Conference Paper

The Effect of UDMA/TEGDMA Mixtures and Bioglass Incorporation on the Mechanical and Physical Properties of Resin and Resin-Based Composite Materials

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Incorporating Bioglass into dental composites may improve biocompatibility and aid tooth and bone tissue remineralisation. This study aimed to determine the impact of Bioglass and silica filler on the mechanical and physical properties of cured photopolymers. Hardness (Vickers microhardness test), flexural strength (FS), and flexural modulus (FM) (three-point bend test) of resins containing various urethane dimethacrylate (UDMA)/triethylene glycol dimethacrylate (TEGDMA) and bisphenol A-glycidyl methacrylate (bisGMA)/TEGDMA concentrations (20–80 mass%) were tested. Degree of conversion (DC), FS, and FM of resin composites containing nonsilanised irregular 45S5-Bioglass (50 μm ; 5–40 mass%) and/or silanised silicate glass filler particulates (0.7 μm ; 30–70 mass%) were tested. Data was analysed using one-way ANOVA. UDMA/TEGDMA resins exhibited increased hardness and FM compared with bisGMA/TEGDMA resins. Addition of Bioglass particles to 60/40 wt% UDMA/TEGDMA or bisGMA/TEGDMA resins may enable the development of new materials that exhibit higher or at least equivalent values of DC, FS, and FM compared with conventional resin composites.

1. Introduction

Conventional light-cured dimethacrylate resin composites undergo free radical photopolymerisation in response to blue light (wavelength 450–500 nm). The resin composites contain monomers such as bisGMA, UDMA, and TEGDMA (used as a diluent) in the organic matrix, a ketone-amine initiator/coinitiator system and inert silicate filler particles [1, 2]. UDMA is increasingly used in the organic matrix of resin composites for dental applications [1], due to the flexibility and strength conferred by the urethane group [2, 3]. These properties may result in enhanced physical and mechanical properties of resin-based UDMA composites

compared with resins containing bulky bisGMA molecules [4]. Although conventional resin composites have been a successful restorative dental material, there is no beneficial biological interaction between the surrounding tissues and the material. By incorporating an optically suited, bioactive glass into these resins, the biocompatibility with the surrounding tissues and remineralisation processes may be improved [3].

The aim of this project was to determine the effect of mixing various comonomer base resin ratios and the impact of the incorporation of silica filler and Bioglass on the mechanical and physical properties of the cured photopolymer composite.

2. Methods

2.1. Resin Synthesis. All materials were supplied by Sigma-Aldrich, UK, and used as received. A variety of UDMA/TEGDMA and bisGMA/TEGDMA concentrations (20 : 80, 30 : 70, 40 : 60, 50 : 50, 60 : 40, 70 : 30, and 80 : 20) were synthesised to determine the optimum polymer conversion. Camphorquinone (CQ, 0.2 wt%) and a coinitiator (2 dimethylaminoethyl methacrylate; DMAEMA, 0.8 wt%) were added as the photoinitiator system to the organic matrix of the resins. The resin formulations were mixed on a magnetic stirrer for 30 min at 60°C and subsequently stored in a lightproof container at 4°C to avoid premature photocuring.

2.2. Resin Composite Synthesis. The bioactive glass was manufactured using an established glass melt process producing the 45S5 Bioglass composition of $(\text{CaO})_{26.9}(\text{Na}_2\text{O})_{24.4}(\text{SiO}_2)_{46.1}(\text{P}_2\text{O}_5)_{2.6}$ [5]. Silica and irregular Bioglass ($<50\text{ }\mu\text{m}$, passed through a $50\text{ }\mu\text{m}$ sieve) particles (Figure 1) were added to 60 : 40 wt% UDMA/TEGDMA or bisGMA/TEGDMA in concentrations 70 : 0, 65 : 5, 60 : 10, 50 : 20, 40 : 30, and 30 : 40.

