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Original research article

Monomer Conversion, Dimensional Stability, and Biaxial Flexural Strength of Flowable Dental Composites Containing Beta-Tricalcium Phosphate and Andrographolide

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ABSTRACT

The aim of this study was to develop flowable dental composites containing beta-tricalcium phosphate (TCP) and andrographolide (Andro). The effect of these additives on monomer conversion, dimensional stability (mass/volume changes), and biaxial flexural strength was examined. The composites were prepared with a powder to liquid mixing ratio of 1.7:1 (mass ratio). Liquid phase contained light curable methacrylates. Powder phase contained dental glass, TCP (5 or 2.5wt%), and Andro (5 or 2.5wt%). Monomer conversion was assessed using FTIR-ATR (n=5). Mass and volume changes were assessed using gravimetric studies ($n = 3$). Biaxial flexural strength was assessed using a mechanical testing frame ($n = 6$). Fracture surface was assessed using SEM-EDX. The commercial controls were resin-based materials (Z350 and Riva). The highest conversion was observed with Riva (81%). The conversion of composites containing TCP and Andro (~53%) was comparable with that of Z350 (51%). The additives reduced monomer conversion of the composites by ~10%. Rising level of TCP and Andro showed minimal effect on the conversion. Mass/volume changes of the experimental composites (1.3wt%, 1.7vol%) were higher than that of Z350 (0.4wt%, 0.6vol%). The additives showed minimal effect on mass/volume changes but reduced BFS of the composites from 183 to 137 MPa. Rising level of Andro reduced BFS by 17% whilst rising TCP level showed negligible effect. Fracture surface revealed calcium phosphates precipitated in the composites. In conclusion, the experimental composites containing TCP and Andro showed comparable monomer conversion but lower strength than Z350. The additives reduced monomer conversion and strength of the composites, but their strength was higher than specified that in the standard of dental composite.

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Keywords: Andrographolide; Biaxial flexural strength; Monomer conversion; Resin composite; Tricalcium phosphate

1. Introduction

Dental caries is currently affecting almost 2.3 billion adults and 558 million children globally [1]. The progressed lesions will eventually form uncleanable carious cavities which require restorative treatments. Dental composites will become the most commonly used restorative materials due to the phasing down of dental amalgam brought by the Minamata Convention on Mercury in 2013 [2]. Current composites exhibit excellent esthetic outcomes and high mechanical strength properties. A recent study, however, reported a high prevalence (up to 44%) of recurrent/secondary caries around composite restorations [3]. This could be due to the lack of mineralizing and antibacterial properties of the composites, leading to continued tooth demineralization and bacterial penetration at tooth-composite interfaces [4]. Another study also suggested that the release of unreacted monomers from the composites could enhance cariogenicity of dental biofilm [5].

Previous studies have demonstrated that the incorporation of phosphates such as monocalcium phosphate (MCPM) with tristrontium phosphate or beta-tricalcium phosphate (TCP) promoted apatite formation, which could potentially help to repair the demineralized dentine. The addition of these phosphates, however, reduced monomer conversion upon light activation [6-7]. The addition of high soluble MCPM (Ca/P ratio=0.5) also promoted hygroscopic expansion that may help to reduce polymerization shrinkage stress [8]. However, the excessive water sorption led to a continuous decline in strength of the composites [9-10].

Antimicrobial agents were incorporated into dental composite to enable antibacterial actions. Chlorhexidine provides a wide range of antimicrobial activities [11-12]. However, the major concern with chlorhexidine is its potential to cause serious allergic reaction resulting in death [13]. Andrographolide (Andro), the major active component of the traditional herb *Andrographis paniculate*, exhibited antimicrobial activity against a wide range of microorganisms [14-15]. Andro interfered with the quorum sensing system in biofilm formation and inhibited the adhesion of cariogenic bacteria, such as *Streptococcus mutans*, to hydroxyapatite [16].

