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**A low viscosity urethane-based composite for improved dental restoratives**

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## ABSTRACT

Several new urethane-based dimethacrylates were synthesized, characterized and used to formulate the resin composites. Compressive strength (CS) was used as a screen tool to evaluate the mechanical property of the formed composites. Flexural strength, diametral tensile strength, water sorption, degree of conversion and shrinkage of the composites were also evaluated. The results show that most of the synthesized urethane-based dimethacrylates were solid, which are not suitable to dental filling restorations. However, it was found that liquid urethane-based dimethacrylates could be derivatized using asymmetrical methacrylate synthesis. Not only the newly synthesized urethane-based dimethacrylates showed lower viscosity values but also their constructed composites exhibited higher mechanical strengths. Without TEGDMA addition, the new urethane-constructed composites showed significantly lower water sorption and shrinkage.

*Keywords:* Urethane-based dimethacrylates, compressive strength, viscosity, composite, evaluation

## INTRODUCTION

Direct dental filling restoratives or dental resin composites have been used in dental clinics for more than 50 years since its invention by Dr. Bowen in 1962.<sup>1</sup> The traditional liquid resin components in resin composites are a mixture of bisphenol A glycidyl methacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA).<sup>2</sup> Due to its extremely high viscosity, low viscosity TEGDMA is always incorporated in order for BisGMA to be practically useful. However, TEGDMA incorporation leads to increased polymerization shrinkage, increased water sorption and reduced flexural strength.<sup>3-7</sup> Other than BisGMA-based resin composites, alternatives including BisEMA (bisphenol A ethoxy methacrylate), UDMA (1,6-bis-(methacryloyloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane) and other dimethacrylates have also been formulated to form composites and used in dental clinics.<sup>2,7</sup> UDMA-based composites are found to be the most popular.<sup>2</sup> Unlike BisGMA, UDMA-based liquid resin showed a reduced viscosity, increased filler loading and greater toughness because of its flexible urethane linkages.<sup>8,9</sup> Due to commercial availability of a number of diisocyanates - a precursor for synthesis of urethane-based oligomers, the attempts have been made to make the urethane-based oligomers or polymers.<sup>5,8-13</sup> These include incorporating high MW polyurethane methacrylate, adding various side groups to a urethane dimethacrylate, using a urethane to partially replace the ester-linkage on BisGMA, using low-shrinkage urethane dimethacrylate monomer, etc.<sup>8-12</sup> Adding various side groups to a urethane dimethacrylate monomer led to the formed polymer to have similar physical properties to UDMA.<sup>8</sup> Incorporating high molecular weight polyurethane methacrylate showed improved toughness and slight reduction in water sorption with compromise of a reduction in mechanical properties as compared to BisGMA-based composite.<sup>9</sup> Using a low-shrinkage urethane dimethacrylate to dental composite led to minimization of polymerization shrinkage.<sup>12</sup> Nevertheless, none of the above has ever been formulated without addition of TEGDMA or other diluents due to high viscosities or solid states of the synthesized or modified oligomers.<sup>7</sup> Although commercial UDMA shows a relatively low viscosity as compared to BisGMA, the oligomer itself still cannot be used alone when mixing with inorganic glass fillers.<sup>2</sup> It was also found that neither TEGDMA- nor BisGMA-containing composite is enzymatically stable in oral environment due to easy access of oral esterases.<sup>13,14</sup> On the other hand, it has been reported that urethane linkages can slow down the enzyme-initiated ester-linkage degradation due to unique urethane hydrogen bond intervention.<sup>15</sup> In this study, we proposed to use an asymmetrical synthesis strategy to synthesize liquid urethane dimethacrylates from different diisocyanates and use

them to formulate the composites without using TEGDMA or other low MW monomers as a diluent, in order to achieve the goal of utilizing commercially available diisocyanates to construct a new urethane-based resin composite system with reduced shrinkage, decreased water-sorption and improved mechanical strength.

The objective of this study was to synthesize new low viscosity liquid urethane-based dimethacrylates, use them to formulate the resin composite, and evaluate the properties of the formed composite.

## MATERIALS AND METHODS

### *Materials*

Isophorone diisocyanate (IPDI, mixture of isomers), 4,4'-methylenebis(phenyl isocyanate) (MBPI), 4,4'-methylenebis(cyclohexyl isocyanate) (MBCI, mixture of isomers), 1,3-bis(1-isocyanato-1-methylethyl)benzene (BIMEB), hexamethylene diisocyanate (HDI), hydroxyethyl methacrylate (HEMA), hydroxypropyl methacrylate (HPMA, mixture of isomers), triethylene glycol dimethacrylate (TEGDMA), dibutyltin dilaurate (DBTL), camphorquinone (CQ), N,N-dimethylaminoethyl methacrylate (DMAEMA), hydroquinone monomethyl ether (MEHQ), acetone and diethyl ether were used as received from Sigma-Aldrich Chemical Co (Milwaukee, WI, USA). The untreated barium borosilicate glass fillers (Herculite XRV, 0.7 microns) were supplied by Kerr Dental Corp (Orange, CA, USA). BisGMA and UDMA were used as received from Esstech Inc (Essington, PA, USA).

### *Synthesis and characterization*

Synthesis of urethane-based oligomers is described below. Briefly, to a flask containing BIMEB (0.05 mol), HEMA (0.05 mol), HPMA (0.05 mol), MEHQ (0.1 mmol) and acetone (30 ml), DBTL (0.5 mmol) was added. After stirring at room temperature for 30 min, the reaction mixture was heated to 60 °C for 4 h. Then the mixture was cooled down to room temperature and purified with ether. After washing with ether for 3 times and vacuum-drying overnight, the purified product HEMA-HPMA-1,3-bis(1-methylethyl)benzene dicarbamate (EPBD, yield > 95%) was obtained. The other studied oligomers were synthesized similarly. The synthesis scheme is shown in Fig. 1a. The synthesized oligomers were characterized by Fourier transform-infrared (FT-IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The proton NMR (<sup>1</sup>HNMR) spectra were obtained on a 500 MHz Bruker NMR spectrometer (Bruker Avance II, Bruker BioSpin Corporation, Billerica, MA) using deuterated dimethyl

sulfoxide as solvent and FT-IR spectra were obtained on a FT-IR spectrometer (Mattson Research Series FT/IR 1000, Madison, WI).

