

Biomechanical Effects of New Resin Matrix System on Dental Fiber-Reinforced Composites

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There are concerns that dental materials based on *bis*-phenol-A-glycidylmethacrylate (*bis*-GMA) may be hazardous. Alternative monomers such as 1,6-hexanediol dimethacrylate (HDDMA) is under research. This research aimed to determine the effect of resin matrix compositions on the biomechanical properties of E-glass fiber-reinforced composite (FRC) using *bis*-phenol-A-glycidylmethacrylate (*bis*-GMA), methylmethacrylate (MMA), 1,6-hexanediol dimethacrylate (HDDMA), camphorquinone (CQ) and N,N-cyanoethyl methylaniline (CEMA). The ratios of the resin matrices (weight %) were 78.4 % *bis*-GMA + 19.6 % MMA + 1 % CQ + 1 % CEMA (control-group), 78.4 % HDDMA + 19.6 % MMA + 1 % CQ + 1 % CEMA (EXP1-group) and 49 % HDDMA + 49 % MMA + 1 % CQ + 1 % CEMA (EXP2-group). E-glass fibers were embedded in matrix and light-cured for 3 × 40 s. Three-point bending (2 × 2 × 25) mm and Vicker's hardness (2 × 2 × 5) mm were examined (n = 6) by a universal testing machine (Torse's UTM, Japan) and a micro-hardness tester (MTX70 Matsuzawa, Japan). The data were analyzed by ANOVA. Bending measurement revealed the mean value of control-group (674.1 ± 9.9) MPa was higher than EXP1-group (638.1 ± 8.6) MPa and EXP2-group (448.3 ± 7.8) MPa. The ANOVA showed significant difference in bending values among the groups (p < 0.05). Hardness measurement proved EXP1-group mean value (179.1 ± 2.5) VHN was higher than control-group (181.5 ± 11.5) VHN and EXP2-group (168.2 ± 7.9) VHN. The ANOVA proved there was significant difference (p < 0.05) in hardness values. In conclusion, a resin matrix system based on HDDMA-MMA (EXP1-group) showed comparable flexural strength and hardness properties to *bis*-GMA-MMA (control-group) system.

Keywords: Biomechanics, Fiber-reinforced composites, 1,6-Hexanediol dimethacrylate.

INTRODUCTION

Recently, there are some materials developed for crown and bridge. The most commonly used material which is preferred by the clinicians is the porcelain fused-to metal, a metal ceramic glass like material that is enameled on top of metal shell [1]. Unfortunately, as popular and successful as this material is, it still exhibits shortcomings which frequently causes clinical problems. The metal alloys commonly used may corrode and the ceramic materials such as porcelain is also brittle [2]. Over the last few years, the development of fiber-reinforced composite (FRC) has offered the dental profession the possibility of fabricating resin-bonded, esthetically good and metal-free tooth restorations for single and multiple teeth replacement [3]. Fiber-reinforced composite is a composite material with fine thin fibers as reinforcement which is good in its tensile strength and flexural modulus [4]. Basically FRC has at least two distinct constituents. The reinforcing component gives good strength and stiffness, while the surrounding matrix supports reinforcement [2]. Generally glass fibers have high tensile strength, excellent impact and compression properties

which make them more desired reinforcing material [5]. In FRC with an interpenetrating polymer network (IPN) structure, the matrix consists of a crosslinking polymer, a linear polymer and a photoinitiator to react the polymerization [6]. One of the most widely used resin matrix which forms highly crosslinking polymer structures is *bis*-phenol-A-glycidylmethacrylate (*bis*-GMA) [7] (Fig. 1). A linear polymer such as methyl methacrylate (MMA) [6] is joined or bridged to form a crosslinking polymer [8]. The photoinitiator includes a photosensitizer and a reducing agent. Camphorquinon (CQ) and N-N-cyanoethyl methylaniline (CEMA) are the common used photosensitizer and reducing agents [6]. Released compounds might cause biological reactions [9] and a case of allergic contact from *bis*-GMA was reported [10]. Since the use of *bis*-GMA is considered to be relatively hazardous, nowadays the use of other matrices are gaining more and more interest. Resin matrix of 1,6-hexanediol dimethacrylate (HDDMA), Fig. 2 has similar reactive groups to *bis*-GMA. The HDDMA properties are low viscosity, fast curing monomer with low volatility, hydrophobic backbone and good solvency for use in free radical polymerization [11,12].

