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Development of Novel Fluoride-releasing Composites

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Abstract

Due to the development of secondary caries, resin-based composites (RBCs) have short life spans. Several modifications have been studied to overcome this problem, such as incorporating ion-releasing fillers. In this study a previously lab-made fluoridated bioactive glass (F-BAG) was scaled-up industrially to establish whether scaling-up affected the fluoride release and flexural properties of RBCs containing this glass. Next, the effect of different monomers and F-BAG concentrations was assessed on selected physical and mechanical properties of RBCs.

Materials and methods: One batch of the lab-made F-BAG and three nominally identical but separately made batches, made by a contract manufacturer (GTS, Glass Technology Services, UK), were initially assessed. First, RBCs made from 50:50 UDMA:TEGDMA and a barium aluminium-silicate glass as primary filler with 20wt% of the different F-BAG batches added. Additionally, an RBC was made with only the primary filler added and one in which the three GTS batches were mixed was made. Next the effect of different monomers (UDMA, HEMA, TEGDMA) was established on RBCs containing the same concentration of F-BAG. Finally, the effect of F-BAG concentration was established when the monomer concentrations were fixed.

All RBCs were assessed in terms of degree of conversion (DOC), water sorption, fluoride release, flexural strength (FS) and flexural modulus (FM).

Results: For DOC and fluoride release RBCs containing the GTS F-BAGs were not significantly different to the lab-made glass containing RBCs and exhibited significantly lower water sorption and higher flexural properties after 1 month storage in distilled water. While the addition of HEMA significantly increased the fluoride release of the RBCs it detrimentally affected the flexural properties over storage time. Finally, there was an

increase in fluoride release as the F-BAG concentration increased but when 30wt% or 40wt% F-BAG was added the flexural properties were reduced.

Conclusion: The experimental F-BAGs composites made in this study represents promising results. Incorporating F-BAGs fillers in 10-40wt% showed good initial flexural properties which decreased over storage time especially for 30wt% and above.

Table of Content

Abstract	I
Dedication	VI
Acknowledgement	VII
List of Figures	VIII
List of Tables	XI
List of Abbreviations	XII
1. Chapter 1. Introduction	1
2. Chapter 2. Literature review.....	3
2.1 Dental conditions requiring restorations.....	3
2.1.1 Dental caries.....	3
2.1.2 Tooth surface loss	7
2.1.3 Dental trauma	10
2.1.4 Treatment strategies	11
2.2 Composition of conventional resin-based composites	19
2.2.1 Organic matrix	19
2.2.2 Inorganic fillers	23
2.2.3 Coupling agents	26
2.2.4 Initiators and activators	28
2.2.5 Other additives	29
2.3 Polymerisation of conventional resin-based composites	30
2.3.1 Free radical addition polymerisation	30
2.3.2 Methods of activation	30
2.3.3 Degree of polymerisation	31
2.3.4 Depth of cure	32
2.4 Properties of conventional composites	33
2.4.1 Polymerisation shrinkage	33
2.4.2 Mechanical properties	34
2.5 Evaluation of the Physical and Mechanical Properties of the resin composite	34
2.5.1 Attenuated total reflection Fourier transform infrared spectroscopy ...	34
2.5.2 Flexural strength and flexural modulus	37
2.5.3 Water sorption	37
2.6 Bio-active resin-based composites	38
2.6.1 Currently used fluoride-releasing materials	38
2.6.2 Fluoride-releasing composites	38
2.6.3 Bio-active glasses	40
2.6.4 Fluoride release and its measurement	47
2.7 Summary	49
3. Chapter 3: Aims, Objectives and program of work.....	50
3.1 Aims	50
3.2 Objectives	50
3.3 Program of work	51
4. Chapter 4: Preparation of Model Experimental Composites and Bio-active glass-based Composites	52

4.1 Introduction.....	52
4.2 Materials and method	53
4.2.1 Composite preparation	53
4.2.2 Monomer preparation	55
4.2.3 Mixing glass fillers with the monomer	55
4.2.4 Model composites physical and mechanical properties	58
4.2.4.1 Degree of conversion	58
4.2.4.2 Water sorption	59
4.2.4.3 Fluoride release	60
4.2.4.4 Flexural strength and flexural modulus	63
4.2.4.5 Statistical analysis	65
4.3 Results	65
4.3.1 Degree of conversion	65
4.3.2 Water sorption	66
4.3.3 Fluoride release	68
4.3.4 Flexural strength and flexural modulus	70
4.4 Discussion	74
4.4.1 Preparation of the F-BAGs composites	74
4.4.2 Degree of conversion	75
4.4.3 Water sorption	76
4.4.4 Fluoride release	77
4.4.5 Flexural strength and flexural modulus	79
4.5 Summary	84
5. Chapter 5: Effect of Different Concentrations of Monomers on the Physical and Mechanical Properties of the F-BAGs Composites	85
5.1 Introduction	85
5.2 Materials and methods	85
5.2.1 Composite preparation	85
5.2.2 Monomer preparation	86
5.2.3 Mixing glass fillers with the monomer	86
5.2.4 Physical and mechanical properties of the different monomer's composites	87
5.2.4.1 Degree of conversion	87
5.2.4.2 Water sorption	87
5.2.4.3 Fluoride release	88
5.2.4.4 Flexural strength and flexural modulus	88
5.2.4.5 Statistical analysis	88
5.3 Results	88
5.3.1 Degree of conversion	88
5.3.2 Water sorption	91
5.3.3 Fluoride release	94
5.3.4 Flexural strength and flexural modulus	97
5.4 Discussion	102
5.4.1 Monomer selection and preparation of the composites	102
5.4.2 Degree of conversion	103
5.4.3 Water sorption	104
5.4.4 Fluoride release	106

5.4.5	Flexural strength and flexural modulus	107
5.5	Summary	109
6.	Chapter 6: Effect of the Concentration of F-BAGs fillers on the Physical and Mechanical Properties of the F-BAGs Composite	111
6.1	Introduction	111
6.2	Materials and methods	111
6.2.1	Composite preparation	111
6.2.2	Monomer preparation	112
6.2.3	Mixing glass fillers with the monomer	112
6.2.4	Physical and mechanical properties of the different F-BAGs glass concentration composites	113
6.2.4.1	Degree of conversion	113
6.2.4.2	Water sorption	113
6.2.4.3	Fluoride release	114
6.2.4.4	Flexural strength and flexural modulus	114
6.2.4.5	Statistical analysis	115
6.3	Results	115
6.3.1	Degree of conversion	115
6.3.2	Water sorption	116
6.3.3	Fluoride release	117
6.3.4	Flexural strength and flexural modulus	119
6.4	Discussion	122
6.4.1	Preparation of the F-BAGs composites	122
6.4.2	Degree of conversion	123
6.4.3	Water sorption	123
6.4.4	Fluoride release	124
6.4.5	Flexural strength and flexural modulus	124
6.5	Summary	127
7.	General discussion and summary	128
7.1	General discussion	128
7.2	Summary	135
7.3	Limitations of the study	136
7.4	Future work	137
7.5	Covid statement	139
8.	References.....	140
9.	Appendices	182

Dedication

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List of Figures

Figure 2-1: Caries risk factors	5
Figure 2-2: Structure of Bis-GMA, UDMA and TEGDMA (Lavigueur C, 2012)	20
Figure 2-3: Structure formula of HEMA (Sigma-Aldrich)	22
Figure 2-4: Structure of TCD-urethane (A) and dicarbamate dimethacrylate (B) (Boaro LCC, 2010)	23
Figure 2-5: Classification of fillers (Ferracane JL, 2011)	26
Figure 2-6: Chemical structures of MPS (Sigma-Aldrich)	27
Figure 2-7: Champhorquinone (Sakaguchi R, 2012)	29
Figure 4-1: The three batches of the GTS glass and the lab-made glass	55
Figure 4-2: Speed-Mixer™, DAC 150.1 FVZ, Hauschild Engineering, Germany	56
Figure 4-3: A. 55F composites. B. 55F composites when a high-speed mix was used (3000 rpm) it shows a heterogeneous mixture. C. The lab-made composites. D. The GTS-mix composites	57
Figure 4-4: 55F When a low-speed mix was used (1000 rpm) it shows a dry and unmixed.	57
Figure 4-5: FTIR samples	59
Figure 4-6: Fluoride ion test specimen in 5ml DW	61
Figure 4-7: Ion-selective electrode	63
Figure 4-8: Custom spilt steel mould	64
Figure 4-9: The sample in DW before stored in incubator	64
Figure 4-10: 55F sample before (A), During (B) and after (C) FS test	65
Figure 4-11: DOC (%) of 55F, lab-made, GTS 1,2 3 and GTS-mix composites, GTS-mix showed a significantly lower D.O.C compared to GTS2 at 60s (P<0.05)	66
Figure 4-12: Figure 4-12: Water sorption ($\mu\text{g}/\text{mm}^3$) of the 55F, lab-made glass and the GTS composites. The lab-made glass composites showed a significantly higher sorption in most of the time points (P<0.05)	68
Figure 4-13: Cumulative fluoride release ($\mu\text{g}/\text{cm}^2$) of the 55F, lab-made and the GTS composites. Despite the significantly lower daily fluoride release by the Lab-made F-BAGs composites up to 96hrs compared to the GTS based composites (P<0.05), the cumulative fluoride release at week 4 were similar (P>0.05)	70
Figure 4-14: Flexural strength values (MPa) of the six tested composites with their standard deviation. The lab-made F-BAGs composites showed a significant decrease over storage time (P<0.05)	73

Figure 4-15: Flexural modulus values (GPa) of the six tested composites with their standard deviation. Only lab-made and GTS2 showed a significant decrease in the FM at day 7 (P<0.05), with no change up to 28 days (P>0.05)	73
Figure 4-16: The DOC of the unsilanised GTS-mix glass composites compared to the silanised one. No significant differences were detected (P>0.05)	82
Figure 4-17: The FS (MPa) of the unsilanised GTS-mix composites compared to the silanised one. No significant differences were shown (P>0.05)	82
Figure 4-18: The FM (GPa) of the unsilanised GTS-mix glass composites compared to the silanised one. No significant differences were shown (P>0.05)	83
Figure 4-19: Water sorption of the unsilanised GTS-mix glass composites and silanised one after 28 days of storage. No significant differences were shown (P>0.05)	83
Figure 4-20: Cumulative Fluoride release of the unsilanised GTS-mix glass composites and silanised GTS-mix glass composites. GTS-mix silanised showed significantly higher cumulative release compared to the unsilanised GTS-mix glass composites (P<0.05)	84
Figure 5-1: The seven F-BAGs containing composites	86
Figure 5-2: Flexural specimens before and after applying the test	88
Figure 5-3: Degree of conversion of the non-F-BAGs composites, no significant differences when increasing the curing time from 10 seconds for all the composites (P>0.05)	90
Figure 5-4: Degree of conversion of the F-BAGs composites, 50:50 UH-BG showed a significant lower DOC compared to the rest of the tested composites until 40s curing time (P<0.05) but no differences were shown at 60s curing time (P>0.05)	90
Figure 5-5: Water sorption ($\mu\text{g}/\text{mm}^3$) of the non-F-BAGs composites, 50:50 UH composites showed higher water sorption which was significant in most of the time points (P<0.05) ..	93
Figure 5-6: Water sorption ($\mu\text{g}/\text{mm}^3$) of the F-BAGs composites, 50:50 UH-BG composites showed higher water sorption which was significant in most of the time points (P<0.05) ..	93
Figure 5-7 The cumulative fluoride ion release for the F-BAGs composites, A- U100-BG and 75:25 UT-BG, B- the UDMA:HEMA F-BAGs composites and C- is the UDMA:TEGDMA:HEMA F-BAGs composites the 50:50 UH-BG composites significantly released more fluoride than the rest of the F-BAGs composites (P<0.05).	95
Figure 5-8: The flexural strength (MPa) of the non-F-BAGs composites, from day 7 up to 28 days of storage, 50:50 UH composites showed a significant lower FS values compared to the rest of the materials (P<0.05)	97
Figure 5-9: The flexural strength values (MPa) of the F-BAGs composites, 50:50 UT-BG showed a significantly lower FS values compared to the rest of the materials at all time points (P<0.05)	99
Figure 5-10: The flexural modulus values (GPa) of the non-F-BAGs composites, 100U, 75:25 UH and 75:12.5:12.5 Composites showed no significant change in the FM over storage time (P>0.05)	100

Figure 5-11: The flexural modulus values (GPa) of the F-BAGs composites, 100 U-BG and 75:25 UT-BG showed a significant higher FM than the rest of the tested composites at day 1 and day 7 test (P<0.05), 50:50 UH-BG showed a significantly lower FM compared to the rest of the materials at all time points (P<0.05)	101
Figure 6-1: The five experimental composites used in this chapter	113
Figure 6-2: Degree of conversion (%) of the different F-BAG composites when light-cured for 10-60 seconds. No significant differences were shown when increase in the DOC when light-cured more than 10 seconds	116
Figure 6-3: Water sorption ($\mu\text{g}/\text{mm}^3$) of the F-BAG composites, 40BG showed a significantly higher water sorption than the tested composites at most of the time points (P<0.05) ...	117
Figure 6-4: Cumulative fluoride release ($\mu\text{g}/\text{cm}^2$) of the different F-BAG composites, increasing the amount of incorporated F-BAGs led to significant increase in the fluoride release (P<0.05)	119
Figure 6-5: Flexural strength values (MPa) of the different F-BAGs concentrations composites, the F-BAGS composites showed a significant decrease at day 7 (P<0.05) with no significant change up to 28 days (P>0.05)	121
Figure 6-6: Flexural modulus values (GPa) of the different F-BAGs concentration composites, 0BG and 10BG showed no significant change throughout the testing period (P>0.05)	121
Figure 7-1: The 21 days cumulative fluoride release from four different GIC, one RMGIC and one giomer (Mousavinasab and Meyers, 2009)	130
Figure 7-2: Cumulative fluoride release of two commercial GIC, compomer, giomer and flouride containing flowable composites in comparison to the F-BAGs composites made in this research (Dionysopoulos;Koliniotou-Koumpia;Helvatzoglou-Antoniades and Kotsanos, 2013)	131
Figure 7-3: The flexural strength (MPa) of the HEMA-containing F-BAGs composites made in this project compared with four commercial pit and fissure sealants (Beun;Bailly;Devaux and Leloup, 2012)	133
Figure 7-4: The flexural modulus (GPa) of the HEMA-containing F-BAGs composites made in this project compared with four commercial pit and fissure sealants (Beun;Bailly;Devaux and Leloup, 2012)	134

List of Tables

Table 2-1: Table 2-1: The compositions of the nine bioactive glass containing fluoride made, the bolded text show the composition of the glass used in this project	46
Table 4-1: List of the materials used in the preparation of the model composite with their manufacturers	54
Table 4-2: Composition of the experimental composites	54
Table 4-3: The fluoride release ($\mu\text{g}/\text{cm}^2$) and SD for the six experimental composites. The green coloured numbers showed significant higher release from the lab-made glass composites ($P<0.05$), the red indicated some significant differences between the GTS glass composites ($P<0.05$), and the blue numbers indicated a significant lower daily fluoride release from the lab-made glass composites compared to the GTS composites ($P<0.05$) ...	69
Table 4-4: The flexural strength (MPa) mean and standard deviation values of the six tested composites. The 55F showed no significant decrease over storage time ($P>0.05$), but the FS of the F-BAGs lab-made and GTS composites decreased significantly at day 7 ($P<0.05$), with no further differences up to 28 days ($P>0.05$)	72
Table 4-5: The flexural modulus (GPa) mean and standard deviation values of the six tested composites. Only lab-made and GTS2 showed a significant decrease in the FM at day 7 ($P<0.05$), with no change up to 28 days ($P>0.05$)	72
Table 5-1: The daily fluoride release of the F-BAGs containing composites. The red text indicated a significant fluoride release from the 50:50 UH-BG ($P<0.05$)	96
Table 6-1: F-BAG composites with different glass concentrations	112
Table 6-2: Daily fluoride ion release ($\mu\text{g}/\text{cm}^2$) of the different F-BAGs concentration composites, the blue numbers show the initial significant increase, and the green numbers show the second significant increase in daily fluoride release	118
Table 6-3: Flexural strength (MPa) of the different F-BAGs concentration composites	120
Table 6-4: Flexural modulus (GPa) of the different F-BAGs concentration composites	121

List of Abbreviations

ATR-FTIR:	Attenuated total reflection Fourier transform infrared spectroscopy.
Bis-GMA:	Bis-phenol –A-glycidyl dimethacrylate.
BAG:	Bioactive glass
C=C:	Carbon double bond
CQ:	Camphorquinone.
CaO:	Calcium oxide
CaF ₂ :	Calcium fluoride
DOC:	Degree of Conversion.
EDAB:	4-ethyl dimethyl aminobenzoate.
F-BAG:	Fluoridated bioactive glass.
FS:	Flexural strength.
FM:	Flexural modulus.
GICs:	Glass ionomer cements.
HEMA:	2-hydroxyethyl methacrylate.
ISO:	International Organisation for Standardisation.
LED:	Light-emitting diode.
Na ₂ O:	Sodium hydroxide
NaF:	Sodium fluoride
PET:	Polyethylene terephthalate.
RBCs:	Resin-based composites.
RMGIC:	Resin-modified glass ionomer cements.
SEM:	Scanning electron microscopy.
SiO ₂ :	Silica
TEGDMA:	Tri-ethylene glycol dimethacrylate.
TISAB:	Total ionic strength adjustment buffer.
U:	UDMA containing composites.

U-BG:	UDMA containing bioactive glass composites.
UDMA:	Urethane dimethacrylate.
UT:	UDMA:TEGDMA containing composites.
UT-BG:	UDMA:TEGDMA containing bioactive glass composites.
UTH:	UDMA:TEGDMA:HEMA containing composites.
UTH-BG:	UDMA:TEGDMA:HEMA containing bioactive glass composites
UV:	Ultraviolet.
Vol%:	Volume percentage.
Wt%:	Weight percentage.
XRD:	X-ray powder diffraction.

1 Introduction

Dental caries is one of the most prevalent diseases (Mahfouz and Abu Esaid, 2014) and a major problem in populations around the world (Kamberi *et al.*, 2016). Caries is a multifactorial disease that causes the destruction of tooth tissues as a result of demineralisation by acids from the bacterial biofilm. Bacteria produce these acids by metabolising carbohydrates which then spread into tooth tissues and break down the mineral content (Dawes, 2003; Angel Villegas *et al.*, 2019). Dental caries can be managed at an early stage. Remineralisation of the dental tissues can occur by the application of fluoride, for example (Abou Neel *et al.*, 2016). In cavitated lesions, surgical intervention is mandatory to remove caries and restore teeth's function and aesthetics.

For decades, different materials have been used for direct restorations, such as composites and amalgams. Amalgam restorations have great clinical longevity, are relatively low cost, and have less technique sensitivity when compared with composites. The use of amalgam has been questioned because of the possible effects of mercury content on people's health. However, there is no evidence to show that the amount of mercury released affects the health of the population; amalgams are safe and effective dental materials (AFFAIRS, 1998; Uçar and Brantley, 2011). However, the use of amalgam restorations has been declining following the Minamata convention call to phase down amalgam use due to the mercury content and its effect on the environment (Kessler, 2013; Spiegel *et al.*, 2015; Joy and Qureshi, 2020). Amalgam cavity preparations are not as conservative as composites; more extensive tooth preparation is needed to enhance the resistance and retention of the restoration. In addition, an increase in the demand for more aesthetic restorations, due to

the variety of tooth colour shades, makes composites a better choice for treatment (Lynch *et al.*, 2014b; Moraschini *et al.*, 2015).

Resin-based composites (RBCs) can be used as cavity liners, provisional restorations, pit and fissure sealants, luting cements for crowns and bridges, inlays, onlays, endodontic sealers and as posts and cores (Ferracane, 2011). Dental composites are made of an organic polymer matrix (mainly methacrylate-based), inorganic fillers such as silica or glass, a coupling agent that binds the filler to the matrix, and initiators and accelerators that control the polymerisation process (Klapdohr and Moszner, 2004). Current composites have sufficient mechanical properties to restore all types of cavities. Several studies have shown composites to show good performance over 10 to 20 years with a low annual failure rate (Gaengler; Hoyer and Montag, 2001; Pallesen and Qvist, 2003; da Rosa Rodolpho *et al.*, 2006).

Secondary caries is one of the most common reasons for the replacement of composite restorations. This occurs at the restoration-tooth margin as a result of polymerisation shrinkage combined with cyclic occlusal loading leading to failure of the adhesive interface between the restoration and the tooth. This leads to increased levels of bacteria at the interface, and eventually to caries (Hansel *et al.*, 1998; Kuper *et al.*, 2013). This problem suggests there is a need for composites with antimicrobial and remineralisation properties to reduce the formation of caries and increase the survival rate of composite restorations (Choi; Condon and Ferracane, 2000; Khvostenko *et al.*, 2016). A few years ago, researchers started exploring the possibility of using bioactive glasses (BAGs) in resin-based composites. BAGs are inorganic fillers containing components with antimicrobial or remineralisation properties such as zinc, copper or silver. BAGs have been found to have an antimicrobial

effect and can remineralise adjacent tooth tissues (Zehnder *et al.*, 2004; Vollenweider *et al.*, 2007b; Waltimo *et al.*, 2007; Brown *et al.*, 2011; Manfred *et al.*, 2013b). Fluoride has been used as antibacterial agent to enhance polymerisation and prevent the demineralisation (Hicks *et al.*, 2003b). Fluoride-releasing materials such as glass ionomers sealants have more potential to prevent pit and fissure caries when compared to resin sealants (Zhang *et al.*, 2014). Due to the superior aesthetic and mechanical properties, fluoride-releasing composites has been studied in the last two decades to produce materials with a higher physical and mechanical properties than other fluoride releasing material such as GIC and compomer (Wiegand;Buchalla and Attin, 2007; Francois *et al.*, 2020). However, incorporating fluoride might reduce the mechanical properties of the materials, as shown in clinical studies(Braun;Frankenberger and Krämer, 2001; Merte;Schneider and Merte, 2004). Previous work at Newcastle University (Merie, 2023) has involved developing a bioactive glass capable of releasing large concentrations of fluoride when placed in an aqueous environment. The currently proposed project will involve developing composites using this glass, which are designed to release fluoride when placed in a neutral aqueous environment. The effect of the material's composition on the flexural strength (FS), flexural modulus (FM), degree of conversion (DOC), water sorption and fluoride release will be studied.

2 Literature review

2.1 Dental conditions requiring restorations.

2.1.1 Dental Caries

Dental caries is considered to be one of the most common oral diseases worldwide causing pain and eventually tooth loss. In the early stage of the disease, caries can be arrested and

reversed. However, disregarding the disease can lead to the destruction of tooth tissues and tooth loss (Featherstone, 2000; Health and Services, 2000; Kidd;Giedrys-Leeper and Simons, 2000; Kidd and Fejerskov, 2003; Pitts, 2004). Dental caries involves the localised destruction of the enamel and dentine by the acids formed by the bacterial metabolism of carbohydrate(Marsh and Martin, 1999; Kidd;Giedrys-Leeper and Simons, 2000; Kidd and Fejerskov, 2003). The disease starts within dental plaque and early changes in the tooth tissues are not noted clinically or radiographically. Dental caries is a chronic disease that can be seen in the crown and root surfaces of primary and permanent dentitions (Selwitz;Ismail and Pitts, 2007).

The four main factors that contribute to the development of dental caries are: time, diet, susceptible tooth surface, and saliva and bacterial biofilm where the interaction of bacterial biofilm with the fermentable carbohydrates occurs on the tooth surface over time (Figure 2-1) (Selwitz;Ismail and Pitts, 2007). Dental plaque on the tooth surface consists of a bacterial biofilm which produces acids as a by-product of carbohydrate metabolism. Calcium and phosphate minerals within the enamel and dentin can be broken down by these acids in a process called demineralisation (Featherstone, 1990; Featherstone, 2000).

A white-spot lesion is the first clinical appearance of enamel demineralisation under dental plaque. Demineralisation continues each time carbohydrates are present in the oral cavity and metabolised (Featherstone, 2000). In the early stage of dental caries, remineralisation can take place through the uptake of fluoride, calcium, and phosphate. The progression of caries depends on the balance between remineralisation and demineralisation. This process might lead to cavitation, reversal, or maintenance of the current status. The remineralised spot has less microporous enamel and a higher amount of fluoride than the original enamel,

thus more resistant to acid attack since the fluorapatite formed in the remineralised spot is less soluble and stronger than hydroxyapatite (Axelsson, 2000; Featherstone, 2004).

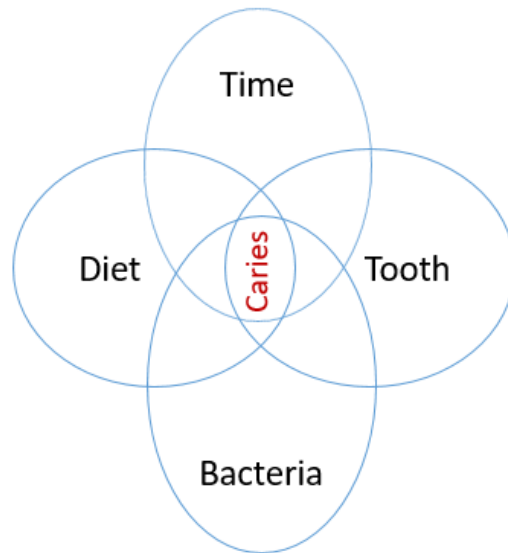


Figure 2-1: Caries risk factors.

Mutans streptococci and lactobacilli are the most important groups of microorganisms found within the bacterial biofilm. The mutans streptococci group includes different cariogenic species such as *Streptococcus mutans* and *Streptococcus sobrinus*. The lactobacilli and mutans streptococci species tend to produce lactic acid, which appears in the dental plaque before the development of caries (Loesche, 1986; Leverett *et al.*, 1993a; Leverett *et al.*, 1993b).

Biological and physical risk factors for tooth structure comprise a high concentration of bacteria, low salivary flow, inadequate fluoride exposure, gingival recession, and genetic factors. Moreover, a person's lifestyle and behaviour, which is under their control, may increase their risk factors. Examples of these factors are poor dental care, poor dietary

habits, such as increased consumption of carbohydrates, sugar, and medicines containing sugar (Featherstone, 2003; Kidd and Fejerskov, 2003; Touger-Decker and Van Loveren, 2003; Thomson, 2004). Other risk factors for caries include a lower socioeconomic status, poverty, availability of dental insurance coverage, use of orthodontic appliances and poorly designed or ill-fitting dentures (Kidd; Giedrys-Leeper and Simons, 2000; Ramos-Gomez *et al.*, 2003; Curzon and Preston, 2004).

Dental caries can be prevented by increasing the use of protective methods and decreasing the presence of pathological factors (Featherstone, 2004). Bacteria and the frequency of ingestion of fermentable carbohydrates are pathological factors (Featherstone, 2000).

Several studies have shown a greater amount of mutans streptococci and lactobacilli in the saliva or biofilm of patients with high caries rate (KLOCK and KRASSE, 1977; Alaluusua *et al.*, 1987; SEPPÄ and HAUSEN, 1988; Klock *et al.*, 1989; Featherstone, 2000). Protective factors include saliva, fluoride application, pit and fissure sealants, and antibacterial therapy such as treatment by mouth rinse containing chlorhexidine gluconate (Featherstone, 2000; Featherstone, 2004; Selwitz; Ismail and Pitts, 2007).

Early carious lesions can be successfully prevented through removal of the bacterial biofilm, the application of fluoride, the placement of pit and fissure resin sealants. However, if the lesion cannot be remineralised and demineralisation has progressed to dentin, restorative intervention is required (Selwitz; Ismail and Pitts, 2007). However, the durability of restorations without preventive strategies are short, and recurrent caries can be seen if the causes are not managed (Mjör and Toffentti, 2000). Fluoride toothpaste is the best method to maintain a constant fluoride level in the mouth (Frencken *et al.*, 2012). Fluoride-containing products, such as mouth rinses, varnishes and toothpastes, can decrease the

incidence of caries by up to 70% compared with no fluoride. Furthermore, a water fluoridation system has been shown to be effective in decreasing the severity of the disease (Featherstone, 2004). Toothpastes containing fluoride has been shown to be effective in caries prevention when used for one year (Marinho *et al.*, 2003). In another study, fluoride gel showed a caries inhibitory effect in children when compared with a placebo or no treatment (Marinho *et al.*, 2015).

Saliva plays an important role in caries prevention or reversal. Saliva provides calcium, phosphate and proteins. These components are able to neutralise the acids from bacterial metabolism, clear carbohydrates from the dental plaque and prevent demineralisation (Featherstone, 2000). A lack of saliva production will cause fast progressive caries. Head and neck radiotherapy, diseases like Sjögren's syndrome and some medication can reduce the production of saliva. Therefore, patients who are on these medications or receiving radiotherapy should be examined regularly and undertake preventive programmes to reduce the incidence of caries (Selwitz;Ismail and Pitts, 2007)

2.1.2 Tooth surface loss

Tooth surface loss (TSL) or tooth wear (TW) is a condition that affects the tooth tissues. TW is caused by factors other than dental caries (Hattab and Yassin, 2000; Mehta *et al.*, 2012; Hemmings *et al.*, 2018). Physiological TW has been found to be 20-38 μm annually (Lambrechts *et al.*, 1989). Factors that cause pathological TW are attrition, erosion, abrasion and abfraction (Mehta *et al.*, 2012). The causes of TW are multifactorial. Patients can have TW due to simultaneous erosion, abrasion and attrition. Each condition should be addressed for better diagnosis, prevention and treatment (Hemmings *et al.*, 2018).

Attrition is loss of tooth tissues as a result of masticatory forces. The early sign of attrition is small facet on the cusps of molars and premolars, and the flattening of the incisal edge of anterior teeth. Shortening of the clinical crown with exposure of dentine and pulp can occur in advanced stages (Kelleher and Bishop, 1999; Mehta *et al.*, 2012). Attrition has been shown to be a result of parafunctional activity. Some researchers have argued that premature contact can cause attrition (Ramfjord, 1961; Smith and Robb, 1996), but there is no evidence to support this theory (Singh and Jindal, 2010).

Erosion is the loss of tooth tissues as a result of the exposure to intrinsic or extrinsic acids (Bishop *et al.*, 1997). The early signs of this condition appear as a shallow smooth surface in the palatal or lingual surfaces of upper or lower teeth. Cupping on the occlusal surface or incisal edge can occur in severe cases (Hattab and Yassin, 2000). Erosion can occur when the pH is below 5.5 (Smith, 1984). It can be divided into external or internal erosion (Eccles, 1982; Mehta *et al.*, 2012; Hemmings *et al.*, 2018). Extrinsic erosion involves the consumption of acidic food and drink, and some medications such as aspirin, which contain salicylic acid (Van't Spijker *et al.*, 2009). Intrinsic erosion is caused by gastric acid, which can be voluntary or involuntary. Excessive alcohol intake and pregnancy can cause involuntary vomiting (Reid *et al.*, 1988).

Gastro-oesophageal reflux disease (Frencken *et al.*, 2012) can cause the regurgitation of stomach acids; these have a low pH and are very erosive to tooth tissues (Schmidt and Treasure, 1997). Moreover, eating disorders such as bulimia increase the incidence of voluntary vomiting, which leads to erosive TW (Milosevic, 1999).

Abrasion is caused by external mechanical process, such as an external object repeatedly contacting the tooth tissues. It can be caused by habits such as pipe-smoking, pen-chewing

and, most commonly, aggressive tooth brushing (Mehta *et al.*, 2012; Hemmings *et al.*, 2018). Abrasion can appear as a V-shaped or rounded ditch on the cervical area of the tooth (Mehta *et al.*, 2012).

Abfraction is a TW caused by eccentric occlusal forces, leading to a tensile and compressive load on the cervical area of the tooth (Mehta *et al.*, 2012; Hemmings *et al.*, 2018) and is claimed to be a result of a combination of erosion, abrasion and attrition; these conditions can accelerate the cervical wear caused by eccentric occlusal force (Munoz *et al.*, 1999).

Prevention of TW

Dentists should educate the patient about the need to reduce the quantity and frequency of acid-containing foods or drinks (Mehta *et al.*, 2012; Hemmings *et al.*, 2018). Beverages can be modified, for example, by adding calcium lactate into carbonated drinks, to decrease the erosive potential. In the case of acute pain due to TW, a desensitising agent or fluoride varnish can be applied to the exposed dentine. Fluoride application can protect the teeth from further erosion by increasing the hardness of the dentin through the formation of fluorapatite, which is less soluble than hydroxyapatite under acidic conditions (Munoz *et al.*, 1999). Desensitising agents can effectively decrease dentine sensitivity and can be applied to the exposed dentine at home or at a dental clinic (Thrash;Dodds and Jones, 1994).

Potassium fluoride toothpaste can decrease dentin hypersensitivity by the penetration of the ions into the dentinal tubules and decreasing the excitability of the tooth nerve transmitting the pain (Chu and Lo, 2010; Mehta *et al.*, 2012).

Occlusal splints are a very successful tool in preventing further TW from attrition (Hemmings *et al.*, 2018). Where restoration of the tooth is needed Glass ionomer cements (GIC) can be used to temporarily restore the exposed tissue until a treatment plan has been finalised.

However, in severe cases root canal treatment or tooth extraction might be needed (Mehta *et al.*, 2012).

2.1.3 Dental trauma

Dental trauma refers to injuries to the teeth and periodontal tissues such as injuries to dental soft tissues, the maxilla and mandible, and facial tissues (Andreasen;Andreasen and Andersson, 2019). There are several classification systems for dental trauma. Some only include tooth trauma and some include the supporting structures and jaw bones (Bastone;Freer and McNamara, 2000). The gold standard classification of dental trauma was developed by Andereasen, by modifying the World Health Organisation (WHO) classification (Organization, 1994; Andreasen;Andreasen and Andersson, 2019). This classification can easily be used in dental office with the help of diagnostic tools, such as illumination lights, sensitivity test and radiographs (Lauridsen *et al.*, 2012). Andreasen classified injuries of the hard tooth tissues and pulp into:

1. Enamel infraction includes crack on the enamel without chipping.
2. Uncomplicated enamel fracture.
3. Uncomplicated enamel and dentine fracture with no pulp involvement.
4. Complicated crown fracture includes enamel, dentine, and pulp.
5. Uncomplicated crown-root fracture which includes enamel, dentine with pulp exposure.
6. Root fracture including dentine, cementum and pulp.

Andreasen also classified periodontal injuries, and injuries to the supporting bony tissues, gingiva and oral mucosa (Andreasen;Andreasen and Andersson, 2019).

Sports, violence and road accidents are the most common causes of dental trauma (Bastone;Freer and McNamara, 2000). Children with a low socioeconomic status were found to be at higher risk of receiving injuries (Hamilton;Hill and Holloway, 1997). A maxillary overjet greater than the 0-3.5mm normally seen, as in case of a class II occlusal relationship, and incomplete lip closure are the most common predisposing factors for traumatic injuries (Burden, 1995; Stokes *et al.*, 1995; Kania *et al.*, 1996).

Since playing sports is the most common cause of dental trauma, it is very important to use mouthguards or faceguards or other protective devices during these activities (Andreasen;Andreasen and Andersson, 2019). Mouthguards have been found to decrease the incidence of trauma during football games by 50% (Jolly;Messer and Manton, 1996). In addition, wearing seatbelts in a car or a helmet when riding a bicycles or motorbike can provide good protection (Bastone;Freer and McNamara, 2000).

2.1.4 Treatment strategies

Dentists should provide dietary advice to their patients to reduce their consumption of sugary food and drinks, which will significantly help reduce the risk of caries (Moynihan, 2002). Food or drinks containing sugar should be avoided close to bedtime due to the reduced salivary flow and therefore low buffering function (Wikner and Söder, 1994; Moynihan, 2002). Cheese and sugar-free chewing gum have been found to help neutralise the acidic pH after meals (Moynihan, 2002). Several studies have found that sugar-free gum can help prevent the occurrence of caries (Hayes, 2001). In addition, hard cheese can help protect the teeth from dental caries (Gedalia *et al.*, 1994).

The prevalence of dental erosion in children is very high. Amongst children aged four to six, 65% have dental erosion, as do 62% of high school students (Smithers *et al.*, 2000). Drinking citrus juice two or more times a day has been shown to increase the risk of dental erosion (Jarvinen; Rytomaa and Heinonen, 1991). Patients should be aware of the type of food or drink that may cause harm to their teeth. Food and drink that have a low potential for caries or erosion should be recommended especially for high risk patients (Moynihan, 2002).

Good oral hygiene has an impact on overall health. It can prevent dental caries, gingivitis and periodontitis. Preventing the formation of plaque on tooth surfaces in order to prevent caries and gingival diseases is the main objective of dental hygiene. Dentists and dental hygienists should educate every patient about oral cleaning methods and check on them regularly (Lindenmüller and Lambrecht, 2011). It is recommended to replace toothbrushes every three to four months (Association, 2002).

Fluoridated toothpastes must be used for tooth cleaning. Most fluoride-containing toothpastes contain sodium fluoride, amine fluoride and sodium monofluoride, which help remineralise the enamel and decrease the formation of dental plaque. Fluoridated toothpastes usually have 1500 ppm of fluoride. They also contain substances such as silicate, magnesium or aluminium oxide which help remove plaque and discolouration. The amount of previous substances should be low to avoid the abrasive effect on the enamel surface (Association, 2002).

In cases of dentin hypersensitivity, potassium nitrate and amine fluoride help protect against sensitivity by forming a layer of calcium fluoride on the exposed dentinal tubules (Pettersson and Kambara, 2004). Fluoride gels usually have a high fluoride (12500 ppm), and

can be used weekly in addition to regular oral care, especially in patients at a high risk of caries (Altenburger *et al.*, 2008).

One of the many ways to provide fluoride is by adding fluoride to the public water (Iheozor-Ejiofor *et al.*, 2015). Fluoride levels in public water supplies should be set at 1 ppm (Edition, 2011). Fluoride level of 1.5 ppm has been found to cause fluorosis (Cury *et al.*, 2019). Water fluoridation can prevent dental caries. It has been shown to decrease the incidence of caries in children by 70% and decreased tooth loss in adults by up to 60% (Burt and Eklund, 1999). Finally, water fluoridation is a good way to maintain a constant level of fluoride in the oral cavity, although it should not exceed the optimal level as this might cause dental and skeletal fluorosis (McDonagh *et al.*, 2000).

Dental restorations are regularly used to restore severely carious teeth, tooth wear, or fractured enamel and dentine. Direct restorations are usually placed when a small amount of tooth structure is lost. However, in large defects in which cusps are lost, for example, indirect restorations may be the treatment of choice (Opdam;Frankenberger and Magne, 2016). Composite restorations have been shown to be suitable to restore large anterior and posterior defects including cusp coverage (Opdam *et al.*, 2010; Attin *et al.*, 2012). A systematic review evaluating the longevity and performance of direct and indirect materials found no difference between direct and indirect techniques in the treatment of tooth wear (Mesko *et al.*, 2016). In cases that require full mouth rehabilitation and an increasing vertical dimension of occlusion, indirect restoration techniques are preferred as they offer better control of occlusal reconstruction (Opdam;Frankenberger and Magne, 2016). Available indirect restorations include inlays, onlays and crowns using gold, metal and ceramic materials.