Fig. 1

### *Evaluation*

#### *Viscosity, degree of conversion, polymerization shrinkage and water-sorption determination*

The viscosity of the liquid formulated with oligomer or oligomer/diluent was determined at 23 °C using a cone/plate viscometer (RVDV-II + CP, Brookfield Eng. Lab. Inc., Middleboro, MA).<sup>16</sup> Degree of conversion (DC) was measured following the published protocol elsewhere.<sup>17</sup> Briefly, a drop of the formulated photo-initiator-containing oligomer liquid was cast in two KBr crystals, followed by directly scanning in FT-IR or photo-curing with blue light (30W, EXAKT 520 Blue Light Polymerization Unit, EXAKT Technologies, Inc., Oklahoma City, OK) for 2 min and then scanning in FT-IR. In the acquired FT-IR spectra, the areas under the peaks at 1637 (assigned to C=C on methacrylate), 1607 cm<sup>-1</sup> (to aromatic C=C, internal standard for the BisGMA-based resin) and 3366 cm<sup>-1</sup> (to urethane hydrogen, internal standard for the urethane-based resin) of uncured and cured specimens were used to calculate DC. DC (%) was calculated based on the equation  $[1 - (\text{area}_{\text{cured}} \text{ at } 1637 \text{ cm}^{-1} / \text{area}_{\text{cured}} \text{ for the internal standard}) / (\text{area}_{\text{uncured}} \text{ at } 1637 \text{ cm}^{-1} / \text{area}_{\text{uncured}} \text{ for the internal standard})] \times 100$ . The mean values were averaged from three readings. The polymerization shrinkage (%) was determined following the published protocol<sup>17</sup> using an equation  $(1 - d_{\text{uncured}}/d_{\text{cured}}) \times 100$ , where  $d_{\text{cured}}$  and  $d_{\text{uncured}}$  = the densities of cured and uncured composites. The densities of the uncured and cured composites were determined by weighing the uncured composite paste injected from a calibrated syringe and weighing the cured cylindrical specimens whose volumes were measured in water with a calibrated buret, respectively. The mean values were averaged from three readings. Water sorption was determined according to ISO 4049. Briefly, disc specimen (15 mm in diameter x 1 mm in thickness) of the resin composite was prepared in a metal ring mold with glass slides covered on both sides, followed by photo-curing with blue light for 2 min on each side. Upon removal, the specimen was placed in a desiccator and maintained at 37 °C until its weight was constant. The weight was recorded as  $m_0$ . Then the specimen was immersed in distilled water at 37 °C for 1 week, followed by removing from water, blotting dry, weighing and recording as  $m_t$ . Water sorption was calculated according to the equation  $(m_t - m_0)/V$ , where  $V$  = volume of the disc specimen. The mean values were

averaged from three readings.

### *Mechanical strength determination*

The resin composite was prepared as described previously.<sup>18</sup> Briefly, the composite was formulated with a two-component system (liquid and powder). The liquid was formulated with dl-camphoroquinone (photo-initiator, 1% by weight), 2-(dimethylamino)ethyl methacrylate (activator, 2%), and liquid oligomers. The newly synthesized liquid oligomers were either formulated alone (100%) or with TEGDMA at 50/50 by weight. Commercial oligomers BisGMA and UDMA were formulated with TEGDMA at 50/50. The untreated glass powders (Herculite XRV, 0.7 microns) were used as fillers and treated with  $\gamma$ -(trimethoxysilyl)propyl methacrylate as described elsewhere.<sup>16</sup> A filler level at 75% (by weight) was used throughout the study. The reason that we chose 75% is because it is closer to the filler content in real natural teeth.<sup>2</sup> Specimens were fabricated at room temperature according to the published protocol.<sup>19</sup> Briefly, the cylindrical specimens were prepared in glass tubing with dimensions of 4 mm in diameter by 8 mm in length for compressive strength (CS) and 4 mm in diameter by 2 mm in length for diametral tensile strength (DTS). The rectangular specimens were prepared in a split Teflon mold with dimensions of 3 mm in width by 3 mm in thickness by 25 mm in length for flexural strength (FS) test. All the specimens were exposed to blue light for 2 min, removed from the mold and conditioned either in distilled water at 37 °C prior to testing. The schematic structures of the representative oligomers used in the study are illustrated in Fig. 1b.

CS, DTS and FS tests were performed on a screw-driven mechanical tester (QTest QT/10, MTS Systems Corp., Eden Prairie, MN), with a crosshead speed of 1 mm/min.<sup>19</sup> A three-point bending fixture with a span of 20 mm between supports was used to conduct the FS test. Six specimens were tested to obtain a mean value for each material or formulation in each test. CS was calculated using an equation of  $CS = P/\pi r^2$ , where P = the load at fracture and r = the radius of the cylinder. DTS was determined from the relationship  $DTS = 2P/\pi dt$ , where P = the load at fracture, d = the diameter of the cylinder, and t = the thickness of the cylinder. FS was obtained using the expression  $FS = 3Pl/2bd^2$ , where P = the load at fracture, l = the distance between the two supports, b = the breadth of the specimen, and d = the depth of the specimen. Compressive yield strength (YS), compressive modulus (CM), toughness (T), energy to yield (ETY) and flexural modulus (FM) were obtained from the stress-strain curves of the CS and FS tests.

One-way analysis of variance (ANOVA) with the post hoc Tukey-Kramer multiple range test was used to determine significant differences of the measured properties among the materials in each group. A level of  $\alpha = 0.05$  was used for statistical significance.

