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Development of new diacrylate monomers as substitutes for Bis-GMA and UDMA

Abstract

Objectives: Bisphenol A-glycidyl methacrylate (Bis-GMA) and urethane dimethacrylate (UDMA) are widely used as the primary components of (meth)acrylic monomers. However, the use of Bis-GMA, which is a bisphenol A derivative, in dentistry is being questioned after bisphenol A was found to exhibit estrogenic activity. Although UDMA is being considered as a substitute for bis-GMA, the mechanical properties of cured resin composites containing UDMA are less than desirable. Therefore, in this study, we developed new alternative (meth)acrylic monomers to enhance the mechanical strength of cured composite resins.

Methods: Five urethane acrylic monomers were synthesized in this study as (meth)acrylic monomer substituents to replace Bis-GMA and UDMA. The elastic modulus, strength, and breaking energy values of cured resins consisting of mixtures of the urethane acrylates and diluting monomers were determined using the three-point flexural test. The data obtained were analyzed using one-way ANOVA and the post-hoc Tukey HSD tests ($p < 0.05$). Viscosities of the urethane acrylic monomers were measured with a cone-plate viscometer. Refractive indices of the urethane acrylic monomers were determined with an Abbe refractometer.

Results: The results of the three-point flexural tests revealed that the cured urethane acrylic monomer-based resin exhibited higher elastic modulus (up to 40%) and strength (up to 21%) compared to the cured UDMA-based resin. Viscosity and refractive index of the urethane acrylic monomers were between those of UDMA and Bis-GMA.

Significance: The developed urethane diacrylates prepared from diisocyanates which have an aromatic or aliphatic ring, 1,3-bis(1-isocyanato-1-methylethyl)benzene (TMXDI), 1, 3-bis(isocyanatomethyl)benzene (XDI) , or norbornane diisocyanate (NBDI) are worth considering as alternative options of Bis-GMA and UDMA for restorative resin composites.

Keywords: dental monomer, bending test, high-strength dental materials, diacrylate monomer, urethane acrylates, composite resin, light-curing resins

1. Introduction

Resin composites are used widely as tooth-color restorative materials in dental restorations and essentially consist of (meth)acrylic monomers and additives such as fillers, polymerization initiators, and polymerization inhibitors, among others [1]. In a composite resin containing such components, a filler usually has the largest weight fraction, followed by the (meth)acrylic monomers. Thus, these two components represent the major proportion of the weight of the composite resin [2]. The (meth)acrylic monomers serve as the binder for the filler. The properties of the monomer used as well as those of the cured product have a significant effect on the properties and performance of the resin composite formed using the monomer and thus those of the cured product as well [3].

With respect to the biological safety of monomers and the mechanical strength and wear resistance of their cured products, (meth)acrylic monomer compositions frequently contain radically polyfunctional methacrylates. Typically, these polyfunctional methacrylate compositions are based on Bisphenol A diglycidyl methacrylate (hereafter referred to as Bis-GMA) or dimethacryloxyethyl 2,2,4-trimethylhexamethylene diurethane (hereafter referred to as UDMA) [3]. Bis-GMA was incorporated into composite dental resins in 1962 by Rafael Bowen and is the most commonly used resin in dental composites, dental sealants, and dental cements [4]. It is a diester derived from methacrylic acid and bisphenol A diglycidyl ether [5]. Bearing two polymerizable groups, it is prone to forming a crosslinked polymer, which is used in dental restorations. However, the use of Bis-GMA poses a problem because one of its base materials, namely, bisphenol A, is an endocrine disruptor [6, 7]. In addition, because of the considerably high viscosity of Bis-GMA, a low-viscosity monomer, such as triethylene glycol dimethacrylate (TEGDMA), must always be incorporated to ensure that Bis-GMA is practical for use as a base resin for resin composites [8, 9]. However, incorporating excess TEGDMA leads to increased polymerization shrinkage and water sorption, decreasing in the mechanical properties [10].

As an alternative dimethacrylate monomer to Bis-GMA, UDMA is being used to prepare Bis-GMA-free dental resin composites [1, 11, 12]. However, the mechanical properties of cured resin composites containing UDMA are less than satisfactory [13]. In particular, the poor strength of these resin composites prevents their use at sites subjected to high stress. Thus, they are unsuitable for use as the crowning material for molar teeth.

In light of these problems, we aimed to develop dental acrylic monomers that can be used to produce cured products with good mechanical properties.