Different materials have been used to directly restore carious teeth, such as amalgams, composites, glass ionomer cements and compomers. Amalgam has been used successfully for decades as the main dental restoration. However, increasing demand for more aesthetic and conservative restorations with improved physical and mechanical properties has made the composites the material of choice for anterior and posterior teeth (Arola;Galles and Sarubin, 2001; Wille *et al.*, 2016).

Dental amalgam:

Dental amalgam has been used in dentistry for more than 150 years. The material is composed of mercury, silver, tin, and copper. Dental amalgam offers high durability, wear resistance, low cost, and high compressive strength in comparison with resin composites. On the other hand, amalgam restorations are brittle materials, are less conservative, are subject to corrosion, and their use has been questioned due to their mercury content (AFFAIRS, 2003; Rathore;Singh and Pant, 2012; Moraschini *et al.*, 2015). However, the amount of mercury released per day in patients with high amalgam load was 7.4 µg which is below the maximum dose of 30 µg suggested by the WHO (Halbach *et al.*, 2008) Major health organisations have declared dental amalgams to be safe and effective material. The use of amalgams is now decreasing for a range of reasons, such as the demand for more aesthetic restorations and improvements in resin-based composites (Dodes, 2001; AFFAIRS, 2003).Furthermore, the use of dental amalgam will be phased out following the Minamata convention agreement on mercury that works toward the decrease and suspension of the use of mercury containing products such as dental amalgam due to the health concern about mercury exposure to individuals and environment (Kessler, 2013; Coulter, 2016).

Resin-based Composites (RBCs):

RBCs were first developed in the 1960s. The first composites were chemically activated, before photo-polymerised composite with ultraviolet (UV) light were developed. UV was then replaced by visible light cure composites (Sakaguchi and Powers, 2012). RBCs can be used as restorations, cavity liners, pit and fissure sealants, posts and cores. Resin composites are the treatment of choice for posterior teeth in many countries (Lynch *et al.*, 2014a). The major advantages of using RBCs are the variety of colour shades and the ability to chemically bond to the tooth structure, which offers more conservative cavity preparation (Chan *et al.*, 2010). A meta-analysis of 12 studies showed a good survival rate of 97.6% after 10 years (Opdam *et al.*, 2014). Furthermore, composites show a better 12 year survival rate compared with amalgam, and 10 years comparable survivability (Opdam *et al.*, 2010). Moreover, posterior composites showed a low annual failure rate of 1-3% in clinical studies at more than five years follow-up (Manhart *et al.*, 2004; Demarco *et al.*, 2012).

Glass ionomer cements:

GICs contain polyalkenoic acids and silicate glass. The glass is composed mainly of silica, alumina and fluoride (termed fluoroaluminosilicate glasses). This material sets by an acid-base reaction. The fluoride and other ions are released from the glass after mixing with the acid. In the first 24-48 hours, the maximum amount (ranging from 5-155 ppm) of fluoride is released from the glass (HÖRSTED-BINDSLEV and LARSEN, 1990; Creanor *et al.*, 1994; De Araujo *et al.*, 1996; Bell *et al.*, 1999; Attar and Önen, 2002; Yap *et al.*, 2002; Attar and Turgut, 2003a; Wiegand; Buchalla and Attin, 2007; Anusavice; Shen and Rawls, 2012). It has been shown that the amount of fluoride decreased from 15-155 ppm at day 1 to 0.9-4 ppm

after 2 months (Perrin;Persin and Sarrazin, 1994). Long term fluoride release can occur up to 3 years after placement (FORSTEN, 1990; Creanor *et al.*, 1994; Preston *et al.*, 1999; Williams;Billington and Pearson, 2001; Asmussen and Peutzfeldt, 2002b). Metal reinforced GICs release less fluoride compared to conventional ones which may be due to silver fluoride ions tend to bind the fluoride to the cement, thus decreasing the fluoride release (Olsen *et al.*, 1989; El Mallakh and Sarkar, 1990).

The fluoride released from GICs is a result of the degradation of the glass during the setting reaction. The fluoride is then released into the matrix and leached from the cement (O'Brien, 2002). The mechanism of fluoride release from GICs is unclear, but researchers agree on a kinetics consisting of short-term and long-term processes. Short-term fluoride release occurs within 1-2 days, declines in the first week, and stabilizes after 2-3 months. Long-term fluoride release is significantly lower (Luo;Billington and Pearson, 2009).

GICs can also recharge and re-release fluoride to the surrounding tooth structures. These materials act as fluoride reservoirs to maintain fluoride and help preventing secondary caries (Dionysopoulos *et al.*, 2013). The recharging ability of these materials depends on the intrinsic factors such as the material composition and environmental factors such as the frequency of fluoride exposure and intensity (Han *et al.*, 2002; Preston *et al.*, 2003). Fluoride released from GIC after recharging showed a significant increase after 24 hrs followed by significant decrease after few days, and the amount released is lower than the initial fluoride release (De Witte *et al.*, 2000; Peng *et al.*, 2000; Attar and Önen, 2002; Attar and Turgut, 2003b).

GICs are commonly used as luting agents for crowns and bridges, cavity liners, and primary teeth restorations. Also, GICs are usually used to restore small cavities such as class V and

class III carious lesions. However, due to inferior mechanical properties compared to RBCs, GICs are not usually used as permanent filling for posterior teeth where strength and resistance to wear is crucial (Berg, 2002). The flexural strength (FS) of different commercially available GIC has been shown to range between 15-51 MPa (De Witte *et al.*, 2000; Peng *et al.*, 2000; Bapna;Gadia and Drummond, 2002; Berg, 2002; Lohbauer *et al.*, 2003), which is lower than the FS of commercial resin-based composite (RBCs) that showed a range between 62-160 MPa (Ilie and Hickel, 2009a; Ilie and Hickel, 2009b; Ilie *et al.*, 2013).

Resin-modified glass ionomer cements and polyacid-modified resin composites:

In RMGICs, methacrylate monomers are added to the polyalkenoic acid. The acid-base reaction starts first followed by the polymerisation reaction after light-activation. Polyacid-modified resin composites (termed compomers) are composed of composite monomers such as Bis-GMA with small amounts of acidic monomers, such as methacrylated phosphoric acid. The glass filler particles used are the same as in conventional GICs but smaller in size. RMGICs and compomers were developed to solve the problems of low mechanical properties and high solubility of the conventional GICs. Giomers are a hybrid materials in which the acid-base reaction completed before incorporating the resin matrix (Wiegand;Buchalla and Attin, 2007).

It has been found that RMGICs can release similar amounts of fluoride to conventional GICs. However, the type and amount of the resin used can have an effect. For example, when HEMA is used as a co-monomer it has a strong affinity to water, thus allowing more diffusion of fluoride ions (Momoï and McCabe, 1993; Musa;Pearson and Gelbier, 1996; Robertello *et al.*, 1999; Tjandrawinata;Irie and Suzuki, 2004). As with GICs, the highest fluoride release occurs during the first day and decreased afterwards (Creanor *et al.*, 1994;

De Araujo *et al.*, 1996; Karantakis *et al.*, 2000). RMGICs continue to release fluoride for up to 2.7 years (Karantakis *et al.*, 2000; Williams;Billington and Pearson, 2001).

Compomers release small amounts of fluoride in the first 24 hours which then increases in the next few days, but in lower amount compared to conventional GICs and RMGIC (Yip and Smales, 2000; Attar and Önen, 2002; Dionysopoulos;Kotsanos and Pataridou, 2003).

Compomers of different brands with high fluoride content and smaller filler size can release higher amounts of fluoride than GICs (Attin *et al.*, 1996). Compomers release a significantly lower amount of fluoride compared to GICs in the first year, but after one year, the daily fluoride release has been shown to be similar to GICs (Asmussen and Peutzfeldt, 2002b).

The reason of the delayed and low amounts of fluoride release is the high crosslinked and less hydrophilic composite resin matrix. The fluoride release increases over time due to water diffusion, which forms hydrogen ions that attack fluoride-containing glass particles to release fluoride. This reaction occurs only after sufficient water has been absorbed for a certain period, allowing the release of fluoride to be more noticeable.(Asmussen and Peutzfeldt, 2002a; Wiegand;Buchalla and Attin, 2007).

Giomers are resin-based materials containing pre-reacted glass ionomer fillers. The fluoroaluminosilicate glass has been reacted with polyacid forming a glass ionomer matrix before mixing it with the resin system (Colceriu Burtea *et al.*, 2019). Similar to compomers, giomers have no initial burst release and the material release low amount of fluoride in the first 12 months, but the cumulative fluoride release is significantly higher than the compomer, but lower than the conventional GIC and RMGIC (Itota *et al.*, 2004b; Bansal and Bansal, 2015). The mechanical strength of the giomers is significantly higher than the

conventional GIC and RMGIC with a FS value more than 100MPa (Abdel-Karim;El-Eraky and Etman, 2014; Ilie, 2016; Colceriu Burtea *et al.*, 2019)

2.2 Composition of Conventional Resin-based Composites

RBCs have four major components: organic matrix, inorganic filler, coupling agent, and initiators and accelerators (Ferracane, 2011).

2.2.1 Organic matrix

Dimethacrylate monomers are the most common organic matrix used in most composite materials (Sakaguchi and Powers, 2012). Bisphenol A-glycidyl methacrylate (Bis-GMA) is the most commonly used monomer in dental composites. Bis-GMA has a higher molecule weight and the molecular structure with hydroxyl groups and an aromatic core reduces the flexibility of this materials (Figure 2-2) (Barszczewska-Rybarek;Chrószcz and Chladek, 2020). Using Bis-GMA has an advantage of increased mechanical properties of dental composites, but the high viscosity of this material can reduce the amount of filler loading in the polymer matrix (Barszczewska-Rybarek;Chrószcz and Chladek, 2020; Alrahlah *et al.*, 2021). Therefore, low molecular weight monomers such as triethylene glycol dimethacrylate (TEGDMA), hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EDMA) are added to dilute the viscosity and obtain a clinically acceptable paste material (Peutzfeldt, 1997; Lavigueur and Zhu, 2012; Anusavice, 2013; Noort, 2013).

Urethane dimethacrylate (UDMA) monomer contains peripheral carbon double bonds which can undergo an addition reaction through free-radical polymerisation. UDMA has lower viscosity and higher flexibility compared to Bis-GMA (Asmussen and Peutzfeldt, 1998). The flexible aliphatic core the UDMA has will enable hydrogen bonding resulting in greater

reactivity and double bond concentration (Barszczewska-Rybarek, 2009). UDMA monomers allow more filler loading compared to Bis-GMA (Cho *et al.*, 2022). Since UDMA has a lower molecular weight and viscosity than Bis-GMA it can be used alone. However, it is usually incorporated with other low viscosity monomers to increase the handling properties and overall performance of the material (Chen, 2010; Lavigueur and Zhu, 2012).

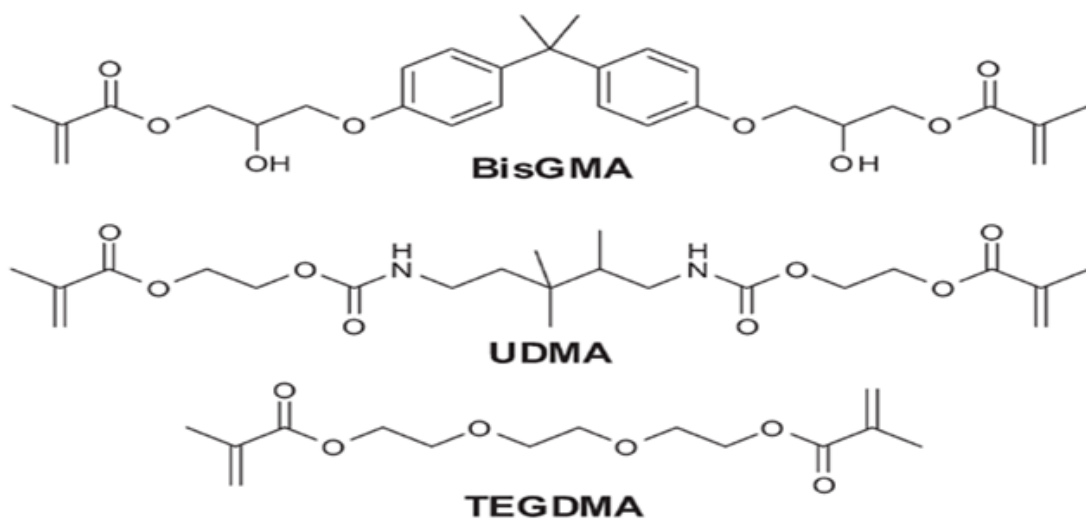


Figure 2-2: Structure of Bis-GMA, UDMA & TEGDMA (Lavigueur and Zhu, 2012).

TEGDMA, the most commonly used co-monomer, is known to reduce the viscosity of mixtures containing monomers such as Bis-GMA and UDMA, which results in improving the degree of polymerisation by enhancing the monomer's mobility during the polymerisation process (DOC) (Atai and Watts, 2006; Floyd and Dickens, 2006). This increase in the polymerisation rate leads to polymerisation shrinkage (Sideridou;Tserki and Papanastasiou, 2003; Gajewski *et al.*, 2012). TEGDMA contains ethylene oxide groups at each end of the

monomer chain that increase the monomer reactivity (Sideridou;Tserki and Papanastasiou, 2002).

The high molecular weight and the multiple functional groups and the in the Bis-GMA and UDMA affect the physical and handling properties of the materials. Also, Bis-GMA has a rigid benzoic ring which affect the material's displaceability, flexibility, and intermolecular forces when compared to UDMA that has an ester group. When these materials are light-cured, they show a low double bond conversion and the network formed will lower the monomer and oligomeric molecule mobility. This result in unreacted monomer becoming trapped in the materials, lowering the DOC, which may affect the physical properties and strength. Adding the low molecular weight TEGDMA monomer leads to less stiff polymers than the higher molecular weight polymers (Lovell *et al.*, 2001a; Sideridou;Tserki and Papanastasiou, 2002; Dickens *et al.*, 2003; Floyd and Dickens, 2006).

HEMA (Figure 2-3), which is used as a co-monomer, is commonly used in dental adhesives, resin-modified glass ionomer cements (RMGICs), and luting composites (Moszner and Hirt, 2012; Sidhu and Nicholson, 2016). This material decreases viscosity of BisGMA and UDMA containing mixtures due to its lower molecular weight and also improves the adhesive resin infiltration and the bond strength to the dentin when used in dental adhesive system (Szczesio-Wlodarczyk *et al.*, 2022). HEMA, due to the hydrophilicity, can absorb water and facilitate the ion exchange which can help in ion-releasing restorative materials. However, high water sorption of the HEMA containing materials lead to low mechanical strength and degradation of the polymer matrix (Takahashi *et al.*, 2011).

HEMA helps to decrease the phase separation and enhance the miscibility between the hydrophilic and hydrophobic materials when used in self-etch adhesive resin (Van Landuyt

et al., 2005; Felizardo *et al.*, 2011). When the water molecules diffuse through the intermolecular spaces within the polymer chains, the phase separation take place where the distance between the chains increase, with swelling of the resin matrix and degradation of the silane interface (Wilson;Zhang and Antonucci, 2005). HEMA is commonly used in RMGIC to activate the acid-base reaction (Francois *et al.*, 2020), produce higher fluoride release, water sorption and ion exchange when compared to HEMA-free adhesives (Malacarne *et al.*, 2006). However, the increased water sorption caused by HEMA leads to hydrolytic bond breakdown which impact on the longevity of the adhesion (Ahmed *et al.*, 2021; Pimentel de Oliveira *et al.*, 2022). Furthermore, HEMA has shown a cytotoxic effect towards the dental tissues considering the fact that the material can release from the adhesives and transfer into the dental pulp (Bakopoulou;Papadopoulos and Garefis, 2009; Gallorini;Cataldi and Di Giacomo, 2014).

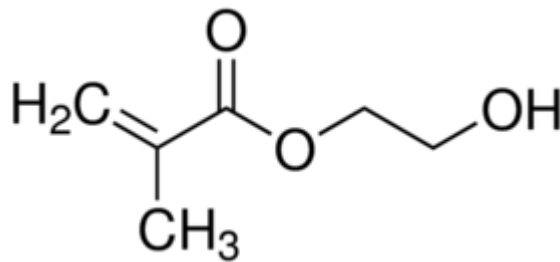


Figure 2-3: Structural formula of HEMA (Sigma Aldrich).

Polymerisation shrinkage is a big concern for the performance of dimethacrylate-based composites (Boaro *et al.*, 2010). The higher the monomer's molecular weight, the lower the carbon double bonds per unit volume, which lead to a lowering of the DOC and

polymerisation shrinkage (Sideridou;Tserki and Papanastasiou, 2002; Kleverlaan and Feilzer, 2005; Dewaele *et al.*, 2006). Some manufacturers have worked to develop a low-shrinkage resin composite. Some composites have been made based with Bis-GMA alone in an attempt to reduce shrinkage, however, the results showed high polymerisation stresses (Boaro *et al.*, 2010). Other materials have used Bis-GMA or UDMA in combination with new high molecular weight monomers such as tricyclodecane-urethane dimethacrylate (TCD-urethane) or dimer dicarbamate dimethacrylate, these materials showed a decrease in the polymerisation shrinkage (Figure 2-4) (Trujillo-Lemon *et al.*, 2006; Boaro *et al.*, 2010).

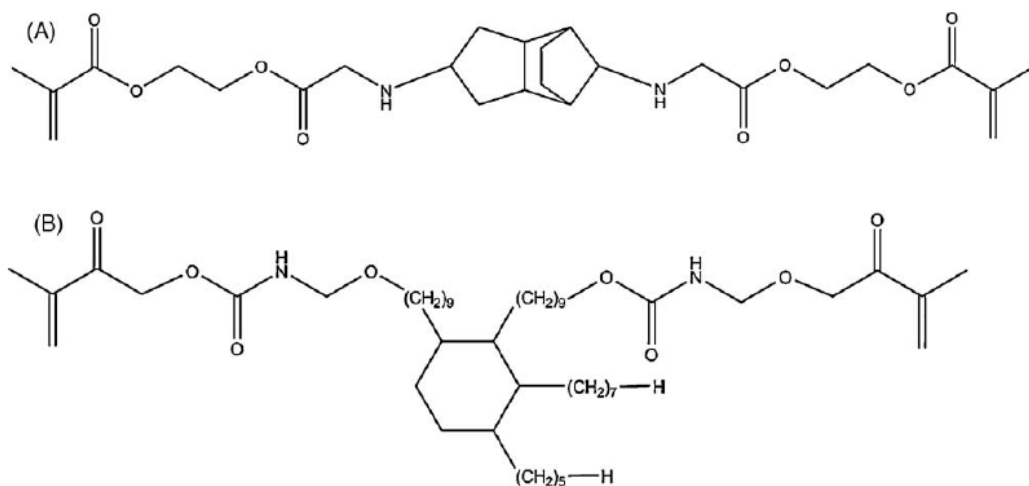


Figure 2-4 Structure of TCD-urethane (A) and dicarbamate dimethacrylate (B)(Boaro LCC, 2010)

2.2.2 Inorganic fillers:

Filler materials are particles added to increase the strength, provide a different degree of translucency and control the curing shrinkage of the composites. The filler's size, type and concentration affect the physical and mechanical properties of the material. Fillers include borosilicate glass, aluminium silicate, lithium aluminium silicate and fused quartz. Moreover, most fillers contain barium, ytterbium fluoride, strontium, zirconium and zinc glasses, which

gives the material radiopacity (Anusavice;Shen and Rawls, 2012; McCabe and Walls, 2013).

Quartz is a very hard filler that cannot be ground into fine particles. In contrast, amorphous silica has the same composition as quartz, but is less hard and therefore decreases the abrasiveness and increases the polishability of the composites (Anusavice;Shen and Rawls, 2012).

The filler particles come in different shapes such as round, irregular, splinter and spherical.

Due to the different surface area, different particle shapes can affect the amount of the resin matrix incorporated into the intra-particles spaces (MIYASAKA and YOSHIDA, 2000).

Moreover, the particle size distribution can affect the mechanical properties of the RBCs. A uniform particle size results in higher voids within the matrix, while a broad spectrum of particle sizes can improve the mechanical properties (Willems *et al.*, 1992; Ferracane, 1995; Ferracane, 2011).

RBCs can be classified based on the filler size such as micro- or macrofilled composites, or based on the physical characteristics such as flowable or packable composites. The most commonly used classification is the one based on the filler size.

Conventional macrofilled composites have an average particle size ranging from 1-50 μm and contain around 75-80% inorganic fillers by weight. Due to the large size and increased hardness of the particles, these composites are hard to finish and polish. Furthermore, the organic resin matrix wears off faster than the fillers, which causes roughening of the surface and discoloration (Harold *et al.*, 2012).

Microfilled composites were developed to overcome the aesthetic problems of conventional composites. Microfilled composites have a filler content of around 35-60% by weight and contain colloidal silica with a diameter of 0.01 to 0.05 μm . These small fillers size combined

with low filler content result in an aesthetically acceptable restoration that is easy to polish and maintain the smooth surface, but are not as strong as macrofilled or hybrid composites which have filler content exceeding 70% by weight (Ferracane, 2011; Anusavice; Shen and Rawls, 2012; Harold *et al.*, 2012).

In an attempt to develop a material with adequate strength and high polishability, hybrid composites were introduced. These composites are a mixture of microfilled and macrofilled composites produced after grinding the large filler particles to small particles of 1 μm diameter. Further grinding of the small fillers results in microhybrid composites with average particle size of 0.4- 1 μm . These composites are considered universal composites and can be used to restore anterior and posterior teeth because they are combining strength and polishability. Nanohybrid composites are a modification of microhybrid composites developed by adding nanoparticles such as pre-polymerised fillers (Ferracane, 2011; Anusavice; Shen and Rawls, 2012; Sakaguchi and Powers, 2012).

Nanofilled composites have a small particle size in the range of 1-100 nm. The small nanoscale particles allow an increased filler load due to increased surface area, which produced a material with high mechanical properties and low polymerisation shrinkage (Figure 2-5) (Moszner and Salz, 2001; Beun *et al.*, 2007; Ferracane, 2011).

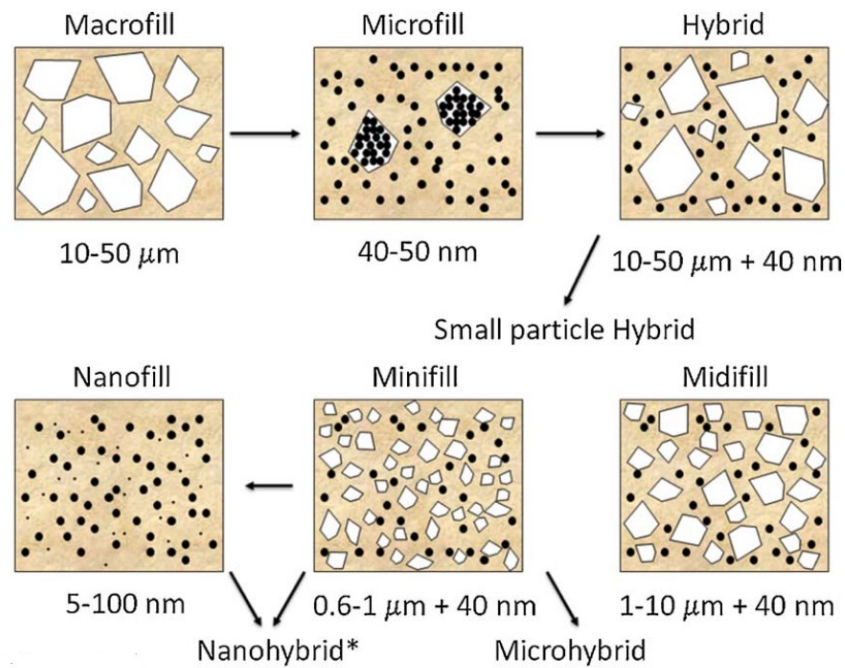


Figure 2-5: Classification of fillers (Ferracane, 2011).

2.2.3 Coupling agent:

Coupling agents are materials used to bond inorganic fillers with the organic matrix of the resin composites (Sakaguchi and Powers, 2012). The most commonly used coupling agents in dental materials include titanate, zirconate and silane (Chen *et al.*, 2018b), of which silane coupling agents are the most commonly used, due to their structural similarity with silica and quartz (Matinlinna and Vallittu, 2007). The most common silane coupling agent is 3-methacryloxypropyltrimethoxysilane (3-MPS) due to the presence of the functional polymerisable methacrylate end group (Matinlinna *et al.*, 2004; Antonucci *et al.*, 2005) (Figure 2-6).

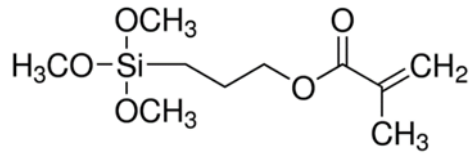


Figure 2-6: Chemical structure of MPS (Sigma Aldrich).

Silane coupling agents contain two functional groups that connect the inorganic fillers to the organic resin matrix. During the surface treatment of the filler particles, the methoxy group undergoes a hydrolysis process, resulting in the formation of a hydroxyl group. This hydroxyl group reacts with the hydroxyl group on the filler and creates a covalent bond. During the polymerisation, the unreacted double bonds on the methacryloxy group react with the monomer (Sakaguchi and Powers, 2012).

Several studies have found that silanisation of the filler particles improves the physical and mechanical properties of the RBCs (Lin *et al.*, 2000; Park and Jin, 2003; Tham;Chow and Ishak, 2010; Lung *et al.*, 2016). Furthermore, coupling agents have been shown to have a positive effect on the stability of the composites over time and prevent the degradation of the filler particles (Matinlinna *et al.*, 2004; Elshereksi *et al.*, 2017). Surface treatment of the filler by a coupling agent can decrease both the surface energy of the fillers and the resin viscosity to promote good diffusion of the filler into the resin. Furthermore, the surface treatment will improve interfacial bonding by providing a functional group on the filler to bond with the matrix (Bose and Mahanwar, 2005).

Fillers such as calcium salts and sodium glasses cannot be treated with a silane coupling agent (Antonucci *et al.*, 2005). There are some limitations in using a silane coupling agent to treat the filler surface. If there is no hydroxyl group on the filler surface, the reaction will not occur efficiently (Goyal, 2006). Modification of the silane by increasing the length of the

alkylene chain has been shown to make the silane more hydrophobic, thus increasing bond stability (Fuchigami *et al.*, 2016). While a silane coupling agent is still the material of choice for surface treatment of the filler, improvement of hydrolytic stability is needed to increase the durability of the bond (Chen *et al.*, 2018a; Matinlinna;Lung and Tsoi, 2018).

2.2.4 Initiators and activators:

The organic matrix of RBC contains initiators and accelerators which are responsible for polymerising the resin. The polymerisation process is activated either by chemical reaction after mixing two pastes together, or by a visible light cure system. In the chemically cured composites (self-cure composites), two paste systems are used, one containing the benzoyl peroxide which initiates the curing process and the second paste has the tertiary amine activator (Ferracane, 2011; Sakaguchi and Powers, 2012; Noort, 2013). Most of the light cure composites contain photoinitiators and amines as co-initiators in the same paste. The initiators do not react before exposure to a light source. Camphorquinone (CQ) (Figure 2-7), is the most common photoinitiator used in RBCs. It absorbs light at a wavelength of 468 nm. CQ is typically added in a very small amounts of 0.1- 1.0 % by weight. Once the light source hit the composites, CQ interacts with the co-initiator tertiary amine and produces free radicals, which initiate the polymerisation. When the CQ absorbs the light, it forms a photoexcitation complex with the tertiary amine and producing two free radicals: cetyl and amino, in which the amino is the one responsible for initiating the polymerisation process (Ikemura and Endo, 2010). N, N-dimethyl-p-toluidine (DMPT), ethyl-4-(dimethylamino) benzoate (EDAB) and dimethylaminoethyle methacrylate (DMAEMA) are an example of amine used as a co-initiator (Anusavice;Shen and Rawls, 2012). Some companies have introduced other photoinitiators that are more colour-stable (less yellow) than CQ, such as

1-phenyl-1,2-propanedione (PPD), bisacylphosphine oxide (Irgacure 819), and monoacylphosphine oxide (Lucirin TPO) (Park;Chae and Rawls, 1999; Stansbury, 2000; Neumann *et al.*, 2005).

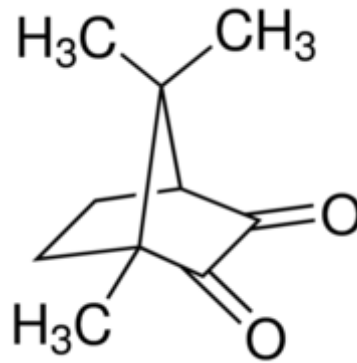


Figure 2-7: **Camphorquinone** (Sakaguchi and Powers, 2012)

2.2.5 Other additives

Pigments such as iron oxides are added in very small amounts (usually 1% or less) to provide the materials with a variety of shades. Fluorescent agents, such as 1,4-double-(benzoxazole group-2-group) naphthalene, are added to provide translucency in case of anterior restorations. High concentration of fluorescent agent will allow more light to pass through the restoration, therefore, less light will be scattered back to the observer, making it appear darker. Therefore, opacifiers such as titanium dioxide are added in small amounts to provide an acceptable aesthetic by increasing the light reflected to the dentists or observers (Haas *et al.*, 2017). It should be noted that darker shades need more light cure exposure time to ensure optimal polymerisation due to the presence of higher amounts of optical modifiers and pigments that affect the light transmission through the composite restorations (Anusavice; Shen and Rawls, 2013).

Inhibitors increase the shelf-life of the RBCs and maintain light stability. These materials are added to decrease the spontaneous polymerisation of the monomers. When the materials is dispensed, the inhibitor will react with the free radical before free radical react with the monomer and this will prevents the chain propagation and prevent the free radical from initiating the polymerisation process and ensure sufficient working time (Anusavice;Shen and Rawls, 2013). The most common inhibitor is butylated hydroxytoluene (BHT), which has good antioxidant properties and this will help to extend the resin's storage life (Anusavice;Shen and Rawls, 2013). The free radical polymerisation reaction occurs at a low level until the inhibitor is totally consumed (Hadis;Shortall and Palin, 2012).

2.3 Polymerisation of conventional RBCs

2.3.1 Free radical addition polymerisation

RBCs polymerisation is by free radical addition polymerisation. Addition polymerisation simply refers to connecting two molecules together to create a larger molecule. The reaction consists of four stages: activation, initiation, propagation and termination (Anusavice;Shen and Rawls, 2012; Sakaguchi and Powers, 2012; McCabe and Walls, 2013).

2.3.2 Methods of activation

The activation of RBCs can occur chemically by mixing materials together, radiation through light cure activation, or both. The polymerisation of self-cure composites is initiated using benzoyl peroxide and activated using tertiary amine such as N, N' dimethyl-p-toluidine. When mixed together, these two materials form a free radical followed by addition polymerisation (Anusavice;Shen and Rawls, 2012; Noort, 2013).

The first light-activated composites used ultraviolet light (UV) to produce free radicals. UV has since been replaced by visible light cure (VLC), which shows a better depth of cure and better control over the working time. VLC composites come in a single paste containing photoinitiator such as CQ and tertiary amine as a co-initiator. Composites are sensitive to oxygen inhibition during the initial phase of the polymerisation. Oxygen reacts with the monomer and prevents the conversion, forming a layer of unpolymerized surface. Dual cure materials use both chemical and light activation (Anusavice;Shen and Rawls, 2012; Noort, 2013).

2.3.3 Degree of Conversion

At the initiation stage of light activated composites, the free radical species reacts with monomer radicals. In the propagation stage, an addition of another monomer molecule occurs to form a polymer chain. This theoretically continues until the polymer chain is terminated, and all the free radicals react. The presence of carbon double bonds makes the resin highly crosslinked (Anusavice;Shen and Rawls, 2012). In reality, not all of the monomers react and so, the degree of conversion (DOC) is measured by comparing the amount of remaining carbon double bonds in the polymer chain compared to unpolymerised monomers (Sakaguchi and Powers, 2012; Leprince *et al.*, 2013). The DOC of RBCs has been found to vary from 35-77% (Schmalz, 2009). The most commonly used technique to measure the DOC is the Fourier Transform Infra-red Spectroscopy (FTIR) (Vandewalle *et al.*, 2004)

DOC is influenced by several factors such as light-cure source, curing time and size of the light-cure tip. Lower DOC affects the performance of the RBCs (Rastelli;Jacomassi and Bagnato, 2008). The higher the DOC, the better the physical and mechanical properties of

the RBCs (Lovell *et al.*, 2001b). When a higher amount of monomer is cured, the resulting material will be more biocompatible, since free residual monomer can cause serious health problems such as skin, eye and mucosal irritation (Asmussen and Peutzfeld, 2001; Gosavi;Gosavi and Alla, 2010). The minimum DOC of methacrylate-based materials for use as a permanent restoration is not known yet, however, it has been found that DOC below 55% result in a weak degradable material (Yap;Wong and Siow, 2003; Galvão *et al.*, 2013). Most methacrylate-based composites show a degree of polymerisation ranging from 55-75% (Galvão *et al.*, 2013).

2.3.4 Depth of cure

The depth of penetration of light-cure source into the resin materials is affected by the wavelength, irradiance, and scattering of the light in the composites. Several factors can reduce the depth of cure, such as the concentration of the photoinitiators used and the size and quantity of the filler particles. For example, microfilled composites tend to scatter more light than hybrid composites, and thus need more curing time to achieve adequate monomer conversion (Sakaguchi and Powers, 2012).The shade and opacity of the RBCs affect the depth of the cure. As composites with a high concentration of pigment scatter more light, longer light curing with an incremental build-up of the restorations will help to attain sufficient polymerisation (Hyun *et al.*, 2017; Rooz, 2020).The tip of the light-cure unit should be placed as close to the restoration as possible (within 1mm) to ensure optimal exposure. Light curing for 20 seconds is the standard exposure time, although this time is often only sufficient to cure an RBC of a light shade to 2mm depth. A curing time of 40 seconds improves the DOC at a depth of 2-3mm. In the case of large restorations, it is important to move the light tip across all the surfaces. Regardless of the light intensity, 2-3

mm is the maximum depth of cure unless a longer curing time is applied (Anusavice;Shen and Rawls, 2012).

2.4 Properties of conventional composites

2.4.1 Polymerisation shrinkage

Polymerisation shrinkage is the major disadvantage associated with all RBCs (Sakaguchi and Powers, 2012). The shrinkage results in stresses between the tooth and the restoration leading to gap formation, which allows for the penetration of bacteria and the formation of secondary caries. The stress can result in the failure of the bond, cracking and fracture of the enamel and post-operative sensitivity, and eventually failure of the restoration (Dauvillier;Aarnts and Feilzer, 2000; Braga and Ferracane, 2004; Tantbirojn *et al.*, 2004; Ferracane, 2008).

Using high molecular weight monomers such as Bis-GMA or UDMA has been found to decrease polymerisation shrinkage (Stansbury *et al.*, 2005). Polymerisation shrinkage of large molecular weight monomers is below 1% when compared to mixed monomers used with methacrylate-based composites, which range between 1.5% to 3 (Anusavice;Shen and Rawls, 2012). However, Bis-GMA and UDMA are very viscous and difficult to blend and handle resulting in poor manipulated materials (Braga and Ferracane, 2004; Stansbury *et al.*, 2005; Ferracane, 2008).

Applying composite restorations using the incremental technique has been shown to reduce polymerisation shrinkage (Lee *et al.*, 2007; Park *et al.*, 2008). In addition, a soft start curing method can reduce the shrinkage. In this method, the intensity of the light cure unit slowly increases to allow for slow polymerisation (Ilie *et al.*, 2005). It has been suggested that using

flowable composites as a liner would decrease shrinkage due to the low modulus of elasticity (Alomari;Reinhardt and Boyera, 2001; Leevailoj *et al.*, 2001). However, other studies have reported that flowable composites have no effect on polymerisation shrinkage (Neme *et al.*, 2002; Cadenaro *et al.*, 2009).

2.4.2 Mechanical properties

RBCs have sufficient mechanical properties and can be used to restore any type of cavity, or as a core for indirect restorations. The wear resistance of the composite materials is questionable specially when placed in patients with parafunctional habits or when placed in large preparations or to replace missing cusps (Krämer *et al.*, 2009). It has been found that the filler content in RBCs has a major effect on the mechanical properties, and that the materials with the highest filler content are stronger, tougher and stiffer than low filler content materials. However, composites have a lower modulus of elasticity compared to amalgams, which explains the deformation that takes place under occlusal forces (Ferracane, 2011).

Filler loading, morphology and particle size have an impact on the mechanical strength of the composite materials. Filler loading more than 40vol% has been found to reinforce the mechanical properties of the composites (Le Strat *et al.*, 2013; Rueda *et al.*, 2017).

2.5 Evaluation of the Physical and Mechanical Properties of the resin composites

2.5.1 Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

Fourier Transform infrared (FTIR) spectroscopy is the most commonly used technique to determine the DOC. FTIR can be used to investigate the materials in liquid and solid phases

(Chung and Greener, 1988; Lovell *et al.*, 2001b). FTIR spectroscopy is a technique sensitive, which requires careful sample preparation to get the spectral data that will produce an accurate DOC reading (De Moraes *et al.*, 2008).

FTIR spectroscopy is based on the interactions that occur between electromagnetic radiation and natural vibrations of the chemical bonds within the atoms of the material. The frequencies of the natural vibration of a chemical bond depend on the masses of the atoms and the stiffness of the chemical bond. Molecular vibrations have two types: stretching and bending. Stretching changes the length of the bond, whereas, bending changes the angle of the bond (De Moraes *et al.*, 2008). Infrared (IR) is usually divided into three spectral areas: the near (NIR) from 4,000 to 14,000 cm^{-1} , the mid (MIR) from 400 to 4,000 cm^{-1} , and far-IR which is from 25 to 400 cm^{-1} .

The IR source, IR detector and Michelson interferometer are the main components of spectrometer. In order to obtain a spectrum, the background (bg) spectrum should be recorded first. Background spectrum captures the source of light or the molecules in the air. Then, another spectrum is recorded with the material sample in place. This spectrum has absorptions from both the air and the sample. After subtracting the background spectrum, the absorption peaks in the final spectrum are mainly due to the sample (De Moraes *et al.*, 2008).

Degree of conversion (DOC) has been widely investigated in dental research (Porto *et al.*, 2010; Collares *et al.*, 2011; Zhang and Wang, 2012; Marovic *et al.*, 2013; Wu;Zhang and Wang, 2013). A high DOC promotes good mechanical properties of resin-based materials (Palin *et al.*, 2003; Ferracane, 2006). Conversion of all the aliphatic carbon-carbon double bond (C=C) is not possible, some monomers remain unreacted (Collares *et al.*, 2014b).The

remaining unpolymerised double bonds are called unreacted monomers (Collares *et al.*, 2014b).