2.3. Hardness of Cured Resins. The cured surface hardness of each unfilled resin sample (10 mm diameter, 2 mm thick) was measured with a hardness tester (Duramin, Struers, UK). Each resin disc was subjected to a load of 100 kgf for 15 s. The size of the indentations caused by the pyramid-shaped diamond indenter on the resins disc surface was recorded. The 2 diagonals of each square were measured and an average was calculated. Equation (1) was employed to calculate the Vickers hardness number:

$$\text{HV} = \frac{1.854F}{d^2} \text{ (kgf/mm}^2\text{)}, \quad (1)$$

where HV is Vickers hardness number, F is force applied to the specimen, and d^2 is surface area determined by taking the average of the 2 diagonals of the square left by the indenter [6].

2.4. Degree of Conversion of Resin Composites. The degree of conversion (DC) of resin composite samples was measured statically using a Fourier transform near-infrared technique (4 scans; 8 wave number resolution; Nicolet 6700, Thermoscientific) [7]. The resin composite mixture was exposed to curing light for 40 s (Optilux 501, wavelength maxima 470 nm; irradiance 850 mW/cm²).

2.5. Flexural Strength and Modulus of Resins and Resin Composites. Rectangular bars (25 mm length, 2 mm breadth, and 2 mm thickness) of 60/40 U/T and B/T resins and each resin composite were polymerised using an overlapping curing protocol with a 12 mm diameter curing tip for 40 s. FS and FM of resin composite samples (25 × 2 × 2 mm) were determined using the three-point bend test by subjecting each resin bar to loading using a universal testing machine (Instron 5544, UK)

at a cross head speed of 1 mm/min and 1 kN load. FS of resin samples was calculated using

$$\text{FS} = \frac{3PL}{2bd}. \quad (2)$$

FM of resin samples was calculated using

$$\text{FM} = \frac{(3PL/2bd)}{(6Dd/L^2 * 100)}, \quad (3)$$

where P is load at fracture, L is support span, b is specimen width, d is specimen thickness, and D is midspan deflection [8].

One-way ANOVA and post hoc Tukey tests were used to determine significant differences between sample conditions (95% significance level).

3. Results

3.1. Unfilled Resins. Resins containing bisGMA/TEGDMA exhibited significantly decreased values for hardness (Figure 1), FS, and FM (Table 1) compared with UDMA/TEGDMA resins ($P < 0.005$). For bisGMA/TEGDMA resins, 60/40 wt% ratio exhibited significantly higher hardness values compared with the other formulations ($P < 0.005$) (Figure 1). Resins containing 50/50, 60/40, and 70/30 wt% UDMA/TEGDMA exhibited significantly higher hardness values compared with any other UDMA/TEGDMA mixture ($P < 0.001$) (Figure 1).

The FS and FM of 50/50, 60/40, and 70/30 wt% UDMA/TEGDMA- and bisGMA/TEGDMA-based resins were significantly higher compared with the other formulations ($P < 0.005$) (Table 1). Resins containing 50/50, 60/40, and 70/30 wt% UDMA/TEGDMA mixtures exhibited significantly higher FS values compared with resins containing 50/50, 60/40, and 70/30 wt% bisGMA/TEGDMA mixtures (Table 1).

The optimum concentration of bisGMA/TEGDMA and UDMA/TEGDMA based on DC (data not shown), hardness (Figure 1), FS, and FM (Table 1) was determined to be 60/40 wt%. Therefore, this concentration was used for Bioglass addition experiments.

3.2. Resin Composites. The DC of bisGMA/TEGDMA-based resins containing 20 wt% Bioglass was significantly higher compared with the other bisGMA/TEGDMA-based resin composites ($P < 0.05$). Although UDMA/TEGDMA-based resin composites containing 20 wt% Bioglass exhibited the highest DC, it was not significantly different compared with the other UDMA/TEGDMA-based resin composites ($P > 0.1$) (Figure 2). The addition of 5 wt% Bioglass resulted in a decrease in the DC of composites compared with unfilled resins; however, no additional decrease was observed up to 30 wt% Bioglass (Figure 2).

