPM functional group(s) onto FDM and FM. As the first step to functionalize HPM group(s) onto FDM and FM, glycidylation was carried out using excess equivalents of epichlorohydrin and 50% aqueous NaOH as a base to scavenge produced HCl under biphasic solvent system (epichlorohydrin-H₂O). In addition, TBABr was added as phase transfer catalyst to accelerate the reaction. Under this condition, glycidylation of FM and FDM was successful to afford the desired products, FmE and FdE in good yields (86 and 74%, respectively) within several hours (2–4 h). Next, methacrylate groups were introduced to the glycidylated furanic compounds using excess equivalents of methacrylic acid and triethylamine as a base at 100 °C for 2 h to give the final products, FmHPM and FdHPM in considerable yields (68 and 86%) (Scheme 2).³⁵

Photo-Polymerizing Rate

To evaluate photo-polymerizing patterns of synthesized bio-based furanic compounds (FmHPM and FdHPM), their kinetic profiles were investigated on the basis of heat generated from propagation of HPM group(s) during photo-polymerization. The heat flow according to time was measured using photo-DSC and the time integral of heat flow was calculated. The presence of the aromatic rings could compete with photo-initiator on UV light absorption with a consequent decrease of the reactivity of the systems.³⁶ Especially, the effect of furan ring on

photo-polymerization should be considered to realize the applicability of bio-based furanic compounds to photo-polymerizable materials. Initial photo-polymerizing rate of each compound was evaluated by half time value ($t_{1/2}$) defined as the time to reach the half of maximum value of heat flow integral. The maximum value of heat flow integral (MHI) was determined according to the following equation:

$$MHI = \int_0^{t_F} H(t) dt$$

where t_F is the time to complete conversion and $H(t)$ is heat flow at time t .

When 1 wt% of TPO was used as a photo-initiator at 20 mW/cm² of UV intensity, both synthesized bio-based furanic compounds showed acceptable photo-polymerizing rates for the purpose of photo-polymerizing process. The $t_{1/2}$ of FmHPM and FdHPM was 10.4 s and 3.0 s, respectively (Figure 2). It indicated that FdHPM bearing two HPM groups was more rapidly photo-polymerized than FmHPM in the initial stage. On the other hand, the maximum value of heat flow integral of FdHPM was lower than that of FmHPM (190 vs. 262 J/g). Since the heat flow occurs mainly by exothermic reaction of methacrylate radicals, this result showed that HPM groups of FdHPM were less reacted. It could be understood that the resulting polymer obtained from FdHPM gave a dense network structure to prevent free diffusion of unreacted FdHPM.

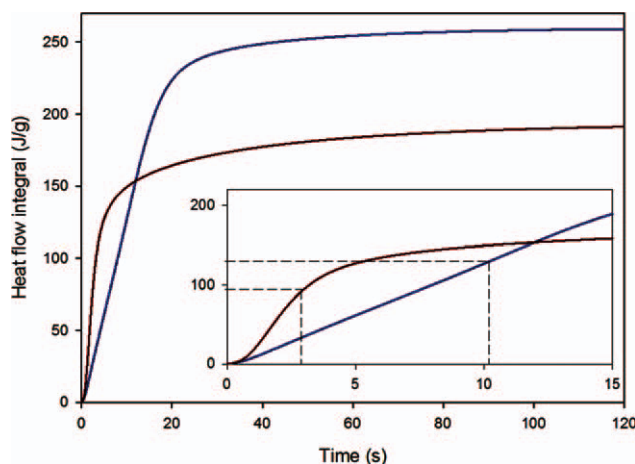


Figure 2. Heat flow integral of synthesized bio-based photo-polymerizable compounds, FmHPM (blue) and FdHPM (red) according to time when irradiated by UV light (intensity: 20 mW/cm²) using 1 wt% of TPO as a photo-initiator. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Shrinkage