The degree of polymerisation of any methacrylate monomer-based material is calculated by comparing the amount of the remaining C=C in the polymer structure. The DOC is affected by different factors such as the chemical structure of the methacrylate monomers and type of photoinitiator used (Leprince *et al.*, 2013). Furthermore, filler size, loading and geometry have an effect on the DOC. Light cured composites reach a DOC ranging from 35 to 77% depending on the composition of the material, the intensity and exposure time of the light curing system (Halvorson; Erickson and Davidson, 2003; Schmalz, 2009).

To determine degree of polymerisation in methacrylate-based resins, NIR or MIR spectral IR regions can be used. In NIR, two aliphatic bands can be used one at 4743 cm⁻¹ and the second at 6165 cm⁻¹. In MIR area, DOC can be calculated by measuring the decrease of the C=C stretch absorption band at 1638 cm⁻¹. It has been found that determination of polymerisation is facilitated when the tested material shows a stable absorption band. This band can be used as an internal standard of normalisation (De Moraes *et al.*, 2008). When a material has an internal standard, the percentage of the remaining unpolymerised aliphatic C=C can be obtained by using the equation:

$$(\% \text{ C=C}) = \frac{\text{Abs aliphatic} / \text{Abs (aromatic)polymer}}{\text{Abs aliphatic} / \text{Abs (aromatic)monomer}} * 100$$

Abs is the height or area of absorption band. DOC can be calculated by subtracting the remaining percentage of aliphatic C=C from 100%:

$$\text{DOC \%} = 100 - (\% \text{ C=C})$$

FTIR spectra of methacrylate resins show other peaks at 1715 and 1580 cm^{-1} . These peaks may be used as internal standards in IR spectrometry to determine the degree of polymerisation (Collares *et al.*, 2011).

2.5.2 Flexural strength (FS) and Flexural modulus (FM)

Flexural testing is a common method to test the mechanical performance of the RBCs (Ilie *et al.*, 2013). ISO4049 has classified the RBCs according to the flexural strength into two types: Type 1: for posterior occlusal restorations when flexural strength should be at least 80 MPa, and type 2: for anterior restorations and other indications when flexural strength is 50 MPa. These values can be used as a baseline to compare when testing or evaluating composite materials (Ilie *et al.*, 2017). It has been found that a minimum of 60vol% filler content is needed for a good mechanical properties (Ilie and Hickel, 2009b), however, increasing the filler volume above 80% will decrease the tensile strength and will have no impact on the flexural strength (Htang;Ohsawa and Matsumoto, 1995). Furthermore, the morphology and filler loading has been shown to have an impact on the flexural strength of the RBCs. For example, rounded fillers will facilitate a higher loading and result in high FS, on the other hand, irregular shaped fillers will not allow a high filler loading and will result in a lower mechanical strength (Kim;Ong and Okuno, 2002).

2.5.3 Water sorption

Water sorption has a high impact on the mechanical performance of the dental composites (Sideridou;Tserki and Papanastasiou, 2003). Some of the RBCs absorb water during their setting reaction, but most of these materials show water sorption by diffusion controlled process (Martin;Jedynakiewicz and Fisher, 2003). Most commonly used monomers such as TEGDMA, are hydrophilic, thus increase the possibility of water sorption in the RBCs (Yiu *et*

al., 2004; Sideridou;Karabela and Vouvoudi, 2008). On the other hand, UDMA and Bis-GMA showed more rigid network and lower water sorption (Sideridou;Tserki and Papanastasiou, 2003). The hydrophilic monomers enable the hydrogen to bond with the surrounding fluids and increase the water in the resin matrix, thus induce swelling , release of unreacted monomers, increase roughness and decrease the mechanical strength of the materials (Szczesio-Wlodarczyk *et al.*, 2020) (Martin;Jedynakiewicz and Fisher, 2003). Water sorption has shown to decrease the mechanical properties and colour stability of the RBCs (Yiu *et al.*, 2004; Mansouri and Zidan, 2018).

2.6 Bioactive Resin-based Composites

2.6.1. Currently used fluoride releasing materials

Fluoride is a well-known anticariogenic agent that exists naturally in the environment. It can be found in food, drinks, and fluoride supplements. Fluoride interferes with bacterial metabolism, decreasing demineralisation of underlying tooth tissues and enhancing remineralisation (Wiegand;Buchalla and Attin, 2007). Fluoride releasing restorative materials are considered to be a way to keep the fluoride permanently in the oral cavity. GICs, for example, can release fluoride for a long time and recharged with fluoride when applying fluoride dentifrice. Fluoride containing restorative materials available are GICs, resin modified GICs (RMGICs), compomers, and composites (Vieira and Modesto, 1999; Wiegand;Buchalla and Attin, 2007; Cury *et al.*, 2016).

2.6.2. Fluoride-releasing composites:

RBCs can contain fluoride in different forms such as inorganic salts, leachable glasses or organic fluoride (Wiegand;Buchalla and Attin, 2007). The factors which contribute to the

fluoride release are: type and size of the filler, type of resin, amount of fluoride and silane treatment (Dijkman *et al.*, 1993; Arends;Dijkman and Dijkman, 1995; Xu *et al.*, 2000a; Xu *et al.*, 2000b; Xu and Burgess, 2003). The more the hydrophilicity and acidity of the polymer matrix, the more fluoride release. The addition of HEMA and acidic monomer, such as HEMA and maleic anhydride were mixed to produce HEMAN, to the fluoride containing composites results in increase the fluoride release due to the acidic character of the resin matrix that will lead to more water sorption and degradation of the filler particles (Asmussen and Peutzfeldt, 2002b). Fluoroaluminosilicate glasses used in GICs and RMGICs are more soluble than composites glasses (mainly barium aluminium silicate glasses) which contribute to more fluoride ion release. The calcium in the GICs and RMGICs, which is responsible for the reaction with the acids or polyacids to create the crosslinked network, make the glass more soluble and weaker compared to the glass of the conventional composites. In addition, smaller fillers particle size releases more fluoride due to larger surface area (Xu and Burgess, 2003). The larger surface area of the small size particles will lead to increase in the acid-base reaction and the degradation of the filler particles, thus more fluoride release (Vermeersch;Leloup and Vreven, 2001; Neelakantan *et al.*, 2011).

Fluoride-releasing composites can be developed following three approaches involving the use of fluoride-containing filler particles, matrix bound fluoride or addition of soluble fluoride salts (Arends;Dijkman and Dijkman, 1995). Ytterbium trifluoride (YbF_3) and leachable glass fillers are used in RBCs as fluoride releasing filler system. YbF_3 , the radiopaque fluoridated filler, releases fluoride in an exchange reaction. When water diffused into composites, the fluoride released from the particles (Arends;Dijkman and Dijkman, 1995; Yap;Khor and Foo, 1999; Xu and Burgess, 2003).

Organic matrix bound fluorides such as acrylic-amine-HF- salts have been incorporated into the resin matrix to enhance the fluoride release (Hicks *et al.*, 2003a). Water-soluble fluoride salts such as sodium fluoride (NaF) and stannous fluoride (SnF₂) have been added to the composites resin matrix. These soluble salts dissolve in water and then fluoride ions leach out of the composites (Arends;Dijkman and Dijkman, 1995). It has been shown that fluoride release from composite resins is lower than fluoride released from compomers, GIC and RMGIC (Carvalho and Cury, 1999; Preston *et al.*, 1999; Karantakis *et al.*, 2000; Attar and Önen, 2002; Preston *et al.*, 2003).

The cause of the clinical failure of the fluoride releasing composites is mainly due to high water uptake and high matrix diffusivity (Braun;Frankenberger and Krämer, 2001; Merte;Schneider and Merte, 2004). High water solubility of the filler and high water uptake and diffusivity of polymer matrix play an important role in increase the fluoride release (Dijkman *et al.*, 1993; Attar and Turgut, 2003a; Xu and Burgess, 2003). The high water sorption negatively affects the mechanical and **physical** properties of the fluoride containing materials (Xu *et al.*, 2004a; Xu *et al.*, 2004b; Xu *et al.*, 2006; Wiegand;Buchalla and Attin, 2007; Ling *et al.*, 2009). For example, Ariston[®], a commercially available fluoridated composite, showed high water uptake which affect the physical and mechanical properties and lead to the failure of the restoration (Ferracane, 2011; van Dijken;Pallesen and Benetti, 2019). Therefore, new composites with a good mechanical properties and release fluoride and other ions continuously should be developed.

2.6.3 Bio-active glasses

The first bioactive glass (BAG), 45S5[®], was developed in 1969 by Larry Hench. 45S5[®] is a silicate glass with the composition in wt.%: **SiO₂ 45.0, CaO 24.5, Na₂O 24.5 and P₂O₅ 6.0**

(Hench, 2006). Since then, hundreds of bioactive glasses have been developed. BAGs react with physiological-like fluids and form hydroxycarbonated apatite (HCA) (Hench, 2006), with a composition similar to the inorganic component of the natural bone. BAGs have been used successfully to treat the bone defects such as trauma, and osteoporosis (Kucera;Urban and Ragkou, 2012; Jones, 2013). 45S5[®] has been used in pit and fissure sealants and showed promising results for caries inhibition (Yang *et al.*, 2013). Another BAG, S53P4, with composition in wt% SiO₂ 53%, Na₂O 23%, CaO 20%, and P₂O₅ 4%, was used as a filler for GIC, and it showed higher remineralisation properties compared to commercial GICs (Xie *et al.*, 2008). Adding the 45S5 BAG to the toothpastes showed the ability to occlude the dentinal tubules and therefore decrease the dental hypersensitivity (Mitchell;Musanje and Ferracane, 2011; Da Cruz *et al.*, 2018; Kanwal *et al.*, 2018).

BAGs are considered to be bioactive due to their ability to bond to the bone tissue (Hench, 2006; Hench, 2013), through formation of the bone-like layer (HCA) on their surface. Other definitions stated that BAGs are considered bioactive due to their ability to release ions and have remineralising and antimicrobial activity when used in dental materials (Liang *et al.*, 2019; Tiskaya *et al.*, 2021).

Several modifications to the original 45S5 have been made. Fluoride-containing BAGs were made by substituting CaF₂ for CaO (based around: SiO₂ 46.1%, Na₂O 24.4%, P₂O₅ 2.6%, CaO 13.45-20.2%, and CaF₂ 6.7-13.45%), resulting a slow formation of the apatite or no formation at all (Hench;Spilman and Hench, 1988). Another study added CaF₂ without substituting CaO from the glass compositions (based around: SiO₂ 33.3-49.5%, Na₂O 17.8-26.4%, P₂O₅ 0.7-1.07%, CaO 15.50-44.9%, and CaF₂ 4.8-32.70%), and the glass formed fluorapatite (FAp) and also showed a fluoride release (Brauer *et al.*, 2009). However, if the

CaF₂ content is more than 5 mol%, the glass will form fluorite instead of forming FAp due to the low phosphate content (Brauer *et al.*, 2010). Fluoride release and FAp formation has been shown when high phosphate fluoride containing BAGs was studied after the addition of 5-9 mol% of CaF₂ (based around: SiO₂ 29.61-44%, Na₂O 6.7-10%, P₂O₅ 3.36-5%, CaO 10-15%, and CaF₂ 2.4-16.4%) (Mneimne *et al.*, 2011b; Lynch *et al.*, 2012).

Several studies have investigated the substitution of CaO by MgO in the BAGs and found that MgO can delay the apatite formation and prevent the growth of the FAp crystals, especially when added at high concentrations (Watts *et al.*, 2010; Ding *et al.*, 2014; Araújo *et al.*, 2016). The addition of the zinc oxide (ZnO) in small amount of 0.4 mol% to the BAGs have been shown to speed up the apatite formation (Salinas *et al.*, 2011); however, when the amount of ZnO was added at 4-6 mol% there was no evidence of apatite formation (Sánchez-Salcedo *et al.*, 2014). Incorporation of ZnO into BAGs showed a high fluoride release and signs of apatite formation under acidic medium only (Blochberger; Hupa and Brauer, 2015). The addition of MgO and ZnO can prevent crystallisation during the quenching of the glass (Tiskaya *et al.*, 2021). Strontium when added to the BAGs has shown a faster degradation and apatite formation (Fredholm *et al.*, 2012). When SrO replaced the CaO in the glass compositions, the glass showed low bioactivity and degradability (O'donnell and Hill, 2010). However, substituting SrO for CaO showed evidence of apatite formation (Hesaraki *et al.*, 2010). Higher sodium (Na) content in the original 45S5 BAGs reduces the melting temperature, but due to its hygroscopic nature, (Na absorbs water readily), it decreases the mechanical properties of the composites (Chen *et al.*, 2017).

Two methods can be used to fabricate BAGs: melt-quenching and sol-gel techniques. The melt-quenching technique is the traditional and the most common method used for the

fabrication of commercial BAGs that occurs through melting the oxides in platinum crucible at $\geq 1300^{\circ}\text{C}$ and then quenching the glass in water. The commercially available glasses such as 45S5 Bioglass[®] are made using melt-quenching route. The newer technique is sol-gel in which silica precursors such as calcium nitrate is used to create gel with nanoparticles at room temperature (Polini; Bai and Tomsia, 2013). After drying then heating the gel at 600°C , the glass is formed (Jones, 2013). BAGs formed by melt-quenching technique are dense, whereas, glasses formed by sol-gel technique show more porosity that results in more surface area and cell response (Khurshid *et al.*, 2015). In addition, fewer chemical components are used to form glasses by sol-gel route. For instance, Na_2O is used only in melt-quenching technique to help reducing the melting temperature and to increase the solubility which is important for the bioactivity of the glass. As there is no melting in the sol-gel and no need to incorporate Na, the sol-gel glasses have a high surface area lead to high dissolution of the glass (Jones, 2013).

The release of calcium, phosphate and, in some formulation, fluoride from BAGs enhances the antimicrobial activity, and have the ability to neutralise the acidic pH in the oral cavity (Vollenweider *et al.*, 2007a; Gubler *et al.*, 2008; Manfred *et al.*, 2013a; Davis *et al.*, 2014a). Calcium and fluoride ions can remineralise and strengthen the tooth structures, and fluoride in particular, has shown a biocide effect against streptococcus mutans in the oral cavity (Davis *et al.*, 2014b). Several studies have shown the effect of fluoride releasing materials on increasing the fluoride concentrations in plaque adjacent to the restorations (Forss; Näse and Seppä, 1995). BAGs composites that can release fluoride and calcium ions have shown to increase the FAp formation that will help in caries prevention (Caldeira *et al.*, 2013). The mechanism of action of the BAG against bacteria is not clearly investigated, but it might be due to the rise of the pH (Khvostenko *et al.*, 2016). When BAGs are immersed in a

physiological solution, the pH increases, due to ionic exchange between the glass surface and aqueous solution. The concentration of calcium and phosphate ions released in physiological solution increases. When the solution became saturated in calcium and phosphate, HAp will precipitate on the glass surface. Phosphate and calcium ions in the glass and saliva play important role in remineralisation process (Jones, 2013). It has been shown that adding fluoride to silicate BAGs lead to the fluorapatite formation which is more stable at low pH than hydroxyapatite (Brauer *et al.*, 2010). Also, BAGs can form a dense layer on the dentine surface which can seal the dentinal tubules and prevent the dentine hypersensitivity (Yli-Urpo; Närhi and Söderling, 2003).

Incorporation of BAGs into the RBCs has been previously studied (Khvostenko *et al.*, 2013; Chatzistavrou *et al.*, 2014; Tauböck *et al.*, 2014). In composite restorations, BAGs were added and showed a significant decrease in the bacterial penetration through the marginal leakage compared to BAG-free composites (Khvostenko *et al.*, 2013; Chatzistavrou *et al.*, 2014; Tauböck *et al.*, 2014). It has been found that adding 15wt% BAG with composition SiO₂ 65mol%, CaO 31mol% and P₂O₅ 4mol% to composites did not significantly affect the mechanical properties of the material (Davis *et al.*, 2014a; Khvostenko *et al.*, 2016). In addition, incorporating up to 10wt% BAGs into composites did not affect the mechanical properties of the composites, however, 30wt% of BAGs added showed a significant decrease in the mechanical properties (Korkut; Torlak and Altunsoy, 2016). Furthermore, incorporating 45S5 BAGs to the composites up to 20wt% showed no significant effect on the FS, however, increasing the concentration to 30wt% significantly decreased the FS values (Nicolae *et al.*, 2014). Another study when 45S5 BAGs and F-BAGs (composition SiO₂ 33.5wt%, CaO 33wt%, Na₂O 10.5wt%, CaF₂ 12wt% and P₂O₅ 11wt%) were incorporated into the composites at 5-40wt%, showed no significant decrease of mechanical properties

when 45S5 BAGs and F-BAGs were added up to 10wt% and 20wt%, respectively (Par *et al.*, 2022).

It has been investigated that fluoridated BAGs (F-BAGs) can form fluorapatite (FAP) which is more resistant to the acidic environment compared to hydroxyapatite. When high concentration of fluoride salts are added, fluorite (CaF₂) will form which decreases the formation of fluorapatite, and therefore decreases the fluoride ion release (Fuji *et al.*, 2003; Lusvardi *et al.*, 2009). To solve this problem, it has been found that adding phosphorus pentoxide (P₂O₅) by 6wt% to the fluoridated glasses will favour the fluorapatite deposition (Brauer *et al.*, 2010; Mneimne *et al.*, 2011a).

F-BAGs containing composites showed a higher modulus of elasticity (MOE) and higher dentine stiffness compared with conventional BAGs. . In the F-BAG, the most common alterations to the glass composition to produce higher fluoride BAGs is to replace either Na₂O or CaO with CaF₂. Replacing Na₂O by CaF₂ can form Si-O-Ca-O-Si groups which reinforce the glass network and results in decreased the non-bridging oxygens with high network connectivity, which in return will reduce the reactivity and bioactivity of the glass (Brauer *et al.*, 2009; Lusvardi *et al.*, 2009; Al-Noaman; Rawlinson and Hill, 2012). However, adding the CaF₂ to the glass composition without substituting CaO or Na₂O showed to increase the FAP formation (Brauer *et al.*, 2010). It has been found that high sodium content, as in the conventional 45S5 Bioglass[®], can cause high water uptake which will affect the properties of the composites. For that, decreasing the amount of the Na and incorporating other materials such as fluoride or calcium are important for the apatite formation (Hench and Polak, 2002; Al-Eesa *et al.*, 2017).

F-BAGs have been shown to be a good source for providing calcium and fluoride ions, which can remineralise the tooth tissues and have a cariostatic effect (Davis *et al.*, 2014a). However, materials with high fluoride release such as GICs have significantly lower mechanical properties, and materials such as compomer is mechanically stronger but releases small amount of fluoride (Xu and Burgess, 2003). Development of materials with high fluoride release and recharge ability along with excellent physical and mechanical properties are highly desirable.

Glass oxides	SiO ₂	CaO	Na ₂ O	P ₂ O ₅	NaF	CaF ₂	AlF ₃
BG5NaF	42.90	23.30	23.30	5.70	4.80	-	-
BG10NaF	40.90	22.30	22.30	5.40	9.10	-	-
BG20NaF	37.50	20.4	20.4	5.00	16.70	-	-
BG5CaF	42.90	23.30	23.30	5.70	-	4.80	-
BG10CaF	40.90	22.30	22.30	5.40	-	9.10	-
BG20CaF	37.50	20.4	20.4	5.00	-	16.70	-
BG5AlF	42.90	23.30	23.30	5.70	-	-	4.80
BG10AlF	40.90	22.30	22.30	5.40	-	-	9.10
BG20AlF	37.50	20.4	20.4	5.00	-	-	16.70

Table 2-1: The compositions of the nine bioactive glass containing fluoride made, the bolded text show the composition of the glass used in this project.

Previous work at Newcastle has focussed on developing a BAG that will release high amounts of fluoride for incorporation in an RBC (Merie, 2023). A number of BAGs containing fluoride were by incorporating 5, 10, 20wt% of NaF, CaF₂ and AlF₃. A total nine glasses were prepared using melt-quenching technique at 1400°C (Table 2-1). The amorphous structures of the BAGs have been confirmed using the XRD without evidence of crystalline phases. All

the glasses released fluoride during the test period of 12 weeks, and the highest amount released from BAG with 20wt% NaF (BG20NaF), while the BAG with 5wt% of CaF (BG5CaF) release the lowest amount.

Composites based on either 100% UDMA or 90% UDMA:10% HEMA were then made using the BAGs with highest fluoride release, the BG20NaF and the BG20CaF. The composites showed no significant differences in the DOC, however, the depth of cure significantly decreased with HEMA-containing BAG composites. The flexural properties were significantly decreased with the addition of the BAGs fillers, but there were no significant differences between the flexural properties of the HEMA-free and HEMA containing BAGs composites. The FS values of the composites made were below the values of at least 80 MPa recommended by the ISO4049 (Standardization, 2019) to make them acceptable for occlusal restoration. So, based on these outcomes, BG20NaF was chosen to be used in this project for the high fluoride release this material showed.

2.6.4 Fluoride release and its measurement

Measuring fluoride release from the restorative materials has been extensively reported in the literature, but there is no standard protocol to follow (Wiegand;Buchalla and Attin, 2007). The fluoride release process can be affected by different factors such as the composition of filler particles and monomer composition of the RBC. Other factors that affect the fluoride release are storage solutions and the frequency of the solution change, pH and composition of the saliva (Lucas;Arita and Nishino, 2003; Osinaga *et al.*, 2003). Specimens with different size and shape are used in fluoride release measurement, and it has been found that the weight has no impact on the fluoride release, and only the surface

of the specimen has more effect on the release of fluoride (Williams;Billington and Pearson, 1999).

Fluoride release can be measured in different storage solutions: artificial saliva, water or acidic solutions (Wiegand;Buchalla and Attin, 2007). The pattern of fluoride release has been shown to be similar under different media, but the differences was in the daily and cumulative fluoride release (Garcez;Buzalaf and Araújo, 2007). The highest fluoride ion release was detected under the acidic media due to the dissolution of the fluoridated component by the effect of the low pH. However, the lowest fluoride release is found in artificial saliva, due to the different ions in saliva that will affect the diffusion of the fluoride from the materials into the storage media (Williams;Billington and Pearson, 2001; Moreau and Xu, 2010; Ozmen, 2020). Natural saliva can form a pellicle on the material surface which decreases the release of ions (REZK-LEGA;ÖGAARD and RÖLLA, 1991; Levallois *et al.*, 1998). The pellicle formed on the surface of fluoridated composites can decrease the fluoride ion release by 15-20% (Arends;Dijkman and Dijkman, 1995). It has been found that artificial saliva decreases the fluoride release from GICs to 17-25% compared to water (Bell *et al.*, 1999). Coating the surface of the restoration with bonding agent can decrease the fluoride release significantly. The bonding agent can form a barrier preventing the water and fluoride ion diffusion between the restoration and the medium (Hattab and Amin, 2001; Vercruysse;De Maeyer and Verbeeck, 2001; Miranda *et al.*, 2002).

Ion release *in-vitro* can be measured using an ion selective electrode (ISE) (Michalska, 2012). ISE is the most commonly used method for its simplicity and reliability (Itota *et al.*, 2004a). ISE can measure the concentrations of different ions such as sodium, calcium, chloride and fluoride, and can also measure the amount of both fluoride complexes and free fluoride ions

in solution (McCabe;Carrick and Sidhu, 2002). A buffer solution is used to decomplex the bound fluoride, so the total ionic strength adjustment buffer (TISAB III) is used to prevent the formation of the fluoride complexes and controlling the pH (Itota *et al.*, 2004a).

2.7 Summary:

Due to the continuous development and modification to enhance the aesthetic, physical and mechanical properties, RBCs became the treatment of choice to directly restore anterior and posterior teeth. However, secondary caries and fracture of the restorations remain the primary causes of failure. Incorporating F-BAGs in the composites potentially provides a bioactive material capable of releasing antibacterial agents that will help to remineralise the affected tissues. Some studies have shown F-BAGs based composites as a promising material that might reduce the incidence of secondary caries and therefore increase the longevity of the material. The recently developed at Newcastle F-BAGs has shown that when made on a lab-scale it can release high amounts of fluoride and can be incorporated into RBCs, however, the mechanical properties of those RBCs were below those recommended for permanent restorations by the ISO standards.

3. Aims, Objectives and program of work.

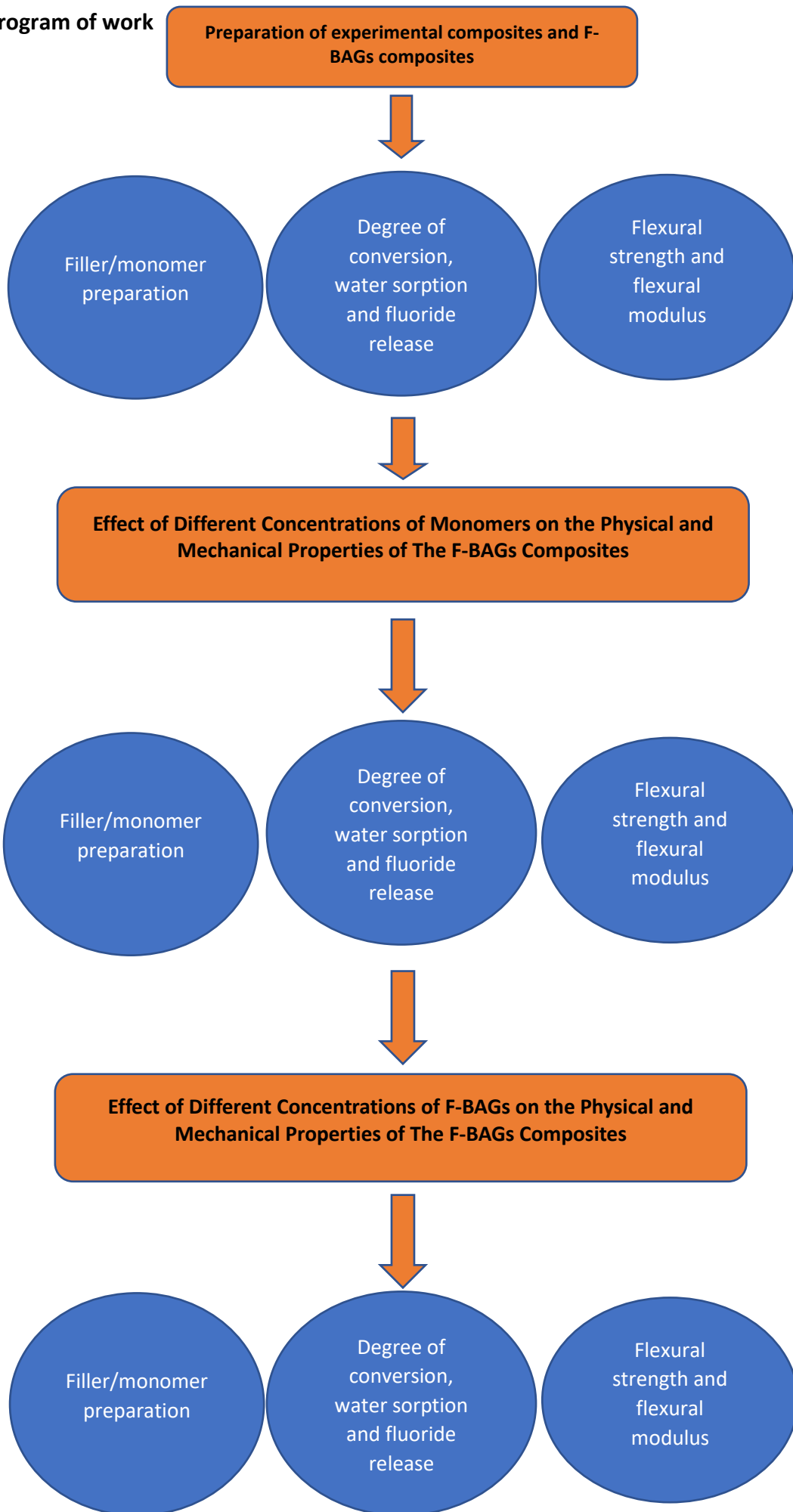
3.1 Aims

The F-BAG previously made at Newcastle University (Merie, 2023) showed potential for use in an RBC but the mechanical properties were not sufficiently high. Additionally, the glass was only made at a laboratory scale, while if it going to be translated into a commercial product the glass will need to be made at a larger industrial scale. Consequently, the overall aim of this work was to establish what types and concentrations of the monomers and F-BAGs produced the best RBC for use as a restorative material.

3.2 Objectives

- Establish that scaling up production of the F-BAGs to an industrial scale did not detrimentally affect the fluoride release, water sorption, degree of conversion, flexural strength and flexural modulus of RBCs made with them.
- Determine the best combination of monomers to provide the best compromise of fluoride release with adequate mechanical properties.
- Measure the effect of F-BAGs concentration on the fluoride release, water sorption, degree of conversion, flexural strength and flexural modulus of the RBC after one month of aging.

3.3 Program of work



Chapter 4: Preparation of Model Experimental Composites and Bio-active glass-based Composites

4.1 Introduction

The aim of this project is to develop novel resin composites based on fluoride containing bio-active glass fillers (F-BAGs) as a secondary filler. The first step in the project is the development of model dental composites that will contain secondary glass fillers. This part of the experiment aims to prepare and characterise the mechanical and physical properties of the model composites. A new F-BAG has been previously developed at Newcastle University (Merie, 2023) and was shown to release high levels of fluoride after storage in water. An important step in the translation of laboratory research to a commercial product is to assess the effect of scaling-up the production of the components from small lab-scale quantities to a larger industrial scale. In this chapter model composites based around the monomers UDMA and TEGDMA were made with silanised barium borosilicate glasses as the primary filler and the F-BAG as the secondary filler. Four batches of the F-BAG were assessed, one batch being made at Newcastle University and the other three being made, at a larger scale, by a commercial glass producer (Glass Technology Services, Sheffield, UK). Composites made with these different batches of glass were compared in terms of their degree of conversion, water sorption, fluoride release and flexural properties both at the time of manufacture and at a number of time-points after storage in distilled water for 28 days.

4.2 Materials and Methods

4.2.1 Composites preparation

The model composites were made using UDMA and TEGDMA monomers 50:50 wt% (Sigma-Aldrich Ltd., Dorset UK). The photo-initiators used were 1wt% camphorquinone (CQ) and 1wt% ethyl 4-dimethylamino benzoate (EDAB) (Sigma-Aldrich Ltd., Dorset UK) (Table 4-1). The main fillers used in these composites were 0.7 μ m silanised barium-aluminium-borosilicate glass (BBS) (GM27884, SCHOTT AG, Germany), the secondary fillers used were the lab-made F-BAGs (Newcastle University, UK), and the industrially made F-BAGs (GTS, Glass Technology Services, UK) (Figure 4-1). The GTS glass was made by a commercial glass producer and came in three separate batches of the same glass composition, each batch made on a different day and at an increased scale of 250g per batch compared to the maximum batch size capable in our lab, 50g. Six composites were made, with an overall filler concentration of 55vol% filler. While one composite was made using only the BBS filler and contained no F-BAG (termed 55F), the other composites were made from 80:20 weight ratio of BBS to F-BAG and were named according to the batch of glass they contained. To establish the effect of combining the different GTS batches on composite properties a composite termed **GTS-mix** was also made in which equally quantities of each GTS batch were mixed together prior to adding to the BBS filler. Table 4-2 shows the amount of each material used in making the model composites.

Materials	Description	Manufacture
UDMA	Urethane dimethacrylate	Sigma-Aldrich Ltd., Dorset UK
TEGDMA	Triethylene glycol dimethacrylate	Sigma-Aldrich Ltd., Dorset UK
CQ	97% Camphorquinone	Sigma-Aldrich Ltd., Dorset UK
EDAB	≥99% Ethyl 4-(dimethylamino)benzoate	Sigma-Aldrich Ltd., Dorset UK
Glass	<p>1-Silanised Barium borosilicate glass</p> <p>$D_{50} = 0.7 \mu\text{m}$</p> <p>2- Bio-active glass with 20% NaF</p> <p>3- Bio-active glass with 20% NaF (Industrially made)</p>	<p>SCHOTT AG, Germany</p> <p>Newcastle University, UK</p> <p>GTS, Glass Technology Services, UK</p>

Table 4-1: List of the materials used in the preparation of the model composite with their manufacturers.

Composites (vol%)	Filler (wt%)	Monomer (wt%)	Composites code
<p>55F composites (55vol% BBS glass)</p> <p>Glass Density= 2.8</p>	75	25	55F
<p>Lab-Made F-BAGs (40% Barium glass, 20% F-BAGs)</p> <p>Glass Density= 2.427</p>	<p>60 BBS</p> <p>15 F-BAGs</p>	25	Lab-made
<p>GTS glass (GTS1,2 and 3)</p> <p>Glass Density= 2.427</p>	<p>60 BBS</p> <p>15 F-BAGs</p>	25	GTS1, GTS2, GTS3 and GTS-mix

Table 4-2: Composition of the experimental composites.



Figure 4-1: The three batches of the GTS glass and the lab-made glass.

4.2.2 Monomer Preparation

50:50wt% of UDMA:TEGDMA were mixed in an amber glass bottle (500mL, Sigma-Aldrich) and then mixed by a magnetic stirrer (VELP, Scientifica, Italy) for 30 minutes at 35°C to enable easier mixing of the materials. Next 1wt% CQ and 1wt% EDAB were then added and further mixed for 30 minutes until a homogeneous mixture was visible. The bottle was sealed with parafilm and stored at 4 °C until use.

4.2.3 Mixing glass fillers with the monomer

Development of composite mixing protocol

To achieve a homogenous distribution of the fillers in the monomer mixture three mixing protocols were tried. First, the monomers were added to the mixing cup (Cole-Parmer, Neots, UK) then fillers were added by increments of 25wt% each and then mixed after each increment for 3mins at 3000 rpm in a centrifugal mixer (Speed-Mixer™, DAC 150.1 FVZ, Hauschild Engineering, Germany) (Figure 4-2). This resulted in a dry and powdery mixture that was not able to be used to make composites (Figure 4-3C). In the second protocol, after adding the monomer, the fillers were added incrementally of 25wt% each and mixed at speed 1000 rpm for 3 minutes, and the result showed a dry mix with visible unmixed fillers

(Figure 4-4). In the third protocol, after adding the monomers, the fillers were added at 25wt% incrementally and then mixed with a speed of 2000rpm for 3 minutes, the result showed a well-dispersed filler and a homogeneous mixture (Figure 4-3D). 25g of each composite was made in polypropylene (PP) containers.

The following is the mixing protocol followed to prepare all subsequent composites discussed in this thesis:

First, mix the monomer and initiator mixture with 25wt% of the fillers for 3 minutes at 2000 rpm.

2nd mix 25wt% of fillers added then mixed for 3 minutes at 2000 rpm.

3rd mix 25wt% of fillers added and mixed for 3 minutes at 2000 rpm.

4th mix the last 25wt% of the fillers added and mixed for 3 minutes at 2000 rpm.

For the 55F composite only the BBS filler was added, for all other composites the BBS filler was added first and then the F-BAG was added in the final increment. After mixing was finished the PP container was sealed with parafilm and wrapped in aluminium foil to prevent light exposure then stored at 4 °C until use.



Figure 4-2: Speed-Mixer™, DAC 150.1 FVZ, Hauschild Engineering, Germany.

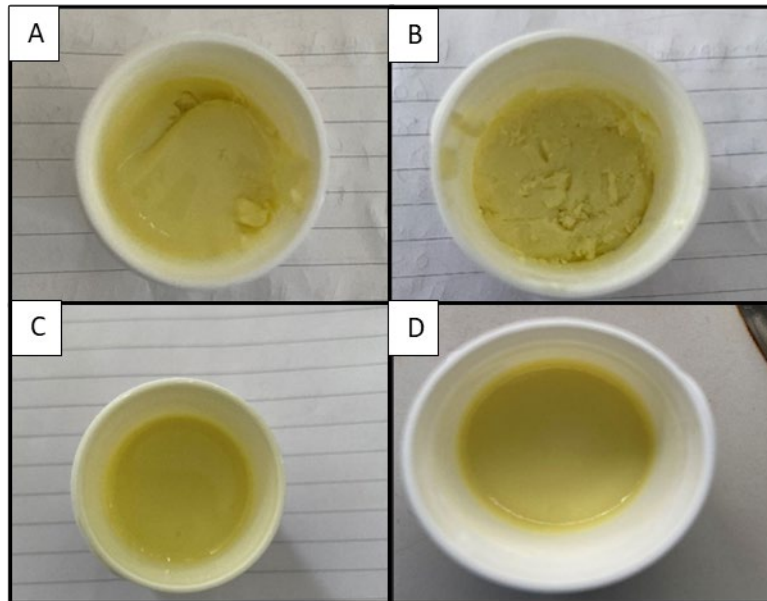


Figure 4-3: A. 55F composites. B.55F composites when a high-speed mix was used (3000 rpm) it shows a heterogeneous mixture. C. The lab-made composites. D. The GTS-mix composites.

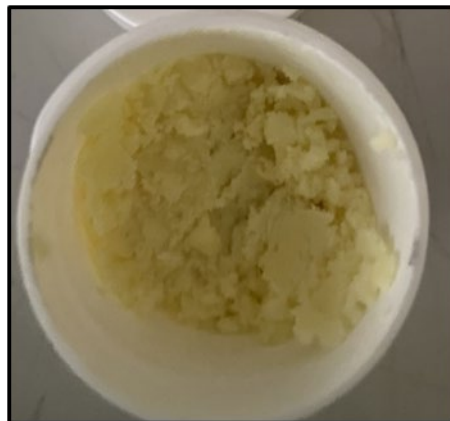


Figure 4-4: 55F When a low-speed mix was used (1000 rpm) it shows a dry and unmixed filler.

4.2.4 Model Composites physical and mechanical property measurements

4.2.4.1 Degree of Conversion

The samples were made by packing the composites into a stainless-steel washer (6.4mm diameter, 0.8mm thickness, RS PRO, UK) using a plastic spatula. The washer was sandwiched between two transparent polyethylene terephthalate (PET) films (0.17mm thickness, PET Goodfellow Cambridge Ltd., Huntingdon, UK) after adding the material and then pressed between two glass slides to extrude the excess material and ensure a flat and smooth surface.

Five specimens were made for each group (n=5), and each group was light cured for specific times of 10, 20, 30, 40, and 60 seconds using an LED light cure unit (10mm tip, 3M EPSE Elipar™) with an irradiance of 1000-1100 mW/cm². The intensity was measured using a curing light radiometer (Bluephase Meter II, Ivoclar Vivadent, UK).