The aim of this study was, therefore, to develop flowable dental composites containing TCP (Ca/P=1.5) and Andro. The effect of increasing the level of TCP and Andro on the degree of monomer conversion, dimensional stability (mass and volume changes), and biaxial flexural strength of the materials were examined.

2. Materials and Methods

2.1 Materials preparation

Liquid phase of the experimental composites contained 70wt% urethane dimethacrylate (UDMA, Sigma-Aldrich, USA), 25wt% triethylene glycol dimethacrylate (TEGDMA, Sigma-Aldrich, USA), 4wt% 2-hydroxyethylmethacrylate (HEMA, Sigma-Aldrich, USA), and 1wt% camphorquinone (CQ, Sigma-Aldrich, USA). Powder phase consisted of silanated boroaluminosilicate glass fillers (0.7 and 2 μm in diameter, Esstech Inc, USA), beta-tricalcium phosphate (TCP, Sigma-Aldrich, USA), and andrographolide (Andro, Nanjing NutriHerb Bio-Tech, China). The composition of powder phase in the experimental composites is provided in Table 1.

Table 1. Composition of powder phase in experimental composites.

Formulation (F)	Glass fillers (wt%)		TCP (wt%)	Andro (wt%)
	2 μm	0.7 μm		
F1	45	45	5.0	5.0
F2	46.25	46.25	5.0	2.5
F3	46.25	46.25	2.5	5.0
F4	47.5	47.5	2.5	2.5
F5	50	50	0	0

The components were weighed and mixed using a powder to liquid mass ratio of 1.7:1 to produce flowable composites. The mixed composite pastes were each placed in a composite syringe (Sulzer MIXPAC™ ONE 1cc syringe, SULZER, Switzerland) and left at room temperature for 24 hr.

Filtek Z350 XT flowable restorative (3M-ESPE, USA) and resin modified glass ionomer restorative material (Riva, Riva LC, Riva SDI, Australia) were used as commercial controls. Samples of the commercial materials were prepared according to the manufacturer instructions. The composition of the commercial materials is provided in Table 2. The materials were purchased from the respective suppliers.

Table 2. Composition of commercial materials.

Materials	Compositions
Filtek Z350 XT Flowable Restorative	Bisphenol glycidyl dimethacrylate, Triethylene glycol dimethacrylate, Bisphenol glycidyl dimethacrylate, Silane-treated ceramic, Silica, Zirconium oxide
Riva LC	Liquid: Poly(acrylic acid), Tartaric acid, 2-Hydroxyethyl methacrylate, Dimethacrylate crosslinker, light initiator, acidic monomer Powder: fluoroalumino silicate glass

2.2 Degree of monomer conversion

An FTIR-ATR (Nicolet iS5 FT-IR Spectrometer and ID7 ATR accessory, Thermo Scientific, USA) was used to measure monomer conversion of the materials $(n=5)$. The uncured materials were placed on the ATR diamond and covered with an acetate sheet. They were light activated from the top surface using an LED light curing unit (light intensity 1,100–1,330 mW/cm^2, SMACO, China) for 40 s. The FTIR spectra from 700 to 4000 cm^{-1} of the bottom surfaces before and after light cured were recorded. Monomer conversion (D_c) was obtained using Eq. (1).

$$D_c = \frac{100(\Delta C_0 - \Delta C_t)}{\Delta C_0}, \qquad (2.1)$$

Where Δc_0 is initial absorbance of the peak at 1320 cm^{-1} (C-O) compared with the background level at 1335 cm^{-1}, Δc_t is the peak at 1320 cm^{-1} above the peak at 1335 cm^{-1} after time *t* [6,10].

2.3 Mass and volume change

The materials were injected into a metal circlip (10 mm in diameter and 1 mm in thickness). The materials were covered by an acetate sheet and light activated on both sides for 40 s in a circular motion. The specimens were left to cure at 25±1 °C for 24 hr. The disc samples $(n=3)$ were placed in 10 mL of simulated body fluid (SBF) [17]. The specimens were incubated at 37 °C for up to 4 weeks. Mass and volume of the specimens were measured at various time points (0, 1, 4, 24 hr; 2, 3, 4 days; 1, 2, 3, 4 weeks) using a balance equipped with a density kit (MS204TS/00, METTLER TOLEDO, USA) [7]. The measurements were performed for up to 4 weeks because previous studies had demonstrated that the changes tend to plateau after 4 weeks[6, 18].