2. Materials and methods

2.1. Synthesis of monomers

A thoroughly dried 1 L four-necked flask equipped with a stirring blade and a thermometer was filled with 270.0 g (2.325 mol) of 2-hydroxyethyl acrylate (HEA), 0.55 g of dibutyltin dilaurate (DBTDL) (0.1 wt% relative to the total weight of HEA and 1,3-bis(1-isocyanato-1-methylethyl)benzene (TMXDI)), and 0.28 g of dibutylhydroxytoluene (0.05 wt% relative to the total weight of HEA and TMXDI). The mixture was stirred to ensure uniformity and then heated to 60 °C. Subsequently, 284.0 g (1.163 mol) of TMXDI was added in drop-by-drop for 1 h. The dropwise addition of

TMXDI was accompanied by an increase in the temperature of the reaction mixture owing to the reaction heat. Thus, the rate of dropwise addition was controlled such that the temperature did not exceed 80 °C. After all the TMXDI had been added, the reaction occurred for 10 h; the reaction temperature was maintained at 80 °C. During this process, the progress of the reaction was tracked with high-performance liquid chromatography, which was used to determine the end point of the reaction. Finally, the product was discharged from the reactor. In this manner, 530 g of the urethane acrylate TMXDI-HEA was obtained.

The urethane (meth)acrylates were synthesized from hydroxyalkyl (meth)acrylates and diisocyanates, as illustrated in Table 1, under conditions similar to those for TMXDI-HEA (Scheme 1).

TMXDI, 1, 3-bis(isocyanatomethyl)benzene (XDI), trimethylhexamethylene diisocyanate (TMHDI), 2-hydroxyethyl acrylate (HEA), 2-hydroxy propyl acrylate (HPA), 4-hydroxybutyl acrylate (HBA), 2-hydroxyethyl methacrylate (HEMA), diethylene glycol dimethacrylate (DEGDMA), and tetraethylene glycol dimethacrylate (4EGDMA) were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. Norbornane diisocyanate (NBDI) was supplied by Mitsui Chemicals Inc. and used without purification. Bis-GMA and TEGDMA were purchased from Shin-Nakamura Chemical Co., Ltd. and used without further purification.

2.2. Preparation of resin formulations

First, 10.0 g (21.3 mmol) of the urethane acrylate TMXDI-HEA, which was synthesized as described above, and 4.53 g (15.8 mmol) of triethylene glycol dimethacrylate (TEGDMA) were added to a container. This mixture was then stirred at 50 °C to ensure uniformity, resulting in a (meth)acrylic monomer solution.

TMXDI-HEA has two acryloyl groups while TEGDMA has two methacryloyl groups. Thus, the proportion of acryloyl groups from TMXDI-HEA were 57% relative to the (meth)acryloyl groups in the (meth)acrylic monomer solution.

Finally, 0.5 w% camphorquinone and 0.5 w% 2-butoxyethyl 4-(dimethylamino)benzoate were added to the (meth)acrylic monomer solution. The mixture was stirred to uniformity at room temperature to obtain a polymerizable dental monomer mixture.

2.3. Measurement of mechanical properties

The dental polymerizable monomer mixture was poured in a 2 × 2 × 25 mm^3 stainless steel mold and irradiated with light from a visible-light irradiator (Solidilite V, SHOFU, Kyoto, Japan) for 3 min on each side, that is, for a total of 6 min. The irradiated specimen was then removed from the mold and heat-treated in an oven at 110 °C for 15 min. The specimen was then cooled to room temperature. Thereafter, the specimen was soaked in distilled water in a closable sample bottle and stored at 37 °C for 24 h. The thus-fabricated specimen was then subjected to testing.

The specimens fabricated using the procedure described above were subjected to the three-point bending test using a universal testing machine (AUTOGRAPH EZ-S, Shimadzu Corporation, Kyoto, Japan). During the tests, the distance between the supports was 20 mm, and the crosshead speed was 1 mm/min.

The urethane (meth)acrylates synthesized in this study were also evaluated under the same conditions as described above.

The data obtained were analyzed using one-way ANOVA and the post-hoc Tukey HSD tests ($p < 0.05$).

2.4. Measurement of viscosity

The viscosities of the urethane (meth)acrylates and the mixtures of TMXDI-HEA and the diluting monomers were measured with a cone-plate viscometer (TVE-22H, TOKI SANGYO Co., Ltd.) at a rotation speed of 10 rpm, the cone diameter was 53mm. The temperature was controlled at 23 and 65 °C using a circulation thermostatic tank.

2.5. Measurement of refractive index

The refractive indices of the urethane (meth)acryl monomers were measured at 589 nm and 23 °C using an Abbe refractometer (DR-M2, ATAGO Co., Ltd.).