The DOC was measured using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Perkin-Elmer, Spectrum Two, UK). Background measurement was recorded at the start of each session and at 2 hourly intervals. After that the unpolymerised materials were recorded as a reference. The DOC was measured under the following conditions: wavelength between 400-4000 cm⁻¹ with 16 scans and spectral resolution of 4 cm⁻¹. The percentage of uncured C=C was determined from the ratio of absorbance intensities of the aliphatic C=C peak at 1640 cm⁻¹ and the C=O stretching peak at 1720 cm⁻¹ for the polymerised specimens, then compared to the same ratio for the uncured composites. The following equations were used to calculate the DOC:

$$1- (\% C=C) = \frac{[Abs (aliphatic)/Abs (C=O peak)]_{polymer}}{[Abs (aliphatic)/Abs (C=O peak)]_{monomer}} \times 100$$

$$2- DOC\% = 100 - (\% C = C)$$



Figure 4-5: FTIR samples

4.2.4.2 Water sorption

Specimens were prepared from the six experimental composites (n=5) by pouring the materials into a plastic PTFE mould (10mm diameter, 1mm thickness) using plastic spatula. The mould was placed on PET film on the top of a glass slide (Goodfellow Cambridge Ltd., Huntingdon, UK). After pouring the material into the PTFE, another layer of PET was placed on the top of the mould and a glass slide was used to press the specimens to extrude the excess materials and provide a flat and smooth surface). Each specimen was light cured in one cycle for 20s (10mm tip, 3M EPSE Elipar™, intensity 1000-1100 mW/cm²) then polished using silicon carbide grinding papers (P600, Norton, Abrasive Technological Excellence, France). The thickness (the mean of four equally spaced points on the circumference) and diameter (the mean of two measurements at right angle to each other) of each specimen was measured using a digital calliper (0.01mm accuracy, Mitutoyo Digimatic, Japan). Each disk was weighed to determine the initial mass (M1) using a digital balance (Mettler AE 240, 0.01 mg accuracy, Leicester, UK). All specimens were then placed in the incubator at 37±1 °C for 24hrs. After 24hrs, each specimen was placed into an individual plastic bottle containing 5mL of distilled water (DW) and stored in an incubator at 37±1 °C for 4 weeks. Mass after immersion (M2) was taken after 1hr, 4hrs, 24hrs, 48hrs, 72hrs, 96hrs, and then weekly up to

week 4. At the time of measurement, each specimen was removed from the storage bottles with tweezers, blotted dry with paper towel until free of visible moisture, then weighed (M2) and placed in the bottle with a fresh 5mL of DW and stored in the incubator for the next measurement. Water sorption was calculated according to the ISO 4049 (ISO, 2019) using the following equation:

$$\text{Water sorption } (\mu\text{g}/\text{mm}^3) = \frac{M2 - M1}{V}$$

Where:

M1 is the initial mass before immersion in water in μg .

M2 is the mass of the specimens after the immersion in μg .

V is the volume of the specimens in mm^3

4.2.4.3 Fluoride release

Specimens used in water sorption test were used in the fluoride release test (n=5). On the day of the experiment, specimens were taken out from the incubator and placed in plastic bottles with 5 mL of DW and stored at 37 ± 1 °C. The bottles were placed at an angle to ensure specimens are fully immersed in DW (Figure 4-6). The DW was changed at each time point of the measurement at 1 hr, 4hrs, 24hrs, 72hrs, 96hrs then weekly up to 4 weeks. During the measurement, specimens were taken out of the plastic bottle, blotted dry with paper towel, then weighed before placing them in a fresh DW solution and stored in an incubator at 37 ± 1 °C for the next measurement.



Figure 4-6: Fluoride ion test specimen in 5ml DW

The fluoride ion release was measured using an ion-selective electrode (ISE) (ORION 4 STAR, Orion Research, Thermo Scientific, Waltham, MA, USA) (Figure 4-7). 0.5 mL of the total ionic strength adjustment buffer (TISAB III) (TISAB III concentrate with CDTA, Thermo Fisher science) was added to each sample solution before testing. A magnetic stirrer (VELP, Scientifica, Italy) was used to mix the solutions for three minutes before recording the measurements at 1hr, 4hrs, 24hrs, 48hrs, 72hrs, 96hrs, then weekly up to 4 weeks.

Before each analysis of the storage solutions, the ISE was calibrated using the standard sodium fluoride solutions (Fluoride ISE standard solution, Reagecon, Switzerland) made from a serial dilution series starting from 1000 ppm to 0.001 ppm, diluted with DW so that a calibration curve could be constructed. The ISE was calibrated every 2 hours at the day of the fluoride measurement. The concentration readings recorded in millivolts (mV) were converted to ppm using the following equations:

$$\frac{mV1 - mV2}{\log C1 - \log C2} = \frac{mVs - mV2}{\log Cs - \log C2}$$

$$\frac{\log Cs - \log C2}{\log C1 - \log C2} = \frac{mVs - mV2}{mV1 - mV2}$$

$$\log Cs - \log C2 = \left(\frac{mVs - mV2}{mV1 - mV2} \right) X (\log C1 - \log C2)$$

$$\log Cs - \log C2 = \left(\frac{mVs - mV2}{mV1 - mV2} \right) X (\log C1 - \log C2)$$

$$\log Cs = \left(\frac{mVs - mV2}{mV1 - mV2} \right) \log C1 - \left(\frac{mVs - mV2}{mV1 - mV2} \right) \log C2 + \log C2$$

$$Cs = 10^{\log Cs}$$

Where mV1 and mV2 represent mV of the standard solutions, C1 and C2 standard solutions' concentration, mVs is the mV of the testing sample, Cs is the concentration of the testing sample.

logCs is the concentration of the testing sample in ppm, and mV is the measured value in millivolts.

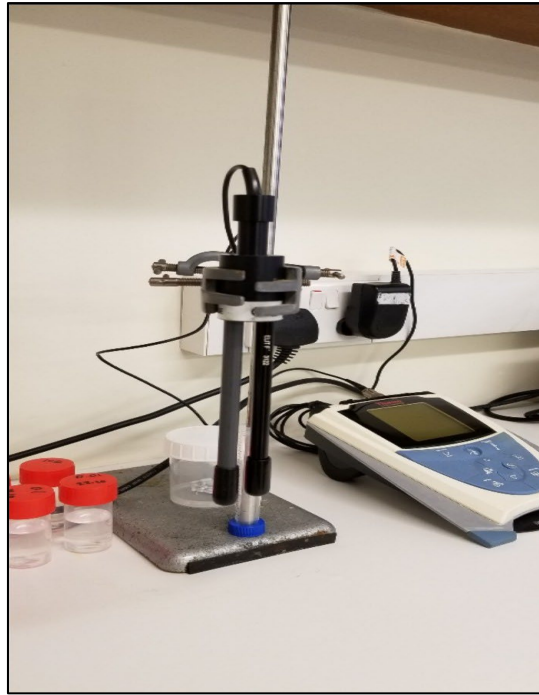


Figure 4-7: Ion-selective electrode

4.2.4.4 Flexural strength (FS) and flexural modulus (FM):

Following ISO 4049, ten specimens of each composite were made using a custom-made split mould with a dimension of 25 X 2 X 2 mm (Figure 4-8). Composites were packed incrementally, then covered with the PET sheet and a glass slab used to compress and level the material. Each specimen was light cured using 5 overlapping 20s exposure using a light cure unit (3M EPSE Elipar™ irradiance= 1000-1100 mW/cm²). Each specimen was removed from the mould and polished using silicon carbide grinding papers (P600, Norton, Abrasive Technological Excellence, France) then stored in 5ml DW in an incubator at 37± 1°C before testing at day 1,7, 14 and 28 (Figure 4-9).

The 3 point-bending tests were performed using a universal testing machine (Instron 5567, Instron, UK) with three-point bending equipment. Before testing, dimensions (thickness and width) of each sample were recorded using a digital calliper (CD-6, Mitutoyo Corporation,

Japan). The maximum load applied to the sample until the fracture point was recorded and the flexural strength and flexural modulus calculated using the following equation.

$$FS (MPa) = \frac{3FL}{2wh^2}$$

$$FM (GPa) = \frac{F}{d} * \frac{L^3}{4wh^3}$$

Where:

F → maximum force (N) applied on the specimen at the fracture point.

L → the length (mm) of the testing span.

w → the width (mm) at the centre of the specimen.

h → the height (mm) at the centre of the sample (mm)

d → the deflection results from the load applied at the centre of the specimen.

F/d → the slope in the linear region of the stress strain curve.



Figure 4-8: Custom split steel mould.

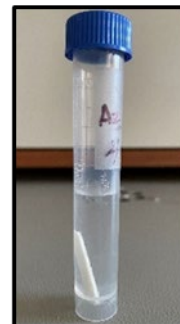


Figure 4-9: The sample in DW before stored in incubator.



Figure 4-10: 55F sample before (A), During (B) and after (C) FS test.

4.2.4.5 Statistical Analysis

All data were analysed with the same statistical software (SPSS version 27, IBM, Chicago, USA). Normality was determined using Shapiro-Wilk test. For normally distributed data a mean and standard deviation were used as summary statistics. Where comparisons between multiple groups were required, the parametric mixed ANOVA and post hoc Bonferroni were used with $P < 0.05$ considered statistically significant. For non-normally distributed data, a median and interquartile range were used to summarise data. When comparisons between groups were required the Kruskal Wallis test used to compare between materials at each time point and Friedman's ANOVA was used to compare within each material with $P < 0.05$ considered statistically significant.

4.3 Results:

4.3.1 Degree of conversion

The data were normally distributed. The mean percentage of the DOC of composites are shown in appendix A and figure 4- 11. The mean DOC ranged from 47-72%. Up to 40s of light exposure, no differences in DOC were found between the six composites ($P > 0.05$).

However, GTS-mix showed a lower DOC compared to GTS2 at 60 seconds curing time

($P < 0.05$). Within each material, no significant differences were found when increasing the curing time from 10 seconds to 60 ($P > 0.05$).

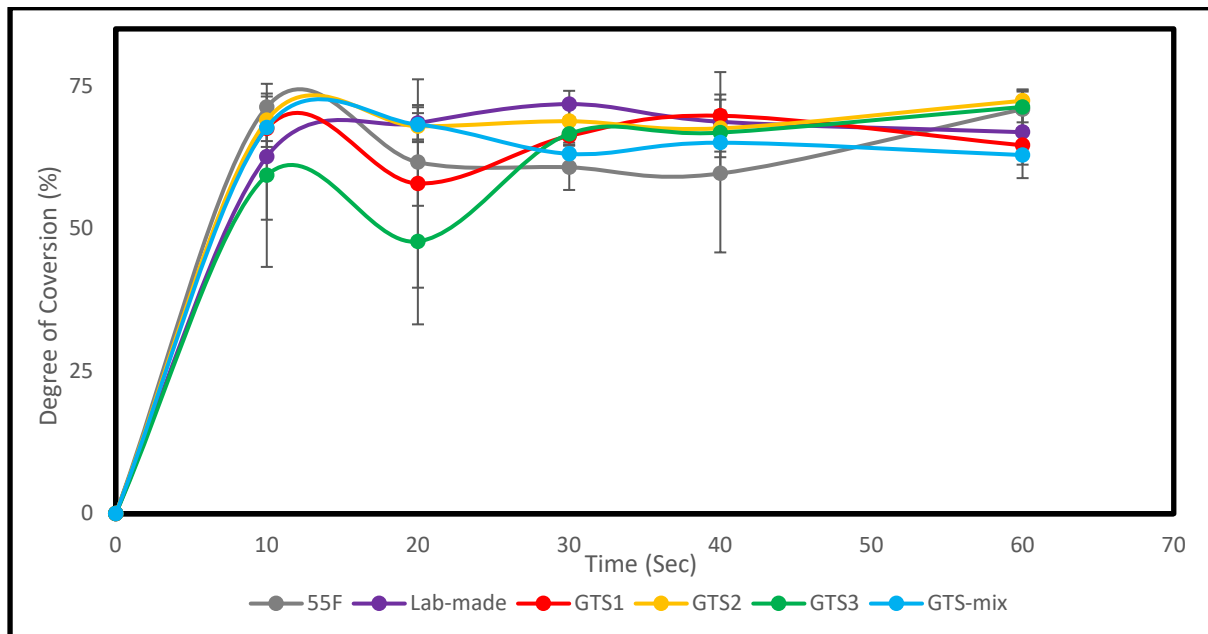


Figure 4-11: DOC (%) of 55F, lab-made, GTS 1,2 3 and GTS-mix composites, GTS-mix showed a significantly lower DOC compared to GTS2 at 60s ($P < 0.05$).

4.3.2 Water sorption

The water sorption data were not normally distributed. The water sorption results are shown in appendix B and figure 4-12. In general, all the six tested composites increased in weight. The pattern of the water sorption of the of the 55F composite specimens showed a significant increase in the water sorption at week 1 ($P < 0.05$) but then no further significant change up to 4 weeks ($P > 0.05$). The lab-made glass composites specimens sorption increased significantly at 48 hours ($P < 0.05$), then no significant

changes were shown ($P>0.05$). The specimens made with GTS glasses showed a similar pattern to each other where the significant increase was shown at 72 hours ($P<0.05$), except GTS-mix that showed the significant increase at 96 hours ($P<0.05$), with no significant change when stored up to 4 weeks. The lab-made glass composites showed a higher water sorption than the 55F and all GTS composites which was significant at most of the time points ($P<0.05$).

At day one, no significant differences were shown between all the tested composites ($P>0.05$). While there were some significant differences between the water sorption of the 55F and lab-made glass composites against the 4 GTS composites, there were no significant differences found between GTS1, GTS2, GTS3 and GTS-mix at all time points ($P>0.05$). The lab-made glass composites showed a significantly higher sorption at most of the time points compared to all the tested composites ($P<0.05$).

55F composites showed a significantly lower water sorption than the lab-made glass composites at all time points between 48 hours and 3 weeks ($P<0.05$). 55F showed also a significantly lower sorption than some of the GTS composites at different time points ($P<0.05$). At 72 hours, it showed a lower sorption than GTS1, then at 96 hours, it was lower than all GTS composites except GTS-mix ($P<0.05$). At week 2, 55F showed a lower sorption than all GTS composites except GTS3 ($P<0.05$) and at week 3, the value was lower than GTS1 and GTS2 ($P<0.05$). At week 4, 55F showed a lower sorption than all the tested composites ($P<0.05$).

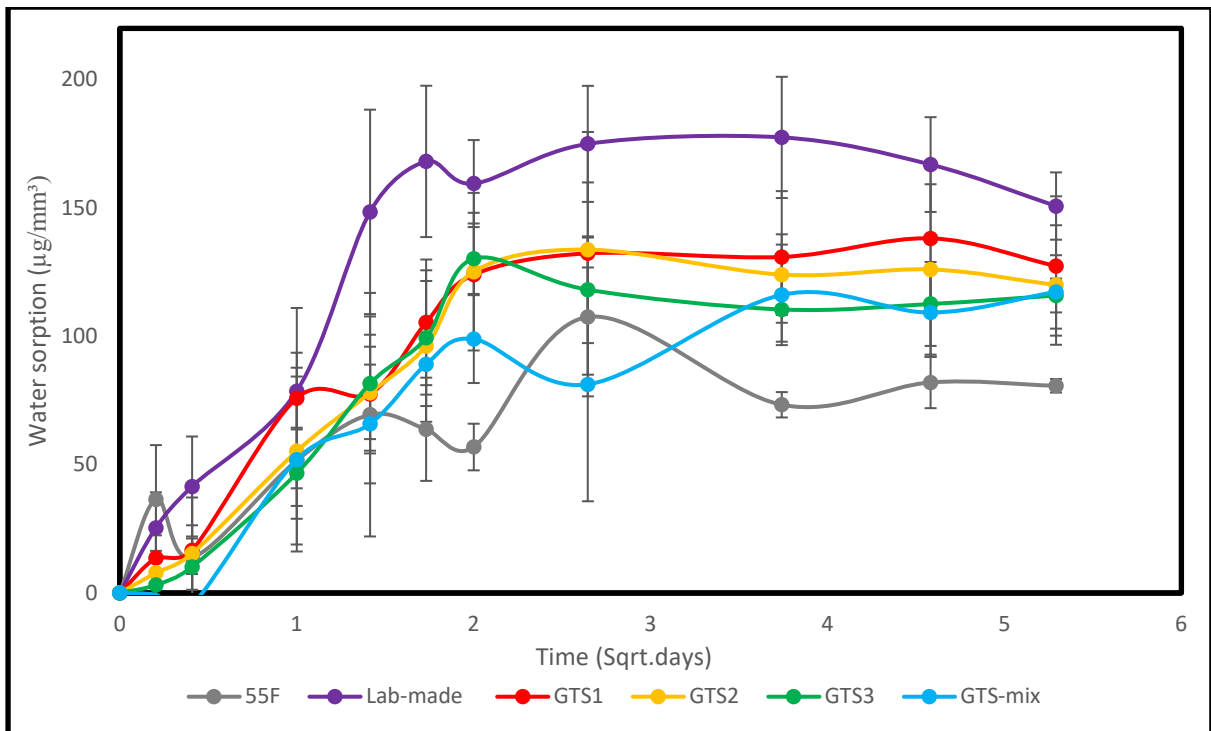


Figure 4-12: Water sorption ($\mu\text{g}/\text{mm}^3$) of the 55F, lab-made glass and the GTS composites. The lab-made glass composites showed a significantly higher sorption in most of the time points ($P < 0.05$)

4.3.3 Fluoride release

The data distribution was evaluated and showed that the fluoride release data were not normally distributed. The pattern of the fluoride ion release was similar among the lab-made and GTS composites with initial high release at 24 hours and the highest release at week 2 (Table 4-3). The 55F composites released negligible amount of fluoride ion up to 4 weeks which was significantly lower than the F-BAGs based composites ($P < 0.05$).

While there were some significant differences between the measured fluoride released after 4 hours, 24 hours, 96 hours and one week ($P < 0.05$, shown in red in table 4-3), the overall fluoride release pattern was similar for all four GTS composites. On the other hand, the lab-made glass composites showed a significantly higher release at 4 hours, and from week 1 until week 4 ($P < 0.05$, shown in green in table 3), and showed a significant lower amount of fluoride release at 24, 48, 72 & 96 hours compared to the GTS composites

($P < 0.05$, shown in blue in table 4-3). The cumulative fluoride release for the four GTS composites was very similar over the 4 weeks ($P > 0.05$). The cumulative release of fluoride ion for the lab-made glass composites was significantly lower up to week 2 compared to the GTS composites ($P < 0.05$), however, at week 4, the fluoride release of the all the composites (except the 55F) was between 57 and 63 $\mu\text{g}/\text{cm}^2$ with no significant differences ($P > 0.05$) (Figure 4-13).

Time	55F		Lab-made		GTS1		GTS2		GTS3		GTS-mix	
	Median	IQR	Median	IQR	Median	IQR	Median	IQR	Median	SD	Median	IQR
1 hour	0.00	0.00	0.26	0.03	0.22	0.07	0.29	0.03	0.24	0.05	0.26	0.03
4 hours	0.00	0.00	1.01	0.15	0.76	0.05	0.83	0.07	0.79	0.05	0.68	0.05
24 hours	0.00	0.00	2.59	0.28	8.67	0.77	7.61	0.43	8.52	0.48	7.5	0.42
48 hours	0.00	0.00	2	0.1	6.29	0.51	5.92	0.28	6.61	0.63	5.91	0.42
72 hours	0.01	0.02	2.26	0.19	5.28	0.26	5.18	0.43	5.62	0.36	5.19	0.24
96 hours	0.00	0.00	1.75	0.17	4.48	0.19	4.13	0.18	4.77	0.43	4.12	0.18
Wk1	0.12	0.07	7.27	0.41	5.13	0.28	4.39	0.11	4.96	0.38	4.59	0.18
Wk2	0.00	0.00	17.54	1.72	12.3	0.64	11.79	0.49	12.11	0.69	11.16	0.26
Wk3	0.05	0.10	14.43	3.93	7.35	0.56	6.85	0.49	7.74	0.79	6.71	0.54
Wk4	0.04	0.08	10.01	1.3	8.32	1.13	7.39	0.21	8.57	0.53	7.88	0.87

Table 4-3: The fluoride release median and IQR ($\mu\text{g}/\text{cm}^2$) for the six experimental composites. The green coloured numbers showed significant higher release from the lab-made glass composites ($P < 0.05$), the red indicated some significant differences between the GTS glass composites ($P < 0.05$), and the blue numbers indicated a significant lower daily fluoride release from the lab-made glass composites compared to the GTS composites ($P < 0.05$)

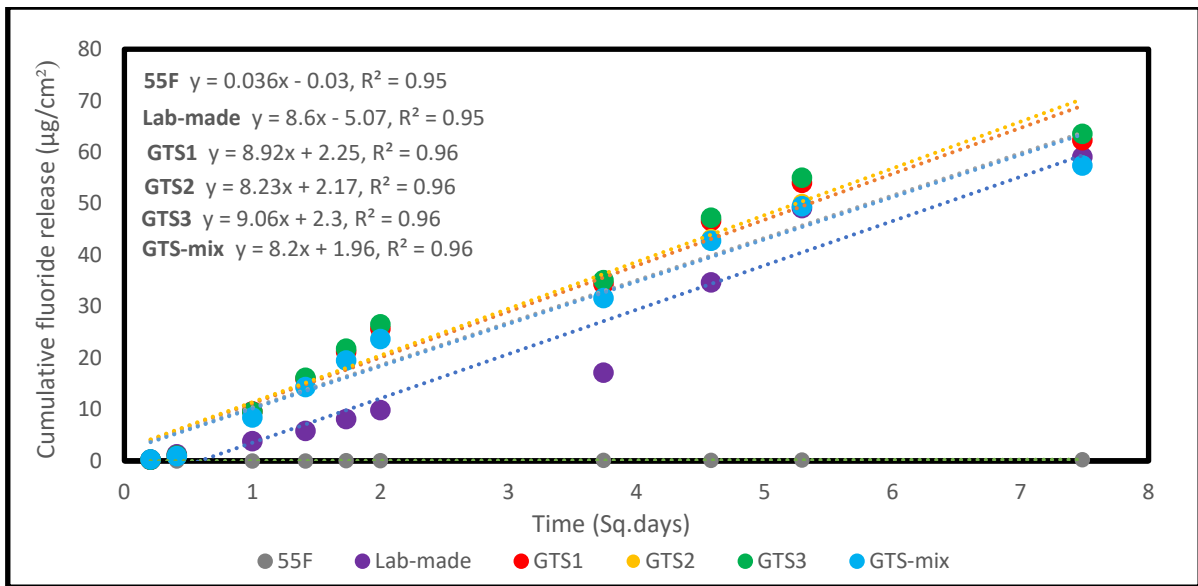


Figure 4-13: Cumulative fluoride release ($\mu\text{g}/\text{cm}^2$) of the 55F, lab-made and the GTS composites. Despite the significantly lower daily fluoride release by the Lab-made F-BAGs composites up to 96hrs compared to the GTS based composites ($P < 0.05$), the cumulative fluoride release at week 4 were similar ($P > 0.05$).

4.3.4 Flexural strength and flexural modulus:

The data were normally distributed. The FS and FM data are shown in table 4-4 and 4-5 and figure 4-14 and 4-15. Initially, all composites had a strength above 80MPa, 55F showed a significantly higher FS value compared to GTS2 and lab-made glass composites ($P < 0.05$), and no significant differences were found between the lab-made glass and the GTS-based composites ($P > 0.05$). At day 7, 55F showed a significantly higher FS value compared to the rest of the composites ($P < 0.05$). At day 14 and 28, lab-made glass composites showed a significantly lower FS compared to 55F and GTS composites ($P < 0.05$) with no differences shown between the 55F and the GTS composites ($P > 0.05$).

Within the groups, 55F showed no significant decrease in the FS when stored up to 28 days ($P > 0.05$). On the other hand, with lab-made glass composites, the strength decreased significantly over time ($P < 0.05$). GTS1,2,3 and GTS-mix showed a significant decrease in the strength at day 7 ($P < 0.05$), then no significant decrease was shown up to 28 days ($P > 0.05$).

For the FM, initially no differences were found between the 55F, the lab-made glass composites and the all the four GTS composites ($P>0.05$). At day 7, 55F showed a significantly higher FM compared to the lab-made, GTS1 and GTS2 ($P<0.05$), but no differences when compared to GTS3 and GTS-mix ($P>0.05$). The lab-made glass composites showed a significantly lower FM when compared to 55F and the GTS composites ($P<0.05$) except GTS2 ($P>0.05$). At day 14, 55F composites showed a significantly higher FM compared to the lab-made, GTS2 and GTS3 ($P<0.05$), and the lab-made glass composites had a significantly lower value compared to all the tested composites ($P<0.05$). At day 28, 55F showed a significantly increased FM strength compared to the lab-made and GTS-mix ($P<0.05$). The lab-made glass composites showed a significantly lower value compared to GTS3 and 55F ($P<0.05$). GTS1,2,3 and GTS-mix showed no significant differences over the storage time ($P>0.05$).

Within each group, 55F, GTS1, GTS3 and GTS-mix showed no significant differences when storing the material up to 28 days ($P>0.05$). The lab-made glass and GTS2 composites decreased significantly when tested at day 7 ($P<0.05$), then no significant change for up to 28 days ($P>0.05$).

Days	55F		Lab-made		GTS1		GTS2		GTS3		GTS-mix	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	100.3	18	82.2	9.3	88.8	8.8	84.3	5	86.6	9.8	88.2	10.4
7	88	24.9	57.4	5	68.7	11.1	68.9	7.1	69.7	9.6	71	9.5
14	80	18.6	49.4	5.4	66.9	7.6	72.1	7.1	73.6	8.4	73.3	6.4
28	82.4	20.3	41.1	4.9	68.4	8.8	68.8	9.6	73.9	8.2	69.9	7.2

Table 4-4: The flexural strength (MPa) mean and standard deviation values of the six tested composites. The 55F showed no significant decrease over storage time ($P>0.05$), but the FS of the F-BAGs lab-made and GTS composites decreased significantly at day 7 ($P<0.05$), with no further differences up to 28 days ($P>0.05$).

Days	55F		Lab-made		GTS1		GTS2		GTS3		GTS-mix	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	8.1	1.5	7.1	0.5	7.7	1.5	7.6	0.3	7.8	0.4	8.1	0.8
7	8.3	1.6	5.7	0.5	6.9	0.3	6.5	0.9	7.4	0.5	7.3	0.4
14	8.4	1.1	5.7	0.6	7.5	1	7.1	0.7	7	0.7	7.4	0.4
28	8.8	1.5	5.3	0.6	6.9	1.2	6.9	1.2	7.4	1	6.4	2.4

Table 4-5: The flexural modulus (GPa) mean and standard deviation values of the six tested composites. Only lab-made and GTS2 showed a significant decrease in the FM at day 7 ($P<0.05$), with no change up to 28 days ($P>0.05$).

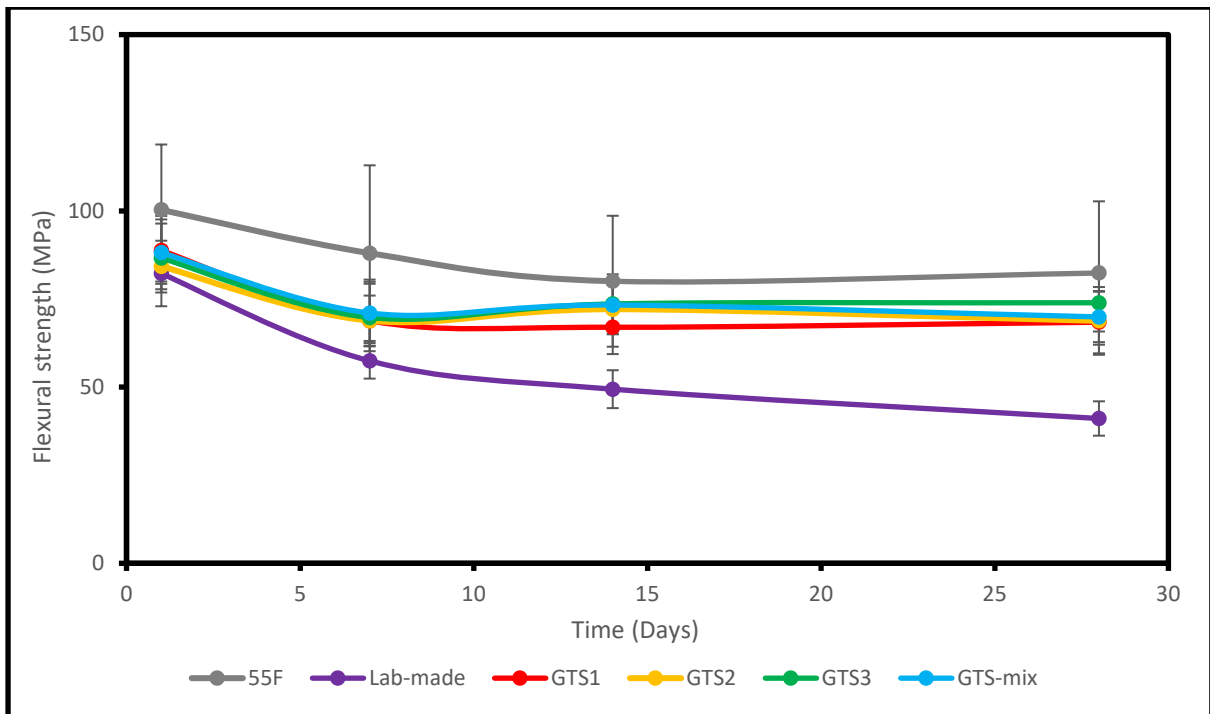


Figure 4-14: Flexural strength values (MPa) of the six tested composites with their standard deviation. The lab-made F-BAGs composites showed a significant decrease over storage time ($P < 0.05$).

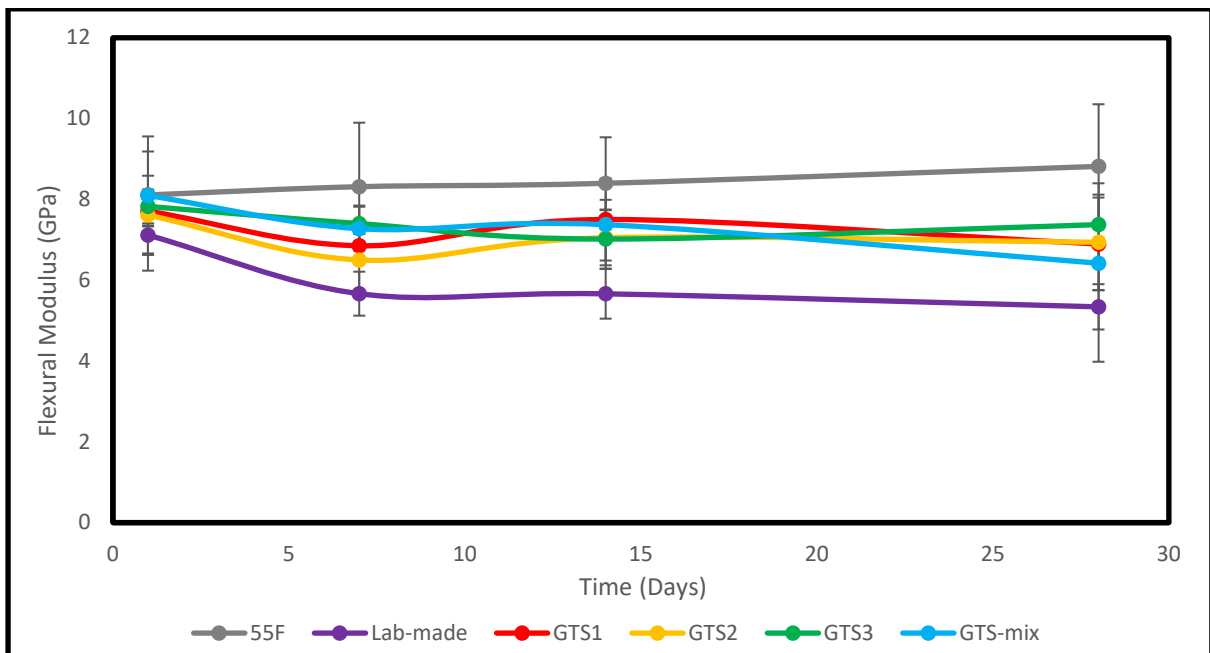


Figure 4-15: Flexural modulus values (GPa) of the six tested composites with their standard deviation. Only lab-made and GTS2 showed a significant decrease in the FM at day 7 ($P < 0.05$), with no change up to 28 days ($P > 0.05$).

4.4 Discussion

4.4.1 Preparation of the F-BAGs composites

In this chapter, six different composites were made. The first composites were the 55F which contain barium silicate glass fillers without the F-BAGs fillers. The second composites were the lab-made glass composites containing the F-BAGs made at Newcastle University added as a secondary filler. Then three composites were made containing industrial GTS glasses as secondary fillers (GTS1, GTS2, GTS3) and the last composites were a mix of the three GTS glasses (GTS-mix). The monomer mixture 50:50 UDMA: TEGDMA was chosen, and the filler volume was 55vol%.

The experimental composites were successfully made with lab-made and industrially made F-BAGs incorporated at 20wt% in addition to the primary barium-aluminium-silicate glass.

The materials were prepared using a centrifuge speed mixer which has been widely used in making experimental composites (Schneider *et al.*, 2009). The speed of mixing influenced the homogeneity of the mixture. The first two attempts to incorporate the fillers to the monomer mixture were not successful when a low speed of 1000 rpm was used, showing dry and unmixed filler particle, and the 3000 rpm also showed a heterogeneous mix even with the extended time of mixing. Whereas, at 2000 rpm for 3mins mixing, along with the incremental mixing technique, the outcome was a homogenous composite paste. It has been reported that incorporating unsilanised fillers can affect the integration and adhesion of the resin matrix that could result in heterogenous composite mix (Zanchi *et al.*, 2015). However, the addition of the F-BAGs into the experimental composites did not affect the homogeneity of the composite mixtures.

4.4.2 Degree of conversion:

Degree of conversion has been previously shown to affect a number of key properties of RBCs, such as strength and modulus (Hofmann *et al.*, 2002; Durner *et al.*, 2012). The addition of BAGs to RBCs has been shown by some authors to lead to a reduction in DOC when compared to BAG-free comparators, and the cause of this reduction is the inhibition effect caused by the water on the surface of BAG, or by the oxides on the particle surface that cause inhibition of the free radical polymerisation (Par *et al.*, 2019b; Par *et al.*, 2020a; Par *et al.*, 2020b). Consequently, the DOC of the RBCs made using the lab-made glass, the three GTS batches and the mixed batch were compared with a BAG-free RBC with the same overall monomers and same filler concentration. Up to 20s there were no significant differences between any of the materials ($P > 0.05$). However, at 30s and 60s the composites made with GTS-mix exhibited a slightly lower DOC compared to GTS2 ($P < 0.05$). The DOC of GTS-mix was quite variable for GTS-mix being particularly variable at 30s and 60s curing time. It is not clear why there was this variability at this time compared to 40s. It has been previously recommended that the minimum DOC for acceptable RBCs recommended for posterior restorations is 55%. Below this the RBCs have been shown to have lower wear resistance (Ferracane *et al.*, 1997; Silikas; Eliades and Watts, 2000; Yap; Wong and Siow, 2003; Galvão *et al.*, 2013). However, a number of studies have shown that the actual range of DOC for commercially available RBCs is between 35% and 77%, clearly indicating that some RBCs are used with much lower DOC than this 55% threshold (Schmalz, 2009; Schmalz and Arenholt-Bindslev, 2009; Galvão *et al.*, 2013). The recommended exposure times for light activation for commercially available composites is between 20-40s. Extended curing time is recommended for light-cure units with lower than 500 mW/cm² light intensity, whereas 20s polymerisation time is enough when higher output levels LED are used (Ernst *et*

al., 2004; Bala;Ölmez and Kalayci, 2005; Kramer *et al.*, 2008). Consequently, at the recommended clinical exposure time (20s and 40s) all the GTS composites performed similarly to the lab-made glass material and the F-BAG free composites.

4.4.3 Water sorption:

Water sorption is an important factor controlling the physical and mechanical properties of the composite materials (Sideridou;Tserki and Papanastasiou, 2003). Increase the water sorption has been shown to reduce the wear resistance and flexural properties of the RBC restorations (Leprince *et al.*, 2013; Cornelio *et al.*, 2014). Incorporating BAGs (one based around SiO₂ 45%, Na₂O 25%, CaO 25%, P₂O₅ 5%, particle size 4 µm) to the dental composites has been shown to increase the water sorption significantly when compared to the BAG-free composites (Par *et al.*, 2019a). In the current work, the water sorption of the composites made using the lab-made glass, the three GTS batches and the mixed batch were compared with a BAG-free RBC with the same monomer and fillers concentrations. No significant differences in water sorption were shown between the GTS batches after 28 days of storage (Appendix B) (P>0.05). The lab-made glass composites showed significantly higher water sorption of 117 µg/mm³ (P<0.05), and the 55F showed the lowest sorption of 57 µg/mm³ after 28 days of storage (P<0.05). The highest limit for the water sorption recommended by ISO4049 for dental composites is 40 µg/mm³ (Standardization, 2019), and all the tested materials showed higher than this limit. Also, the ISO standard stipulates measuring the water sorption after only one week of storage, and the ion releasing materials will experience greater filler and matrix degradation with aging in order to release ions suggesting that they will absorb more water over time (Par *et al.*, 2022). The water sorption of the lab-made glass composites and GTS composites were in the range between 65-117

$\mu\text{g}/\text{mm}^3$ which is in the range of the commercially available GIC (50-250 $\mu\text{g}/\text{mm}^3$) (Cefaly *et al.*, 2003; Bhatia *et al.*, 2017), and lower than the water sorption of some BAG-containing composites (ones based around SiO_2 45%, Na_2O 25%, CaO 25%, P_2O_5 5%, particle size 4 μm), with between 10 and 20wt% BAG filler, that showed a range between 100-200 $\mu\text{g}/\text{mm}^3$ (Par *et al.*, 2019a).

The composites made from the lab-made glass and the GTS glass contained a mixture of silanised glass at 80wt% and unsilanised bioactive glass at 20wt%. In the conventional composites, the monomer network is the main cause of water sorption, due to the filler particles having a hydrophobic silane coating. However, in BAG materials, the fillers are hydrophilic and absorb water due to the lack of silane coating (Martin and Jedynekiewicz, 1998; Kangwankai *et al.*, 2017).

4.4.4 Fluoride release

Fluoride is well-known for having an anticariogenic effect through decreasing the demineralisation of the tooth substances by forming an acid-resistant hydroxyapatite or fluorapatite, and enhancing the remineralisation process by inhibiting the microbial growth (Ekstrand; Fejerskov and Silverstone, 1988; Hamilton and Bowden, 1988; Burt and Eklund, 1999). The addition of the different formulation of BAG fillers has been shown to lead to the release of essential ions including fluoride comparable to GIC and compomers (Karantakis *et al.*, 2000; Wiegand; Buchalla and Attin, 2007). The ion selective electrode (ISE) was used to measure the fluoride ions release in distilled water. This method has been used widely by researchers to measure the fluoride release (Itota *et al.*, 2004a; Durner *et al.*, 2012). The acetic buffer solution (TISAB) was added to release the free fluoride ions from the complex

ions. TISAB can also prevent the hydroxide ions interference which has the same ion radius as fluoride ions (Itota *et al.*, 2004a; Itota *et al.*, 2004b).

The fluoride release of the composites made using the lab-made glass, the three GTS batches and the mixed batch were compared with a F-BAG-free RBC with the same monomer and fillers concentrations. Despite some significant differences in terms of daily fluoride release between the lab-made glass composites and all the GTS composites, the cumulative fluoride release was similar up to 28 days ($P>0.05$) (Figure 13). The pattern of fluoride release was the same for all the F-BAGs composites in which the initial burst at 24 hours, followed by slow release before the significant increase at week one and week two ($P<0.05$), and the result of this study showed that the F-BAGs composites can release fluoride in a comparable pattern with the GIC, RMGIC and RBCs (Karantakis *et al.*, 2000; Wiegand; Buchalla and Attin, 2007). The 24-48 hours initial burst followed by diminishing phase has been reported in fluoride containing restorative materials (Okte *et al.*, 2012; Gururaj *et al.*, 2013).