2.4 Biaxial flexural strength and biaxial flexural modulus

Disc specimens were prepared according to section 2.3. They were immersed in 10 mL of SBF $(n=6)$ and incubated at 37 °C for 24 hr. Then, the specimens were removed and placed on a ball-on-ring testing jig. The load was applied using a ball indenter (4 mm in diameter). The test was performed using 2 kN load cell with a crosshead speed of 1 mm.min^{-1} under the mechanical testing frame (AGSX, Shimadzu Corp, Japan). BFS (Pa) was obtained using Eq. (2.2) [7].

$$\mathrm{BFS}=\frac{F}{d^2}\left\{(1+v)\left[0.485\ln\left(\frac{r}{d}\right)+0.52\right]+0.48\right\}, \tag{2.2}$$

where F is the maximum load (N), d is the thickness of disc specimen (m), r is the radius of circular support (m), and v is Poison's ratio (0.3). Additionally, biaxial flexural modulus was calculated using Eq. (2.3).

$$E=\left(\frac{\Delta H}{\Delta W_c}\right)\times\left(\frac{\beta_c d^2}{q^3}\right), \tag{2.3}$$

Where E is biaxial flexural modulus of the specimen (Pa), $\frac{\Delta H}{\Delta W_c}$ is rate of change of load with regards to central deflection or gradient of force versus displacement curve (N/m), β_c is centre deflection junction (0.5024) [19], q is ratio of support radius (4 mm) to the radius of disc.

Surface fracture was assessed under a scanning electron microscope (SEM) (JSM 7800F, JEOL, Japan) equipped with Energy Dispersive X-ray (EDX, Inca X-sight 6650 detector, Oxford Instrument, UK).

2.5 Statistical analysis

Numerical values from monomer conversion, biaxial flexural strength, and modulus of elasticity reported in this study are presented as mean (±SD). Data were analysed using SPSS for Window version 25 (IBM, New York, USA). Levene 's test was employed to assess the homogeneity of variances of results. One-way ANOVA and Tukey multiple comparison were used if variances between materials were equal. Dunnett T3 post-hoc multiple comparison was used when the variances were not equal. The significance level was set at $p = 0.05$. Additionally, post hoc power analysis was examined using G*Power 3.1 Software (University of Dusseldorf, Germany). The results demonstrated that the sample size of each test gave power>0.99 at $\alpha = 0.05$.

Factorial analysis was performed to analyse the effect of a rising level of TCP and Andro on the tested properties. a_1 and a_2 represent the average effect of changing the level of TCP and Andro from 2.5 to 5 wt% on the property P, respectively. The magnitude of interaction is given as $a_{1,2}$. The full factorial equations can be given as following [6].

$$\ln P=\left(\ln P\right)\pm a_1\pm a_2\pm a_{1,2}. \tag{2.4}$$

The percentage effect of each variable (Q) can be additionally calculated using the following equation:

$$Q(\%)=100\left(1-\frac{G_H}{G_0}\right)=100\left(1-\exp\left(2a_i\right)\right), \tag{2.5}$$

where G_H and G_0 are the geometric average property for the samples with the variable at its high versus low value, respectively. CI error bars (95%) for $2a_i$ parameters were calculated. Where these error bars cross zero, the variable i is considered to have had no significant effect on the property P [12]. The effect of variable change was considered significant if the magnitude of a_i was greater than both its calculated 95% CI and interaction terms.

3. Results

3.1 Monomer conversion

The highest monomer conversion was observed with Riva (80.8±2.8 %) whereas the lowest was observed with Z350 (51.8±1.6 %) (Fig. 1). The conversions of F1 (54.2±1.1 %), F2 (53.0±0.8 %), F3 (53.0±0.3 %), and

F4 (53.3±0.7 %) were comparable to that of Z350 ($p>0.05$). The conversion of F5 (59.9±1.2 %) was however significantly higher than that of Z350 ($p < 0.01$). Factorial analysis demonstrated that raising the level of TCP and Andro showed negligible effect on monomer conversion of experimental composites (Fig. 2).