3. Results

3.1. Synthesis of monomers

TMXDI and XDI, which have an aromatic ring, and NBDI, which has an aliphatic ring, were selected as the suitably rigid diisocyanates for this study. The diisocyanates were reacted with hydroxyalkyl acrylates, such as HEA, HPA, and HBA, to obtain urethane acrylates (Table 1). The urethane acrylates exhibit a rigid structure and contain an aromatic or aliphatic ring from the diisocyanates.

A urethane methacrylate TMXDI-HEMA, which has a similar structure with TMXDI-HEA was also synthesized from the reaction of TMXDI and HEMA under similar conditions. UDMA was obtained from the reaction of TMHDI and HEMA under similar conditions. TMHDI does not contain any aromatic or aliphatic rings in its molecular structure.

3.2. Mechanical properties

The elastic modulus, strength, and breaking energy of the cured resins formed using the (meth)acrylic monomer mixture of the urethane acrylates and TEGDMA as determined by the three-point flexural test are shown in Figure 1. As controls, UDMA and TMXDI-HEMA were also tested under the same conditions. The elastic modulus of the cured resins containing TMXDI-HEA, TMXDI-HPA, XDI-HPA, and NBDI-HEA were significantly higher than those of the cured resin containing UDMA. With respect to the strength, the TMXDI-HEA-based resin was significantly superior to the UDMA-based resin. The cured resins containing TMXDI-HPA, XDI-HPA, and NBDI-HEA had higher strength than the cured resin containing UDMA. No statistical difference was observed between the breaking energies of the samples since the standard deviation of the breaking energies as determined from the experiments was large. These results indicate that the cured resins formed using the new urethane acrylates exhibit improved mechanical properties as compared with those of the cured resin formed using UDMA.

TMXDI-HEMA is a methacrylate monomer and its structure is similar to that of TMXDI-HEA. However, TMXDI-HEMA and TMXDI-HEA differ in the terms of their polymerizable functional group. The elastic modulus and strengths of the cured resins formed using TMXDI-HEMA and TMXDI-HEA were similar. Although statistically speaking, the braking energies of the cured resins containing TMXDI-HEA and TMXDI- HPA were not significantly different, the average breaking energy of the TMXDI-HEA-based resin was higher than that of the TMXDI-HEMA-based resin.

3.3. Viscosity

The results of the viscosity measurements of the urethane (meth)acrylates and Bis-GMA are displayed in Table 2. The synthesized urethane acrylates had higher viscosities than UDMA but lower than Bis-GMA.

The effect of the diluting monomers on the viscosity of the (meth)acrylic monomer mixtures was analyzed. The viscosities of the mixtures at 23 °C are shown in Table 3. The viscosity reduction effect of the diluting monomers could be arranged as follows: DEGDMA > TEGDMA > 4EGDMA. The structure of these diluting monomers are show Figure 2.

3.4. Refractive index

The refractive indices of three of the urethane (meth)acrylates, UDMA, and Bis-GMA are shown in Table 4. All urethane acrylates in the table, which contains an aromatic ring and an aliphatic ring, exhibited a higher refractive index than that of UDMA.

3.5. Diluting monomers

TMXDI-HEA was diluted using the monomers to form (meth)acrylic monomer mixtures containing 70 wt% urethane acrylate. Moreover, (meth)acrylic monomer mixtures diluted with DEGDMA or TEGDMA and containing 80 wt% TMXDI-HEA were also prepared to confirm the effect of the weight ratio of urethane acrylate and the diluting monomers. The elastic modulus, strength, and breaking energy of the cured resins formed using the (meth)acrylic monomer mixtures as determined by the three-point flexural test are shown in Figure 3.

The cured resin containing 70 wt% TMXDI-HEA and DEGDMA had a higher elastic modulus than the resins containing TEGDMA and 4EGDMA. Further, the structures of the diluting monomers did not affect the strengths and breaking energies of the cured resins. In addition, with an increase in the weight ratio of urethane acrylate from 70 wt% to 80 wt%, the elastic modulus and strength of the cured resins also increased.

4. Discussion

To develop new (meth)acrylate monomers that can be used as substitutes for Bis-GMA and UDMA, urethane (meth)acrylates from hydroxyalkyl (meth)acrylates and diisocyanates. The general structure of the monomers synthesized in this study is shown in Figure 4.

The central moiety between two carbamate groups of the molecule was derived from isocyanates (hereafter referred to as the CORE). The rest of the structure was derived from hydroxyalkyl (meth)acrylates; the alkyl chains between the carbamate group and the ester group are hereafter referred to as the ARM.

UDMA does not have a rigid structure. For example, it does not contain an aromatic or aliphatic ring in its molecular structure [12]. Further, the C6 aliphatic chain is considered a soft structure as compared with an aromatic or aliphatic ring. This is the reason the cured resins containing UDMA exhibited a low elastic modulus and a moderately high strength [13].