There is no consensus on the amount of fluoride sufficient to be effective to prevent recurrent caries. However, localized fluoridation around a demineralised area, with fluoride released in the range of 0.63-1.3 $\mu\text{g}/\text{cm}^2$ per day, was shown to be effective to inhibit demineralisation (Rawls, 1995; McNeill *et al.*, 2001). The lab-made glass composites and all the GTS composites showed a fluoride release higher than this range and to other commercially available fluoride releasing materials (Wiegand; Buchalla and Attin, 2007; Naoum *et al.*, 2011).

4.4.5 Flexural strength and flexural modulus

Flexural tests are standard means for testing the strength of the RBCs and these test are of the high ranked tests to predict the clinical performance of the dental composites (Ferracane, 2013; Standardization, 2019). Incorporating the a number of different BAG fillers in the resin composites has shown to decrease the mechanical properties in comparison to the BAGs free composites (Nicolae *et al.*, 2014; Par *et al.*, 2022).

The FS and FM of the RBCs made using the lab-made glass, the three GTS batches and the mixed batch were compared with the 55F. Initially, the flexural strength of the 55F was significantly higher than the lab-made glass composites and the GTS glass composites, and no significant decrease was shown when stored in DW up to 28 days ($P>0.05$). On the other hand, the lab-made and the four GTS composites showed values above 80 MPa on day one test with no significant differences between them ($P>0.05$), then the values decreased significantly over storage time for the lab-made glass composites ($P<0.05$), and for the GTS glass composites values decreased significantly at day 7 ($P<0.05$), with no further decrease up to 28 days.

From the results, adding the F-BAGs in 20wt% did affect the FS of the experimental F-BAGs composites. The flexural strength values of different commercially available composites were reported to be between 62-160 MPa, and the composites with higher fillers content showed a higher FS value (Ilie and Hickel, 2009a; Ilie and Hickel, 2009b; Ferracane, 2013; Ilie *et al.*, 2013). However, increasing the filler load above 80vol% result in unworkable composite paste (Anusavice; Shen and Rawls, 2013).

All F-BAGs based composites showed an FS of at least 80 MPa after aging for 24hrs, which based on the limits stipulated by ISO 4049 would make them acceptable for occlusal restoration. The values were, also, comparable to those reported for a range of different commercial composites (Ilie and Hickel, 2009b; Ilie and Hickel, 2009a; Ilie;Rencz and Hickel, 2013). After one week of aging, the F-BAGs composites showed a decrease in the flexural strength as a result of the water sorption that causes degradation of the resin/glass interface. The BAG composites are designed to have ion release from the bioactive glass, which results in the degradation of the glass fillers and eventually reducing the material's strength (Khvostenko *et al.*, 2013). The results of the lab-made glass composites showed a more significant decrease over time compared to the GTS composites, with the GTS composites being stable from day 7 up to 28 days.

The addition of BAG fillers up to 20wt% has been shown to not significantly affect the FS of composites after water storage, although SEM analysis reveals glass dissolution from the composite surface due to water sorption (Soderholm and Roberts, 1990; Lohbauer *et al.*, 2003; Curtis *et al.*, 2008; Khvostenko *et al.*, 2013; Nicolae *et al.*, 2014) . Increasing the BAG concentration to 30wt% and above led to a significantly decreased FS after water storage, due to degradation of the filler particles due to water sorption (Nicolae *et al.*, 2014). Based on the FS results, the lab-made and the GTS composites showed acceptable strength within the value recommended by the ISO4049.

The flexural modulus of the tested composites ranged between 5-8 GPa comparable to most highly filled commercial composites (3-16 GPa) (Leprince *et al.*, 2010; Ilie;Rencz and Hickel, 2013; Jun *et al.*, 2013; Randolph *et al.*, 2016; Ilie *et al.*, 2017) and BAG containing composites (2.5-6.5 GPa) (Par *et al.*, 2019b; Par *et al.*, 2022). After 24 hours in DW, no

significant differences were found between the experimental control composites (55F) and the F-BAGs composites ($P>0.05$). The FM values for the 55F and the four GTS composites showed no significant change over the storage time ($P>0.05$). The addition of the F-BAGs did not have an impact on the FM of the GTS composites. However, the lab-made glass composites showed a significant decrease at day 7 ($P<0.05$), then no significant change up to 28 days ($P>0.05$). These results support the water sorption result where the lab made glass composites showed the highest sorption compared to the GTS composites, and this might be due to the plasticisation effect of the water (Zhao and Li, 2008). Several studies have shown that adding BAG, CaP or HA fillers to the experimental composites decreases the FM values significantly compared to the experimental control composites (Aljabo *et al.*, 2015; Taheri *et al.*, 2015), however, the four GTS composites here did not show a lower FM compared to the 55F.

In an attempt to improve the mechanical properties of the composites one batch of GTS-mix particles were silanised using 2% γ -methacrylo-xypropyltrimetoxysilane following a previously published method (Al-Eesa *et al.*, 2021). There were no significant differences between the silanised and unsilanised GTS glass composites in terms of DOC (Figure 4-16), FS (Figure 4-17), FM (Figure 4-18), and water sorption (Figure 4-19). However, the cumulative fluoride release from the silanised GTS glass composite was significantly higher than the unsilanised one ($P<0.05$) (Figure 4-20). It is not clear why the fluoride release increased but the lack of significant improvement in mechanical properties following this silanisation attempt suggests that further work is required to develop a silanisation protocol for the F-BAG used in this work. Consequently, for the remainder of the work describe in this thesis no silanisation of the F-BAGs was used.

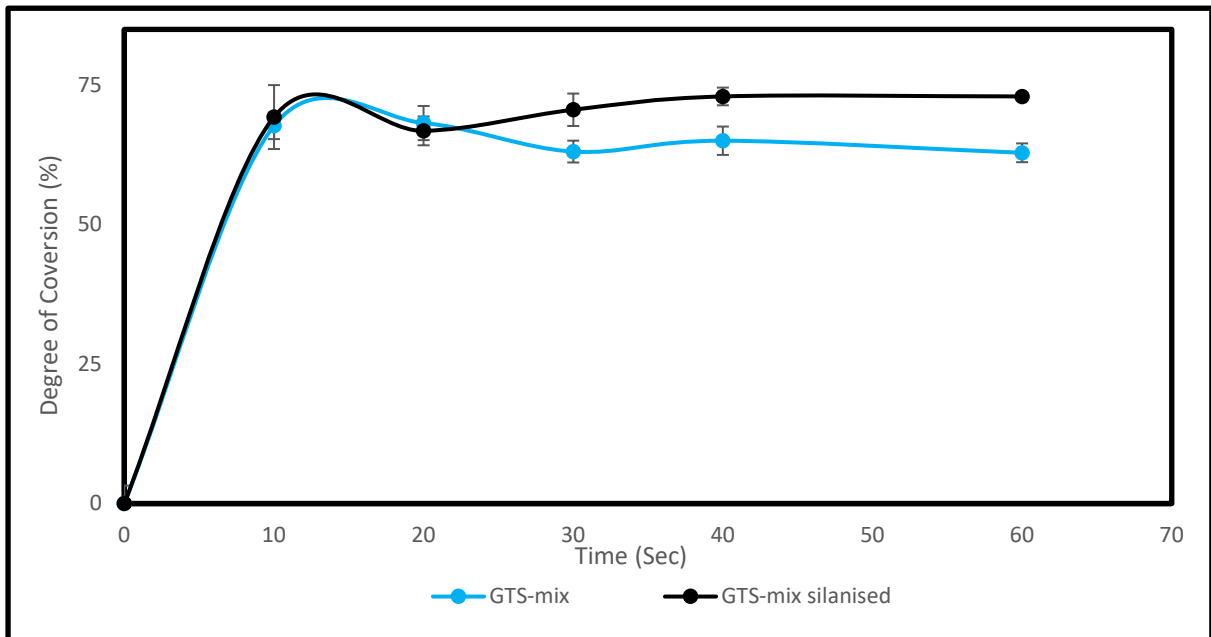


Figure 4-16: The DOC of the unsilanised GTS-mix glass composites compared to the silanised one. No significant differences were detected ($P>0.05$).

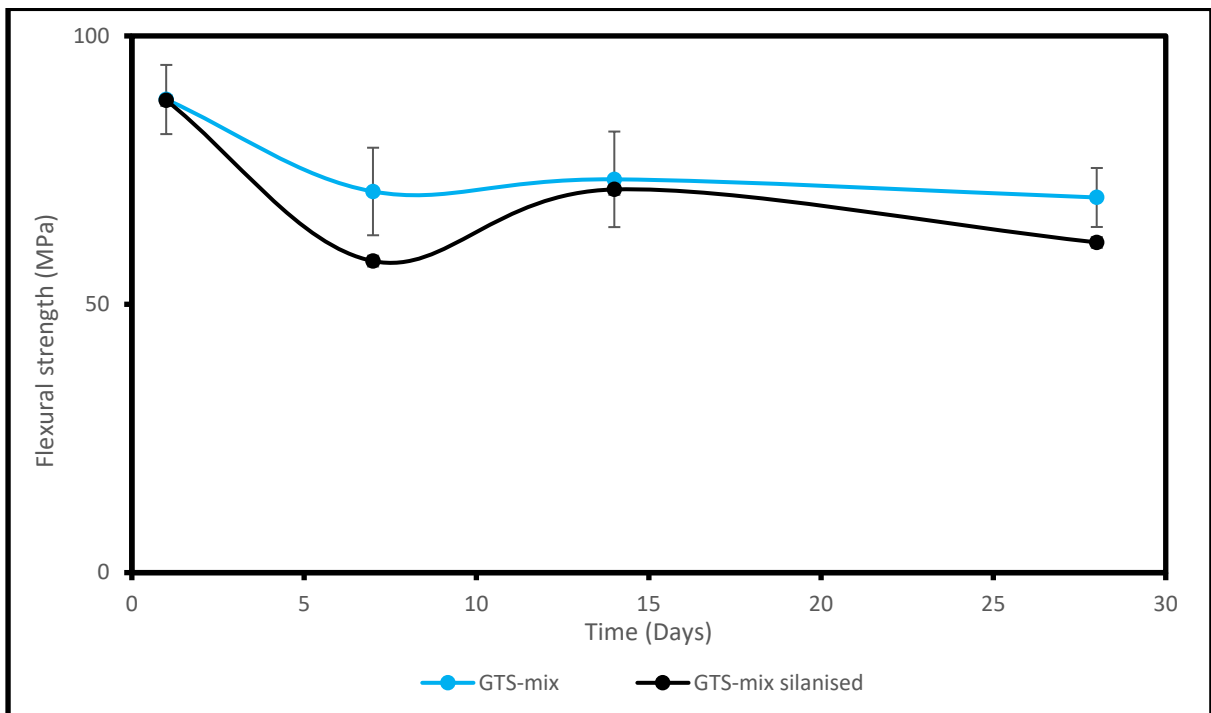


Figure 4-17: The FS (MPa) of the unsilanised GTS-mix composites compared to the silanised one. No significant differences were shown ($P>0.05$).

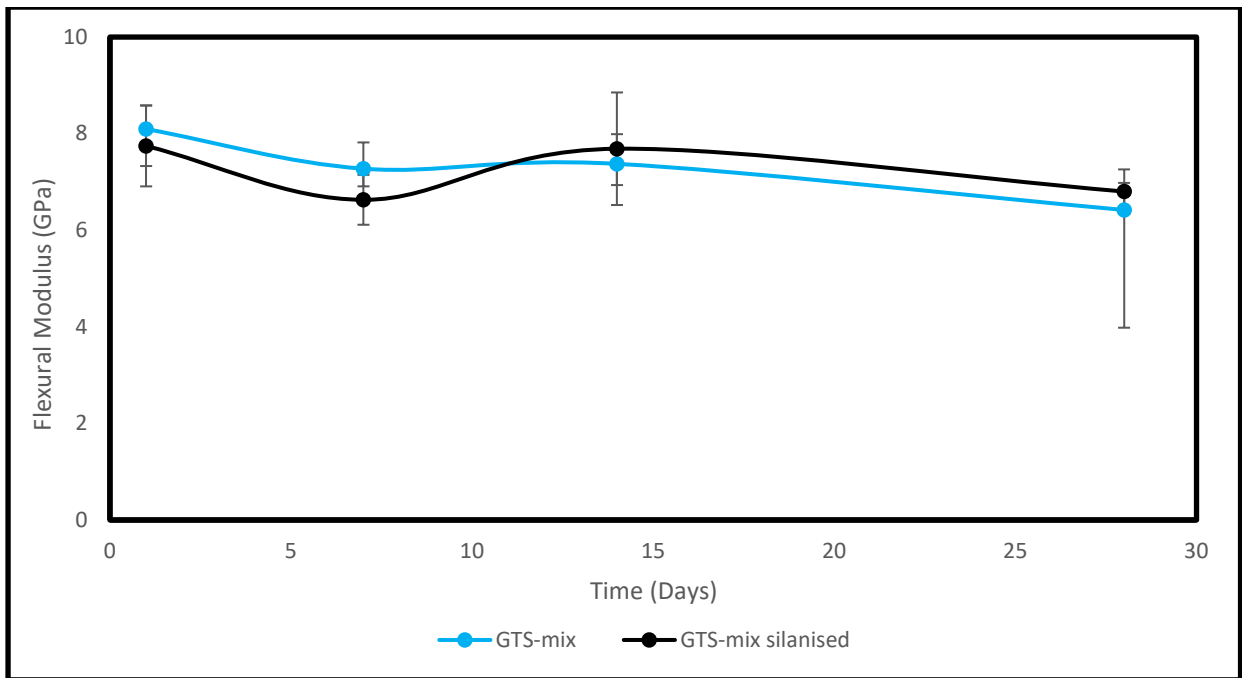


Figure 4-18: The FM (GPa) of the unsilanised GTS-mix glass composites compared to the silanised one. No significant differences were shown ($P>0.05$).

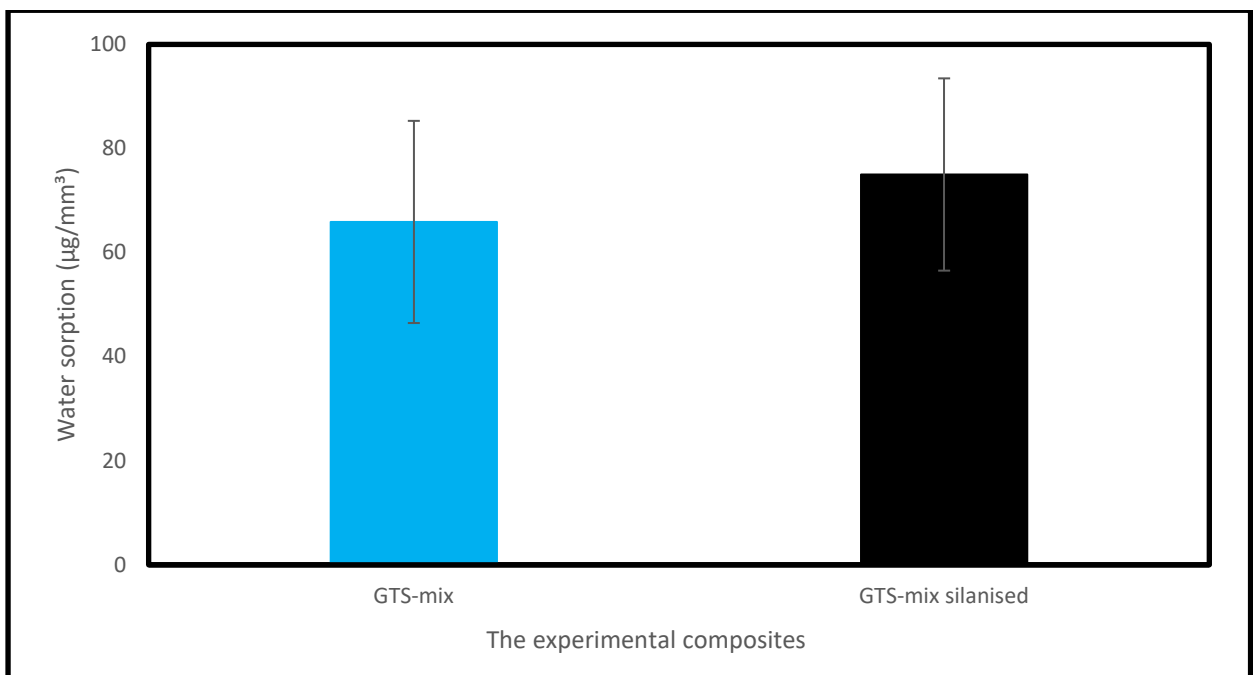


Figure 4-19: Water sorption of the unsilanised GTS-mix glass composites and silanised one after 28 days of storage. No significant differences were shown ($P>0.05$).

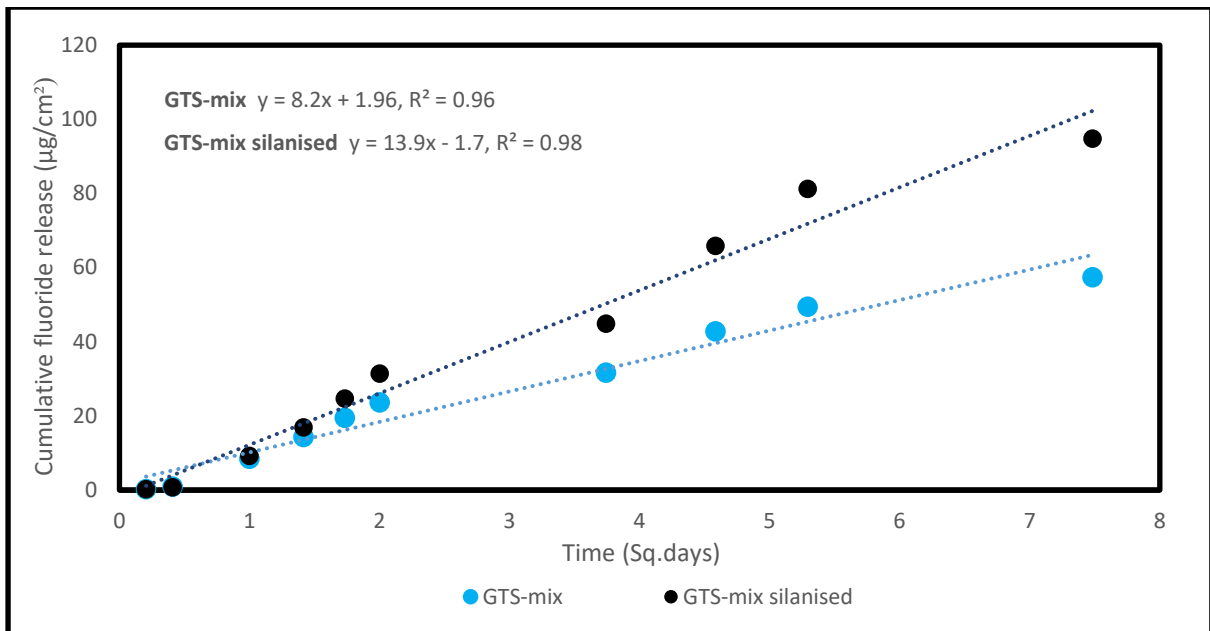


Figure 4-20: Cumulative Fluoride release of the unsilanised GTS-mix glass composites and silanised GTS-mix glass composites. GTS-mix silanised showed significantly higher cumulative release compared to the unsilanised GTS-mix glass composites ($P < 0.05$).

4.5 Summary

Scaling up from lab-made to industrially made glass does not affect the physical and mechanical properties, and composites made with the GTS glasses performed better than the lab-made glass composites. All GTS composites showed high DOC, good mechanical properties, and similar water sorption and fluoride release. While the flexural strength decreased over the first seven days of storage no further differences were shown up to 28 days. Compared to the lab-made, GTS composites had higher flexural properties but lower water sorption ($P < 0.05$) (Appendix B), but no differences were shown in cumulative fluoride release ($P > 0.05$) (Figure 4-13). As no significant differences were found between any of the GTS batches all future work used a mixture of all three batches (GTS-mix).

Chapter 5: Effect of Different Concentrations of Monomers on the Physical and Mechanical Properties of the F-BAGs Composite

5.1 Introduction

The aim of this chapter was to understand the effect of different monomer types and concentrations on the physical and mechanical properties of the composites. Model composites based around the monomers UDMA, TEGDMA and HEMA were made with silanised barium borosilicate glasses as the primary filler incorporated at 80wt%, and the F-BAG as the secondary filler incorporated at 20wt%. Different concentrations of the monomer mixtures were made starting with 100 UDMA then incorporating TEGDMA and HEMA in different concentrations to study the effect of materials concentrations and viscosity on the fluoride release and the physical and mechanical properties. The properties of the composites were compared in terms of their DOC, water sorption, fluoride release and flexural properties.

5.2 Materials and Methods

5.2.1. Composites preparation

The model composites were made using different concentrations UDMA, TEGDMA, and HEMA (Sigma-Aldrich Ltd., Dorset UK). The same photo-initiators as described in section 4.2.1 were used again at 1wt% concentration. Composites made with 55vol% filler concentrations, the main filler used was 0.7 μ m silanised barium borosilicate glass (BBS) (GM27884, SCHOTT AG, Germany), the secondary fillers used was the GTS-mix glass described in the previous chapter. Fourteen composites were made, seven composites using 100% by weight BBS glass with no F-BAGs, and seven composites were made with 80% by weight BBS glass and 20% by weight F-BAGs.

5.2.2 Monomer preparation

The monomers were prepared using different concentrations of UDMA, TEGDMA, and HEMA. All the monomers and photoinitiators were mixed in an identical way to that described in section 4.2.2. Different monomer mixtures were made: 100 U, 75:25 UT, 50:50 UH, 75:25 UH, 75:12.5:12.5 UTH, 50:30:20 UTH and 50:40:10 UTH added by weight percent. The bottle was sealed with parafilm and stored at 4 °C until use.

5.2.3 Mixing glass fillers with the monomer

As with chapter 4, the composites were made with a total filler concentration of 55vol% in 25g PP containers. To achieve a homogenous mixture, the final mixing protocol used in the previous chapter was used here (section 4.2.3). For the F-BAG free composites only the BBS glass was used, while for the F-BAG containing composites the filler was made up of 80wt% BBS and 20wt% F-BAG. The monomer mixtures were added first, then following the incremental mixing protocol mentioned previously (section 4.2.3), the barium silicate glass fillers were added, and then the F-BAGs fillers were added next. The PP container was sealed with parafilm and wrapped in aluminium foil to prevent light exposure then stored at 4 °C until use. Typical examples of homogenous mixtures obtained are shown in Figure 5-1.

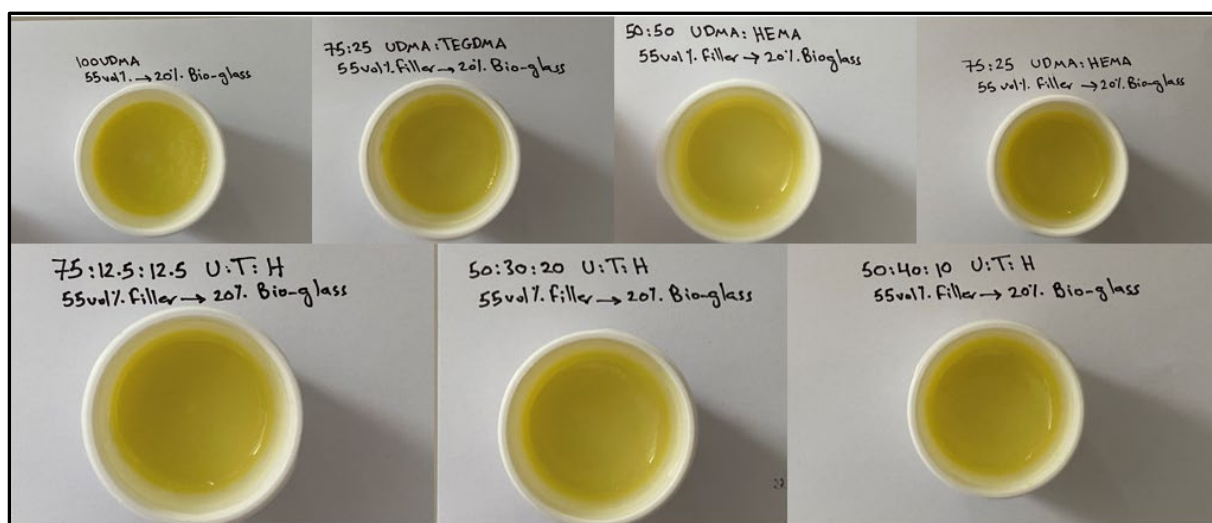


Figure 5-1: The seven F-BAGs containing composites.

5.2.4 Physical and mechanical properties of the different monomer's composites

5.2.4.1 Degree of conversion

The DOC of the fourteen experimental composites was measured using FTIR-ATR (Perkin-Elmer, Spectrum Two, UK). 25 specimens were made from each material. Each group (n=5) was light cured for specific times 10, 20, 30, 40, and 60 seconds using an LED light cure unit (10mm tip, 3M EPSE Elipar™, UK) with an irradiance of 1000-1100 mW/cm². The same methodology was followed as described in the previous chapter (section 4.2.4.1).

5.2.4.2 Water sorption

Water sorption specimens were made following the same methodology previously mentioned (section 4.2.4.2). Each disk was weighed to determine the initial mass (M1) using a digital balance (Mettler AE 240, 0.01 mg accuracy, Leicester, UK). All specimens were then placed in the incubator at 37±1 °C for 24hrs. After 24hrs, each specimen was placed into an individual plastic bottle containing 5mL of distilled water (DW) and stored in an incubator at 37±1 °C for 4 weeks. Mass after immersion (M2) was taken after 1hr, 4hrs, 24hrs, 48hrs, 72hrs, 96hrs, and then weekly up to week 4. At the time of measurement, each specimen was removed from the storage bottles with tweezers, blotted dry with paper towel until free of visible moisture, then weighed (M2) and placed in the bottle with a fresh 5mL of DW and stored in the incubator for the next measurement. The following equation was used to calculate the sorption:

$$\text{Water sorption } (\mu\text{g}/\text{mm}^3) = \frac{M2 - M1}{V}$$

Where M1 is the initial mass before immersion in water in μg , M2 is the mass of the specimens after the immersion in μg and V is the volume of the specimens in mm^3 .

5.2.4.3 Fluoride release

Disc-shaped specimens were prepared from the fourteen experimental composites made. The specimen dimension was 10 x 1 mm using PFTE mould (n=5). The same methodology mentioned previously in Chapter 4 was followed (section 4.2.4.3).

5.2.4.4 Flexural strength (FS) and flexural modulus (FM)

Flexural testing (n=10) (Figure 5-2) and analysis was studied following the same methodology described previously (section 4.2.4.4).

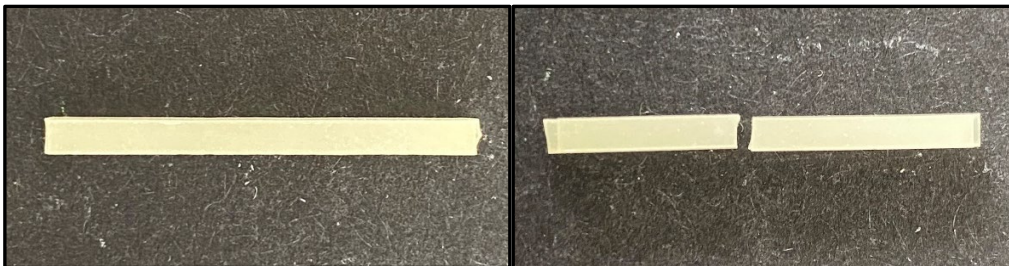


Figure 5-2: Flexural specimens before and after applying the test.

5.2.4.5 Statistical Analysis

All data were analysed as previously described in section 4.2.4.5.

5.3 Results

5.3.1 Degree of conversion

The data were normally distributed. The mean percentage of the DOC of the non-F-BAGs and F-BAGs composites are shown in appendix 2 and figures 5-3 and 5-4. In non-F-BAGs

composites, the DOC ranged between 67% and 83%. After 10 seconds of curing time, 75:25 UH showed a significantly higher DOC than 100U and 75:25 UT ($P < 0.05$). At 20 seconds of curing time, 75:25 UT showed a significantly lower DOC compared to 100U and 50:30:20 UTH ($P < 0.05$). 75:25 UT has a significantly lower DOC compared to all the non-F-BAGs composites at 30 seconds of curing time ($P < 0.05$). At 40 seconds, 75:25 UT has a significantly lower DOC compared to 50:50 UH, 75:25 UH, and 75:12.5:12.5 UTH ($P < 0.05$). Also, 100U showed a significantly lower DOC compared to 75:25 UH and 72:12.5:12.5 UTH at 40 seconds of curing time ($P < 0.05$). At 60 seconds, 75:25 UT has a lower DOC than all the non-F-BAGs composites ($P < 0.05$), and 75:12.5:12.5 UTH showed a higher DOC than all the tested composites except 50:50 UH ($P < 0.05$). Within each material, there were no significant differences when increasing the curing time from 10 seconds for all the non-F-BAGs composites ($P > 0.05$).

For the F-BAGs containing composites, the DOC ranged between 26% to 75%. The 50:50 UH-BG composites showed a lower DOC than all the F-BAGs composites at 10, 20, and 30 seconds of curing time ($P < 0.05$). At 10 seconds, 50:30:20 UTH-BG has a significantly lower DOC than all the F-BAGs composites and a significantly higher DOC than 50:50 UH-BG ($P < 0.05$). 50:40:10 UTH-BG showed a significantly higher DOC value than 100U-BG and 50:30:20 UTH-BG ($P < 0.05$). At 40 seconds, 50:50 UH-BG showed a lower DOC compared to 75:25 UT-BG, 50:30:20 UTH-BG, and 50:40:10 UTH-BG which was significant ($P < 0.05$). At 60 seconds, 100U-BG showed a significantly lower DOC compared to 50:40:10 UTH-BG ($P < 0.05$). Within each material, 50:50 UH-BG showed a significant increase in the DOC from 10s to 40s ($p < 0.05$), but there were no differences when increasing the curing time to 60s ($P > 0.05$). Furthermore, 50:30:20 UHT-BG showed a significantly lower DOC at 10s ($P < 0.05$), but no significant differences were shown when increasing the curing time above 20

seconds ($P>0.05$). The addition of the F-BAGs to the composites affected the DOC significantly for 50:50 UH-BG, 100U-BG, and 75:12.5:12.5 UTH-BG ($P<0.05$).

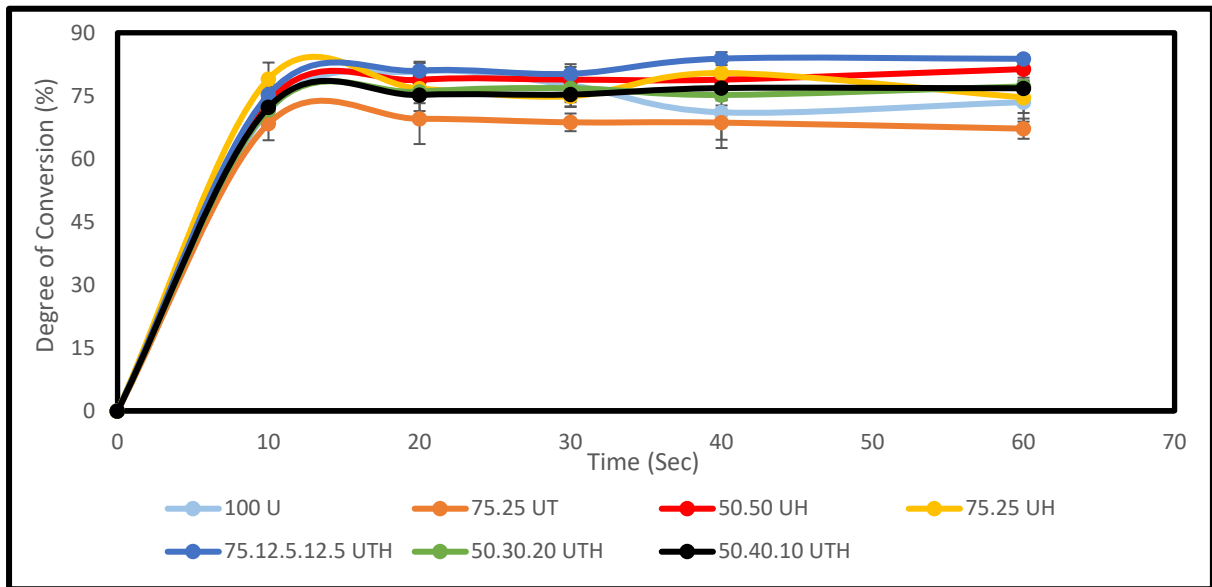


Figure 5-3: Degree of conversion (%) of the non-F-BAGs composites, no significant differences when increasing the curing time from 10 seconds for all the composites ($P>0.05$).

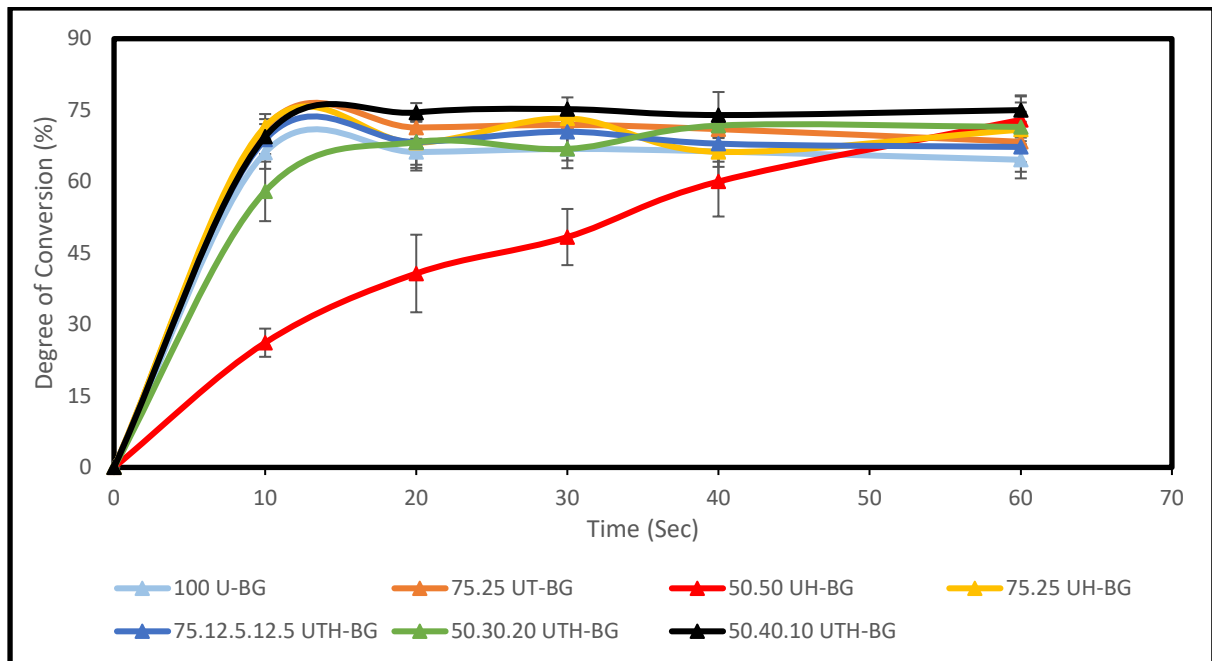


Figure 5-4: Degree of conversion (%) of the F-BAGs composites, 50:50 UH-BG showed a significant lower DOC compared to the rest of the tested composites until 40s curing time ($P<0.05$) but no differences were shown at 60s curing time ($P>0.05$).

5.3.2 Water sorption

The data were normally distributed. The water sorption results are shown in Figures 5-5 and 5-6. Appendix 2 showed the cumulative water sorption for the tested composites up to 28 days. At 1 and 4 hours, no differences were shown between the tested composites ($P>0.05$). For the non-F-BAGs composites, 50:50 UH showed significantly higher water sorption at most of the time points ($P<0.05$). At 24 hours, 50:50 UH showed significantly higher water sorption than 75:25 UT only ($P<0.05$). From 48 hours up to week four, 50:50 UH showed significantly higher sorption when compared to all composites ($P<0.05$), except 50:30:20 UTH at 48, 72, and 96 hours in which there were no significant differences between the two composites ($P>0.05$). Within each material, 100U, 75:25 UT, 75:25 UH, and 50:40:10 UTH showed a significant increase at week one ($P<0.05$), then no significant differences were shown up to week four. 50:50 UH showed a significant increase at 24 hours and 96 hours ($P<0.05$), after 96 hours, there was a non-significant decrease towards week four. 50:30:20 UTH showed a significant increase at 48 hours ($P<0.05$), but no significant change was detected over the storage time ($P>0.05$). 75:12.5:12.5 UTH showed an increase in the water sorption at 72 hours which was significant ($P<0.05$), then no significant increase up to four weeks ($P>0.05$).

For the seven F-BAGs containing composites, initially, no differences were shown between all the composites at 1 hour, however, at 4 hours 50:50 UH-BG showed higher water sorption than all the composites ($p<0.05$) except 50:30:20 UTH-BG in which there were no differences ($P>0.05$). 50:50 UH-BG showed higher sorption compared to all the tested

materials in most of the time points ($P < 0.05$), on the other hand, 100U-BG showed lower water sorption compared to the tested F-BAGs composites in most of the time points ($P < 0.05$). Also, 50:30:20 UHT-BG showed the second highest water sorption after the 50:50 UH-BG, it showed significantly higher sorption than the rest of the composites in most of the time points ($P < 0.05$). Within each material, some materials showed a significant increase in water sorption at 24 hours, some at 48 and 96 hours, and some at the week one test. 50:50 UH-BG showed a significant increase at 24 hours and 48 hours ($P < 0.05$), then the sorption decreased but not significantly toward week four ($P < 0.05$). 50:30:20 UTH-BG also showed a significant increase at 24 hours ($P < 0.05$), then no change was detected before a significant increase at week one took place ($P < 0.05$). After that increase, no significant change was shown ($P > 0.05$). 100U-BG, 75:25 UT-BG showed a significant increase at 96 hours ($P < 0.05$), then no significant change was shown ($P > 0.05$). 75:25 UH-BG and 75:12.5:12.5 UHT-BG showed a significant increase at the week one test ($P < 0.05$), the no significant change up to week four ($P > 0.05$). finally, 50:40:10 UTH-BG showed a significant increase at 48 hours with no change up to week four ($P < 0.05$).

Incorporating F-BAGs into the resin composites shows a significant effect on water sorption. At 1 and 4 hours, no differences were shown between the non-F-BAGs composites and the BAGs containing composites. 100U-BG composites showed no significant differences compared to 100U composites from 1 hour until week two ($P > 0.05$), however, at weeks three and four, a significant increase in water sorption was found from 100U-BG composites when compared to 100U composites ($P < 0.05$). All other composites showed a significant increase from 24 hours until week four from the F-BAGs containing composites compared to non-F-BAGs composites ($P < 0.05$).