## RESULTS

Figs 2 and 3 show the FT-IR and  $^1\text{H}$ NMR spectra of the parent compounds HEMA, HPMA, BIMEB and the product EPBD. Table 1 shows detailed characteristic peaks from the FT-IR spectra and chemical shifts from the  $^1\text{H}$ NMR spectra. Disappearance of hydroxyl group at  $3422\text{-}3428\text{ cm}^{-1}$  as well as isocyanate group at 2256 and appearance of urethane peaks at 3363, 1726 and 1519 confirmed the formation of the EPBD. Disappearance of the chemical shift at 4.82 (-OH) and appearance of the chemical shifts at 7.65 (-OCONH-) as well as 6.04 and 5.68 ( $\text{H}_2\text{C}=\text{C}-$ ) confirmed the formation of EPBD.

Fig. 2

Fig. 3

Table 1

Table 2 shows the physical states of the synthesized dimethacrylates. All the HEMA-derivatized oligomers were solids or paste. Two of the HPMA-derivatives (DPBD and DPID) were liquid and the others were solid. When both HEMA and HPMA were used, all the derivatives were either paste or liquids with high or low viscosities. Table 3 shows the code, name, ratio and viscosity value of the oligomers and tested formulations. The viscosity value was in the decreasing order of BIS > EPMD > EPCD > UD > EPBD > EPID > DPBD > DPID > BIST > EPMDT > EPCDT > UDT > EPBDT > EPIDT > DPBDT > DPIDT > T, where there were no statistically significant differences between BIST and EPMDT and between EPBDT and EPIDT ( $p > 0.05$ ).

Table 2

Table 3

Fig. 4 shows the CS and viscosity values of the composites composed of the liquid oligomers and TEGDMA at 50/50 (wt/wt). CS and viscosity were in the decreasing order of (1) CS (MPa): EPBDT > UDT > EPIDT > DPBDT > EPCDT > BIST > EPMDT > DPIDT, where there were no statistically significant differences among UDT, EPIDT, DPBDT and EPCDT and among BIST, DPIDT and EPMDT ( $p > 0.05$ ); and (2) viscosity (cp): BIST > EPMDT > EPCDT > UDT > EPBDT > EPIDT > DPBDT > DPIDT, where there were no statistically significant differences between BIST and EPMDT and between EPBDT and EPIDT.

Fig. 4

Tables 4 and 5 show detailed compressive properties of three TEGDMA-containing and four urethane-based composites verse time after aging in water up to 90 days, respectively. These properties include compressive yield strength (YS), compressive modulus (M), CS, toughness (T) and energy to yield strength (ETY) accompanying with statistical significance in each category.

Table 4

Table 5

Tables 6 and 7 show the YS, M, flexural strength (FS), flexural modulus (FM), and diametral tensile strength (DTS) (Table 6), and shrinkage, water sorption and degree of conversion (DC) (Table 7) of the selected composites, accompanying with statistical significance in each category.

Table 6

Table 7

## DISCUSSION



Urethane-based polymers have shown excellent biocompatibility in cardiovascular applications.<sup>20</sup> In current dental composite market, there is only one commercially available urethane dimethacrylate (often called UDMA) being used in the formulation. Its viscosity (1320 cp) is lower than BisGMA but much higher than TEGDMA. Like BisGMA-constructed composites, UDMA has to be mixed with TEGDMA to formulate a workable composite. To seek alternative urethane-based dimethacrylates, we synthesized a series of new urethane-based oligomers. We utilized five commercially available diisocyanates to react with HEMA or HPMA to form the urethane-based dimethacrylates. During the study, we found that if HEMA was used to derivatize diisocyanates, the products were solid, except for the IPDI derivative which was an unflowable paste. It is known that to formulate a dental composite, resin portion must be liquid with relatively low viscosity so as to form a workable paste with solid glass fillers to deliver.<sup>2,3</sup> Hence solid or unflowable paste materials are not acceptable to formulation of resin composites. On the other hand, if HPMA was used, only DPBD and DPID were liquid but the rest were solid. We attribute this to the reason that the formed urethane derivatives are too symmetrical and also strong hydrogen bonds from the urethane linkages lead to regularity, which leads to solidification or crystallization of the products. It is known that molecules with strong intermolecular interactions and symmetrical molecular structures are easy to form crystals.<sup>21,22</sup> By carefully analyzing the structure of commercial UDMA which is a viscous liquid at room temperature, one can find that UDMA is really a mixture of a pair of optical isomers having a chiral center at C2 with one methyl substitute on the 9-carbon molecular core, although it is also derivatized with HEMA at both ends.<sup>2,23</sup> Perhaps it is this chiral center to make UDMA to be a mixture of isomers instead of a pure oligomer, leading to formation of a liquid product. Inspired by this analysis, we proposed to synthesize asymmetrical urethane-based oligomers by placing different length of methacrylate on either end of diisocyanate, i.e., HEMA and HPMA were incorporated equally in mole to one diisocyanate molecule. As a result, the newly synthesized oligomers were obtained in the form of low or high viscosity liquid or paste, which dramatically changed the feasibility of these urethane-based oligomers for dental application from impossible to possible. Among these newly synthesized liquid or paste oligomers, we selected the liquid oligomers for initial screening test with CS. During the test, TEGDMA was added to dilute the oligomers at 50/50 (wt/wt), following the formulation commonly used in commercial resin composites.<sup>2,24</sup> EPBDT, EPIDT, DPBDT and DPIDT exhibited lower viscosity values but higher CS values as compared to EPMDT and EPCDT. Therefore we decided to focus on EPBD, EPID, DPBD and DPID for further investigation. By comparing the viscosity values, we found that the newly synthesized EPBD (452 cp), EPID (353),

DPBD (320) and DPID (250) showed much lower viscosity values as compared to commercial urethane dimethacrylate (UDMA, 1320). In other words, without using TEGDMA as a diluent, the four newly synthesized oligomers could be used to formulate resin composites directly. With TEGDMA incorporation, the formulations of all the four new oligomers showed even lower viscosity values.