On the other hand, the urethane acrylates synthesized in this study contain a rigid structure, namely, one with an aromatic or aliphatic ring. For instance, TMXDI-HEA has a phenyl ring as its CORE moiety while its ARM moieties are C2 aliphatic chains, which are moderately soft structures. To ensure that the cured resin exhibits both rigidity and toughness, it is necessary to maintain a balance between the rigid and soft segments of the molecule. The cured this type of urethane acrylates (TMXDI-HEA, TMXDI-HPA, XDI-HPA, and NBDI-HEA) based resin exhibited higher elastic modulus and strength compared to the cured UDMA-based resin. On the other hand, the elastic modulus and strength of the cured TMXDI-HBA-based resin were much lower than those of the cured TMXDI-HEA-based resin and comparable to those of the cured UDMA-based resin. It can be seen that the length of ARM is the cause of this difference between TMXDI-HEA and TMXDI-HBA since the molecular structure of

TMXDI-HBA is similar to that of TMXDI-HEA in all aspects except the length of ARM. The C4 aliphatic chain may be too soft as an ARM moiety for designing this type of urethane acrylate molecule. These results indicate that it is necessary to pay attention to even minor differences in the molecular structure of monomers when designing monomers for dental materials.

Several studies have attempted to use urethane methacrylate monomers containing rigid structures, such as TMXDI-HEMA, in dental materials [13, 14, 15, 16]. However, such monomers have not been employed widely. As shown above, the cured TMXDI-HEMA-based resin was brittle compared with the cured TMXDI-HEA-based resin. From the perspective of striking a balance between the rigid and soft segments, the combination of a phenyl ring in the CORE and methacrylate groups would not be suitable, as methacrylate resins are harder than acrylate resin. Conventionally, acrylate monomers have not been employed as widely in dental materials as methacrylate monomers. Acrylate monomers are generally known to be more toxic than methacrylate monomers, and it is necessary to compare the benefits and risks as a medical device and conduct adequate risk management [17]. However, the results of this study indicate that combination of acrylate groups and a rigid structure in CORE is worth considering as an alternative option to improve mechanical properties of resin.

The urethane acrylates synthesized in the study had much higher refractive indices than UDMA due to an aromatic ring and an aliphatic ring in the molecules of the former [18, 19]. Higher-refractive-index monomers are favorable for radiopaque dental composites since resin layer should have a similar refractive index with radiopaque fillers which have a high refractive index to keep enough curing depth [20].

Generally, viscous monomers are diluted with low-viscosity monomers to ensure that the resulting dental materials exhibit the desired viscosity. TEGDMA, DEGDMA, and 4EGDMA were selected as the diluting monomers to evaluate the effect of the monomer used on the mechanical properties of the resulting resins. The lower viscosities of the urethane acrylates (compared to Bis-GMA) should help overcome the limitations related to the composition of dental materials [20, 21].

The viscosity of TMXDI-HEA can be reduced using a diluting monomer such as DEGDMA, TEGDMA, or 4EGDMA. The viscosity reduction effect of the diluting monomers could be arranged as follows: DEGDMA > TEGDMA > 4EGDMA. This result indicates that short-chained monomers are more effective for reducing viscosity. The structure of these diluting monomers did not give a significant effect on the mechanical properties of the resin except for elastic modulus in this study.

Increasing the weight ratio of urethane acrylate significantly affected the viscosity of the (meth)acrylic monomer mixtures. This was because increasing the proportion of urethane acrylate with respect to that of the diluting monomer caused an increase in the viscosity of the monomer composition, even though it also enhanced the mechanical properties of the resin. Therefore, it is necessary to optimize the monomer composition ratio while striking a balance between the viscosity of the monomer and the mechanical properties of the resin.

5. Conclusion

In summary, the cured resin containing TMXDI-HEA, TMXDI-HPA, XDI-HPA, and NBDI-HEA which are the urethane diacrylates synthesized in this study are exhibited higher mechanical properties compared to UDMA. Therefore, they can be considered as candidates to replace Bis-GMA and UDMA as monomers in dental composite materials although the high toxicity of acrylate monomers compared to methacrylate monomers is a concern. Hybrid resin blocks, in particular, may be a suitable application for these urethane acrylates because they require high mechanical properties and are cured outside the mouth, reducing the risk of monomer toxicity.

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Figure and table captions

Scheme 1. Synthesis of urethane acrylate monomers.