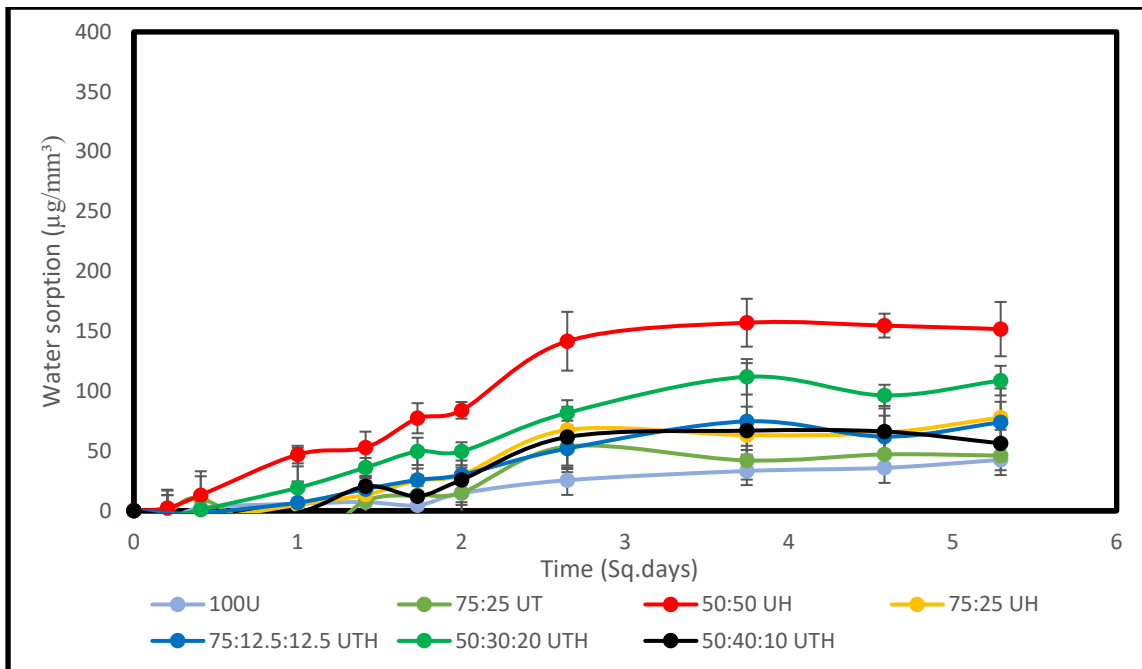


Figure 5-5: Water sorption ($\mu\text{g}/\text{mm}^3$) of the non-F-BAGs composites, 50:50 UH composites showed higher water sorption which was significant in most of the time points ($P < 0.05$).

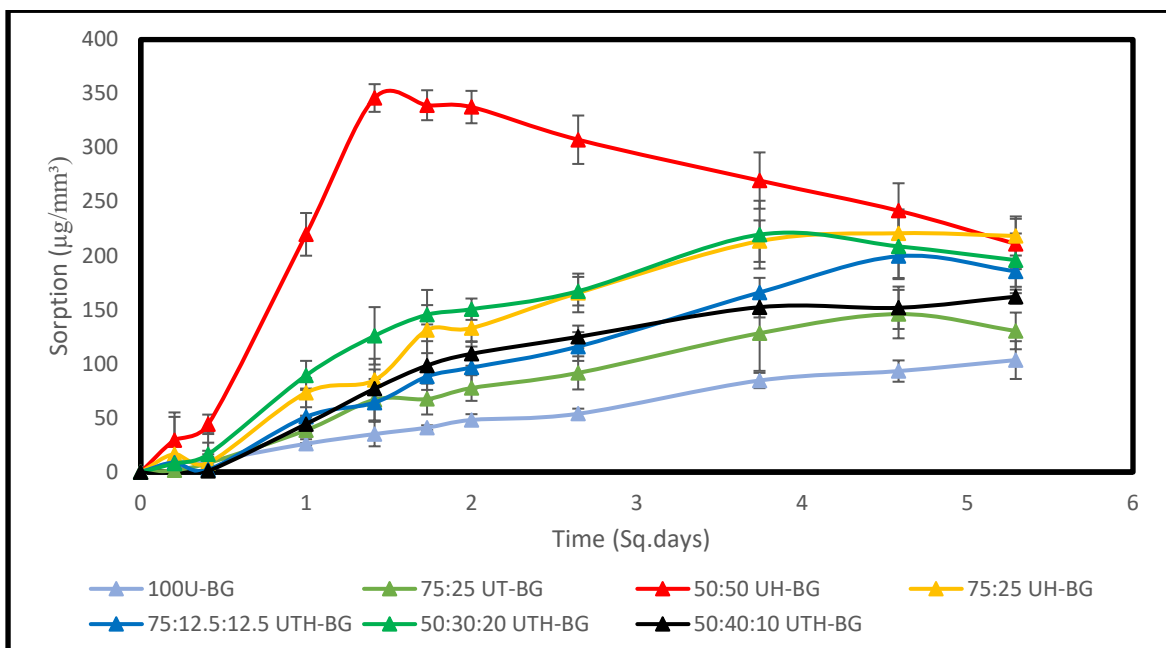


Figure 5-6: Water sorption ($\mu\text{g}/\text{mm}^3$) of the F-BAGs composites, 50:50 UH-BG composites showed higher water sorption which was significant in most of the time points ($P < 0.05$).

5.3.3 Fluoride release

The data were not normally distributed. The non-F-BAGs did not release any fluoride throughout the testing period. The pattern of the fluoride ion release in the F-BAGs composites was similar among all the tested composites with initial high release at 24 hours ($P < 0.05$), and the highest release at week 2 ($P < 0.05$) (Table 5-1). The highest daily fluoride release was by the 50:50 UH-BG, which showed a significant increase in fluoride release from day 1 until 28 days ($P < 0.05$, shown in red in table 5-5) compared to all other materials at all time points ($P < 0.05$). 100U-BG had the lowest fluoride ion release among the tested composites ($P < 0.05$). The cumulative fluoride release showed significantly higher ion release ($300 \mu\text{g}/\text{cm}^2$) from 50:50 UH-BG ($p < 0.05$), whereas 100 U-BG released the lowest amount of fluoride ($P < 0.05$) (Figure 5-8). In figure 5-7 the cumulative fluoride release of the non-BAGs composites was included to show the significant differences between the two groups (with and without F-BAGs).

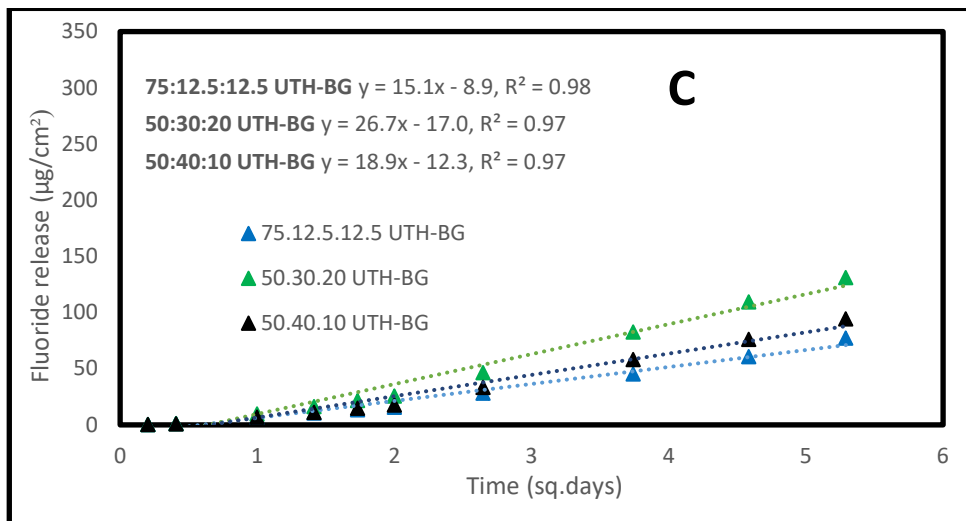
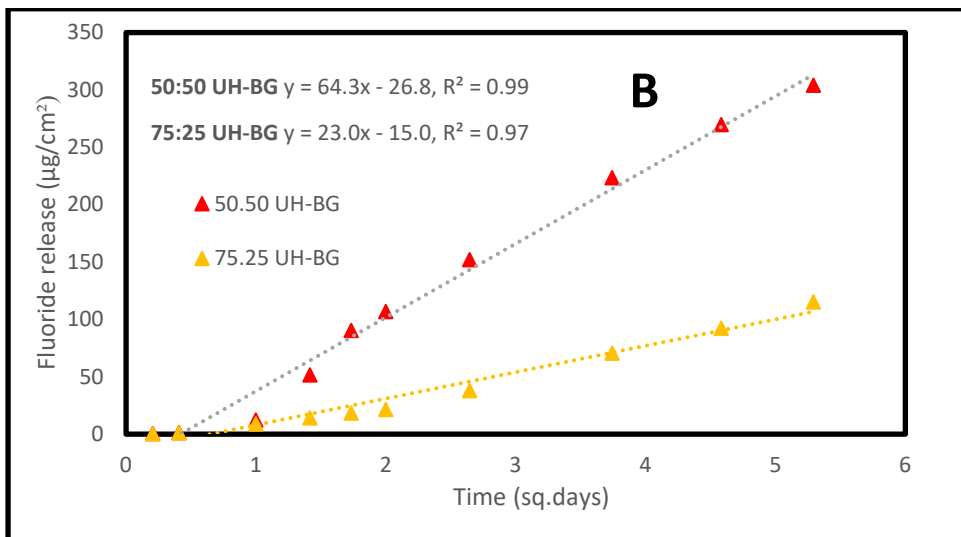
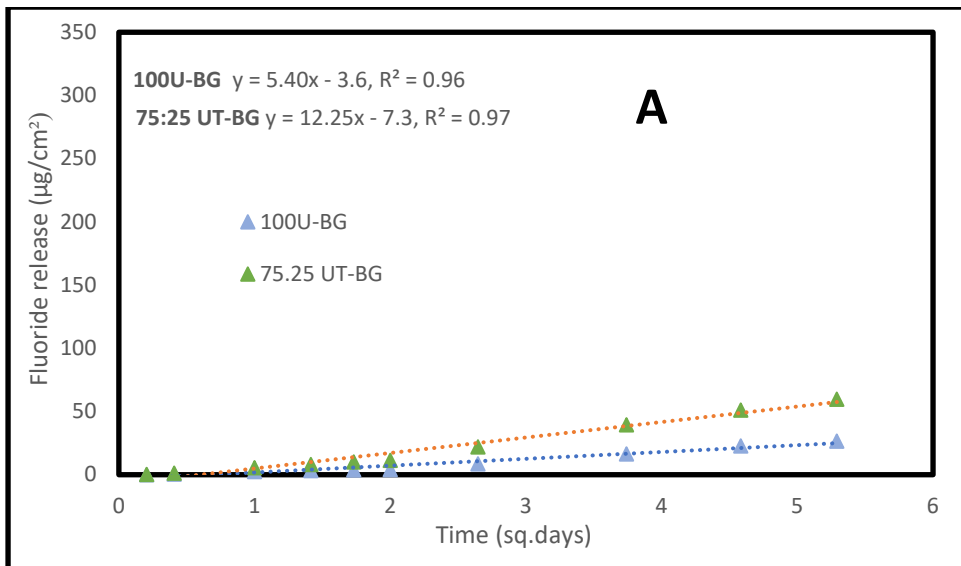


Figure 5-7: The cumulative fluoride ion release for the F-BAGs composites, A- U100-BG and 75:25 UT-BG, B- the UDMA:HEMA F-BAGs composites and C- is the UDMA:TEGDMA:HEMA F-BAGs composites the 50:50 UH-BG composites significantly released more fluoride than the rest of the F-BAGs composites (P<0.05).

Time	100U-BG		75:25 UT-BG		50:50 UH-BG		75:25 UH-BG		75:12.5:12.5 UTH-BG		50:30:20 UTH-BG		50:40:10 UTH-BG	
	Median	IQR	Median	IQR	Median	IQR	Median	IQR	Median	IQR	Median	IQR	Median	IQR
1 hr	0.07	0.06	0.28	0.03	0.39	0.07	0.27	0.09	0.28	0.04	0.31	0.05	0.23	0.06
4hrs	0.43	0.13	0.85	0.05	0.83	0.07	0.78	0.07	0.75	0.16	0.74	0.10	0.68	0.13
24hrs	2.06	1.09	4.36	0.15	10.98	0.81	7.83	0.70	5.83	0.77	8.53	0.98	5.75	0.68
48hrs	0.60	0.67	2.60	0.24	39.47	20.52	5.30	0.64	3.65	0.49	6.72	0.86	4.39	0.40
72hrs	0.50	0.30	1.92	0.39	38.56	4.75	4.07	0.71	2.88	0.38	5.34	1.03	3.60	0.20
96hrs	0.33	0.19	1.37	0.33	16.46	2.06	3.15	0.46	2.11	0.22	3.95	1.00	2.84	0.35
Wk1	4.69	0.96	10.70	1.00	45.41	2.63	16.43	1.71	12.59	1.01	20.69	1.71	15.83	1.30
Wk2	7.64	1.86	17.37	1.11	71.21	6.64	32.58	5.01	17.20	9.40	36.27	2.29	24.83	2.17
Wk3	6.39	1.37	11.67	2.05	46.38	4.57	21.91	3.82	15.44	3.55	26.75	3.68	17.86	1.98
Wk4	3.85	1.23	8.65	1.24	34.27	4.21	22.97	3.88	16.43	3.22	21.56	5.25	18.06	2.93

Table 5-1: The daily fluoride release of the F-BAGs containing composites. The red text indicated a significant fluoride release from the 50:50 UH-BG (P<0.05).

5.3.4 Flexural strength (FS) and flexural modulus (FM)

The data were normally distributed. The FS and FM data are shown in appendix 2 and in figures 5-8, 5-9, 5-10, and 5-11.

Starting with the FS results. Initially, for non-BAG composites, the 50:40:10 UTH composites showed a significantly lower FS value compared to the 75:25 UH and 75:25 UT ($P < 0.05$). The rest of the composites show no significant differences on day 1 ($P > 0.05$). At days 7, 14 and 28, the HEMA containing composites, 50:50 UH, 50:40:30 and 50:40:10 UTH, showed a significantly lower FS compared to the rest of the materials ($P < 0.05$). Despite the slight decrease in the FS on day 7, there were no significant differences in the FS for the 100U, 75:25 UT, 75:25 UH, and 50:40:10 UTH over the storage time ($P > 0.05$). Within each material, 50:50 UH and 50:30:20 UTH showed a significant decrease at day 7 ($p < 0.05$) and 75:12.5:12.5 UTH showed a significant decrease at day 14 ($p < 0.05$) but no significant change was found up to 28 days ($P > 0.05$) (Figure 5-8).

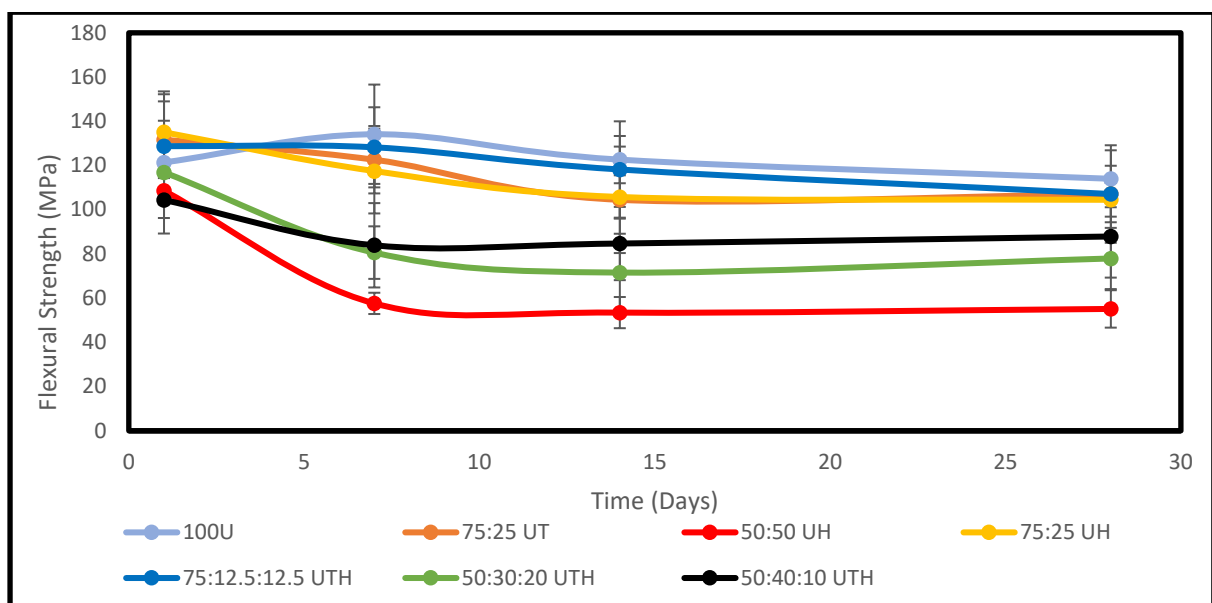


Figure 5-8: The flexural strength (MPa) of the non-F-BAGs composites, from day 7 up to 28 days of storage, 50:50 UH composites showed a significant lower FS values compared to the rest of the materials ($P < 0.05$).

For the F-BAGs composites, 50:50 UH-BG showed significantly lower FS values compared to the rest of the F-BAGs composites at all time points ($P < 0.05$) (Figure 5-9). No differences were found between the other tested composites on day 1 ($P > 0.05$). On day 7, 75:25 UT-BG and 75:12.5:12.5 UTH-BG showed a higher FS than 75:25 UH-BG, 50:30:20 UTH-BG, and 50:40:10 UTH-BG ($P < 0.05$). From day 7 up to 28 days, 100U-BG showed significantly higher FS values compared to the rest of the tested composites ($p < 0.05$). On days 14 and 28, 75:25 UT-BG showed significantly higher FS values than all the materials (Except 100U-BG) ($P < 0.05$).

Except for 100U-BG, the FS values dropped significantly at day 7 for all the composites ($P < 0.05$), then strength remained stable up to 28 days ($P > 0.05$). The 100 U-BG showed no significant differences in the FS value over the storage time ($P > 0.05$). The statistical analysis showed that the addition of the F-BAGs to the composites significantly decreased the flexural strength of all the composites ($P < 0.05$).

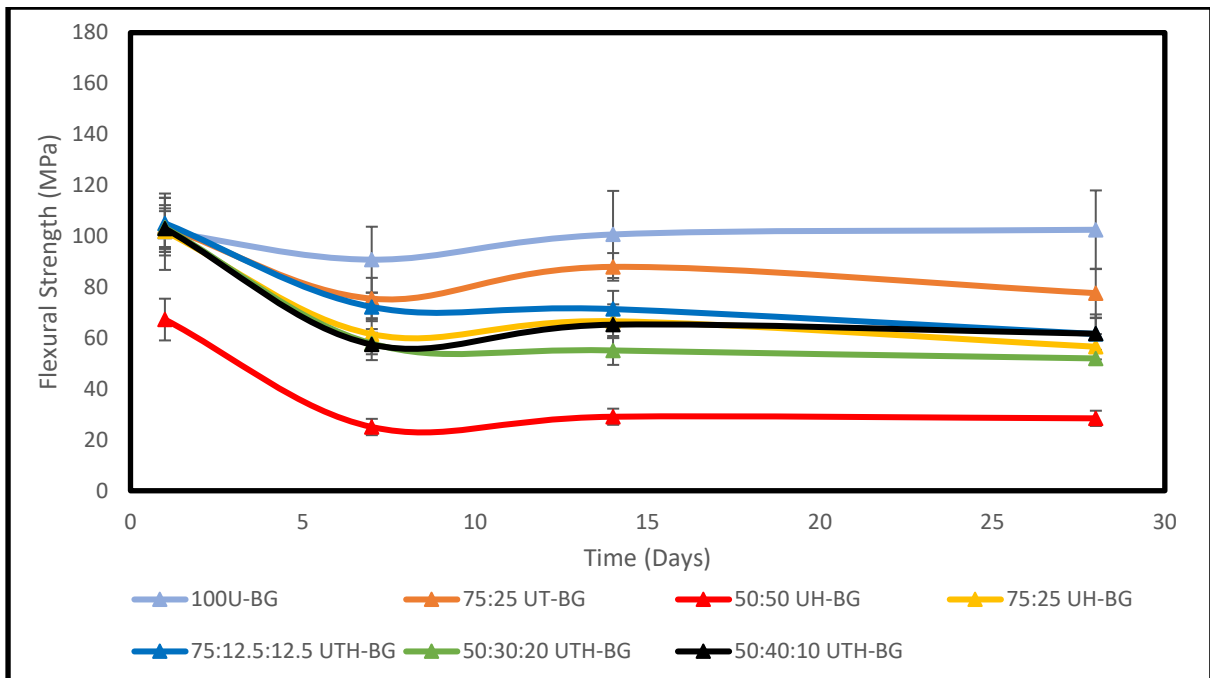


Figure 5-9: The flexural strength values (MPa) of the F-BAGs composites, 50:50 UT-BG showed a significantly lower FS values compared to the rest of the materials at all time points ($P < 0.05$).

The FM of the non-F-BAG composites (Figure 5-10) showed a significantly lower value for the 50:50 UH composites at all time points ($P < 0.05$) except at day 1 there were no significant differences compared to 75:25 UT and 50:30:20 UTH ($P > 0.05$). From day 7 up to 28 days, 75:12.5:12.5 UTH showed a higher FM compared to all the tested composites ($P < 0.05$). Within each material, the 100U, 75:25 UT, and 75:12.5:12.5 UTH composites did not show a significant decrease in the FM over the storage time ($P > 0.05$). On the other hand, 50:50 UH, 50:30:20 UTH, and 50:40:10 UTH composites showed a significant decrease at day 7 ($P < 0.05$), then no significant change was shown up to 28 days ($P > 0.05$). Also, 75:25 UH composites showed a significant decrease at day 14 ($P < 0.05$).

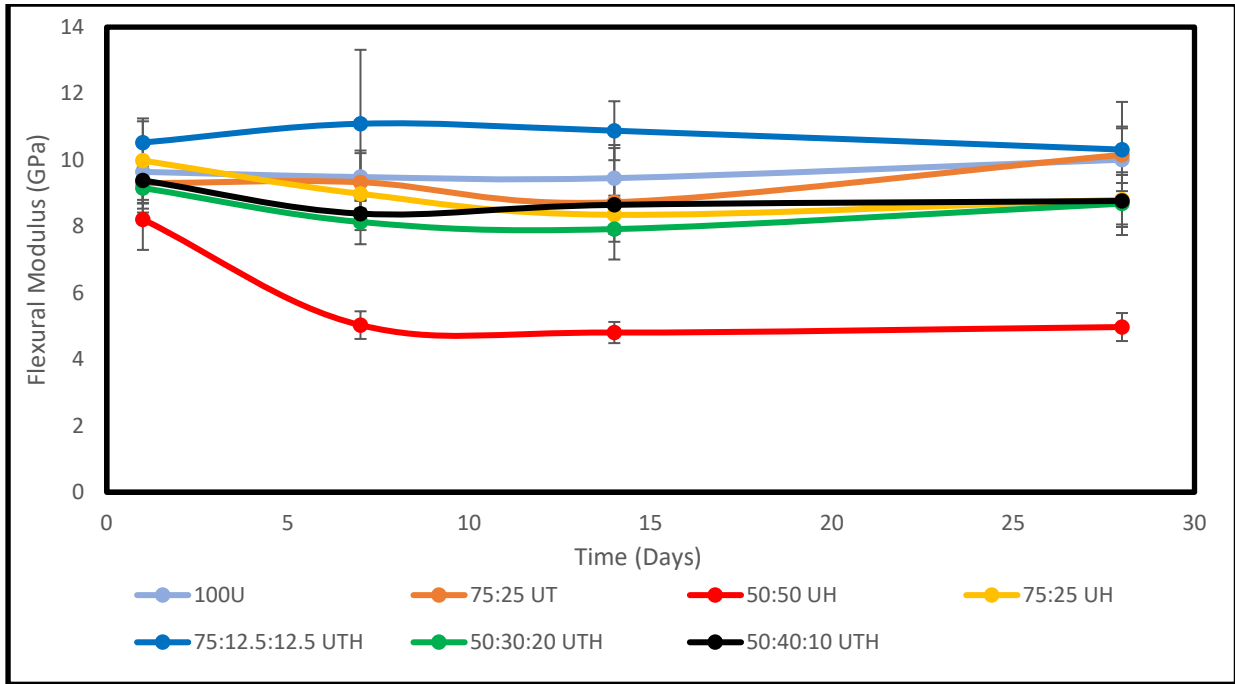


Figure 5-10: The flexural modulus values (GPa) of the non-F-BAGs composites, 100U, 75:25 UH and 75:12.5:12.5 Composites showed no significant change in the FM over storage time ($P>0.05$).

The FM for the F-BAGs composites, 100U-BG and 75:25 UT-BG showed higher FM values, and 50:50 UH-BG showed significantly lower values when compared to the rest of the F-BAGs composites ($P<0.05$) (figure 5-11). Within each material, the FM values for the 100U-BG decreased significantly at day 14 ($P<0.05$). For the 50:50 UH-BG composites, the FM values decreased significantly at day 7 ($P<0.05$), then the materials were stable up to 28 days. For the 75:25 UT-BG and 75:25 UH-BG composites, the values decreased significantly at day 7 and day 28 ($P<0.05$). 50:40:10 UTH-BG composites showed a significant decrease in the FM at day 28 ($P<0.05$). No significant change in the FM was shown for the 75:12.5:12.5 UTH-BG and 50:30:20 UTH-BG composites over the storage time ($P>0.05$). The addition of the F-BAGs fillers to the composites did affect the material's FM significantly ($P<0.05$). However, two materials (100U-BG & 75:25 UT-BG) on day 1, showed no significant

differences when F-BAGs were incorporated, but FM decreased significantly over the storage time compared to non-F-BAGs composites ($P<0.05$)

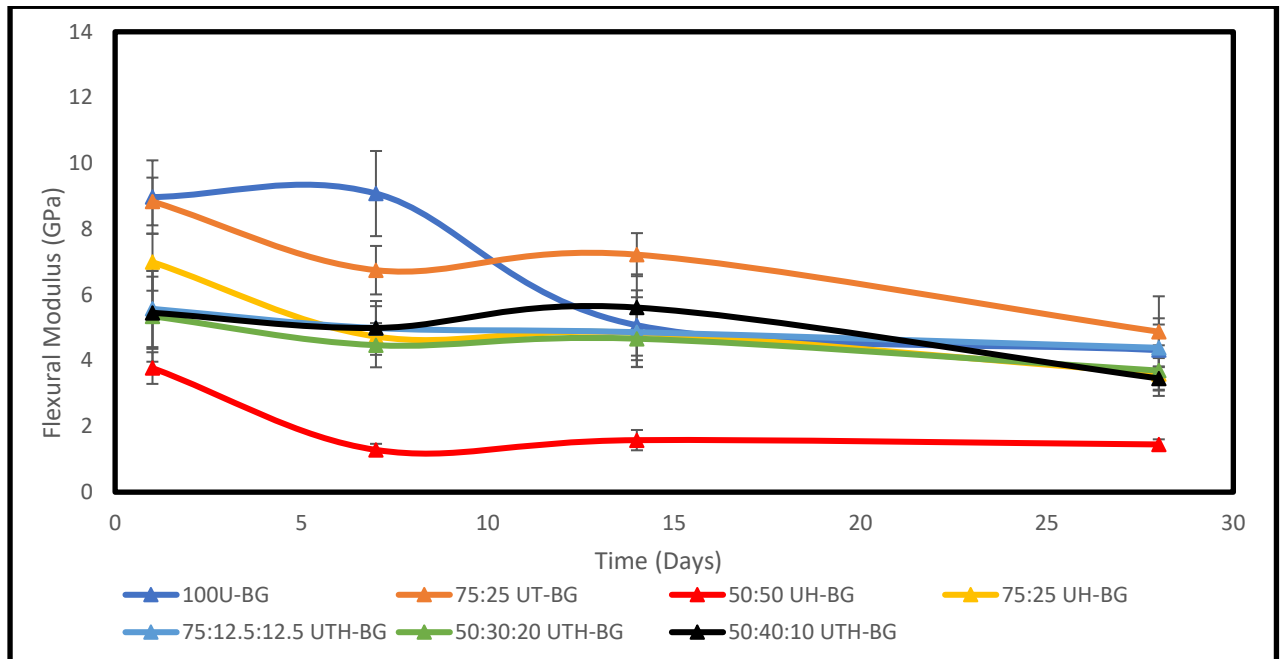


Figure 5-11: The flexural modulus values (GPa) of the F-BAGs composites, 100 U-BG and 75:25 UT-BG showed a significant higher FM than the rest of the tested composites at day 1 and day 7 test ($P<0.05$), 50:50 UH-BG showed a significantly lower FM compared to the rest of the materials at all time points ($P<0.05$).

5.4 Discussion

5.4.1 Monomers selection and preparations of the composites

The experimental F-BAGs composites were successfully made with F-BAGs fillers incorporated at 20wt%. The aim in this chapter is to study the effect of different types and concentrations of monomer mixtures on the physical and mechanical properties of the F-BAGs composites.

In this chapter, three monomers have been used to make the experimental composites. UDMA was used as the main base monomer, TEGDMA and HEMA were used as co-monomers or diluents. Seven monomer mixtures were made. In the seven experimental control composites, barium-aluminium-silicate glass was used at 100wt% with 55 vol% filler loading. On the other hand, the seven experimental F-BAGs composites were made using the barium-aluminium-glass as primary glass at 80wt% and F-BAGs incorporated at 20wt% with a filler loading at 55 vol%. The same mixing protocol used in chapter 4 was used here and homogenous composite mixtures were obtained using the centrifuge mixer.

UDMA is commonly used as a base monomer in some commercially available materials and has a molecular weight of 470 g/mol (Maravić *et al.*, 2023). This material showed a good performance as a main monomer (Sideridou;Tserki and Papanastasiou, 2003; Kerby *et al.*, 2009). TEGDMA, due to the low molecular weight of 286.2 g/mol and low viscosity, was used as diluting monomer for an easier mixing and incorporation of glass. TEGDMA has a carbon double bond at each end which improve the degree of polymerisation by enhancing the monomer's mobility (Dickens *et al.*, 2003). HEMA is a hydrophilic monofunctional monomer with a molecular weight of 130 g/mol. The reason for incorporating TEGDMA was to reduce the viscosity of the composites, and for HEMA to increase the hydrophilicity, which will in turn, increase the ion release from the RBCs. It has been shown that the lower

the viscosity of the monomer mixture the higher the filler loading (Vasudeva, 2009).

However, when making the composites, even with the 100 UDMA based composites, a homogenous composite pastes were obtained at 55vol%.

5.4.2 Degree of conversion

The DOC of the F-BAGs composites and F-BAGS free composites were studied. The monomer mixtures showed no effect on the degree of conversion when the control non-F-BAGs composites were studied. Furthermore, the DOC values for both groups (with or without F-BAGs fillers) were comparable to a range of currently used composites and above the recommended acceptable values of 55%, except for the 50:50 UH-BG that showed a significant lower DOC compared to the rest of the materials (Silikas;Eliades and Watts, 2000; Tarle and Par, 2018). Incorporating HEMA in to composites has been shown to increase the DOC. The flexibility of this monomer enhances the mobility of the reactive species, thus increases the DOC (Skrtic and Antonucci, 2007) HEMA is usually added to dental materials to increase the hydrophilicity and their ability to wet the tooth tissues (Malacarne *et al.*, 2006). However, adding HEMA in high concentration has shown to decrease the DOC and the addition of the F-BAGs and the inhibitory effect these materials has on the polymerisation results in the low DOC (De Carvalho *et al.*, 2016; Par *et al.*, 2018b).

When F-BAGs fillers were added, a reduction in DOC was found, which was significant for 100U-BG, 50:50 UH-BG and 75:12.5:12.5 UTH-BG ($P < 0.05$). The addition of BGs to composites has been shown to effect DOC dependent on BG type and concentration and the monomers used in the composite. For instance, 45S5 BG (a glass based on SiO₂ 45wt%, Na₂O 25wt%, CaO 25wt%, P₂O₅ 5wt%) had no significant effect on the DOC of UDMA:TEGDMA BAGs based composites (Par *et al.*, 2020c) but at concentrations above 20wt% had an effect

on the polymerisation BisGMA/TEGDMA based BAGs composites (Par *et al.*, 2018a; Par *et al.*, 2018b). Additionally, the addition of a calcium fluoride containing BG (based around SiO₂ 33.5wt%, CaO 33wt%, Na₂O 10.5wt%, P₂O₅ 11wt%, CaF₂ 12wt%) showed no effect on the polymerisation process, even when 40wt% was added (Par *et al.*, 2021).

The F-BAGs particles were both much bigger than the primary barium glass filler and were also unsilanised. While the size of the glass filler particles has been shown to not affect the polymerisation process, the surface oxides on unsilanised 45S5 BG fillers has been found to inhibit polymerisation of methacrylate resins (Stansbury, 2012; Par *et al.*, 2018b; Marovic *et al.*, 2022b).

The differences in the refractive index (RI) between the monomers and the fillers can affect the polymerisation. When there is a mismatch between the RI of the resin and the fillers, the scattering of the light at the filler/resin interface is increased which results in decreasing the DOC (Shortall;Palin and Burtscher, 2008). The refractive index of UDMA, TEGDMA and HEMA is 1.45, 1.46 and 1.45 respectively, and for the barium glass is 1.53 (Miletic *et al.*, 2017; Yadav *et al.*, 2022). The refractive index for the F-BAGs fillers is not known, however, the decrease in the DOC of some of the F-BAGs composites could be due to the differences in the RI between the bioactive glass and the monomer mixtures.

5.4.3 Water sorption

Water sorption is an important factor that can affect the physical and mechanical properties of the RBCs (Sideridou;Tserki and Papanastasiou, 2003). Flexural properties and wear resistance have been shown to decrease with increasing water sorption in the composite resins (Leprince *et al.*, 2013; Cornelio *et al.*, 2014). Compared with the BAGs free composites, the addition of the 45S5 BAGs to the dental composites increased the water

sorption (Par *et al.*, 2019a). The water sorption of the seven composites made using the F-BAGs at 20wt% was measured compared with seven non-F-BAGs composites with same monomer and fillers concentrations. Both the non-F-BAGs and the F-BAGs composites showed a significant increase in the water sorption after 24 hours of storage time ($P < 0.05$) and the addition of the F-BAGs fillers to the composite resins significantly increased the water sorption of the tested composites ($P < 0.05$). The water sorption of the non-F-BAGs ranged between 15-80 $\mu\text{g}/\text{mm}^3$ (Appendix E) and ranged between 46-213 $\mu\text{g}/\text{mm}^3$ for the F-BAGs composites (appendix 2), where the lowest values for the 100 UDMA based composites and the highest values for 50:50 UDMA:HEMA based composites. In non-F-BAGs composites, the water sorption occurs mainly in the monomer network as the primary fillers are hydrophobic due to the silane coating, however, in the F-BAGs composites the water sorption significantly increased due to the hydrophilic F-BAGs fillers used. It has been shown that increasing the amount of the BAG fillers (glass based around SiO_2 45wt%, Na_2O 25wt%, CaO 25wt%, P_2O_5 5wt%, particle size 4 μm) increases the water sorption significantly and adding 40wt% BAG increased the water sorption six times compared to the BAG-free control composites (Par *et al.*, 2019a).

Increasing the concentration of HEMA led to increase the water sorption. 50:50 UH-BG composites showed a significantly higher water sorption compared to the rest of the materials followed by 50:30:20 UHT-BG ($P < 0.05$). HEMA has been shown to induce water sorption which cause the polymer matrix to expand (Malacarne *et al.*, 2006). On the other hand, 100 U-BG showed the lowest sorption ($P < 0.05$). HEMA-free composites showed lower sorption than HEMA-containing composites ($P < 0.05$). Highly hydrophilic monomer mixtures containing HEMA have been used in experimental composites to enhance the ion release when the UDMA, Bis-GMA, and TEGDMA based composites did not release ions (Skrtic and

Antonucci, 2007). HEMA is the most hydrophilic monomer used in this project which has lower molecular weight and has one hydroxyl group per molecule that can form hydrogen bonds with the water molecules, thus more water within the polymer system (Venz and Dickens, 1991). TEGDMA, on the other hand, does not contain the hydroxyl group but has the affinity to absorb water because of its hydrophilic ether linkage (Örtengren *et al.*, 2001). The significant differences between the HEMA containing composites and HEMA-free is attributed to the hydrophilicity of the HEMA monomer.

5.4.4 Fluoride release

Fluoride has anticariogenic effect that can decrease the demineralisation of the dental hard tissues and enhance the remineralisation (Ekstrand;Fejerskov and Silverstone, 1988; Fejerskov;Ekstrand and Burt, 1996). Different formulation of F-BAG composites have been shown to release fluoride similar to other fluoride releasing materials such as GIC and compomers (Al-Eesa *et al.*, 2017; Francois *et al.*, 2020). The fluoride release of the composites made using different monomer concentrations with the addition of F-BAGs at 20wt% was measured. The same trend observed with the water sorption was shown in the fluoride release, HEMA-containing composites released more fluoride ions than the HEMA-free composites, especially with the 50:50 UH-BG. HEMA was used in experimental composites to enhance the ion release (O'donnell;Skrtic and Antonucci, 2006; Van Landuyt *et al.*, 2008; Porenczuk *et al.*, 2019). The addition of HEMA allows more water diffusion into the polymer matrix due to the hydrophilicity the material has, thus more water sorption and fluoride release (Tichy *et al.*, 2021). The presence of HEMA increases the flexibility in the polymer network through increasing the water sorption and enhance the glass dissolution and fluoride release (Beriat and Nalbant, 2009; Sokolowski *et al.*, 2018; Panpisut *et al.*,

2020). The cumulative fluoride release from the 100 U-BG was significantly lower than 75:25 UT-BG and the other HEMA containing composite specimens, and this due to the hydrophilicity of the TEGDMA and HEMA. The hydrophilicity of the monomer mixtures, such as TEGDMA and HEMA, play important role in the degradation of the glass particles (May and Donly, 2017; Garoushi;Vallittu and Lassila, 2018; Porenczuk *et al.*, 2019).

5.4.5 Flexural strength and flexural modulus

In order to function well and last longer in oral cavity, RBCs should have a sufficient strength. Flexural strength and flexural modulus are significant mechanical properties to test the clinical performance of the dental composites (ISO, 2009; Ferracane, 2011; Ferracane, 2013). The FS and FM of the experimental composites were evaluated.