In photo-polymerization, total volume of starting materials becomes reduced as they are polymerized. This shrinkage is a generally occurring phenomenon during polymerization because space between single molecules of monomer is disappeared by construction of chemical bonds. Shrinkage ratio is one of most important factors in the applicable area of photo-polymerizable materials. In this study, linear shrinkage ratios of bio-based furanic compounds were analyzed in real-time using LVDT transducer and they were determined by the following equation:

$$\text{Linear shrinkage ratio (\%)} = \frac{\text{Thickness after shrinkage}}{\text{Thickness of initial stage}} \times 100$$

For comparison, shrinkage ratio of bisphenol A-type photo-polymerizable composition, 50% (wt/wt) Bis-GMA in TEGDMA was also analyzed (chemical structure of Bis-GMA and TEGDMA were shown in Figure 3). The shrinkage ratio of FmHPM was ~3.0% but that of FdHPM was reached up to 6.1% (Figure 4). The higher shrinkage of FdHPM could be anticipated because FdHPM with two HPM groups forms a dense network structure. Meanwhile, FmHPM with only one HPM group forms a linear polymer with pendant groups, which

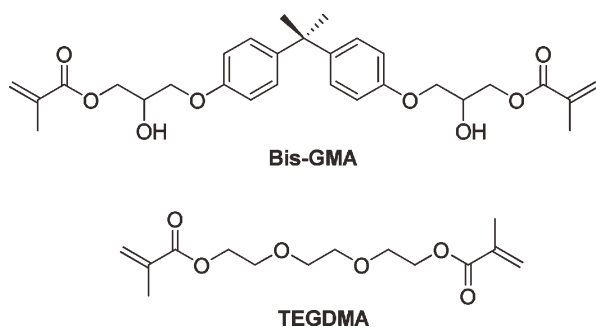


Figure 3. Chemical structures of Bis-GMA and TEGDMA.

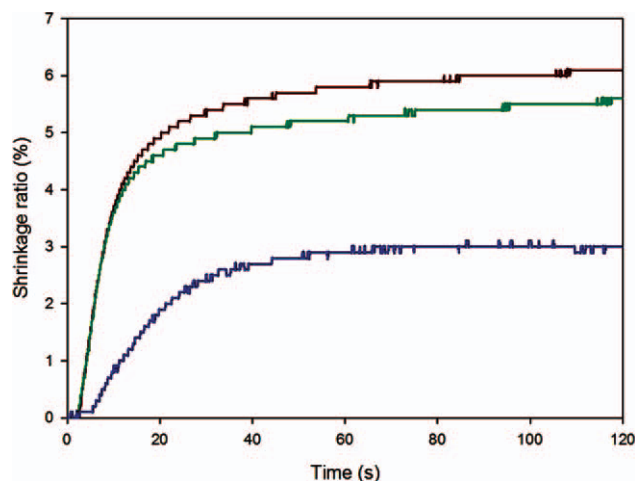


Figure 4. Shrinkage ratio of synthesized bio-based photo-polymerizable compounds, FmHPM (blue) and FdHPM (red) and Bis-GMA/TEGDMA composition (green) according to time when irradiated by UV light (intensity: 4.5 mW/cm²) using 1 wt% of TPO as a photo-initiator. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resulted in lower shrinkage due to loose stacking of molecules. The shrinkage ratio (5.6%) of Bis-GMA/TEGDMA composition, both of that have two HPM groups was also higher than that of FmHPM. In a viewpoint of chemical structure, shrinkage ratio is related with flexibility of backbone structure because flexible backbone could assist an efficient stacking between molecules. In Bis-GMA/TEGDMA composition, backbone of Bis-GMA, bisphenol A moiety, is more rigid than that of FdHPM but backbone of TEGDMA, tetraethylene glycol moiety, is more flexible than that of FdHPM. Therefore, Bis-GMA/TEGDMA composition (50/50 in wt%) showed similar shrinkage ratio to FdHPM.