FS and FM of bisGMA/TEGDMA resin composites containing 20 wt% Bioglass were significantly higher compared with bisGMA/TEGDMA composites containing 70 wt% silica ($P < 0.005$) (Table 2). There was no significant difference

TABLE 1: Flexural strength and modulus of bisGMA/TEGDMA (BT) and UDMA/TEGDMA (UT) resins. UDMA/TEGDMA resins exhibited increased flexural modulus compared with bisGMA/TEGDMA resins. Standard deviation ($n = 9$) is displayed in paranthesis.

BisGMA/TEGDMA (wt%)	FS (MPa)	FM (GPa)	UDMA/TEGDMA (wt%)	FS (MPa)	FM (GPa)
20 : 80 BT	50.9 (4.7)	1.4 (0.0)	20 : 80 UT	43.9 (7.9)	1.2 (0.1)
30 : 70 BT	59.4 (9.6)	1.8 (0.3)	30 : 70 UT	64.1 (6.0)	1.6 (0.1)
40 : 60 BT	61.0 (4.9)	1.7 (0.1)	40 : 60 UT	65.4 (11)	1.7 (0.2)
50 : 50 BT	66.2 (4.1)	1.9 (0.1)	50 : 50 UT	77.5 (5.3)	2.0 (0.1)
60 : 40 BT	64.7 (3.7)	1.7 (0.1)	60 : 40 UT	70.8 (4.1)	1.9 (0.0)
70 : 30 BT	67.4 (8.0)	1.7 (0.1)	70 : 30 UT	74.0 (7.2)	2.0 (0.2)
80 : 20 BT	55.2 (4.8)	1.5 (0.1)	80 : 20 UT	69.0 (6.5)	1.7 (0.1)

TABLE 2: The FS and FM of bisGMA/TEGDMA and UDMA/TEGDMA resin composites. UDMA/TEGDMA- based composites exhibited higher FS and FM compared with bisGMA/TEGDMA-based composites. BG: Bioglass. Standard deviation ($n = 9$) is displayed in parenthesis.

60 : 40 wt% BisGMA/TEGDMA	FS (MPa)	FM (GPa)	60 : 40 wt% UDMA/TEGDMA	FS (MPa)	FM (GPa)
70 wt% Silica	46.1 (9.4)	4.8 (0.5)	70 wt% Silica	84.3 (14)	7.0 (0.9)
5 wt% BG	59.4 (6.4)	5.9 (0.2)	5 wt% BG	80.3 (7.2)	6.4 (0.5)
10 wt% BG	55.1 (5.5)	5.4 (0.4)	10 wt% BG	69.7 (9.8)	6.0 (0.6)
20 wt% BG	56.5 (5.1)	6.8 (0.4)	20 wt% BG	79.3 (8.4)	6.9 (0.9)
30 wt% BG	39.6 (5.3)	5.7 (0.7)	30 wt% BG	57.8 (9.4)	4.4 (0.4)
40 wt% BG	26.0 (3.0)	3.3 (0.9)	40 wt% BG	42.7 (2.9)	3.6 (0.5)

FIGURE 1: The hardness of bisGMA/TEGDMA- (BT-) and UDMA/TEGDMA- (UT-) based resins. UDMA/TEGDMA resins exhibited increased hardness values compared with bisGMA/TEGDMA resins. Error bars represent standard deviation ($n = 9$).

in the FS and FM of UDMA/TEGDMA composites containing 70 wt% silica and UDMA/TEGDMA composites containing 20 wt% Bioglass ($P = 0.673$) (Table 2). However addition of >20 wt% Bioglass to both bisGMA/TEGDMA- and UDMA/TEGDMA-based resin composites resulted in a marked decrease in FS, which was significantly lower compared with the other bisGMA/TEGDMA and UDMA/TEGDMA resin composites ($P < 0.005$) (Table 2).