In general, all the F-BAGs composites showed an acceptable initial FS value of more than 100 MPa which is comparable to a range of currently used RBCs (Ilie and Hickel, 2009a; Ilie and Hickel, 2009b; Ferracane, 2011; Ilie;Rencz and Hickel, 2013). However, the 50:50 UH-BG had a significantly lower FS than the other composites ($P < 0.05$) with a value of 67 MPa at day one. Over the storage time, HEMA containing composites had significantly lower FS compared to the rest of the composites ($P > 0.05$). Generally, the FS is correlated with TEGDMA/HEMA concentrations, the higher their concentration the lower the FS. 75:25 UT, on the other hand, showed a lower water sorption and higher FS when compared to HEMA containing composites which was also shown in a recent study (Szczesio-Wlodarczyk *et al.*, 2022). It has been shown that adding HEMA up to 20wt% in UDMA-based composites does not affect the strength of the materials (Koleganova *et al.*, 2006). However, increasing HEMA concentrations lead to increase water sorption and decrease the materials' strength (Collares *et al.*, 2011). FS values decreased over storage time which is the results of

degradation of the fillers particles (Lohbauer *et al.*, 2003; Curtis *et al.*, 2008; Shah; Ferracane and Kruzic, 2009; Khvostenko *et al.*, 2013). Due to HEMA being monofunctional, increasing the HEMA concentration will reduce the crosslink density of the composites (Collares *et al.*, 2014a).

The addition of the F-BAGs fillers to the experimental composites significantly weakened all the composites ($P < 0.05$). The F-BAG composites showed a significant decrease in the FS when compared to the F-BAGs-free composites ($P < 0.05$). The influence of adding the F-BAGs fillers is a result of the glass morphology, particle size and lack of silane coating. The F-BAGs fillers used in this project have irregular shapes and had a larger particle size ($45\mu\text{m}$) compared to the primary glass barium silicate fillers ($0.7\ \mu\text{m}$) and these morphological and size differences can cause a stress concentration at the resin/fillers interface (Asar *et al.*, 2013). The F-BAGs were also unsilanised which has been suggested to result in larger voids forming in composites compared to than composites with silanised glass fillers, which would again affect the mechanical properties (Tham; Chow and Ishak, 2010).

In general, the FS decreased over storage time for all composites, but this was more significant in the F-BAGs composites. BG fillers dissolve gradually over time in an aqueous environment (Tarle, 2018) weakening the materials.

The FM of the non-F-BAGs composites were higher than the F-BAGs composites ($P < 0.05$).

The FM values for the non-F-BAGs composites ranged between 5-10 GPa and were comparable to commercial composites (3-16 GPa) (Leprince *et al.*, 2010; Ilie; Rencz and Hickel, 2013; Jun *et al.*, 2013; Randolph *et al.*, 2016). However, when the F-BAGs were added, the FM decreased (1.5-9 GPa). The result of the F-BAGs were comparable to a range of currently used GIC materials (Marovic *et al.*, 2022a) and comparable to 45S5 BAG

composites that showed a range between 0.5-4.5 GPa (Par *et al.*, 2019b). It has also been shown that the hydrophilicity of the unsilanised BAGs, in this case one based on SiO₂ 45wt%, Na₂O 25wt%, CaO 25%, P₂O₅ 5wt% leads to the decrease in the FM. Increase HEMA concentration will increase the water sorption and therefore plasticizing the polymer network that will affect the FM (Beriat and Nalbant, 2009). The hydrophilicity of the organic matrix lead to decrease in the FM (Porenczuk *et al.*, 2019) and this was shown by most hydrophilic monomer mixture the 50:50 UH that showed the lowest FM values.

The addition of the unsilanised F-BAGs affected the FM. The hydrophilicity of the BAG composites compared to BAG-free composites lead to degradation of the fillers over time and decrease the FM (Sideridou;Karabela and Bikiaris, 2007; Yang *et al.*, 2013). As described earlier in the FS results, the significant decrease over the storage time from the F-BAGs composites is a results of the size and shape of the filler particles, unsilanisation of the glass fillers and plasticisation of the resin matrix (Tham;Chow and Ishak, 2010; Asar *et al.*, 2013; Tarle, 2018). 75:25 UDMA:TEGDMA and 75:12.5:12.5 UDMA:TEGDMA:HEMA monomer mixtures showed a high DOC, lower water sorption and higher flexural properties compared to the other HEMA-containing composites, beside the good fluoride release.

5.5 Summary

The experimental F-BAGs composites with different monomers mixture and 20% by weight F-BAGs fillers were prepared and evaluated. F-BAGs composites showed good DOC values for all the different monomers used, except the 50:50 UH-BG which showed a lower degree of conversion compared to the rest of the materials tested after 10,20,30 and 40 second curing time (P<0.05). HEMA containing composites showed a higher water sorption, higher fluoride release and lower FS and FM values. Furthermore, incorporating the F-BAGs fillers

increased the water sorption, fluoride release, and decreased the FS and FM of the tested composites. Based on the results obtained, it was concluded that either 75:25 UDMA:TEGDAM or 75:12.5:12.5 UDMA:TEGDMA:HEMA would be suitable to be used in the next part of the research. However, as HEMA is a flexible hydrophilic monomer that shows high water sorption that can affect the material's strength and cause a degradation of the polymer matrix (Beriat and Nalbant, 2009; Collares *et al.*, 2011; Takahashi *et al.*, 2011; Tauscher *et al.*, 2017) it was decided that the 75:25 UDMA:TEGDMA was selected to be used in the next section where different concentrations of the F-BAGs fillers will be used.

Chapter 6: Effect of the Concentration of F-BAGs fillers on the Physical and Mechanical Properties of the F-BAGs Composite

6.1 Introduction

The aim of this part of the experiment was to understand the effect of F-BAG concentration on the mechanical and physical properties of composites. In the previous chapter, the effect of different monomer types and concentrations on the composites' properties were studied and 75:25 UDMA:TEGDMA monomer mixture was chosen to be used in this study. In this chapter, model composites based around the monomers UDMA:TEGDMA were made with the barium-aluminium-borosilicate glass as primary filler and the F-BAG as the secondary filler incorporated at incremental concentrations between 10wt% and 40wt%. The properties of the composites were compared in terms of their DOC, water sorption, fluoride release and flexural properties.

6.2 Materials and Methods

6.2.1. Composites preparation

The model composites were made using 75:25 UDMA: TEGDMA monomers (Sigma-Aldrich Ltd., Dorset UK). The photo-initiators used were 1wt% camphorquinone (CQ) and 1wt% ethyl 4-dimethylamino benzoate (EDAB) (Sigma-Aldrich Ltd., Dorset UK) (Table 6-1).

Composites made with 55vol% filler concentrations, the main fillers used in these composites were 0.7 μ m silanised-Barium borosilicate-glass (BBS) (SCHOTT AG, Germany), the secondary fillers used were the GTS-mix glass (GTS) (Table 4-1). Five composites were made, the first one is the experimental control with no F-BAGs filler used (OBG) (100wt% BBS), and four composites were made by incorporating the GTS glass at 10, 20, 30 and

40wt% (10BG, 20BG, 30BG and 40BG) replacing the primary filler to maintain the overall filler loading at 55vol% (Table 6-1).

Composites	UDMA %	TEGDMA%	CQ%	EDAB%	Sio ₂ glass %	Bioactive glass % (F-BAGs)	Composites code
1	75	25	1	1	100	0	0BG
2	75	25	1	1	90	10	10BG
3	75	25	1	1	80	20	20BG
4	75	25	1	1	70	30	30BG
5	75	25	1	1	60	40	40BG

Table 6-1: F-BAG composites with different glass concentrations

6.2.2 Monomer preparation

The monomers used were 75:25 UDMA:TEGDMA mixed in amber glass bottles to prevent accidental activation of the photoinitiator (500ml, Sigma-Aldrich) and then mixed in a magnetic stirrer (VELP, Scientifica, Italy) for 30 minutes at 35°C to enable easier mixing of the materials. In each bottle, 1% camphroquinone (CQ) and 1% Ethyl 4(dimethylamino) benzoate (EDAB) were then added and further mixed for 30 minutes until a homogeneous mixture was visible. Bottle was sealed with parafilm and stored at 4 °C until use.

6.2.3 Mixing glass fillers with the monomer

As with chapter 4 and 5, the composites were made with a total filler concentration of 55vol% in 25g PP containers. To achieve a homogenous mixture, the final mixing protocol used in the previous chapters was used here (section 4.2.3). For the F-BAG free composites only the BBS glass was used, while for the F-BAG containing composites the filler was made up of 60-90wt% BBS and 10-40wt% F-BAG. The monomer mixtures were added first, then

following the incremental mixing protocol mentioned previously (section 4.2.3), the barium silicate glass fillers were added, and then the F-BAGs fillers were added next. The PP container was sealed with parafilm and wrapped in aluminium foil to prevent light exposure then stored at 4 °C until use. Typical examples of homogenous mixtures obtained are shown in Figure 6-1.



Figure 6-1: The five experimental composites used in this chapter.

6.2.4 Physical and mechanical properties of the different monomer's composites

6.2.4.1 Degree of conversion

The DOC of the fourteen experimental composites was measured using FTIR-ATR (Perkin-Elmer, Spectrum Two, UK). 25 specimens were made from each material. Each group (n=5) was light cured for specific times 10, 20, 30, 40, and 60 seconds using an LED light cure unit (10mm tip, 3M EPSE Elipar™, UK) with an irradiance of 1000-1100 mW/cm². The same methodology was followed as described in the previous chapter (section 4.2.4.1).

6.2.4.2 Water sorption

Water sorption specimens were made following the same methodology previously mentioned (section 4.2.4.2). Each disk was weighed to determine the initial mass (M1) using a digital balance (Mettler AE 240, 0.01 mg accuracy, Leicester, UK). All specimens were then

placed in the incubator at 37±1 °C for 24hrs. After 24hrs, each specimen was placed into an individual plastic bottle containing 5mL of distilled water (DW) and stored in an incubator at 37±1 °C for 4 weeks. Mass after immersion (M2) was taken after 1hr, 4hrs, 24hrs, 48hrs, 72hrs, 96hrs, and then weekly up to week 4. At the time of measurement, each specimen was removed from the storage bottles with tweezers, blotted dry with paper towel until free of visible moisture, then weighed (M2) and placed in the bottle with a fresh 5mL of DW and stored in the incubator for the next measurement. The following equation was used to calculate the sorption:

$$\text{Water sorption } (\mu\text{g}/\text{mm}^3) = \frac{M2 - M1}{V}$$

Where M1 is the initial mass before immersion in water in µg, M2 is the mass of the specimens after the immersion in µg and V is the volume of the specimens in mm³.

6.2.4.3 Fluoride release

Disc-shaped specimens were prepared from the five experimental composites shown in table 6-1. The specimen dimension was 10 x 1 mm using PFTE mould (n=5). The same methodology mentioned previously in Chapter 4 was followed (section 4.2.4.3).

6.2.4.4 Flexural strength (FS) and flexural modulus (FM)

Flexural testing (n=10) and analysis was studied following the same methodology described previously (section 4.2.4.4)

6.2.4.5 Statistical Analysis

All data were analysed as previously described in section 4.2.4.5.

6.3 Results

6.3.1 Degree of conversion

The data were normally distributed. The mean percentage of the DOC of the F-BAG composite specimens (0BG, 10BG, 20BG, 30BG and 40BG) are shown in appendix G and figure 6-2. All 5 composites showed a DOC above 60%, with no significant differences when increasing the curing light for more than 10 seconds ($p>0.05$). At 20 seconds, 0BG composites show a significantly lower DOC than 30BG and 40BG ($p<0.05$). Also, 20BG showed a significantly lower DOC than 40BG ($p<0.05$). Furthermore, 40BG showed a significantly lower DOC than 20BG at 40 seconds ($p<0.05$).

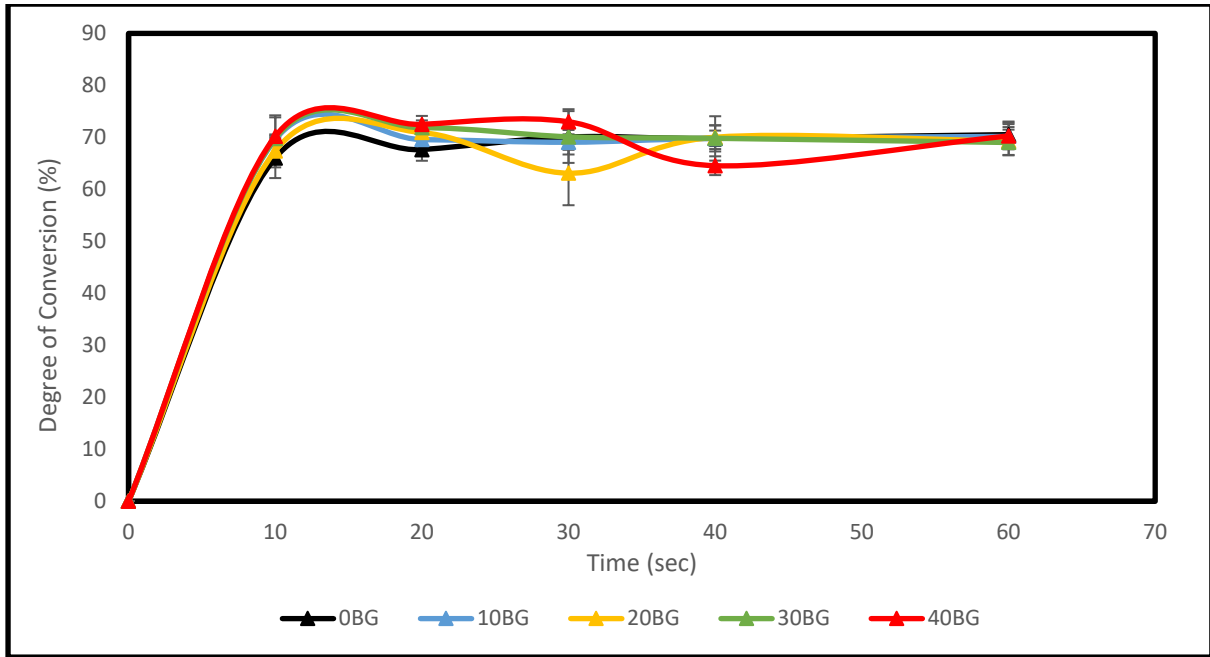


Figure 6-2: Degree of conversion (%) of the different F-BAG composites when light-cured for 10-60 seconds. No significant differences were shown when increase in the DOC when light-cured more than 10 seconds.

6.3.2 Water sorption

The data were not normally distributed. The water sorption results are shown in figure 6-3 and appendix H. 0BG, 10BG and 20BG specimens showed a significant increase in water sorption at week two ($P < 0.05$) with no significant change up to week four ($P > 0.05$). on the other hand, 30BG and 40BG showed a significant increase at week one ($P < 0.05$) with no change up to week four ($P > 0.05$).

Initially, after 1 and 4 hours there were no significant differences in the water sorption between all five tested composite specimens ($P > 0.05$). At 24 hours, 0BG composites showed a significantly lower water sorption than all the F-BAG composites ($P < 0.05$), and 20BG showed a significantly lower sorption when compared to 40BG composites ($P < 0.05$). From 48 hours until 96 hours, the same outcomes were shown in which 0BG and 10BG composites had a significantly lower sorption compared to 30BG and 40BG composites, and

20BG showed a significantly lower value compared to 40BG ($P<0.05$). 20BG continued to show significantly lower water sorption than 40BG up to week three ($P<0.05$), but no differences were shown between the two composites at week four ($P>0.05$). 0BG composites showed significantly lower water sorption compared to 20BG, 30BG, and 40BG at week one up to week four ($P<0.05$). on the other hand, 10BG composites showed a significantly lower value at weeks one and two compared to 30BG and 40BG ($P<0.05$), but at week three and four the values were significant lower compared to 40BG only ($P<0.05$).

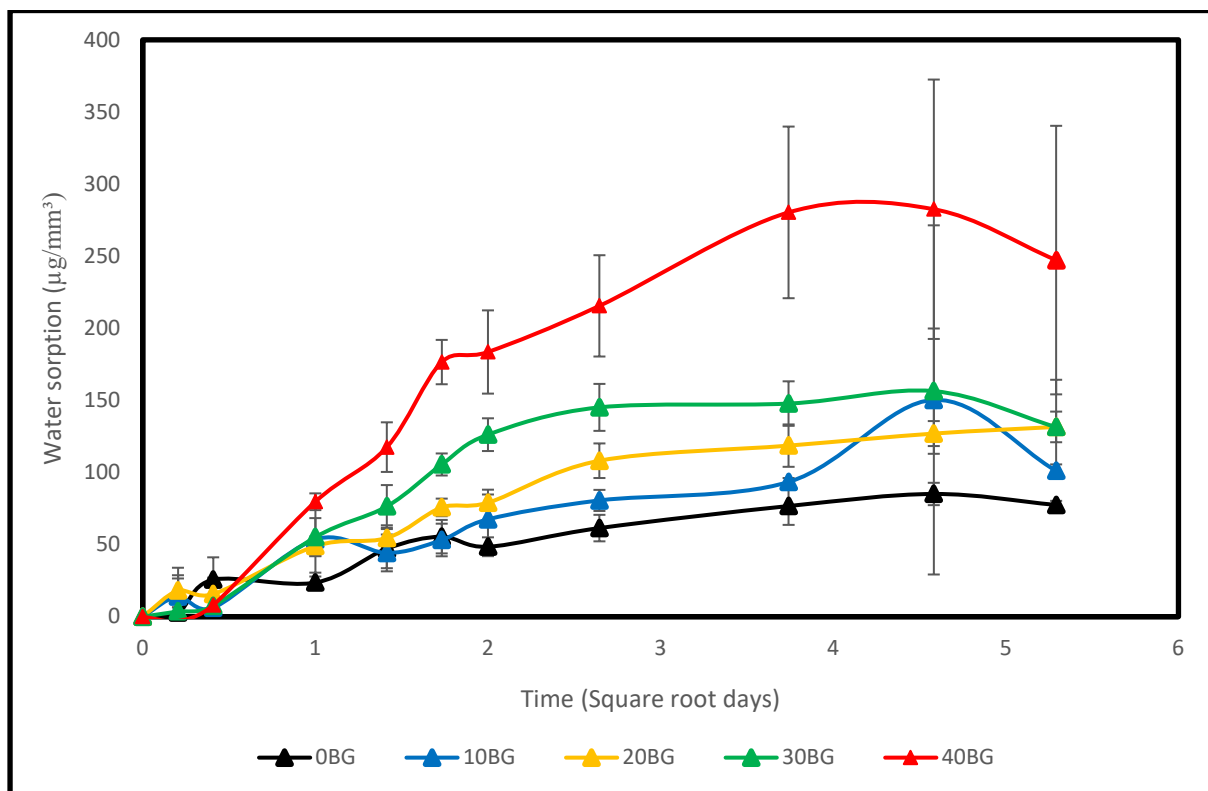


Figure 6-3: Water sorption ($\mu\text{g}/\text{mm}^3$) of the F-BAG composites, 40BG showed a significantly higher water sorption than the tested composites at most of the time points ($P<0.05$).

6.3.3 Fluoride release

The data were not normally distributed. The daily fluoride ion-release data are summarised in table 6-2. There was a clear relationship between the F-BAGs fillers concentrations and

fluoride ion release at each time point with the 40BG composite specimens releasing significantly more fluoride at each time point than the other F-BAGs composites followed by 30BG, 20BG, and 10BG ($P<0.05$). The pattern of the fluoride ion release was similar among all the tested composite specimens with initial high release at 24 hours ($p<0.05$) followed by a significant decrease up to week 1 ($P<0.05$, shown in blue in table 6-2). At weeks 1 and 2, a significant increase in the fluoride release (shown in green in table 6-2) followed by a significant decrease at weeks 3 and 4 ($P<0.05$).

40BG specimens showed a significantly higher cumulative fluoride release ($364 \mu\text{g}/\text{cm}^2$) during the entire testing period followed by 30BG ($193 \mu\text{g}/\text{cm}^2$), 20BG ($91 \mu\text{g}/\text{cm}^2$), and 10BG ($27 \mu\text{g}/\text{cm}^2$) ($p<0.05$). OBG released a significantly smaller amount of fluoride with $3.51 \mu\text{g}/\text{cm}^2$ at 28 days ($p<0.05$) (Figure 6-4).

Time	OBG		10BG		20BG		30BG		40BG	
	Median	IQR	Median	IQR	Median	IQR	Median	IQR	Median	IQR
1 hr	0.14	0.18	0.16	0.06	0.43	0.08	0.35	0.05	0.53	0.15
4hrs	0.53	0.29	1.04	0.25	2.26	0.13	2.58	0.34	2.45	0.00
24hrs	0.26	0.34	3.32	0.36	12.22	1.31	27.07	2.95	44.44	4.22
48hrs	0.01	0.01	0.73	0.35	7.63	1.09	14.78	2.30	30.74	2.27
72hrs	0.01	0.01	1.48	0.25	6.38	0.65	16.08	1.65	32.49	1.94
96hrs	0.00	0.00	1.07	0.13	4.99	1.06	14.52	1.32	31.69	2.85
Wk1	0.11	0.16	4.38	0.73	13.64	1.78	36.18	3.33	64.12	3.06
Wk2	0.19	0.26	6.62	0.48	18.56	1.15	36.36	1.93	61.03	9.44
Wk3	2.09	1.95	4.20	0.30	12.75	1.49	23.51	1.89	54.10	8.44
Wk4	0.17	0.15	3.87	0.89	12.12	1.45	21.65	5.59	42.44	4.15

Table 6-2: Daily fluoride ion release ($\mu\text{g}/\text{cm}^2$) of the different F-BAGs concentration composites, the blue numbers show the initial significant increase, and the green numbers show the second significant increase in daily fluoride release.

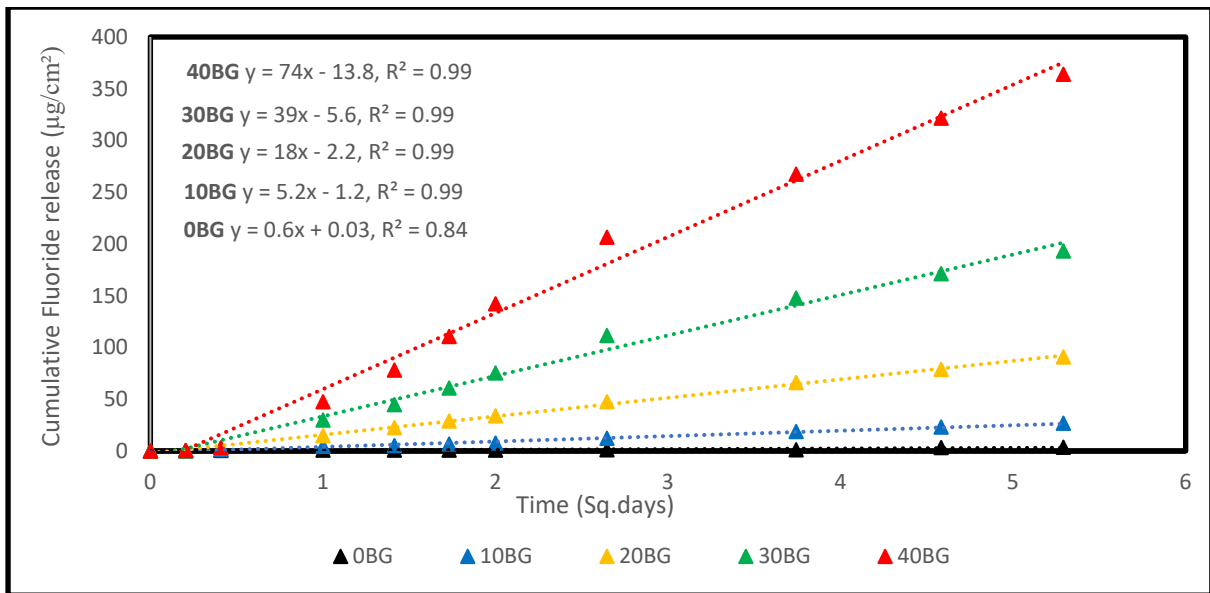


Figure 6-4: Cumulative fluoride release ($\mu\text{g}/\text{cm}^2$) of the different F-BAG composites, increasing the amount of incorporated F-BAGs led to significant increase in the fluoride release ($P < 0.05$).

6.3.4 Flexural strength and flexural modulus

The data of both flexural strength (FS) and flexural modulus (FM) were normally distributed. The FS data are summarised in table 6-3 and figure 6-5. 0BG, at all testing periods, showed a significantly higher FS ($P < 0.05$) except at day 28 which showed no significant differences compared to 10BG ($P > 0.05$). On day 1, 10BG showed a significantly higher FS compared to 20BG, 30BG and 40BG ($P < 0.05$), and no significant differences were found between 20BG and 30BG ($P > 0.05$). 40BG showed a significantly lower FS than the rest of the composites ($P < 0.05$). On day 7, 10BG showed a significantly higher FS compared to 20BG, 30BG, and 40BG ($P < 0.05$), and 20BG showed a significant higher FS value compared to 30BG and 40BG ($P < 0.05$). Also, 30BG had a significantly higher FS than 40BG ($P < 0.05$). The same outcomes were shown on day 14 except there were no significant differences between 30BG and 40BG composites ($P > 0.05$), and on day 28, 20BG showed no significant differences when compared to 30BG ($P > 0.05$). Within each group, FS of the 0BG decreased significantly at day

14 ($P < 0.05$), and all the F-BAGs composites (10-40) showed a significant decrease at day 7 ($P < 0.05$) with no significant differences shown from day 7 up to 28 days ($P > 0.05$).

The FM data are shown in table 6-4 and figure 6-6. On day 1, 40BG composites showed a significantly lower FM value than 0BG and 30BG ($P < 0.05$). On day 7, 0BG had a significantly higher FM compared to the F-BAGs composites, and 40BG had the lowest FM among the tested composites which was significant ($P < 0.05$), 10BG and 20BG showed a significantly higher FM than 30BG ($P < 0.05$). On day 14, 0BG and 10BG showed a significantly higher FM compared to 20BG, 30BG and 40BG composites ($P < 0.05$). On day 28, 0BG showed a significantly higher FM compared to the rest of the tested materials ($P < 0.05$), and 10BG showed a significantly higher values compared to 30BG and 40BG ($P < 0.05$), 20BG had a significant higher value than 40BG ($P < 0.05$). The FM strength of 20BG decreased significantly at day 14, and the value for 30BG and 40BG decreased significantly on day 7 ($P < 0.05$) with no change up to 28 days ($P > 0.05$), on the other hand, the FM of 0BG and 10BG were stable over the storage time ($P > 0.05$).

Time (Days)	0BG		10BG		20BG		30BG		40BG	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	139.8	10.8	124.4	11.1	103.2	8.5	95.9	7.5	79.7	10.5
7	129.2	12.5	101.6	8.3	84.5	8.3	69.8	4.8	51.2	5.1
14	117	16.5	101.3	10.8	78.3	9.1	62.7	5.8	54.4	6.6
28	100.3	14.8	93.7	10.1	77	11.5	67.9	6	51.5	4.6

Table 6-3: Flexural strength (MPa) of the different F-BAGs concentration composites

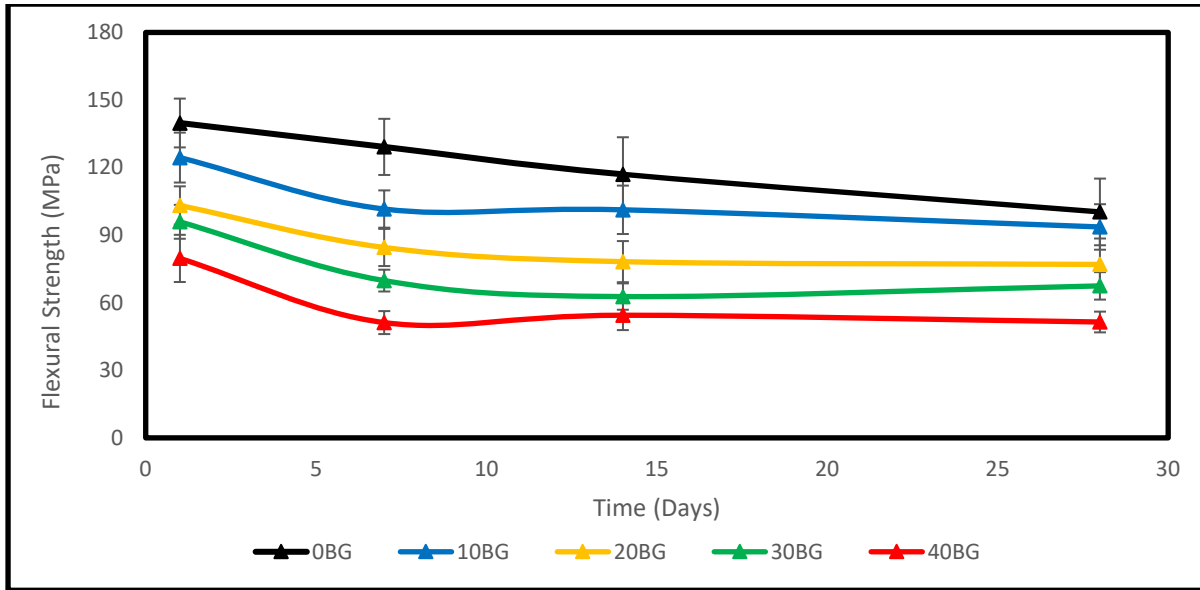


Figure 6-5: Flexural strength values (MPa) of the different F-BAGs concentrations composites, the F-BAGS composites showed a significant decrease at day 7 ($P < 0.05$) with no significant change up to 28 days ($P > 0.05$).

Time (Days)	0BG		10BG		20BG		30BG		40BG	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	9.8	0.8	8.9	0.9	8.9	1	9.2	1	7.8	1.3
7	10	0.9	8.9	0.9	8.3	0.8	7.3	0.6	6.2	0.4
14	10.1	1.2	9	1.2	7.4	0.6	6.8	0.9	6.4	0.6
28	10.3	1.8	8.5	0.7	8.1	0.8	6.9	0.6	5.8	0.4

Table 6-4: Flexural modulus (GPa) of the different F-BAGs concentration composites

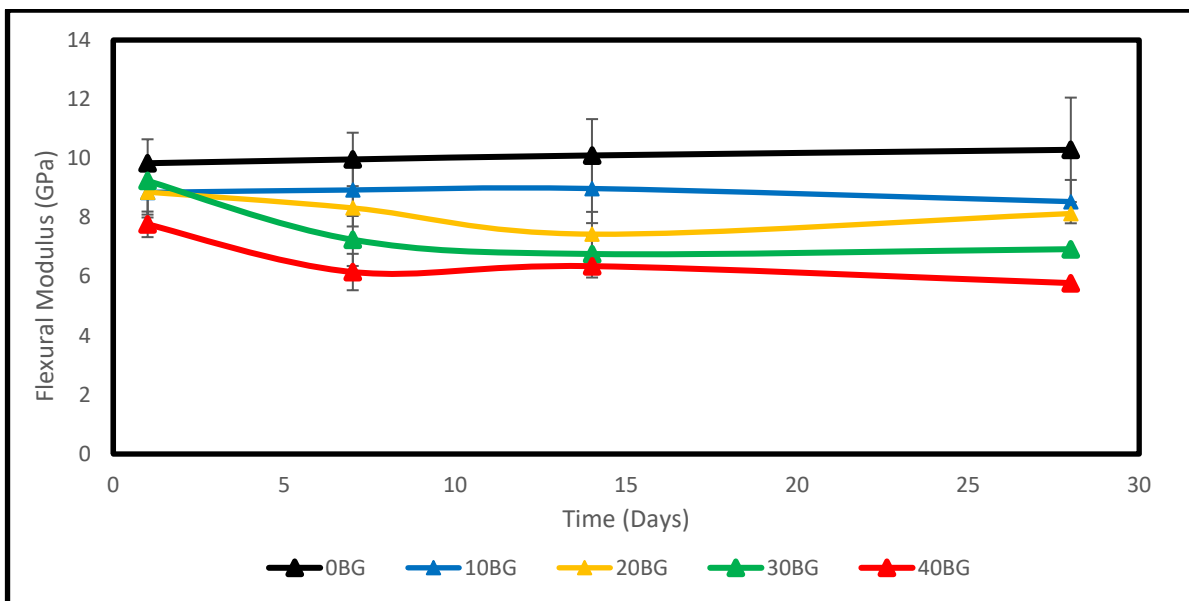


Figure 6-6: Flexural modulus values (GPa) of the different F-BAGs concentration composites, 0BG and 10BG showed no significant change throughout the testing period ($P > 0.05$)

6.4 Discussion

6.4.1 Preparation of the F-BAGs composites

Specimens from the experimental F-BAGs composites with different F-BAGs concentrations were prepared following the same method previously described in chapter 4 section 4.4.3. The monomer mixture 75:25 UDMA:TEGDMA was selected after it has been studied in chapter 5. 75:25 UDMA:TEGDMA monomer mixture, when used to make a F-BAGs composites, showed a good DOC, mechanical strength, and fluoride release. The F-BAGs powder were incorporated at 10, 20, 30 and 40wt% in addition to the barium borosilicate glass powder to produce highly filled composites with filler content of 55vol% (75wt%). The experimental F-BAGs composites prepared here contained silanised primary barium silicate glass and unsilanised F-BAGs fillers. It has been shown that silanisation of the bioactive glass fillers can prevent the ion release, on the other hand, it may result in decreasing the mechanical strength (Oral *et al.*, 2014). However, the mechanical strength can be improved by mixing the bioactive fillers with the silanised barium glass, for example, which can provide the composites with strength whereas the bioactive glass fillers gradually dissolve in the medium to either release ions or converted into hydroxyapatite or fluorapatite (Oral *et al.*, 2014; Marović *et al.*, 2016). Experimental F-BAGs composites were made successfully with F-BAGs incorporated at 0, 10, 20, 30 and 40wt% (0BG, 10BG, 20BG, 30BG and 40BG). The aim of this chapter is to study the effect of different concentrations of F-BAGs concentrations on the physical and mechanical properties of the F-BAGs composites.

6.4.2 Degree of conversion

The DOC of the five tested composites were measured and showed values ranged between 66-73% with no significant effect found between the materials when the F-BAGs added up to 40wt% ($P>0.05$).

6.4.3 Water sorption

Increasing the concentration of F-BAGs significantly affected the water sorption ($P<0.05$), particularly for concentrations of 30wt% and above. Water sorption is an important factor controlling the physical and mechanical properties of the composite materials (Sideridou;Tserki and Papanastasiou, 2003). It has been found that the addition of the BAGs fillers (based around SiO_2 45, CaO 24.5, Na_2O 24.5 and P_2O_5 6 in weight percent and particle size of 25 μm) can increase the water sorption of the composite materials (Yang *et al.*, 2013). The highest limit for the water sorption of the RBCs is 40 $\mu\text{g}/\text{mm}^3$ as recommended by the ISO4049 (Standardization, 2019), and all the tested materials showed higher than this limit, ranging between 60-144 $\mu\text{g}/\text{mm}^3$. The hydrophilicity of the BAG fillers contributed to the increase in the water sorption compared to the conventional composites that contain silanised hydrophobic fillers. Also, the ISO standard stipulates measuring the water sorption after only one week of storage, and the ion releasing materials will subjected to filler and matrix degradation with aging in order to release ions (Par *et al.*, 2019a; Par *et al.*, 2022). The results obtained in this chapter are comparable to a range of currently used ion releasing GIC based materials which showed a sorption ranged between 50-250 $\mu\text{g}/\text{mm}^3$

(Cefaly *et al.*, 2003; Bhatia *et al.*, 2017). Furthermore, the values showed a lower water sorption than a previously reported BAG composites (based around SiO₂ 45%, Na₂O 25%, CaO 25%, P₂O₅ 5%) when the BAGs incorporated at 5-40wt% and showed values between 70-220 µg/mm³ (Par *et al.*, 2019a).

6.4.4 Fluoride release

The pattern of the fluoride release was similar between the F-BAGs composites where the initial significant increase was at day one, then the release decreased before the significant increase at week one. This pattern resembles most of the fluoride releasing materials in which the initial burst of fluoride occurred in the first 24-48 hours (Karantakis *et al.*, 2000; Wiegand; Buchalla and Attin, 2007). The fluoride release of the F-BAGs was proportional to the concentrations of the F-BAGs fillers where 40BG released the highest amount of fluoride ions.

The cumulative fluoride release from the F-BAGs made in this chapter ranging between 27-364 µg/cm² where higher than a range of commercially available fluoride releasing material with values ranging between 8-150 µg/cm² (Dionysopoulos *et al.*, 2013).

6.4.5 Flexural strength and flexural modulus

In the FS test, the addition of the F-BAGs fillers had an impact on the FS value of the tested composites where the values decreased significantly (P<0.05). The OBG showed significantly higher FS than the F-BAGs composites (P<0.05), except after 28 days, no differences were shown compared to 10BG composites (P>0.05). Some studies have shown the same trend

where the experimental control with no BAG fillers showed significantly higher FS (Nicolae *et al.*, 2014; Par *et al.*, 2019b). Initially, the F-BAGs composites showed a value above 80 MPa which is above the ISO- recommended level, except the 40BG that showed a value of 79 MPa (ISO, 2009; Standardization, 2019). When compared with the strengths of a range of currently used dental composites, all the F-BAGs composites including the 40BG were within the range reported in the literature between 62-160MPa (Ilie and Hickel, 2009a; Ilie and Hickel, 2009b; Ferracane, 2011; Ilie;Rencz and Hickel, 2013)

There are several potential reasons for this decrease in strength as F-BAGs concentration increased. Firstly, differences in filler particle size can lead to stress concentrations at the resin/fillers interface (Asar *et al.*, 2013), so the difference in size between the primary BBS filler (0.7 μm) and the F-BAGs filler (45 μm) could have contributed to the decrease in FS as the F-BAG concentration increased. Secondly, increasing the concentration of unsilanised F-BAGs fillers will affect the flexural properties of the composite materials. It has been shown that increasing the amount of 45S5 bioactive glass in the composite resin decreased the FS significantly when the BAG fillers were incorporated at 5-40wt%, and the results at day one were between 17.1 and 121.5 MPa which is lower than the results obtained in this chapter (Par *et al.*, 2022). Other studies have shown a concentration dependent effect of adding BAGs to RBCs. For instance, when BAGS (based around SiO₂ 46.1%, CaO 26.9%, Na₂O 24.4%, P₂O₅ 2.6%) were added to the composites, no detrimental effect was found up to 20wt%, but increasing the concentration to 30-40% significantly decreased the FS values (Nicolae *et al.*, 2014).

All of the F-BAGs composites showed a significant decrease in the FS after one week of storage ($P < 0.05$), but then no change was shown up to 28 days ($P > 0.05$). Again, there are a

number of possible reasons for this, all of which are likely to have contributed to this decrease. Unsilanised filler particles can lead to voids forming within the resin matrix resulting (Tham;Chow and Ishak, 2010), which together with the hydrophilicity of the unsilanised glass used, will lead to an increase water sorption and degradation of the fillers and matrix-filler interface over the storage period (Curtis *et al.*, 2008; Khvostenko *et al.*, 2013; Al-Eesa *et al.*, 2021). Different BAGs show different levels of degradation over time meaning that some previous studies have shown a similar decrease in FS to that found in this study, while others have reported no decrease over 30 days of storage showing that the composition of the BAG has considerable influence on the stability of the RBC in an aqueous medium.