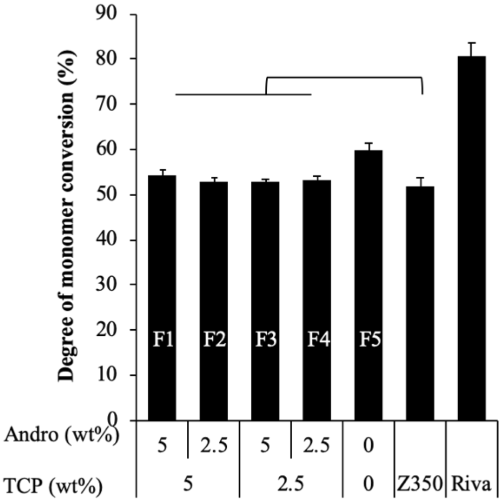

Fig. 1. Monomer conversion of materials after light curing for 40 s. Lines indicate no significant difference ($p > 0.05$). Error bars are 95% CI $(n=5)$.

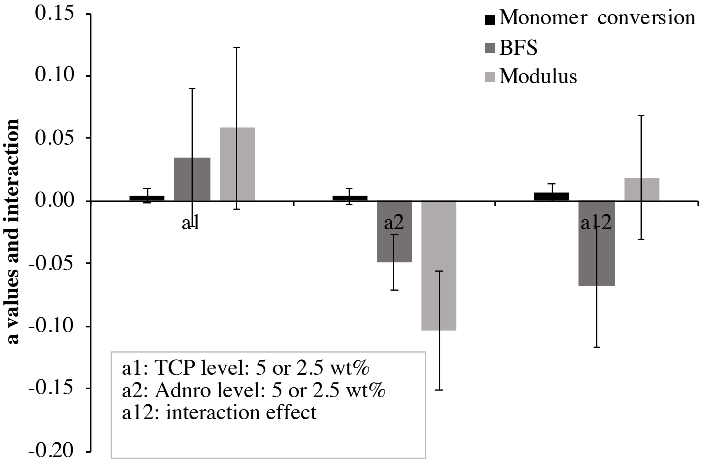

Fig. 2. Factorial analysis describing the effect of TCP (a_1) and Andro (a_2) and their interaction effect ($a_{1,2}$) on monomer conversion, biaxial flexural strength, and modulus of elasticity. Error bars are 95% CI ($n = 5$ for monomer conversion, $n = 6$ for biaxial flexural strength (BFS) and modulus).

3.2 Mass and volume changes

Mass and volume of all materials were increased after immersing in SBF for up to 4 weeks. The highest mass and volume changes were observed with Riva (8.1 wt%, 11.6 vol%) (Fig. 3). The observed mass and volume changes of experimental composites (1.1-1.5 wt% and 1.1-2.0 vol%) were higher than that of Z350 (0.4 wt%, and 0.6 vol%).