Mechanical Properties After Photo-Polymerization

HPM functionalized compounds are widely used as photo-polymerizable adhesives in a variety of applications. To validate photo-polymerized adhesion of bio-based furanic compounds, tensile-shear strength was measured after bonding glass and

Table I. Tensile-Shear Strength of Polycarbonate and Glass Plate Pair Bonded by Photo-Polymerizable Materials Following UV Irradiation^a

Material(s) ^b	Adherend ^c	Tensile-shear Strength (MPa)
FmHPM	Glass	N/A
	Polycarbonate	N/A
FdHPM	Glass	0.6148
	Polycarbonate	0.2067
Bis-GMA/ TEGDMA (1:1)	Glass	0.6771
	Polycarbonate	0.3259

^a190 mW/cm² of UV light intensity was irradiated for 30 s, ^b1 wt% of TPO was contained as a photo initiator, ^cThickness of glass and polycarbonate plates is 1 and 3 mm, respectively.

polycarbonate plate pair by photo-polymerization. 20 μL of each sample containing 1 wt% of TPO as a photo initiator was loaded between plates and UV light (UV intensity: 190 mW/cm²) was irradiated for 30 s. The tensile-shear strengths of joints bonded by photo-polymerization were measured using UTM and the results were summarized in Table I. FmHPM turned a sticky material after photo-polymerization but joints bonded by FmHPM showed too low tensile-shear strength to measure properly by UTM. FmHPM forming a linear polymer after photo-polymerization was unable to give sufficient molecular weight to bond two plates. On the other hand, FdHPM forming a cross-linked polymer after photo-polymerization successfully bonded both glass and polycarbonate plate pair. Compared with tensile-shear strength of joints bonded by Bis-GMA/TEGDMA composition, bio-based FdHPM showed less bonding power but its results was comparable. In influence of adherends, tensile-shear strengths of glass joints were higher than those of polycarbonate joints in both cases of FdHPM and Bis-GMA/TEGDMA composition. It was understood that OH groups on FdHPM and Bis-GMA/TEGDMA composition was more interactive with hydrophilic glass plates existing OH groups on the surface than polycarbonate plates. In addition, lower tensile-shear strength in polycarbonate joints could be affected to some extent by UV stabilizer added during manufacturing polycarbonate plates and difference in thickness.

To evaluate surface hardness of bio-based furanic compounds after photo-polymerization, pencil hardness of FmHPM and FdHPM was examined. Each sample containing 1 wt% of TPO as a photo-initiator was irradiated for 300 s with UV light (UV intensity: 185 mW/cm²) after coating in 4 μm . Pencil hardness of FmHPM was H-2H and that of FdHPM was 2H-3H. These results indicated that cross-linked network structure of photo-polymerized FdHPM led to hard and rigid surface. From the comparison with pencil hardness of Bis-GMA/TEGDMA composition (2H-3H), bio-based FdHPM showed no noticeable dissimilarity. From the results, it is feasible for bio-based furanic compounds to alternate petroleum-based bisphenol A type compounds in photo-polymerizable applications.

CONCLUSIONS

In conclusion, photo-polymerizable bio-based furanic compounds bearing one or two 2-hydroxypropyl methacrylate(s) (FmHPM and FdHPM) were newly synthesized from carbohydrate-derived furanic alcohols (furan methanol and furan dimethanol) in reasonable yields (58 and 64% of overall yields, respectively). Photo-polymerizing behaviors including photo-polymerizing rate and shrinkage were investigated. Photo-polymerizing rate of FdHPM was faster than that of FmHPM. Meanwhile, conversion of FdHPM in photo-polymerization was less than that of FmHPM. It was understood due to the network structure of photo-polymerized FdHPM bearing two photo-polymerizable HPM groups. Higher shrinkage of FdHPM than that of FmHPM could support this phenomenon. In addition, mechanical properties such as adhesive ability and surface hardness of photo-polymerized materials were observed and compared with commonly utilized photo-polymerizable composition, Bis-GMA/TGADMA. From the results, bio-based photo-

polymerizable FdHPM showed similar patterns to Bis-GMA/TGADMA composition in bonding properties and surface hardness. Finally, we could address their feasibility to alternate petroleum-based photo-polymerizing materials.

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