Figure 1. The results of three-point flexural tests of cured resins formed from urethane (meth)acrylates (57 mol%) and TEGDMA (43 mol%) after storage at 37 °C for 24 h. (A) Elastic modulus, values with same letters (a, b, c, or d) are not statistically different (p-value of 0.05). (B) Flexural strength, values with same letters (a, b, or c) are not statistically different (p-value of 0.05). (C) Breaking energy, no statistically significant difference was observed (p-value of 0.05).

Figure 2. Chemical structures of diluting monomers.

Figure 3. The results of three-point flexural tests of cured resins formed from mixtures of TMXDI-HEA and diluting monomers after storage at 37°C for 24 h. (A) Elastic modulus, values with same letters (a, b, or c) are not statistically different (p-value of 0.05). (B) Flexural strength, values with same letters (a, b, or c) are not statistically different (p-value of 0.05). (C) Breaking energy, no statistically significant difference was observed (p-value of 0.05).

Figure 4. General structure of urethane (meth)acrylate monomers.

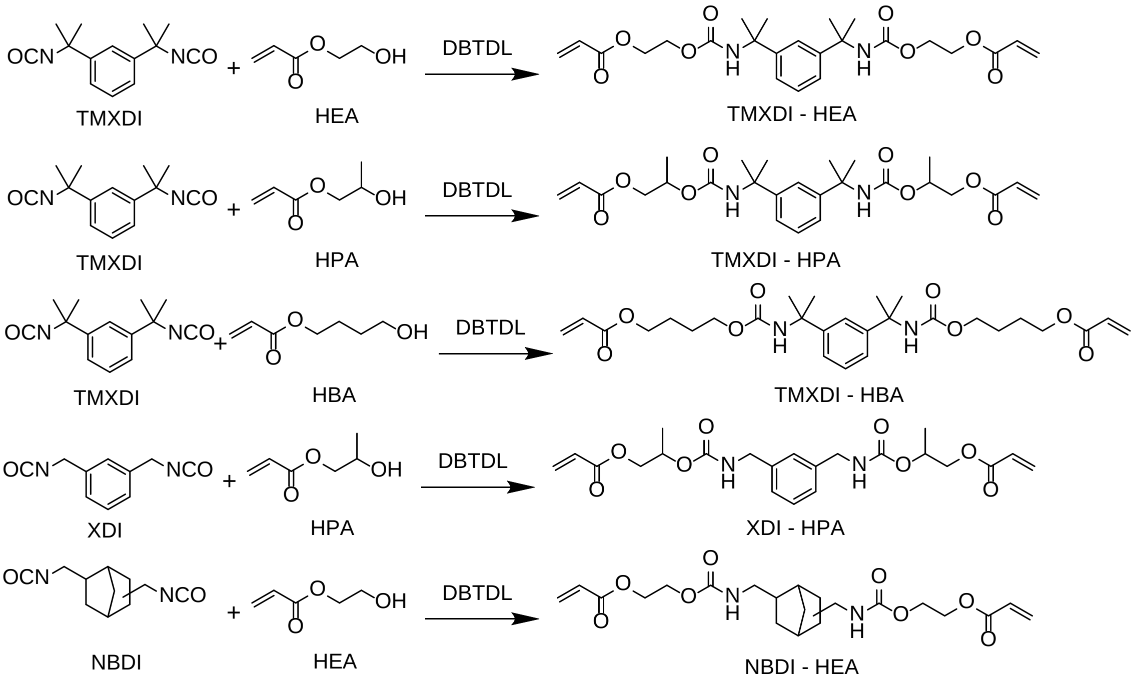
Table 1. Urethane (meth)acrylates synthesized in this study.

Table 2. Viscosities of urethane (meth)acrylates and Bis-GMA.

Table 3. Viscosities of mixtures of TMXDI-HEA and diluting monomers.

Table 4. Refractive indices of urethane (meth)acrylates and Bis-GMA at 589 nm and 23 °C.

Figures



Scheme 1.