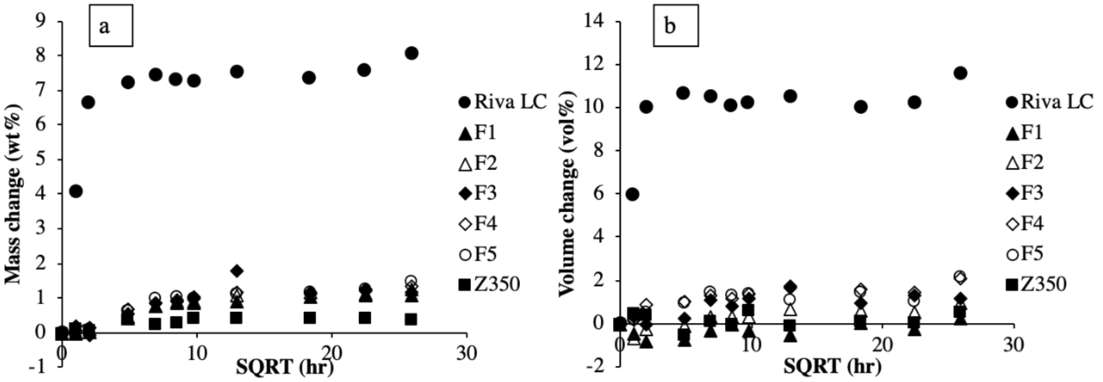

Fig. 3. The average of a) mass and b) volume changes of all materials after immersion in SBF for up to 4 weeks ($n = 3$, error bars are not presented to aid visualization).

3.3 Biaxial flexural strength (BFS) and modulus of elasticity (BFM)

Z350 showed the highest observed mean BFS (230±33 MPa) and BFM (4.4±0.3 GPa) (Fig. 4). The BFS of Z350 was comparable with that of F5 (180±10 MPa) (p=0.228). The BFS of F1 (139±24 MPa), F2 (163±15 MPa), and F4 (151±11 MPa) were comparable to that of F5 (p>0.05). Riva exhibited the lowest BFS (86±32 MPa) which was comparable to F3 (119±17 MPa) (p=0.186). The BFM of all experimental composites was comparable with that of Z350 and Riva (p>0.05). Factorial analysis indicated that raising the level of Andro from 2.5 to 5 wt% reduced BFS and BFM by 9±4 % and 20±7 %, respectively. The effect from raising the TCP level was however, negligible.

The surface fracturing of F1-F4 revealed calcium phosphate precipitate (Ca/P ratio=1.38) (Fig. 5). Multiple cracks were observed within the bulk of Riva.

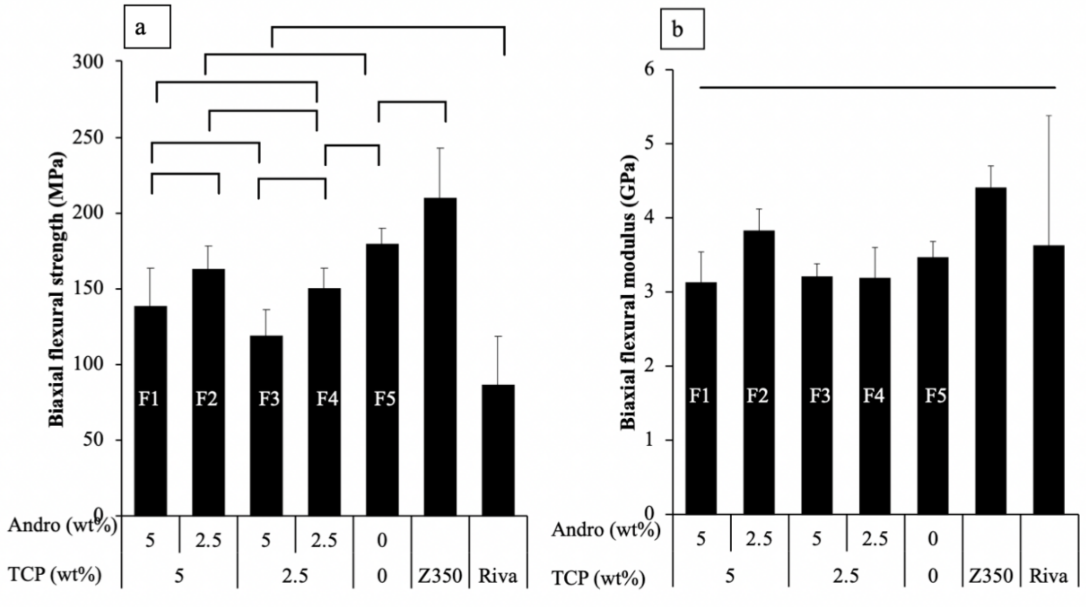

Fig. 4. a) Biaxial flexural strength and b) biaxial flexural modulus of materials after immersion in SBF for 24 hr. Lines indicate no significant difference ($p > 0.05$). Error bars are 95% CI ($n = 6$).