To find out how good the mechanical properties of the newly synthesized resin composite system, CS was used as a screening tool for evaluation. It was found that both BIST and UDT showed nearly no changes in CS after 90 day aging in water at 37 °C but a significant increase from 0 to 1 d is observed for EPBDT. On the other hand, all the three composites showed a dramatic increase in modulus after aging in water for 24 h, followed by no further changes. This may be explained by the reason that the resin composite samples took a 24 h period of time from surface to inside gradually to have water completely absorbed, which allows the modulus to continue to increase due to post-cure or dark-cure.<sup>25</sup> The other properties showed either no changes or a slight increase or decrease after the initial 24 h, meaning that water neither increase nor decrease the strengths. EPBDT was found to be the highest in all the measured properties among the three materials after 90 days.

Since the four newly synthesized urethane derivatives (EPBD, EPID, DPBD and DPID) were low in viscosity values, we decided to try to formulate the composites by using these oligomers only without adding any TEGDMA. Similar to those TEGDMA-containing composites, almost all the four resin composites showed a significant increase in both CS and modulus during the initial 24 h. After that, EPBD and EPID showed nearly no changes in CS but continuous increases in modulus up to 30 days. On the other hand, DPBD and DPID showed a continuous increase in CS up to 30 days but nearly no changes in modulus. All the other properties showed either no change or a slight increase or decrease from 30 to 90 days. EPBD was the highest in all the measured properties, followed by EPID, DPBD and DPID. This may be explained by the following structural differences: (1) both EPBD and EPID are the ethyl and propyl comprised urethane dimethacrylate. Ethyl group contains  $-\text{CH}_2\text{CH}_2-$ , which is shorter than propyl group ( $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ), indicating that EPBD or EPID contains relatively more urethane linkages and methacrylate groups as compared to DPBD or DPID in a mole of the composite. Obviously only urethane-linkages and methacrylate groups make a significant contribution to strength enhancement because the former provides strong hydrogen bonds whereas the latter provides crosslinked covalent bonds. That may be why EPBD or EPID was stronger than DPBD or DPID; (2) EPBD or DPBD contains more rigid aromatic phenyl groups than the

corresponding EPID or DPID which has cyclic hexane groups. That may be why EPBD showed the highest compressive properties, followed by EPID, DPBD and DPID.

Finally, YS, FS, FM, DTS, DC, shrinkage and water sorption of the selected composites were evaluated and compared after 7-day aging in water. The reason that we chose 7-day aging is because the results indicate that most strength values showed no more changes after 7 days. The EPBD-based composite was found to be the highest in almost all the properties except for CS and DTS, followed by the EPID-based one. Its moduli in both compression (M) and three-point bending (FM) were outstandingly high as compared to the others, indicating that the EPBD-based composite is more rigid and has more molecular interactions including covalent and physical crosslinks in it, due to its inherent rigidity from the aromatic phenyl groups, strong hydrogen bonding from the urethane linkages and covalent crosslink from the dimethacrylates. The EPID was the second to the EPBD due to the fact that the 6-membered cyclohexane ring in the EPID is not as rigid as the 6-membered benzene ring in the EPBD.<sup>21</sup> On the other hand, the BIST-, UDT- and EPBDT-ones showed lower YS, M, FS and FM values, which is probably attributed to the fact that they all contain 50% TEGDMA. It is known that TEGDMA contains three ethylene glycol units and is a more flexible and soft molecule.<sup>22,26</sup> Both flexibility and water-sorption after water-aging lead to reduced strengths, especially moduli (M and FM).<sup>27</sup>

Three TEGDMA-containing composites showed much higher polymerization shrinkage values than the four new urethane-based composites without TEGDMA, which can be mainly attributed to the high content of carbon-carbon double bonds in the TEGDMA-containing composites and may be partially attributed to strong urethane hydrogen bonds in the four new urethane-based composites. It is known that conversion of carbon-carbon double bonds to single bonds leads to shrinkage.<sup>23</sup> The more carbon-carbon double bonds in the system the higher the shrinkage would be anticipated. Let's calculate how many moles of C=C in the studied resins. Assume we have one gram of the resin that needs to be calculated. After simple calculation, we found that there exist 5.623, 5.449, 5.43, 3.86, 4.03, 3.76 and 3.92 mmols of C=C in one gram of UDT, BIST, EPBDT, EPBD, EPID, DPBD and DPID neat resins, respectively. That may be why the three TEGDMA-containing composites showed higher shrinkage values. The same explanation is also applied to the reason why the BIST, EPBDT, EPBD and DPBD composites showed lower shrinkage values than the UDT, EPID and DPID ones. Regarding water sorption, all the TEGDMA-containing composites showed much higher values than the non-TEGDMA-containing ones. The result is consistent with that published elsewhere,<sup>8</sup> which can be simply attributed to the nature of TEGDMA because

TEGDMA contains three ethylene glycol units which are considered very hydrophilic.<sup>28,29</sup> The more hydrophobic parts and more aromatic phenyl groups in the system, the less water-sorption would be expected. That is why the EPBDT, EPBD and DPBD composites showed lower water-sorption values than their corresponding counterparts (UDT, EPID and DPID). Due to two hydroxyl groups, the BIST composite showed the highest water-sorption although BIS also contains two hydrophobic aromatic phenyl groups. In the case of DC, all the three TEGDMA-containing neat resins showed higher conversion values than the four non-TEGDMA resins. This can be attributed to the higher viscosity values of the non-TEGDMA resins because high viscosity can interfere with radical motion and chain propagation,<sup>30</sup> thus leading to a lower conversion. By comparing EPBDT and EPBD, adding 50% TEGDMA significantly increased DC from 57.5% to 70.8%.

## CONCLUSIONS

The new liquid urethane dimethacrylate oligomers with lower viscosity values were synthesized and used to formulate the resin composites. It was found that using asymmetrical methacrylate synthesis to form urethane dimethacrylates could be a good strategy to make a liquid oligomer. The newly synthesized urethane dimethacrylates not only showed lower viscosity values but also their corresponding composites exhibited higher mechanical strengths, especially yield strength and modulus. Without TEGDMA addition, the new urethane dimethacrylate-constructed composites showed significantly low water sorption and shrinkage, which may significantly improve current dental composites. It is possible to formulate the composites only using these newly synthesized urethane dimethacrylates without incorporation of diluent TEGDMA or others due to their low viscosities. Future studies will include investigating solubility and cytotoxicity of the unreacted oligomers, studying the effect of filler content on properties of the composites, and enhancing degree of conversion of the resins and composites.