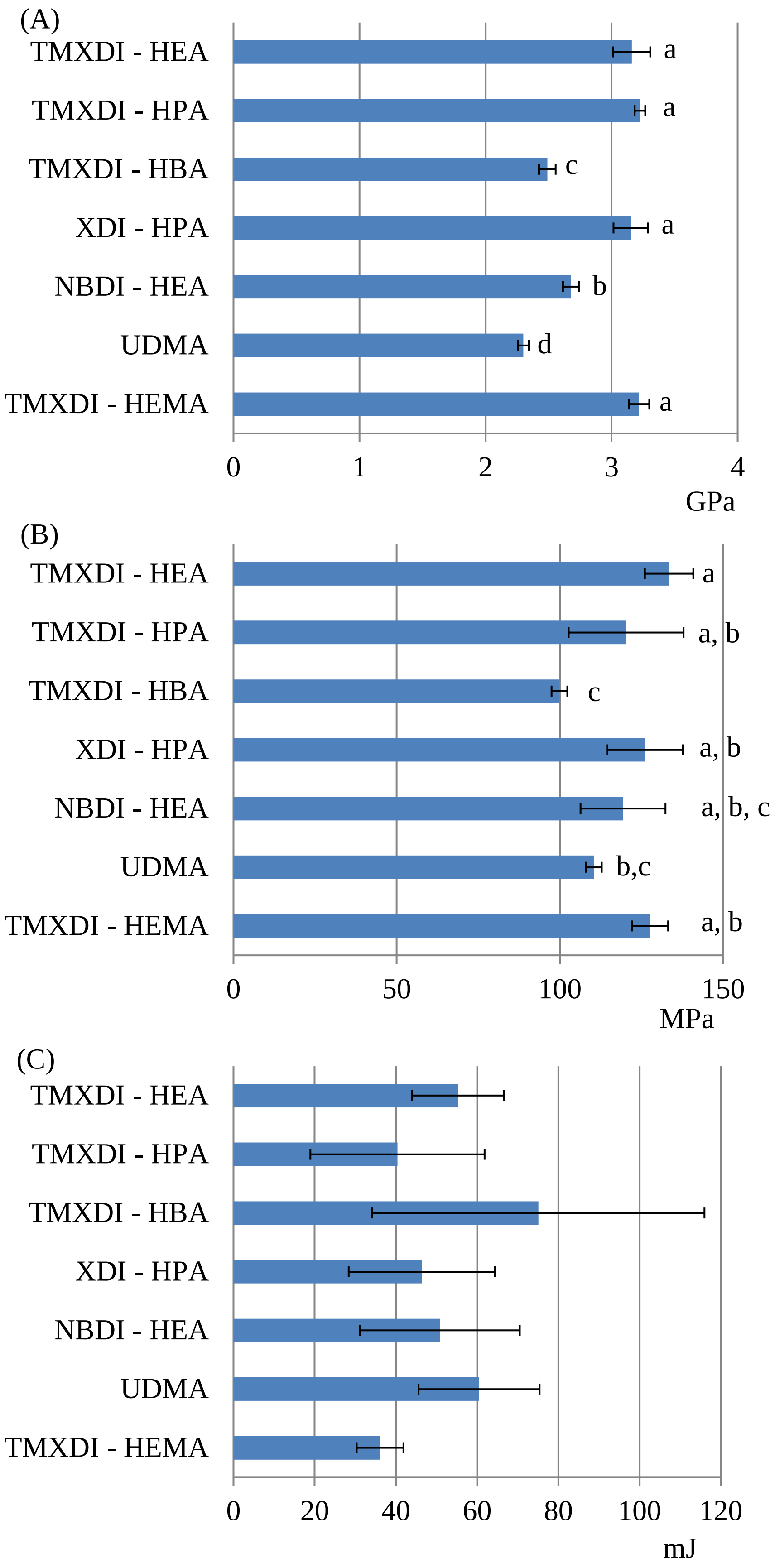

(A)
TMXDI - HEA
TMXDI - HPA
TMXDI - HBA
XDI - HPA
NBDI - HEA
UDMA
TMXDI - HEMA
a
a
c
a
b
d
a
0
1
2
3
4
GPa
(B)
TMXDI - HEA
TMXDI - HPA
TMXDI - HBA
XDI - HPA
NBDI - HEA
UDMA
TMXDI - HEMA
a
a, b
c
a, b
a, b, c
b,c
a, b
0
50
100
150
MPa
(C)
TMXDI - HEA
TMXDI - HPA
TMXDI - HBA
XDI - HPA
NBDI - HEA
UDMA
TMXDI - HEMA
0
20
40
60
80
100
120
mJ

Figure 1.

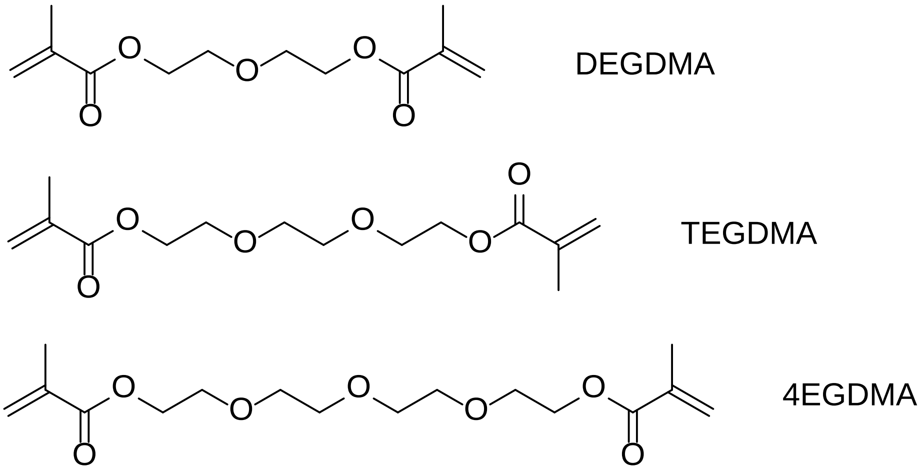


Figure 2.