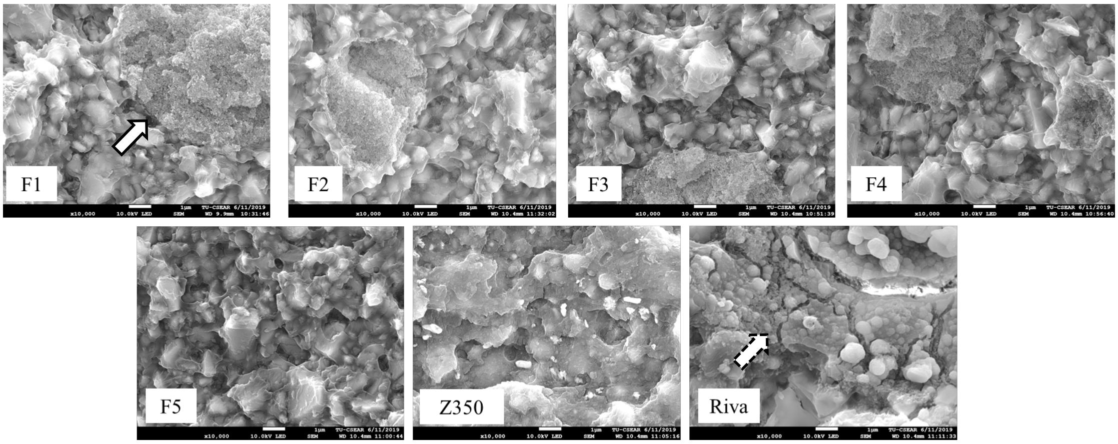

Fig. 5. SEM images of surface fracture from BFS tested specimens (scale bars are 1 μm). Solid arrow indicates calcium phosphates (Ca/P ratio=1.36) observed inside the bulk of F1-F4 samples. Dashed arrow indicates cracks observed in Riva.

4. Discussion

This study aimed to develop novel light curable flowable dental composites containing tricalcium phosphate and andrographolide. The effect of the additives on monomer conversion, mass/volume changes, and biaxial flexural strength were assessed.

4.1 Monomer conversion

High monomer conversion of resin-based restorative materials is required to enable high mechanical strength properties and cytocompatibility of the materials [20]. Additionally, it has been proposed that the release of unreacted monomers affects the balance of bacterial species in dental biofilms, resulting in a high proportion of acid-producing bacteria [21]. This may contribute to the formation of secondary caries around composite restorations [4].

The composition of monomer phase plays an essential role in the level of monomer conversion observed from resin-based restorative materials [22]. In general, a high level of monomer conversion is observed from polymers comprised of flexible and low glass transition temperature (T_g) monomers [23-24]. The primary base monomer of resin-modifed glass ionomer cement such as Riva is hydroxyethyl methacrylate (HEMA, T_g=-60 °C) [25, 26]; therefore, the highest monomer conversion was obtained from this material. The main base monomer of Z350 was Bis-GMA [20] (bisphenol A-glycidyl methacrylate, T_g=-8 °C) whereas the the major base monomer of the experimental composites was UDMA (urethane dimethacrylate, T_g=-35 °C). This may explain the higher momer conversion of experimental composites with no additive, when compared with Z350.

The addition of TCP and Andro reduced the conversion obtained from the experimental composites. This might be due to the increase in light scattering that resulted from the reflective indices mismatch between the additives and glass fillers/polymer in the materials [10]. This could reduce light transmission and negatively affected the polymerization at the bottom of materials [27].

Currently, there is no minimum requirement for the monomer conversion of dental composites. Previous studies have demonstrated that the release of unreacted monomer from composites was markedly reduced when the final monomer conversion of the materials was greater than 50% [28, 29]. All experimental composites exhibited a conversion greater than 50%. This may suggest the risk of toxic monomer released from the materials is low.