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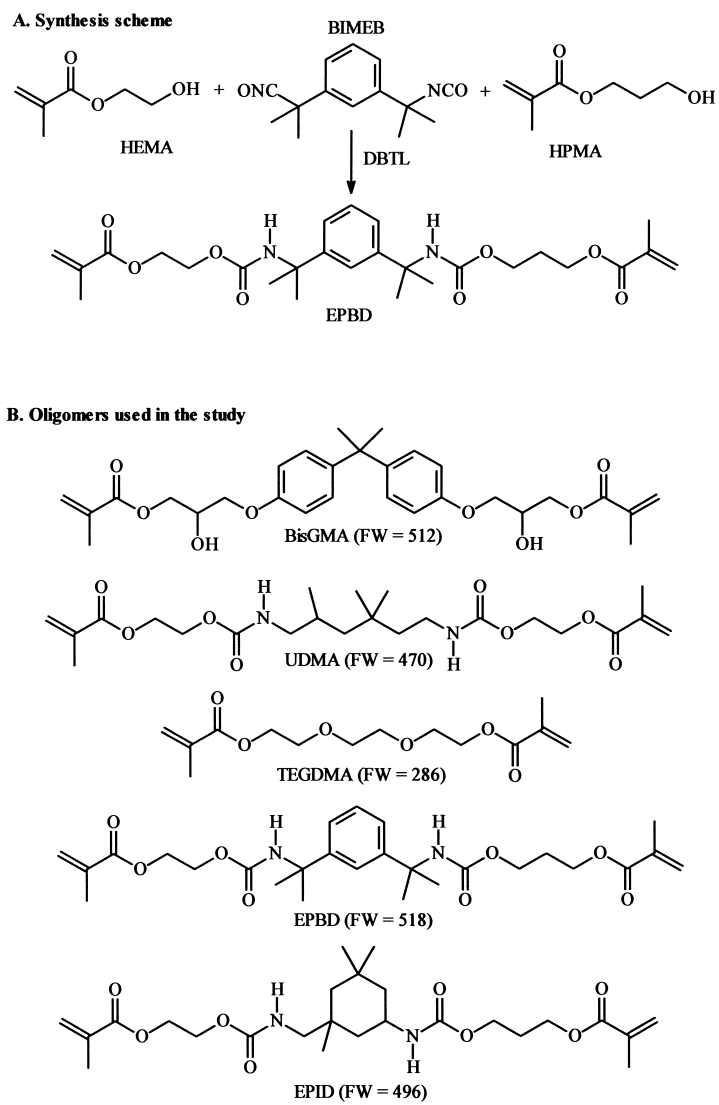


Fig. 1. Schematic diagrams for the synthesis of EPBD and the structures of the selected oligomers used in the study:

A. Synthesis of EPBD; B. Structures of the selected oligomers used in the study.



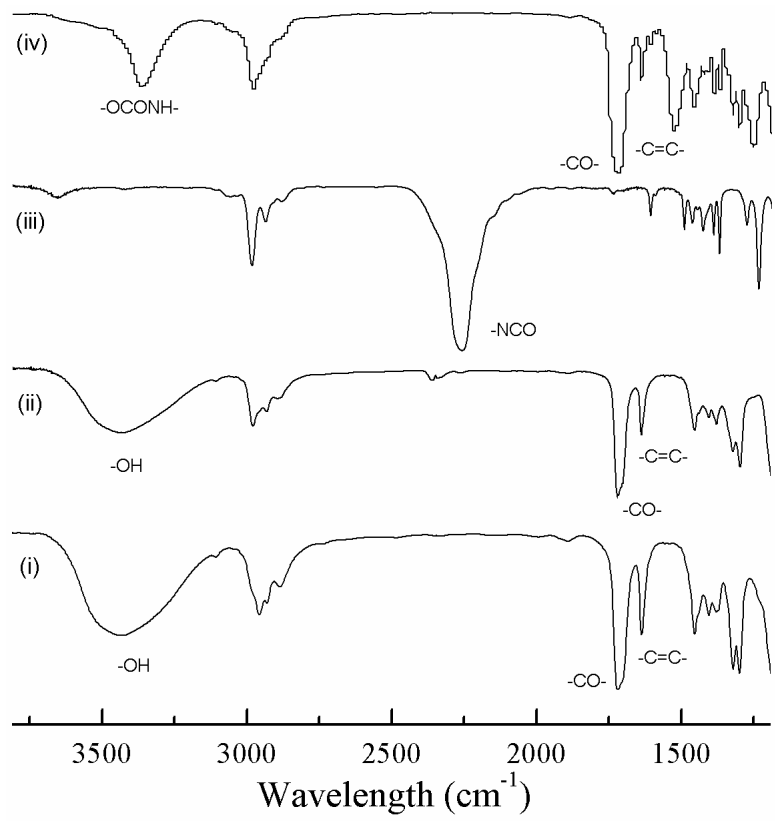


Fig. 2. FT-IR spectra for monomers and synthesized oligomer: (i) HEMA, (ii) HPMA, (iii) BIMEB and (iv) EPBD.