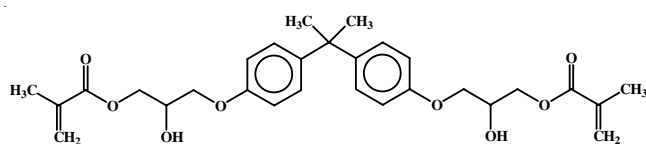
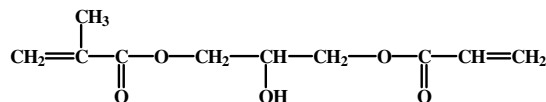
Fig. 1. Structure of *bis*-phenol-A-glycidylmethacrylate (*bis*-GMA)

Fig. 2. Structure of 1,6-hexanediol dimethacrylate (HDDMA)

The 1,6-hexanediol dimethacrylate (HDDMA) features water repellency property (hydrophobic). It is used as a functional monomer for polymers and as a crosslinking agent between the molecular chains of polymers. Applications of HDDMA include adhesives and sealants, coatings, elastomer, photopolymers electronics, improved adhesion, hardness, abrasion and heat resistance. The toxicological properties of HDDMA are reported not to produce mutagenic, embryotoxic, teratogenic, or reproductive effects in humans. Related to the carcinogenicity, it is reported that none of HDDMA components are listed by IARC, NTP, OSHA, or ACGIH as carcinogens [12].

The mechanical strength of FRC depends on the impregnation of fibers within the resin matrix and adhesion of fibers to the matrix [13-15]. Others factors which influence the properties of FRCs are quantity of fibers and orientation of fibers [15-18]. Failure of the FRC by external force can happen by cracking of the polymer matrix, the fiber or at their interface [19,20]. It was known that the chewing forces in human in the range of 98.1-294.3 MPa. The flexural strength of prosthodontic metal alloys typically are around 500-750 MPa and the hardness of gold alloy around 250 VHN [2,21].

The objective of this study was to examine the effect of resin matrix composition including *bis*-GMA based and HDDMA based compositions on the biomechanical properties of E-glass FRC. Moreover this study aimed to determine the best resin matrix ratios of HDDMA-MMA which produced good mechanical properties compared to the *bis*-GMA-MMA matrix system.

EXPERIMENTAL

The materials used in this study were *bis*-GMA (Sigma-Aldrich, USA), MMA (ProSciTech, Australia), HDDMA (Esstech, USA), CQ (Esstech, USA), CEMA (Esstech, USA) and E-glass fibers (Ahlstrom, Finland). The E-glass fibers (R338-2400/V/P) were already silanized by the manufacturer and kept in a desiccator for 24 h prior to specimen preparation. The fibers were sized by immersion in a sizing solution (50 % wt % *bis*-GMA + 50 % wt % MMA for the control-group; 50 % wt % HDDMA + 50 % wt % MMA for the experimental groups for 1 min. The sized fibers were cut into 25 mm long with a surgical steel knife for the preparation of test specimens [22].

Two bundles of 25 mm long fibers were placed along the long axis of the specimen into the mould and embedded into the resin matrix with different compositions as shown in Table-1.

TABLE-1
MATRIX COMPOSITION (wt %)

Group	Component				
	<i>bis</i> -GMA	MMA	HDDMA	CQ	CEMA
Control	78.4	19.6	0	1	1
EXP1	0	19.6	78.4	1	1
EXP2	0	49.0	49.0	1	1

Each group of matrix composition consisted of 6 specimens. Total eighteen specimens with the dimension of (2 × 2 × 25) mm were prepared [6]. All specimens were light-cured on both sides with a light curing unit (Woodpecker, USA) for 3 × 40 s. After light-curing, all specimens were polished by polishing paper (360 grit) [22]. The specimens were immersed in distilled water for 24 h, 37 °C before mechanical testing.

The mechanical tests were carried out (n = 6) for each matrix composition group on three-point bending test and Vickers hardness test. Three-point bending test used a universal testing machine (Torsee's UTM, Japan). The span between the two supports was 20 mm and the crosshead speed was 1 mm/min during testing. Load and deflection were recorded and plotted. The maximum load of the load-deflection curve was used to calculate the flexural strength by the following formulae [23]:

$$\sigma = 3 FL/2bd^2$$

σ = fleksural strength (MPa); F = maximum load in the load-deflection curve (Newton); L = span between the two supports (millimeter); b = width of the specimen (millimeter); d = height of the specimen (millimeter).