4.2 Mass and volume change

Restorative materials will be exposed to oral fluids, resulting in water movement or water sorption that induces mass changes and hygroscopic expansion of the materials[30]. The absorbed water may, however, plasticise the polymer matrix or cause the release of components that may consequently lead to a reduction in mechanical strength [6].

The experimental composites exhibited mass and volume changes comparable to that observed with commercial materials (1-2 wt% and 1-2 vol%) [31]. A previous study showed that the addition of the hydrophillic MCPM fillers significatnly promoted water sorption induced mass/volume changes (final mass chage ranged from -1 to 2 wt% and volume change of 2-5 vol%). This resulted in the loss of components and negatively affected the strength of experimental composites [6]. The results from the current study indicate that the addition of TCP and Andro to dental composites have a negligible effect on mass and volume changes; this may be due to their low water solubility [15, 32].

The experimental composites exhibited mass and volume changes higher than Z350. The possible reason for low water sorption enhanced hygroscopic expansion observed with Z350 could be the low mobility of its primary base monomer (Bis-GMA). Bis-GMA is a stiff molecule due to its isopropylidene-diphenoxy core [33]. In contrast, HEMA is a small molecule with high mobility, which may contribute to the high flexibility of the polymer network [34]. This may promote high water sorption, leading to Riva having the highest observed mass and volume change compared with other materials.

High polymerization shrinkage of the cured composites may create tensile stress at the tooth-composite interface, leading to bond failure and subsequent bacterial microleakage [4]. A previous study showed that the polymerization shrinkage of commercial flowable composites was ~4 vol% [35]. It was shown that the net final expansion of composites may help to reduce shrinkage stress of the materials [8]. Hence, net volume expansion observed with the experimental composites in this study could partially help to balance this stress and reduce the risk of interfacial failure.

4.3 Biaxial flexural strenght and biaxial flexural modulus

Dental composites are generally indicated for load bearing restoration. High mechanical strength of the material is therfore required to ensure the longevity of the restorations. BFS tests were employed in the current study. It was suggested that the the flexural stregth observed in the BFS tests correlated with that from the conventional 3-point bending test, but with less variability in the data [36].

The flexural strength observed with the experimental composites was in the acceptable range compared with that of commercial flowable composites (100-160 MPa) [37]. The modului of the experimental composites were however, slightly lower than that of the commercial materials (6-9 GPa). This could be due to the absorbed water possibly acting as a plasticiser, thereby reducing the stiffness of the polymer matrix in the experimental composites [38]. The lowest strength was obsereved with Riva which could be due to the excessive water sorption of the materials.

The addition of TCP and Andro (F1-F4) reduced the strength of the composites as was expected. This could be due to the lack of silanisation of the additives, which is essential to enable chemical bonding of the resin polymer and additives [39]. The additives were not silanised due to the need to enable their release [7]. However, the experimental composites still exhibited flexural strength greater than the 24 hr-flexural strength (80 MPa) required by BS EN ISO 4049:2019 [40].

Previous studies have shown that a rising level of calcium phosphates reduced mechanical strength properties of the materials [9,10]. In the current study, raising the level of TCP from 2.5 to 5 wt% showed a negligible effect on the strength. A possible explanation could be the low solubility of TCP [32]. Another explanation could be the precipation of small phosphate particles, which could act as reinforcing fillers [41] replacing the reacted TCP. The low solubilty of the additives may be considered beneficial to maintaining suffient mechanical strength properties for the composites. This could however, affect the therapuetic characteristics, such as remineralization or antibacterial activity, of the materials which may need to be investigated in the further studies.

5. Conclusion

The novel flowable dental composites containing TCP and Andro were developed. The experimental composites exhibited monomer conversion in the range of that observed from commercial composites. The additives reduced monomer conversion but showed minimal effect on mass/volume changes. The addition of TCP and Andro reduced strength of the experimental composites. Raising the level of TCP showed negligible effect whilst raising level of Andro reduced the strength of materials. However, the strength of the experimental composites was still greater than that required by the ISO standard.

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