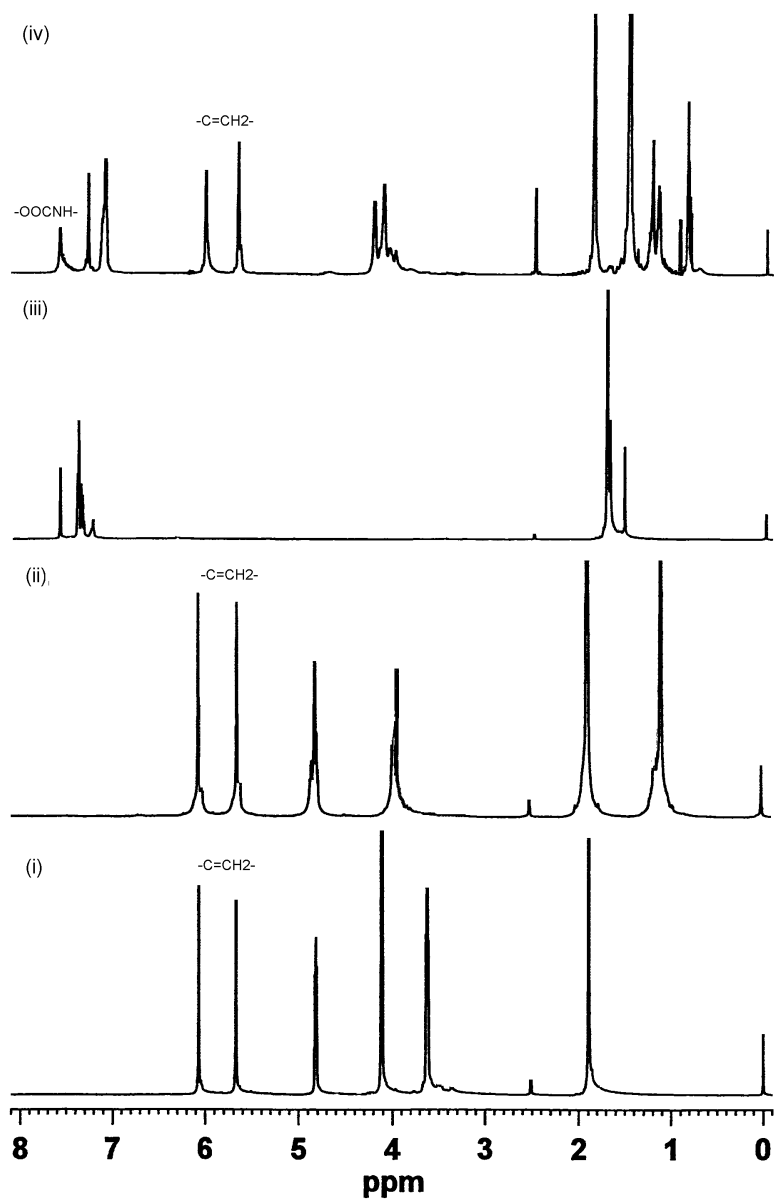


Fig. 3.  $^1\text{H}$ NMR spectra for monomers and synthesized oligomer: (i) HEMA, (ii) HPMA, (iii) BIMEB and (iv) EPBD.

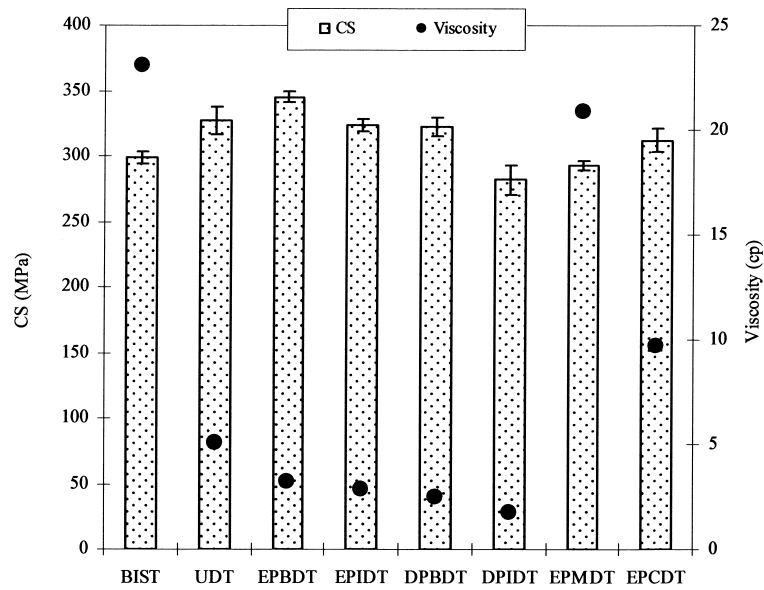


Fig. 4. CS of the composites composed of the liquid oligomers formulating with TEGDMA at 50/50 (by weight) and viscosity of the corresponding resin mixtures. Specimens for CS were light-cured for 2 min and conditioned in distilled water at 37 °C for 24 h before testing.

Table 1. Structure and physical state of the parent compounds and synthesized derivatives

Parent compound	Di-HEMA-dicarbamate	Di-HPMA-dicarbamate	HEMA-HPMA-dicarbamate <sup>1</sup>
MBPI	Solid	Solid	Very viscous liquid
MBCI	Solid	Solid	Viscous liquid
HDI	Solid	Solid	Paste
BIMEB	Solid	Liquid	Liquid
IPDI	Paste	Liquid	Liquid

<sup>1</sup>HEMA-HPMA dicarbamate = reaction product of diisocyanate with 0.5 mole of HEMA and 0.5 mole of HPMA

Table 2. Viscosity values of all the tested formulations

Code	Name	Ratio	Viscosity (cp)
BIS	BisGMA	100	N/M <sup>1</sup>
UD	UDMA	100	1320 (81)
T	TEGDMA	100	N/M
EPBD	HEMA-HPMA-1,3-bis-(1-methylethyl) benzene dicarbamate	100	452 (21)
EPID	HEMA-HPMA-isophorone dicarbamate	100	353 (19)
DPBD	Di-HPMA-1,3-bis-(1-methylethyl) benzene dicarbamate	100	320 (8.0)
DPID	Di-HPMA-isophorone dicarbamate	100	250 (11)
EPMD	HEMA-HPMA-4,4'-methylenebis(phenyl) dicarbamate	100	N/M
EPCD	HEMA-HPMA-4,4'-methylenebis(cyclohexyl) dicarbamate	100	1890 (94)
BIST	BisGMA/TEGDMA	50/50	23.1 (1.8)
UDT	UDMA/TEGDMA	50/50	5.1 (0.9)
EPBDT	EPBD/TEGDMA	50/50	3.2 (0.4)
EPIDT	EPID/TEGDMA	50/50	2.9 (0.6)
DPBDT	DPBD/TEGDMA	50/50	2.5 (0.4)
DPIDT	DPID/TEGDMA	50/50	1.8 (0.1)
EPMDT	EPMD/TEGDMA	50/50	20.9 (2.2)
EPCDT	EPCD/TEGDMA	50/50	9.7 (0.3)

<sup>1</sup>N/M = the viscosity was either too high or too low to be measured.