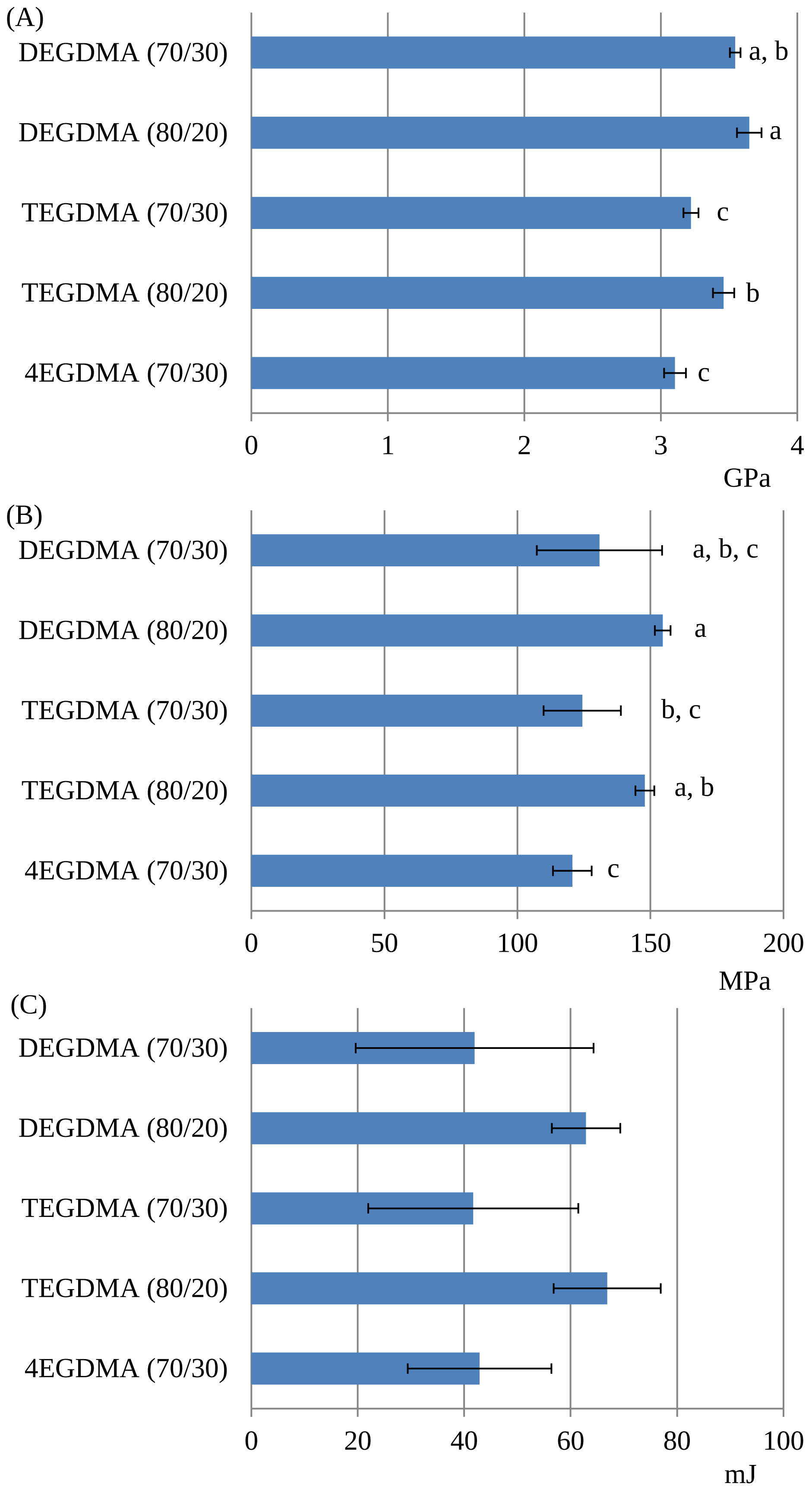

(A)
DEGDMA (70/30)
DEGDMA (80/20)
TEGDMA (70/30)
TEGDMA (80/20)
4EGDMA (70/30)
a, b
a
c
b
c
0
1
2
3
4
GPa
(B)
DEGDMA (70/30)
DEGDMA (80/20)
TEGDMA (70/30)
TEGDMA (80/20)
4EGDMA (70/30)
a, b, c
a
b, c
a, b
c
0
50
100
150
200
MPa
(C)
DEGDMA (70/30)
DEGDMA (80/20)
TEGDMA (70/30)
TEGDMA (80/20)
4EGDMA (70/30)
0
20
40
60
80
100
mJ

Figure 3.