Vickers hardness test was conducted according to ISO 6507-2. A microhardness tester (type MTX 70 Matsuzawa, Japan) was utilized to carry out the test. A load of 0.245 Newton and a loading duration of 20 s were used. Time delay from applying the indenter to the determination of the hardness value was standardized to 10 s [5].

The data on mechanical test were analyzed by SPSS software. The level of statistical significant p was set as 0.05. The data normality was examined by Kolmogorov-Smirnov test. One way analysis of variance (ANOVA) followed by Post hoc least significant different (LSD) test were carried out. The dependent variables (hardness and flexural strength in 3-point bending test) were compared with independent factor (resin matrix composition).

RESULTS AND DISCUSSION

Table-2 showed the mean values of flexural strength of FRC materials with different matrix compositions. Each composition consisted of 6 replication samples.

Table-2 showed the control group had the highest flexural strength value while the EXP2-group had the lowest value. The flexural strength mean value of the control-group and EXP1-group was nearly similar. The data of flexural strength values of FRC with different matrix compositions were tested for normality distribution by Kolmogorov-Smirnov test. It was proved that all of the 3 group matrix compositions had significant value more than 0.05; therefore it was concluded that the data had normal distribution and could be analyzed further by ANOVA. The ANOVA in Table-3 showed statistically

TABLE-2
FLEXURAL STRENGTH OF
FIBER-REINFORCED COMPOSITE (MPa)

Matrix composition	Mean $\pm$ SD
Control-group	674.1 $\pm$ 9.9
EXP1- group	638.1 $\pm$ 8.6
EXP2-group	448.3 $\pm$ 7.8

TABLE-3
ANOVA OF FLEXURAL STRENGTH VALUE
OF FIBER-REINFORCED COMPOSITE

	Sum of squares	Df	Mean square	F	Sig
Between groups	193971.98	2	300.94	4.47	0.03
Within groups	3070.99	15	67.40		
Total	197042.98	17			

significant difference in flexural strength values among the 3 different matrix compositions of FRC ($p < 0.05$). Further analysis with LSD in Table-4 proved that there was significant difference ($p < 0.05$) between the control-group and the EXP1-group, the control-group and the EXP2-group and the EXP1-group and the EXP2-group.

TABLE-4
LSD TEST OF FLEXURAL STRENGTH VALUE
OF FIBER-REINFORCED COMPOSITE

Group (I)	Group (J)	Mean difference (I-J)	Sig
Control	EXP1	51.63	0.01
	EXP2	241.44	0.01
EXP1	Control	51.63	0.01
	EXP2	189.81	0.01
EXP2	Control	241.44	0.01
	EXP1	189.81	0.01

Table-5 showed the hardness value in VHN of the FRC with different matrix compositions. It was shown the EXP1-group had the highest hardness value (181.5 ± 11.5) VHN and the EXP2-group had the lowest hardness value (168.2 ± 7.9) VHN.

TABLE-5
VICKERS HARDNESS VALUE OF
FIBER-REINFORCED COMPOSITE (VHN)

Matrix composition	Mean $\pm$ SD
Control	179.1 $\pm$ 2.5
EXP1	181.5 $\pm$ 11.5
EXP2	168.2 $\pm$ 7.9

The normality test of the hardness value by Kolmogorov-Smirnov test showed all of the data had normal distribution ($p > 0.05$). Further analysis by ANOVA in Table-6 proved there was significant difference ($p < 0.05$) in hardness values among the 3 groups of FRC matrix compositions. Post hoc test by LSD in Table-7 showed that there was no significant difference ($p > 0.05$) between the control-group and the EXP1-group, while between the control-group and the EXP2-group and between the EXP1-group and the EXP2-group showed significant differences in hardness value ($p < 0.05$).