Table 3. Compressive properties of the TEGDMA-containing resin composites verse time

Material	Time	YS [MPa]	M [GPa]	CS [MPa]	T [KNmm]	ETY [Nmm]
BIST	0d	72.7 (2.9)	3.63 (0.18)	300.1 (13) <sup>j</sup>	1.66 (0.14) <sup>o</sup>	83.0 (2.9)
	1d	110.3 (3.9) <sup>a,1</sup>	5.38 (0.11)	298.4 (4.7) <sup>j</sup>	1.50 (0.07) <sup>p</sup>	138.1 (10)
	7d	109.2 (2.8) <sup>a</sup>	4.99 (0.17) <sup>c</sup>	304.5 (19) <sup>j</sup>	1.55 (0.05) <sup>o,p</sup>	110.2 (6.2) <sup>u</sup>
	30d	108.5 (4.3) <sup>a</sup>	5.01 (0.29) <sup>c</sup>	307.7 (10) <sup>j</sup>	1.63 (0.11) <sup>o</sup>	107.7 (4.5) <sup>u</sup>
	90d	108.6 (1.7) <sup>a</sup>	5.29 (0.07)	306.5 (5.6) <sup>j</sup>	1.59 (0.13) <sup>o,p</sup>	121.3 (3.4)
UDT	0d	83.2 (0.9)	4.05 (0.16)	310.9 (4.7) <sup>k</sup>	1.79 (0.04) <sup>q</sup>	99.2 (3.3) <sup>v</sup>
	1d	120.3 (12)	4.96 (0.28)	327.4 (10) <sup>l</sup>	1.91 (0.12) <sup>r</sup>	185.3 (26)
	7d	105.2 (1.8)	4.82 (0.27) <sup>f,g</sup>	326.5 (7.1) <sup>l</sup>	1.88 (0.06) <sup>r</sup>	155.7 (3.3)
	30d	94.5 (2.5) <sup>b</sup>	4.76 (0.09) <sup>f</sup>	323.2 (4.1) <sup>l</sup>	1.70 (0.15) <sup>q</sup>	105.4 (8.9) <sup>v</sup>
	90d	93.8 (4.5) <sup>b</sup>	4.87 (0.06) <sup>g</sup>	310.2 (3.1) <sup>k</sup>	1.51 (0.02)	102.2 (14) <sup>v</sup>
EPBDT	0d	83.2 (2.6)	3.76 (0.11)	289.7 (3.9)	1.64 (0.03)	103.9 (5.6)
	1d	112.1 (9.7) <sup>c</sup>	5.47 (0.12) <sup>h</sup>	345.1 (4.1) <sup>m</sup>	2.02 (0.04)	146.8 (19) <sup>w</sup>
	7d	115.6 (3.3) <sup>c</sup>	5.50 (0.06) <sup>h,i</sup>	348.1 (11) <sup>m,n</sup>	1.90 (0.14) <sup>s</sup>	145.2 (2.6) <sup>w</sup>
	30d	121.0 (1.6) <sup>c,d</sup>	5.56 (0.05) <sup>i</sup>	355.5 (4.2) <sup>n</sup>	1.87 (0.04) <sup>s,t</sup>	147.6 (3.4) <sup>w</sup>
	90d	125.4 (4.3) <sup>d</sup>	5.73 (0.02)	347.5 (7.5) <sup>n</sup>	1.79 (0.11) <sup>t</sup>	154.8 (11) <sup>w</sup>

<sup>1</sup>Entries are mean values with standard deviations in parentheses and the mean values with the same letter in each category were not significantly different ( $p > 0.05$ ). Specimens were conditioned in distilled water at 37 °C prior to testing.

Table 4. Compressive properties of four new resin composites verse time<sup>1</sup>