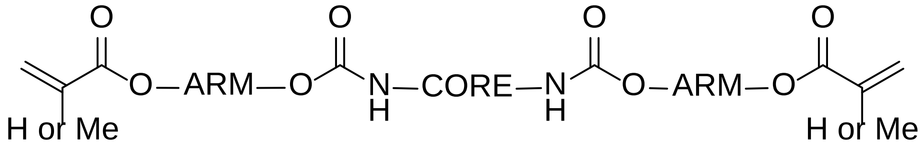


Figure 4.

Table

Table 1.

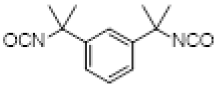
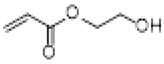
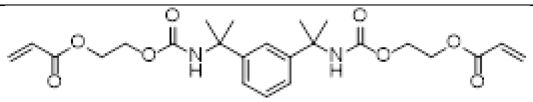
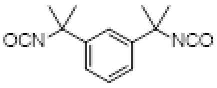
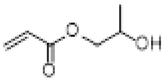
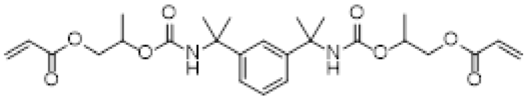
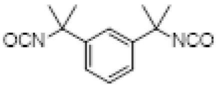
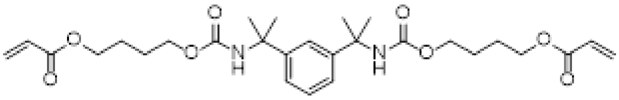
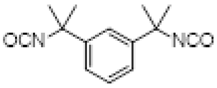
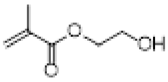
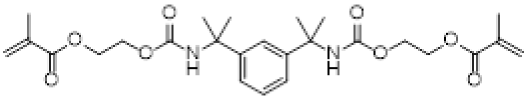
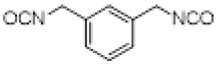
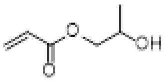
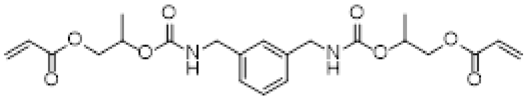
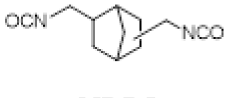
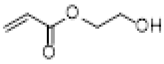
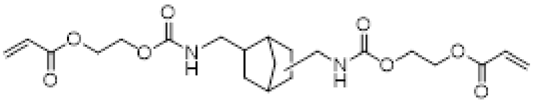
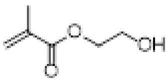
Diisocyanates	Hydroxyalkyl (meth)acrylates	Urethane (meth)acrylates
 TMXDI	 HEA	 TMXDI – HEA
 TMXDI	 HPA	 TMXDI – HPA
 TMXDI	 HBA	 TMXDI – HBA
 TMXDI	 HEMA	 TMXDI – HEMA
 XDI	 HPA	 XDI – HPA
 NBDI	 HEA	 NBDI – HEA
 TMHDI	 HEMA	 TMHDI - HEMA

Table 2.

Monomaers	Viscocity (mPa•s at 65 ^{o}C)
TMXDI - HEA	1670
TMXDI - HPA	1800
TMXDI - HBA	410
XDI - HPA	570
NBDI - HEA	930
UDMA	320
TMXDI - HEMA	1900
Bis-GMA	3660

Table 3.

Diluting monomer (TMXDI - HEA wt / Diluting monomer wt)	Viscosity (mPa•s at 23 ^{o}C)
DEGDMA (70/30)	1320
DEGDMA (80/20)	10260
TEGDMA (70/30)	1800
TEGDMA (80/20)	12250
4EGDMA (70/30)	2180

Table 4.

Urethane (meth)acrylates	Refractive index of monomer
TMXDI - HEA	1.517
XDI - HPA	1.515
NBDI - HEA	1.506
UDMA	1.484
Bis-GMA	1.551