Fiber reinforced composite is a composite material made of a polymeric matrix which is reinforced by fibers. The matrix has several functions, *i.e.* holding the fibers in the composite

TABLE-6
ANOVA OF HARDNESS VALUE OF
FIBER-REINFORCED COMPOSITE

	Sum of squares	Df	Mean square	F	Sig
Between groups	601.87	2	300.94	4.465	0.03
Within groups	1010.99	15	67.40		
Total	1612.86	17			

TABLE-7
LSD TEST OF HARDNESS VALUE OF
FIBER-REINFORCED COMPOSITE

Group (I)	Group (J)	Mean difference (I-J)	Sig
Control	EXP1	2.38	0.62
	EXP2	10.90	0.04
EXP1	Control	2.38	0.62
	EXP2	13.28	0.01
EXP2	Control	241.44	0.04
	EXP1	13.28	0.01

structure, transferring stresses between fibers and protecting fibers from external environment. Thus the matrix in FRC affects the material properties greatly [24]. There are two types of polymer used in FRC, the cross-linked and linear polymers. The cross linking polymer or the thermosetting polymer refers to the multifunctional dimethacrylate resin. The linear polymer or the thermoplastic polymer refers to the monofunctional methacrylate polymer [4]. In FRC with the IPN structure usually the matrix consists of a cross linking polymer, a linear polymer and a photo initiator [25].

There are two kinds of setting reaction on FRC resin matrix, *e.g.* the polymerization reaction and the cross linking reaction. Polymerization reaction refers to the formation of a polymer by sequential adhesion of monomer units. The cross linking reaction in a polymer is the formation of a cross link where chain are bonded together either through direct connection or *via* an intermediary atom, ion, molecule or chain. This produces a three dimensional strongly cross linked system [26].

This study was aimed to replace the matrix of *bis*-GMA (cross linking monomer) which is considered to be relatively hazardous to HDDMA (cross linking monomer) in an FRC material. It was known the combination of *bis*-GMA-MMA matrix produced an IPN structure improved the mechanical strength of FRC material. Structurally, the HDDMA monomer had reactive groups similar to *bis*-GMA. Based on this fact, it was assumed combination of HDDMA-MMA might produce an IPN structure as well. This condition might improve the mechanical properties of FRC.

The result of the study also proved the matrix composition of HDDMA-MMA in FRC produced lower flexural strength value than the *bis*-GMA-MMA matrix system significantly. This fact might be caused by the difference in the viscosity of *bis*-GMA and HDDMA. *Bis*-GMA had the benzene component on its structure which might cause the molecular weight higher and the solvent was more viscous than HDDMA. The less viscosity of HDDMA might cause the impregnation of HDDMA to the fiber be lower than *bis*-GMA. This condition decreased the flexural strength of FRC with HDDMA matrix composition.

The requirement of fixed partial denture alloy for flexural strength was over 500 MPa [21]. In previous study, it was reported that flexural strength value of E-glass FRC with *bis*-GMA-MMA based matrix in three point bending was 461 ± 50 MPa [6]. Even though the current work had different components in the FRC specimens from those of previous studies, the result of the flexural strength value of *bis*-GMA+MMA (control-group) (674.1 ± 9.9 MPa) and HDDMA+MMA (EXP1-group) (638.1 ± 8.6 MPa) fulfilled the requirement of fixed partial denture alloy requirement for flexural strength. It was suggested that the current study result was acceptable for clinical used.

The result showed hardness value of EXP1-group was higher than control-group. The higher value might be caused by the good solvency of HDDMA to MMA. This condition influenced different rapidity in setting time of the resin polymerization. HDDMA will react to MMA faster than *bis*-GMA to MMA; therefore HDDMA will have faster setting time than *bis*-GMA to MMA. This condition influenced the higher hardness value of HDDMA to MMA.

The results of Post hoc test in Table-7 showed that there was not any difference of hardness value between control-group and EXP1-group. Although statistically the hardness value difference is insignificant, the value does not exceed of enamel hardness (230-260VHN) [21]. It is mentioned if the hardness value of an alloy is greater than enamel, it may wear the enamel of the teeth opposing to the restoration [27]. Table-7 showed that the hardness value of all groups fulfilled the requirement of hardness properties for crown and bridge material.

Conclusion

In conclusion, resin matrix based composition of HDDMA-MMA (EXP1-group) showed comparable bending and hardness properties to *bis*-GMA-MMA matrix system (control-group). Further research was suggested to determine the biological properties of the proposed new matrix system of HDDMA-MMA (EXP1-group) to gain biocompatible FRC.

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