Figure 3 shows the fracture surface of the 60/40 wt% U/T containing 20 wt% and 30 wt% Bioglass. There is some evidence of filler “plucking” and filler “shearing,” which may suggest that more energy is required for crack propagation.

The addition of up to 30 wt% Bioglass to bisGMA/TEGDMA and UDMA/TEGDMA resin composites had no detrimental effect on the DC (Figure 3), whereas

FIGURE 2: The degree of conversion of bisGMA/TEGDMA (BT) and UDMA/TEGDMA (UT) resin composites. UDMA/TEGDMA-based composites exhibited higher degree of conversion values compared with bisGMA/TEGDMA-based composites ($P < 0.005$, one-way ANOVA). Error bars represent standard deviation ($n = 5$). BG: Bioglass.

the addition of >20 wt% Bioglass to either bisGMA/TEGDMA or UDMA/TEGDMA resin composites had a negative impact on the FS and FM of the final composites (Table 2).

4. Discussion

The molecular structure and viscosity of the comonomer mixtures significantly affect the mechanical and physical properties of the cured resin. Due to the rigidity of bis-GMA molecules, polymer conversion is limited prior to the

FIGURE 3: SEM micrographs of fracture surface of resin composites containing 20 wt% (a) and 30 wt% (b) Bioglass at 500x magnification.

maximum rate of polymerisation, which limits propagation reactions. The lower viscosity and increased flexibility of UDMA at early stages of polymerisation (controlled by differences in hydrogen bonding interactions and molecular structure) will lead to higher conversion prior to diffusion-controlled propagation [9, 10] and thus higher final DC and network formation evidenced by significantly increased hardness (Figure 1). Thus, the optimum concentration of bisGMA/TEGDMA and UDMA/TEGDMA based on DC, RP (data not shown), hardness (Figure 1), FS, and FM (Table 1) was determined to be 60/40 wt%.

The addition of Bioglass particles reduced the DC of the resin composites compared with the unfilled resins, which was possibly due to particle size, morphology, and increased light attenuation (reflection, refraction, and scattering) and opacity during the polymerisation reaction (Figure 2).

The UDMA/TEGDMA-based resin composites exhibited higher FS and FM values compared with bisGMA/TEGDMA-based composites (Table 2), which is also likely to be a result of increased crosslink density in the polymer network. Increasing Bioglass content (>20 wt%) within the matrix had a detrimental effect on the optical characteristics, which led to a reduction in DC and consequently FS and FM.

At the fracture surface (Figure 3), there is some evidence of filler “plucking” that would be expected for the incorporation of Bioglass fillers without surface modification using a silane agent to achieve a chemical bond between the filler and matrix. There may also be some filler “shearing”

at the fracture surface, which may require more energy for crack propagation thus leading to increased fracture toughness values (not measured), which requires further analysis. For composites containing up to 20 wt% Bioglass no significant deterioration in FS and FM was observed (Table 2). However, lack of filler silanisation may result in significant strength deterioration for composites containing greater than 20 wt% Bioglass. This will remain an important consideration in the development of “bioactive” light-curable resin-based composites where a compromise may exist between ion dissolution/remineralisation potential and strength characteristics of the restorative material. Although 60/40 comonomer mixtures exhibit the most desirable polymerisation characteristics, there exist competing factors associated with viscosity (affecting rheology and handling properties) and optical property combinations with the filler (affecting refractive index and light transmission through depth), which require further consideration.

5. Conclusion

Addition of Bioglass particles to 60/40 wt% UDMA/TEGDMA or bisGMA/TEGDMA resins may lead to the development of new materials that exhibit higher or at least equivalent values of DC, FS, and FM compared with conventional resin composites. Further work in this area is warranted.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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