Material	Time	YS [MPa]	M [GPa]	CS [MPa]	T [KNmm]	ETY [Nmm]
EPBD	0d	89.6 (2.4)	4.80 (0.12)	275.5 (8.4)	2.09 (0.07)	117.8 (6.7)
	1d	126.4 (6.7) <sup>a</sup>	6.01 (0.11)	315.3 (9.7) <sup>l</sup>	2.01 (0.17)	173.8 (11) <sup>y</sup>
	7d	123.2 (6.2) <sup>a</sup>	6.18 (0.34)	323.2 (9.1) <sup>l</sup>	1.69 (0.17) <sup>p</sup>	160.2 (4.6) <sup>y</sup>
	30d	120.9 (3.6) <sup>a</sup>	6.34 (0.32)	320.4 (6.6) <sup>l</sup>	1.63 (0.07) <sup>p</sup>	158.0 (8.4) <sup>y</sup>
	90d	128.8 (3.4) <sup>a</sup>	6.45 (0.45)	325.2 (11) <sup>l</sup>	1.67 (0.08) <sup>p</sup>	164.1 (15) <sup>y</sup>
EPID	0d	90.1 (4.3)	4.60 (0.45)	251.0 (7.4)	1.45 (0.20) <sup>q</sup>	117.3 (12)
	1d	115.9 (2.9) <sup>b</sup>	5.34 (0.07)	317.6 (6.7) <sup>m</sup>	1.90 (0.04)	155.5 (8.1) <sup>w</sup>
	7d	121.0 (5.4) <sup>b,c</sup>	5.71 (0.13)	313.4 (11) <sup>m</sup>	1.61 (0.09) <sup>r</sup>	151.2 (14) <sup>w</sup>
	30d	127.9 (5.5) <sup>c,d</sup>	6.01 (0.21)	315.3 (10) <sup>m</sup>	1.58 (0.05) <sup>r,s</sup>	152.5 (6.7) <sup>w</sup>
	90d	134.6 (5.9) <sup>d</sup>	6.13 (0.19)	314.5 (18) <sup>m</sup>	1.51 (0.13) <sup>q,s</sup>	158.2 (8.8) <sup>w</sup>
DPBD	0d	99.2 (7.9)	5.38 (0.33) <sup>i</sup>	236.2 (7.4)	1.68 (0.13) <sup>t</sup>	141.5 (4.5) <sup>x</sup>
	1d	135.2 (4.1) <sup>e</sup>	5.41 (0.15) <sup>i,j</sup>	255.0 (9.2) <sup>n</sup>	1.64 (0.09) <sup>t</sup>	195.9 (5.7)
	7d	128.1 (5.2) <sup>e,f</sup>	5.33 (0.18) <sup>i</sup>	271.1 (8.4)	1.68 (0.10) <sup>t</sup>	151.3 (6.4)
	30d	116.8 (3.1) <sup>g</sup>	5.47 (0.31) <sup>j</sup>	290.2 (9.3)	1.73 (0.08) <sup>t</sup>	147.8 (6.8) <sup>x</sup>
	90d	122.7 (3.3) <sup>f,g</sup>	5.61 (0.25)	255.8 (8.5) <sup>n</sup>	1.65 (0.09) <sup>t</sup>	149.1 (5.9) <sup>x</sup>
DPID	0d	83.9 (5.1)	4.19 (0.14)	197.6 (5.2)	1.24 (0.05)	117.4 (5.9)
	1d	111.0 (5.3) <sup>h</sup>	4.67 (0.15)	225.1 (19)	1.37 (0.18) <sup>u</sup>	143.2 (8.6) <sup>y</sup>
	7d	104.5 (7.2) <sup>h</sup>	5.08 (0.07) <sup>k</sup>	248.9 (7.4) <sup>o</sup>	1.56 (0.11)	138.2 (17) <sup>y</sup>
	30d	103.2 (4.2) <sup>h</sup>	5.08 (0.30) <sup>k</sup>	265.3 (7.8)	1.64 (0.18)	134.1 (8.6) <sup>y</sup>
	90d	120.1 (2.2)	5.03 (0.11) <sup>k</sup>	252.4 (6.5) <sup>o</sup>	1.38 (0.07) <sup>u</sup>	138.1 (8.3) <sup>y</sup>

<sup>1</sup>EPBD, EPID, DPBD and DPID = four newly synthesized resin-composed composites without TEGDMA addition. Specimens were conditioned in distilled water at 37 °C prior to testing.

Table 5. Comparison of the mechanical properties of the selected resin composites<sup>1</sup>

Materials	YS [MPa]	M [GPa]	CS [MPa]	FS [MPa]	FM [GPa]	DTS [MPa]
BIST	109.2 (2.8) <sup>a,b</sup>	4.99 (0.17) <sup>d,e</sup>	304.5 (19) <sup>g</sup>	84.7 (16) <sup>i,j</sup>	6.03 (0.24) <sup>n</sup>	46.8 (2.8) <sup>p</sup>
UDT	105.2 (1.8) <sup>a</sup>	4.82 (0.27) <sup>d</sup>	326.5 (7.1) <sup>h</sup>	99.4 (7.3) <sup>k</sup>	5.82 (0.96) <sup>o</sup>	68.7 (5.7)
EPBDT	115.6 (3.3) <sup>b,c</sup>	5.50 (0.06) <sup>f</sup>	348.1 (11)	111.3 (13) <sup>l</sup>	6.69 (0.41)	41.2 (2.5) <sup>p</sup>
EPBD	123.2 (6.2) <sup>c</sup>	6.18 (0.34)	323.2 (9.1) <sup>h</sup>	121.9 (11) <sup>l</sup>	7.31 (0.43)	58.9 (2.1) <sup>q</sup>
EPID	121.0 (5.4) <sup>c</sup>	5.71 (0.13)	313.4 (11) <sup>g,h</sup>	91.1 (4.7) <sup>i,k</sup>	6.22 (0.32)	45.2 (1.4) <sup>p</sup>
DPBD	118.1 (5.2) <sup>c</sup>	5.33 (0.18) <sup>f</sup>	271.1 (8.4)	72.1 (4.1) <sup>j</sup>	6.54 (0.36)	53.6 (1.6) <sup>q</sup>
DPID	104.5 (7.2) <sup>a</sup>	5.08 (0.07) <sup>e</sup>	248.9 (7.4)	71.4 (3.9) <sup>j</sup>	5.90 (0.64) <sup>n,o</sup>	46.2 (6.3) <sup>p</sup>

<sup>1</sup>All the materials and their formulations were the same as those described in Tables 3 and 4. Specimens were conditioned in distilled water at 37 °C for 7 days prior to testing.

Table 6. Comparison of the shrinkage, water sorption and DC of the selected resin composites<sup>1</sup>

Materials	Shrinkage (%)	Water sorption [ $\mu\text{g}/\text{mm}^3$ ]	DC (%)
BIST	3.60 (0.31)	24.1 (3.4) <sup>b</sup>	73.2 (0.8) <sup>d</sup>
UDT	4.36 (0.39)	21.9 (2.5) <sup>b</sup>	73.7 (0.6) <sup>d</sup>
EPBDT	3.99 (0.14)	17.4 (1.9)	70.8 (1.1) <sup>d</sup>
EPBD	1.85 (0.06) <sup>a,3</sup>	7.0 (1.3) <sup>c</sup>	57.5 (0.7) <sup>e</sup>
EPID	2.17 (0.09)	8.0 (0.7) <sup>c</sup>	48.5 (1.3) <sup>f</sup>
DPBD	1.69 (0.11)	6.7 (1.7) <sup>c</sup>	54.8 (0.9) <sup>e</sup>
DPID	1.96 (0.13) <sup>a</sup>	7.2 (0.8) <sup>c</sup>	47.2 (1.3) <sup>f</sup>

<sup>1</sup>All the materials and their formulations were the same as those described in Table 5. Both shrinkage and water sorption were measured with the composite specimens. DC = degree of conversion, which was measured with the neat resin specimens without glass filler addition.