The flexural modulus of the tested composites ranged between 7-9 GPa comparable to most highly filled commercial composites (3-16 GPa) (Leprince *et al.*, 2010; Ilie;Rencz and Hickel, 2013; Jun *et al.*, 2013; Randolph *et al.*, 2016). These were higher than the FMs reported in previous studies looking at RBCs containing BGs, for instance an F-BAGs (glass compositions SiO₂ 33.5%, CaO 33%, Na₂O 10.5%, P₂O₅ 11% and CaF₂ 12%) and 45S5 (glass compositions: SiO₂ 45.0%, CaO 24.5%, Na₂O 24.5%, P₂O₅ 6.0%) which had FMs of 0.5-6.5 GPa (Par *et al.*, 2019b; Par *et al.*, 2022)

The addition of the F-BAGs fillers decreased the FM of the F-BAGs composites ($P < 0.05$) in a similar manner to that previously shown when RBCs have been made with other BAG fillers (Nicolae *et al.*, 2014; Par *et al.*, 2019b). At day one, no significant differences were shown between 0BG, 10BG and 20BG ($P < 0.05$), and 0BG and 10BG were stable from day one with no significant increase or decrease in the FM values over the storage time ($P > 0.05$). Over time, however, the RBCs containing 20wt% or more of the F-BAGs started to show a

reduction in FM. While the RBCs used in this chapter were HEMA-free there will still have been some water sorption over storage time. The unsilanised filler is more susceptible to degradation (Arksornnukit;Takahashi and Nishiyama, 2004) and increases the overall hydrophilicity of the RBC, which leads to plasticization of the resin matrix and deterioration of the filler-matrix interface, and decrease in the FM (Lohbauer *et al.*, 2003; Curtis *et al.*, 2008; Shah;Ferracane and Kruzic, 2009).

6.5 Summary

F-BAGs composites with different F-BAGs fillers concentrations were made. All the F-BAGs composites showed an acceptable DOC. The water sorption and fluoride release were dependent on the concentrations of the F-BAGs fillers used. For example, 40BG showed the highest water sorption and fluoride release. Despite the reduction in the values over the storage time, the FS values were acceptable and within the range of the 72 different commercial composites reported in the literature (Ilie and Hickel, 2009a). The FM values were acceptable and showed comparable values to the commercial composites (Leprince *et al.*, 2010; Ilie;Rencz and Hickel, 2013; Jun *et al.*, 2013; Randolph *et al.*, 2016). Based on the results, incorporating F-BAGs fillers in 10-40wt% showed good initial flexural properties which decreased over storage time especially for 30BG and 40BG. Increasing the F-BAGs concentration significantly increases the fluoride release, the fluoride release from 20BG was more than three times higher than the 10BG, on the other hand, the flexural strength of the 20BG is lower.

Chapter 7: General discussion and summary

7.1 General discussion

The aim of this study was to develop a fluoride releasing composite containing fluoridated bioactive glass fillers (F-BAGs) with sufficient mechanical and physical properties for use as a permanent restoration. The F-BAGs fillers were made in the lab in a previous work (Merie, 2023) where several formulations of F-BAGs containing NaF, CaF₂, AlF₃ were investigated to test the ability to release fluoride. The F-BAGs formulations containing 20% NaF (BG20NaF) was chosen for investigation in this thesis due to RBCs made with it having the highest fluoride release.

The first objective of this thesis was to scale-up from the lab-made F-BAGs to industrially made F-BAGs to investigate whether this had an effect on the material's physical and mechanical properties and to investigate if the glass performed as well as the lab-made glass. Therefore, the Glass Technology Service company made three different batches of glass, made on different days, based on the formulation of the lab-made glass. The experimental F-BAGs composites were made successfully using the lab-made and industrially made glass incorporated at 20wt% in a 50:50UDMA:TEGDMA monomer mixture and a total filler loading of 55vol%. The results showed no significant differences in DOC ($P>0.05$). The FS initially were higher than the recommended values by ISO4049 of 80 MPa (Standardization, 2019), however, the values decreased over time significantly for the lab-made glass composites ($P<0.05$). The lab-made glass composites also showed significantly higher water sorption ($P<0.05$), but no differences in cumulative fluoride release between the lab-made and the GTS glass composites ($P>0.05$). Also, no significant differences were shown between the three batches of the GTS glass composites and when three batches of

glass were mixed (GTS-mix). So, scaling-up from lab-made to industrially made glass did not affect the materials properties and composites made from the GTS glass showed promising results, fulfilling the first objective.

The second objective was to establish the effect different concentrations of UDMA, TEGDMA and HEMA monomer mixtures had on the physical and mechanical properties of the F-BAGs composites. When higher concentration of HEMA was used, higher fluoride release and water sorption was shown. On the other hand, the flexural properties of the HEMA containing composites were lower than HEMA-free composites especially when 50:50% of UDMA:HEMA was used to make the experimental composites. When the fluoride release and mechanical properties were considered, it was decided that the best overall properties were obtained with 75:25 UDMA:TEGDMA monomer combination and this was selected for the third experiment when different concentrations of the F-BAGs fillers were used.

The third objective was to determine the effect of the concentration of F-BAGs on the properties of the RBCs. The addition of F-BAGs between 10wt% and 40wt% had an impact on the water sorption, fluoride release and flexural properties of the tested composites ($P < 0.05$). However, no effect were shown on the DOC when F-BAGs added up to 40wt% ($P < 0.05$). The water sorption and fluoride release of the different F-BAGs composites increased with increased F-BAGs fillers concentrations as shown in figure 6-3 and 6-4. The highest limit for the water sorption recommended by ISO4049 for dental composites is $40 \mu\text{g}/\text{mm}^3$ (Standardization, 2019), and all the F-BAGs composites showed a sorption higher than this, with values between $60\text{-}144 \mu\text{g}/\text{mm}^3$ (Appendix H). Despite the high water sorption, the values were in the range of the commercial available GIC which showed a water sorption

ranged between 50-250 $\mu\text{g}/\text{mm}^3$ (Cefaly *et al.*, 2003; Bhatia *et al.*, 2017) and comparable to experimental composites containing between 5 and 40 wt% BAGs, water sorption between 100-220 $\mu\text{g}/\text{mm}^3$ (Par *et al.*, 2019a).

In terms of fluoride release, the F-BAGs composites showed a cumulative fluoride release between 27-364 ug/cm^2 depends on the F-BAGs concentration. The amount obtained from these composites is within the range of the amount of fluoride release reported in the literature from different fluoride containing composites, compomers, giomers, GIC and RMGIC ranged between 6-361 ug/cm^2 (Figure 7-1 and 7-2).

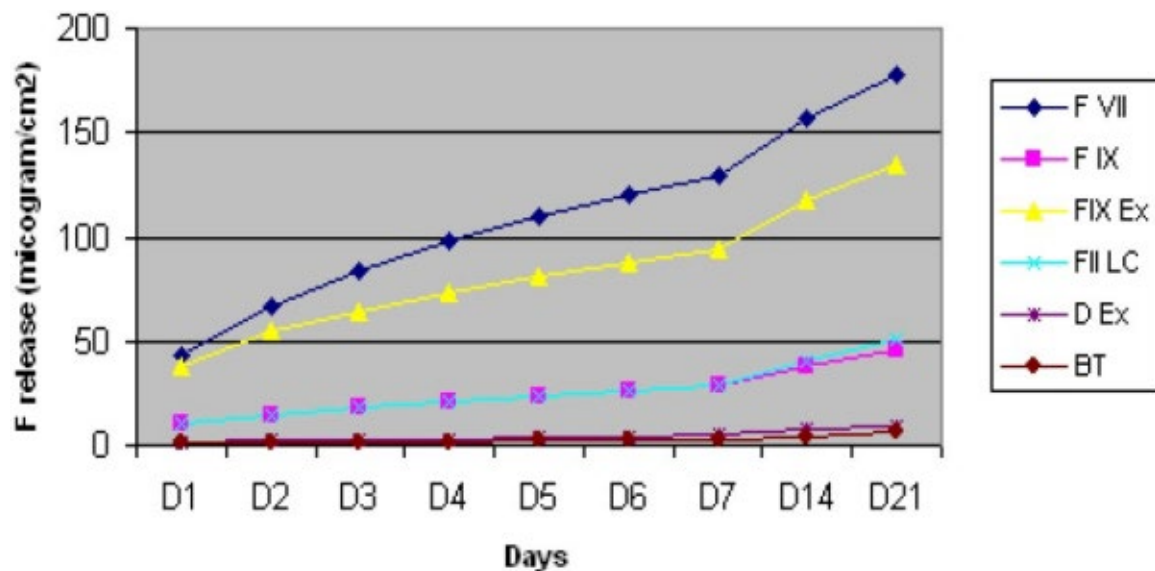


Figure 7-1: The 21 days cumulative fluoride release from four different GIC, one RMGIC and one giomer (Mousavinasab and Meyers, 2009).

The FS and FM of the F-BAGs composites were decreased compared to the F-BAGs-free composites. The FM and FS of the F-BAGs composites made with 10-40wt% F-BAGs fillers performed better or comparable to several studies of commercial composites and BAG containing composites (Ilie and Hickel, 2009a; Ilie and Hickel, 2009b; Ferracane, 2011; Ilie; Rencz and Hickel, 2013; Jun *et al.*, 2013; Khvostenko *et al.*, 2013; Leprince *et al.*, 2013; Nicolae *et al.*, 2014; Par *et al.*, 2019b; Par *et al.*, 2022) and within the range of the ISO recommendation for posterior composites of 80 MPa, except the 40BG that showed 79 MPa

at day one before the values decreased over storage time (Figure 6-5) (Standardization, 2019).

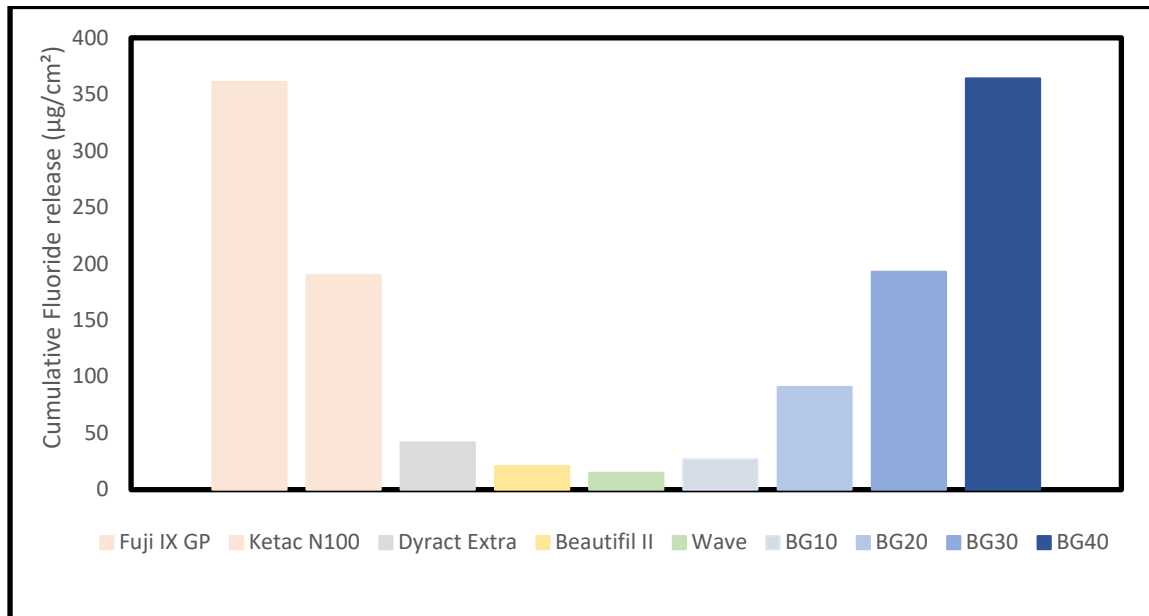


Figure 7-2: Cumulative fluoride release of two commercial GIC, compomer, giomer and fluoride containing flowable composites in comparison to the F-BAGs composites made in this research (Dionysopoulos *et al.*, 2013).

The FS and FM of the F-BAGs composites were lower than the F-BAGs free composites. This is most likely due to the lack of silanisation of the F-BAG particles and their large particle size compared to the primary filler. The differences in the shape and size of the BAG filler particles decreases the flexural properties when compared to BAG free composites (Fu *et al.*, 2008). It has been shown that mechanical strength of the dental composites increases with decreasing the filler size which will have higher filler surface area, thus more filler loading (Fu *et al.*, 2008; Marovic *et al.*, 2021).

Silanisation of the filler particles creates a covalent bond within the fillers and compolymerise with the resin matrix which will impact on the mechanical strength of the dental composites. Incorporating the unsilanised F-BAGs can decrease the mechanical

strength, however, silanising these glass could prevent the reactivity and ion release of the composite materials (Xavier *et al.*, 2015).

While the HEMA-containing materials were unsuitable for use as restorative composites, there are several other potential applications for their use. Firstly, HEMA is commonly used in adhesive resins (Toledano *et al.*, 2004) due to it enhancing the miscibility between the hydrophilic and hydrophobic parts of the adhesive materials (Nakaoki *et al.*, 2000; Moszner;Salz and Zimmermann, 2005; Van Landuyt *et al.*, 2005). BAG fillers have been used in experimental dental adhesives and showed promising results (Sauro *et al.*, 2012; Al-Eesa *et al.*, 2017; Al-Eesa *et al.*, 2018; Jun *et al.*, 2018; Kim *et al.*, 2021). BAG containing adhesives showed a therapeutic effect of remineralisation due to the ion release that can stabilise the caries lesion or repair the demineralised tooth tissues (Sauro *et al.*, 2013). Furthermore, BAG containing adhesives have been shown to increase the hardness and elastic modulus of the dentine interface (Sauro *et al.*, 2012). Therefore, HEMA containing F-BAGs composites made in this project could be useful as dental adhesive composites where high fluoride release can help in remineralising the affected dentine.

Additionally, pit and fissure sealants have been developed that incorporated BAG (Yang *et al.*, 2013; Chen *et al.*, 2018b; AlGhannam *et al.*, 2022; Choi;Han and Yang, 2023). Pit and fissure sealants do not need as high mechanical properties as restorative materials and previous work, in which a BAG filler was added up to 25wt% showed an FS of 54 MPa (Yang *et al.*, 2013). In this project, with 50:50 UH-BG composites, the FS value at day one was 67 MPa, and with 75:25 UH-BG, the value increased to 101 MPa. In comparison to commercially available pit and fissure sealants, the 50:50 UH-BG composites showed inferior properties, whereas all other HEMA containing composites (75:25 UH-BG, 75:12.5:12.5 UTH-BG, 50:30:20 UTH-BG and 50:40:10 UTH-BG) all had comparable FS and

FM (Figure 7-3 and 7-4) (Beun *et al.*, 2012). Consequently, the HEMA containing F-BAGs are promising candidates for use in an ion releasing pit and fissure sealants. In summary, successful novel fluoride releasing composites were produced using F-BAGs fillers which showed adequate fluoride release and mechanical strength. The F-BAGs fillers were shown to be suitable fillers to be used in composite resins.

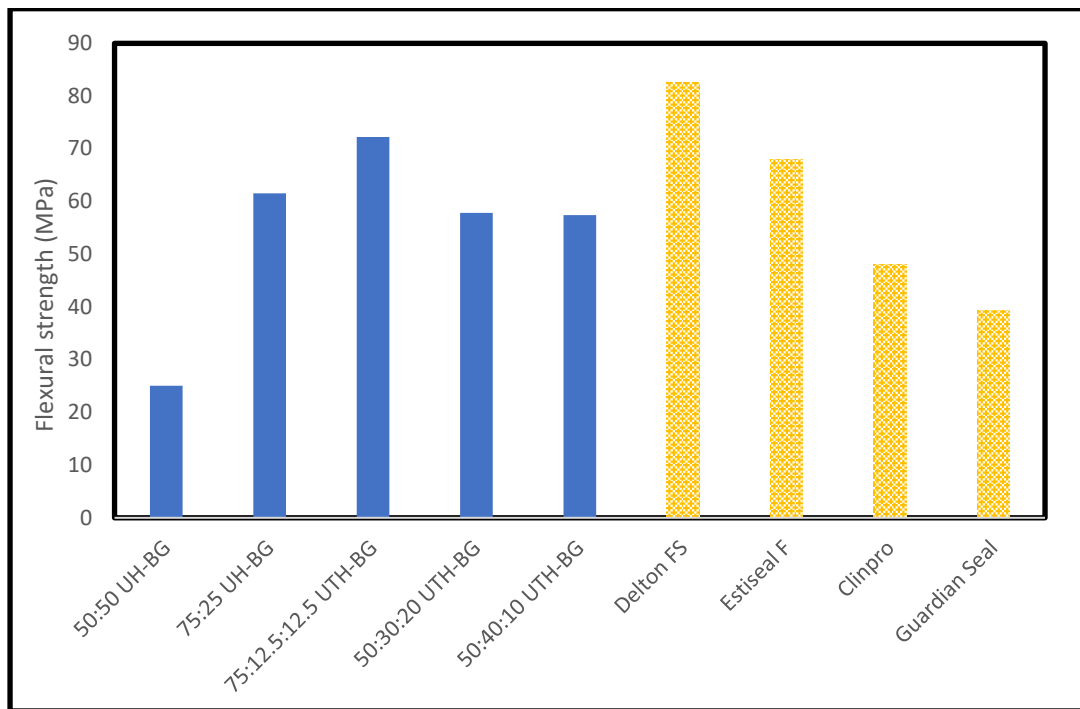


Figure 7-3: The flexural strength (MPa) of the HEMA-containing F-BAGs composites made in this project compared with four commercial pit and fissure sealants (Beun *et al.*, 2012)

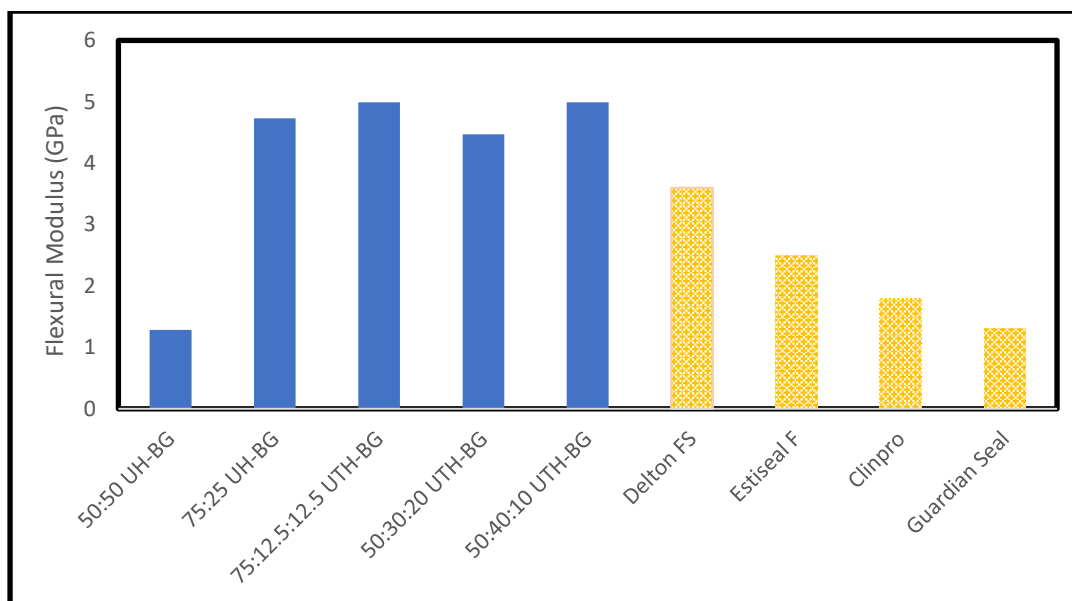


Figure 7-4: The flexural modulus (GPa) of the HEMA-containing F-BAGs composites made in this project compared with four commercial pit and fissure sealants (Beun *et al.*, 2012)

Eventhough evidence has shown the relation between the fracture toughness and marginal breakdown, and between the clinical wear and DOC, FS and fracture toughness. However, multi-factors are related to the clinical success of the RBCs, and in-vitro studies are not accuratley resemble the situation in the oral cavity (Ferracane, 2013). Furthermore, the 80 MPa ISO standards threshold used when testing new composites does not show the reality of the clinical situations. The deterioration in the RBCs is a material-dependant and has shown a 60% in some materials after a year of water exposure (Curtis *et al.*, 2008; Ilie and Hicel, 2009b). Moreover, the one day FS measured by the ISO 4049 are not useful with the more hydrophilic BAG composites that contain soluble fillers (Hashimoto *et al.*, 2010; Yang *et al.*, 2013). Several commercial composites showed higher FS values than the ISO threshold and some experimental BAGs based composites have shown a better values (Ilie and Hicel, 2009b; Par *et al.*, 2022).

7.2 Summary

- Scaled-up glass produces composites that are as good as the composites made with lab-made glass and in some cases better.
- There was no significant differences between composites made with the three batches of the GTS glass and when composite made out of three batches mixed together (GTS-mix).
- The monomer types and concentrations affected the physical and mechanical properties of the F-BAGs.
- When F-BAGs were incorporated at 10-40wt%, no significant effect on the DOC were shown. However, the flexural strength decreased compared to the F-BAGs free composites but still within the recommended ISO standard except when 40wt% F-BAGs fillers added.
- Incorporating the F-BAGs to the composite resins up to 40wt% showed a promising and a comparable results to the commercial composites and to experimental BAG and F-BAGs composites tested in several studies.
- The fluoride release and water sorption increased with increasing the F-BAGs concentrations, the F-BAGs fillers showed the ability to release fluoride under a neutral conditions (DW) which could be a promising finding that this material can reduce the incident of secondary caries and remineralise the carious tissues.

7.3 Limitations of the study

- In this project, it was only possible to measure the water sorption, fluoride release and flexural properties over one month of water storage. However, these materials would be exposed to an aqueous environment in the oral cavity for much longer time. Consequently, it would have been better, had time allowed if the the effects of water storage over longer time periods had been studied. .

- The properties of RBCs are related to the DOC and as was shown in the experiments in this work, there were some differences in the DOC of composites due to composition. However, in making the flexural property specimens it was necessary to use the overlapping curing technique. Consequently, it is possible that these specimens had a much high DOC, due to this overlapping curing technique, than they would have if they were used as a restorative and just cured for 20-40s by the clinician.

- All artificial aging experiments were conducted using DW as the storage medium. Many previous studies have looked at how storage in artificial saliva affects properties, and they often show some differences compared to storage in DW. However, there are many potential different formulations of artificial saliva and none truly mimic natural saliva,so within the time limits of this work it was decided that only the effect of water storage would be considered.

- Despite the high viscosity and cytotoxicity, Bis-GMA is the most commonly used monomer and offer the advantage of higher mechanical properties compared to other base monomers and the mechanical results of the F-BAGs composites could be improved using Bis-GMA monomer mixtures.

7.4 Future work

- Investigate the depth of cure for the F-BAGs composites. The DOC was tested but this does not reflect the depth of cure which can be affected by the differences in RI of the fillers and monomers.
- Further investigate the effect of the filler silanisation on the fluoride release and mechanical strength. The lack of silanisation of the F-BAGs is likely to have been the cause of reduction of mechanical properties over storage in DW. It would be worth investigating whether it is possible to silane coat the F-BAGs and then to see whether the mechanical properties improve and whether the fluoride release is reduced.
- The refractive index of the F-BAG was not matched to the monomers used in this study and that could have an effect on the polymerisation of the composites. While in this work the DOC was measured, it is still not clear how much residual monomer would be released from the composites. Consequently, it would be useful to measure the residual monomer released by the composites, particularly as residual monomer has been shown to be an irritant to oral tissues and potentially to be cytotoxic.
- Investigate the hardness and mechanical wear of the F-BAGs composites. Wear resistance and hardness are important properties that have an effect on the longevity of the composite materials.
- Since F-BAGs composites have released fluoride ions in DW, it is worth studying the solubility. In BAG composites, most of the solubility originates from the BAG fillers beside the residual monomers and higher solubility has been shown in composites

with higher BAG filler concentrations. Consequently, it would be important to see how the solubility changes over time.

- Measure the fluoride release and mechanical properties after storage in different media such as artificial saliva and acidic artificial saliva. The acidic medium will resemble the challenging situation in the oral cavity when the pH decreased

7.5 Covid statement

The COVID-19 had a huge impact on my project. Due to the regulations that reduced capacity in the dental materials labs, my access to the lab was significantly limited during my 2nd year. This reduced the amount of work that I was able to do, compared to my original project plan. In particular, two areas of the work were affected. Firstly, I was not able to do the XRD and SEM analysis of the lab-made and GTS-made glasses. Making sure that the materials were glasses and made similar morphology before making composites was clearly important but gaining training and access to the labs to carry these experiments out was difficult at the time. Consequently, my supervisor Dr Oana Bretcanu, conducted these experiments and the results are presented in Appendix 4. Secondly, due to time constraints, it was decided to only look at the effect of DW storage for 1 month. As mentioned in the Future Work section, the materials will experience far longer times in an aqueous environment if used a restorative material and without the delays caused by COVID-19 I would have looked at longer storage periods in this work.

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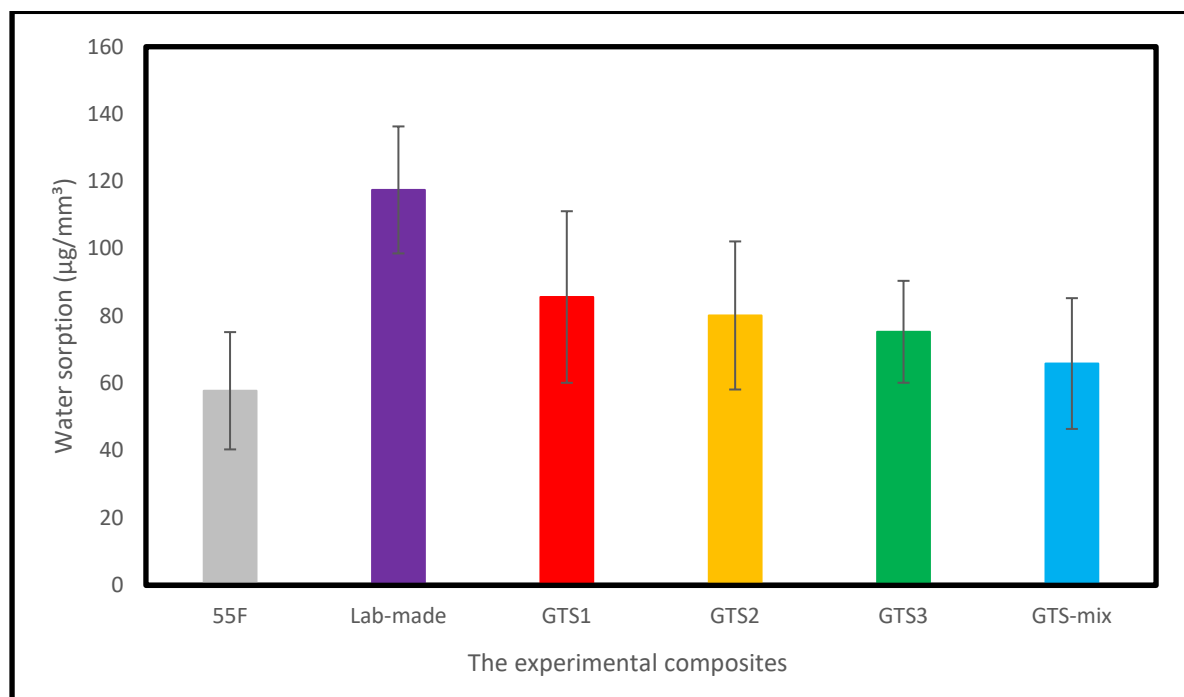
9. Appendices

Appendix 1

A: The DOC (%) of the six experimental composites, the F-BAGs-Free (55F), Lab-made F-BAGs composites, the three batches of the GTS and the GTS-mix composites.

Time(S)	55F		Lab-made		GTS1		GTS2		GTS3		GTS-mix	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
10	71.30	1.85	62.61	11.06	67.55	3.24	68.97	1.60	59.32	16.05	67.72	2.07
20	61.62	7.63	68.48	3.17	57.89	18.27	67.92	2.31	47.74	14.54	68.21	1.60
30	60.73	3.97	71.81	2.33	66.23	3.30	68.81	2.34	66.59	2.07	63.10	2.95
40	59.65	13.84	68.72	8.71	69.77	2.83	67.56	3.12	66.81	3.33	65.04	3.12
60	70.91	3.31	66.89	4.55	64.59	5.75	72.40	1.99	71.32	2.69	62.88	6.67

B: The water sorption ($\mu\text{g}/\text{mm}^3$) of the six experimental composites, the F-BAGs-Free (55F), Lab-made F-BAGs composites, the three batches of the GTS and the GTS-mix composites after 28 days.



Appendix 2

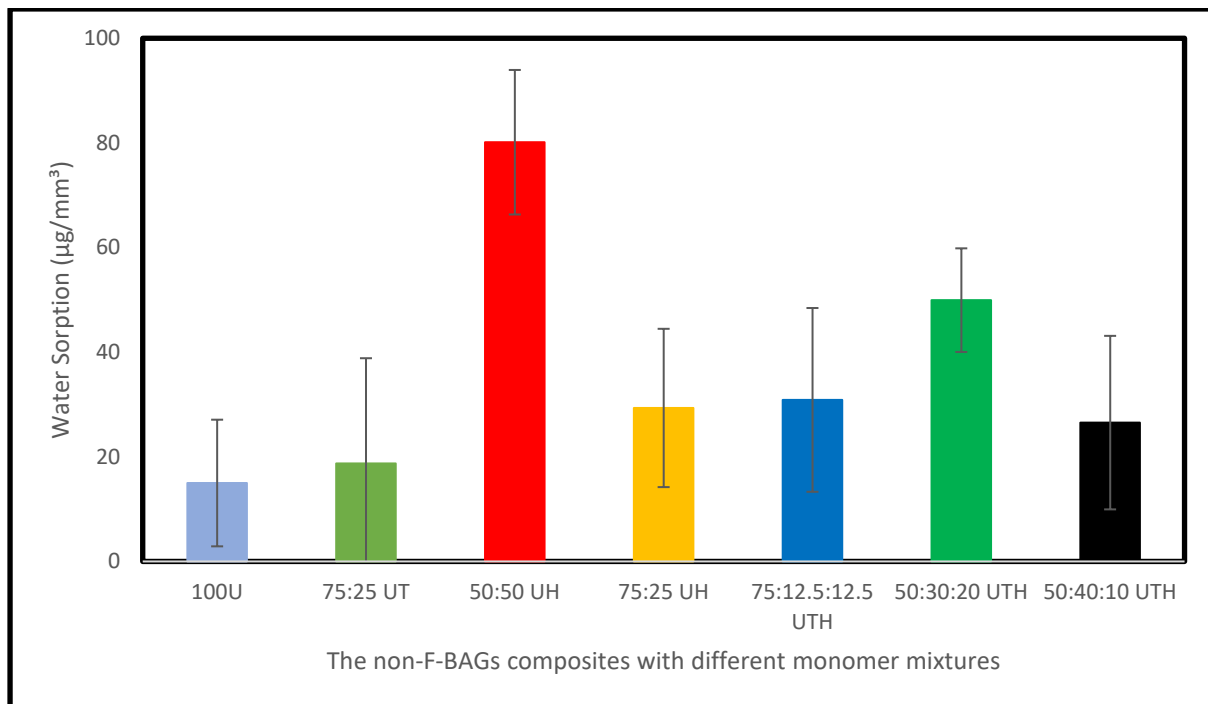
A: The DOC (%) of the seven non-F-BAGs experimental composites with different monomers mixtures.

Time (sec)	100U		75:25 UT		50:50 UH		75:25		75:12.5:12.5 UTH		50:30:20 UTH		50:40:10 UTH	
	Mean	Sd	Mean	Sd	Mean	Sd	Mean	Sd	Mean	Sd	Mean	Sd	Mean	Sd
10	71.42	3.59	68.37	3.96	73.70	4.10	79.02	3.89	75.28	1.88	71.71	1.55	72.25	3.23
20	80.78	2.00	69.51	6.00	78.79	2.71	76.68	3.45	80.97	2.14	75.96	1.69	75.20	3.83
30	77.51	5.02	68.68	2.10	78.85	2.08	74.91	2.58	80.24	1.62	76.81	1.29	75.30	1.83
40	71.06	8.50	68.62	4.08	78.84	1.88	80.41	2.74	83.84	1.55	75.20	1.28	76.84	2.67
60	73.49	4.64	67.17	2.40	81.35	2.03	74.61	3.71	83.80	0.90	77.24	3.01	76.79	1.88

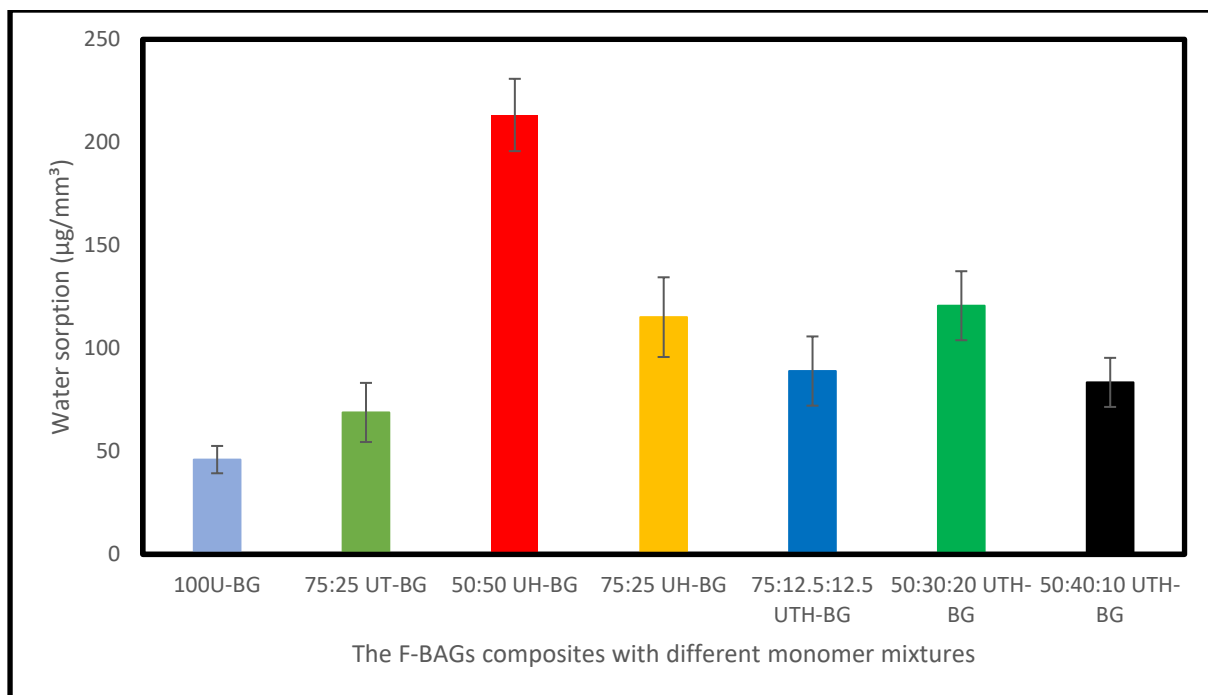
B: The DOC (%) of the seven F-BAGs experimental composites with different monomers mixtures.

Time (sec)	100U-BG		75:25 UT-BG		50:50 UH-BG		75:25 UH-BG		75:12.5:12.5 UTH-BG		50:30:20 UTH-BG		50:40:10 UTH-BG	
	Mean	Sd	Mean	Sd	Mean	Sd	Mean	Sd	Mean	Sd	Mean	Sd	Mean	Sd
10	66.09	3.41	71.28	0.79	26.18	2.96	71.54	2.64	68.81	1.32	57.95	6.25	69.45	3.67
20	66.19	3.86	71.35	2.35	40.71	8.14	68.14	4.60	68.32	2.55	68.30	5.42	74.52	1.97
30	66.84	2.42	71.90	0.79	48.36	5.90	73.28	1.35	70.48	4.96	66.87	4.06	75.21	2.47
40	66.32	3.23	71.01	1.03	60.02	7.35	66.24	6.60	67.97	3.79	71.76	2.34	73.97	4.83
60	64.59	3.91	68.36	6.30	72.96	5.14	70.90	1.65	67.28	3.22	71.48	5.13	75.01	2.87

C: The water sorption ($\mu\text{g}/\text{mm}^3$) of the seven experimental non-F-BAGs composites with different monomer mixtures after 28 days of storage. The water sorption of the 50:50 UH composites was significantly higher than the rest of the tested composites ($P < 0.05$).



D: The water sorption ($\mu\text{g}/\text{mm}^3$) of the seven experimental F-BAGs composites with different monomer mixtures after 28 days of storage. The water sorption of the 50:50 UH-BG composites was significantly higher than the rest of the tested composites ($P < 0.05$).



E: The flexural strength values (MPa) of the non-F-BAGs composites with different monomer mixtures.

Days	100U		75:25 UT		50:50 UH		75:25 UH		75:12.5:12.5 UTH		50:30:20 UTH		50:40:10 UTH	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	121.4	18.9	131.7	17.4	108.6	12.4	135.1	18.5	128.7	23.5	116.9	14.6	104.4	15.2
7	134.1	22.5	122.6	15.2	57.6	4.8	117.5	19.2	128.2	18.1	80.6	11.9	83.9	19.1
14	122.7	10.7	104.5	24.1	53.5	7.1	105.8	9.8	118.2	21.8	71.6	17.6	84.7	16.6
28	114	12.9	107.1	22.1	55.1	8.5	104.5	7.6	107.1	12.8	78	13.8	87.9	18.6

F: The flexural strength values (MPa) of the F-BAGs composites with different monomer mixtures

Days	100U-BG		75:25 UT-BG		50:50 UH-BG		75:25 UH-BG		75:12.5:12.5 UTH-BG		50:30:20 UTH-BG		50:40:10 UTH-BG	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	101.8	15	103.8	11.3	67.3	8.2	101.9	8	105.1	10.0	103.3	7.6	103.0	9.2
7	90.8	13	75.5	8.2	25.1	3.2	61.5	6.3	72.2	5.6	57.9	4.2	57.4	6.1
14	100.7	17.1	88	5.4	29.1	3.2	66.6	6.6	71.4	7.2	55.1	5.7	65.3	5.2
28	102.6	15.5	77.6	9.6	28.5	3	56.6	5	61.6	6.2	52	2.4	61.7	7.6

G: The flexural modulus values (GPa) of the non-F-BAGs composites with different monomer mixtures

Days	100U		75:25 UT		50:50 UH		75:25 UH		75:12.5:12.5 UTH		50:30:20 UTH		50:40:10 UTH	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	9.6	0.9	9.3	0.8	8.2	0.9	10	1.2	10.5	0.7	9.2	0.7	9.4	0.7
7	9.5	0.7	9.3	1	5	0.4	9	0.5	11.1	2.2	8.1	0.7	8.4	0.5
14	9.5	0.9	8.7	1.7	4.8	0.3	8.4	0.6	10.9	0.9	7.9	0.4	8.7	0.8
28	10	1	10.2	0.9	5	0.4	8.8	0.8	10.3	1.4	8.7	0.9	8.8	0.8

H: The flexural modulus values (GPa) of the F-BAGs composites with different monomer mixtures

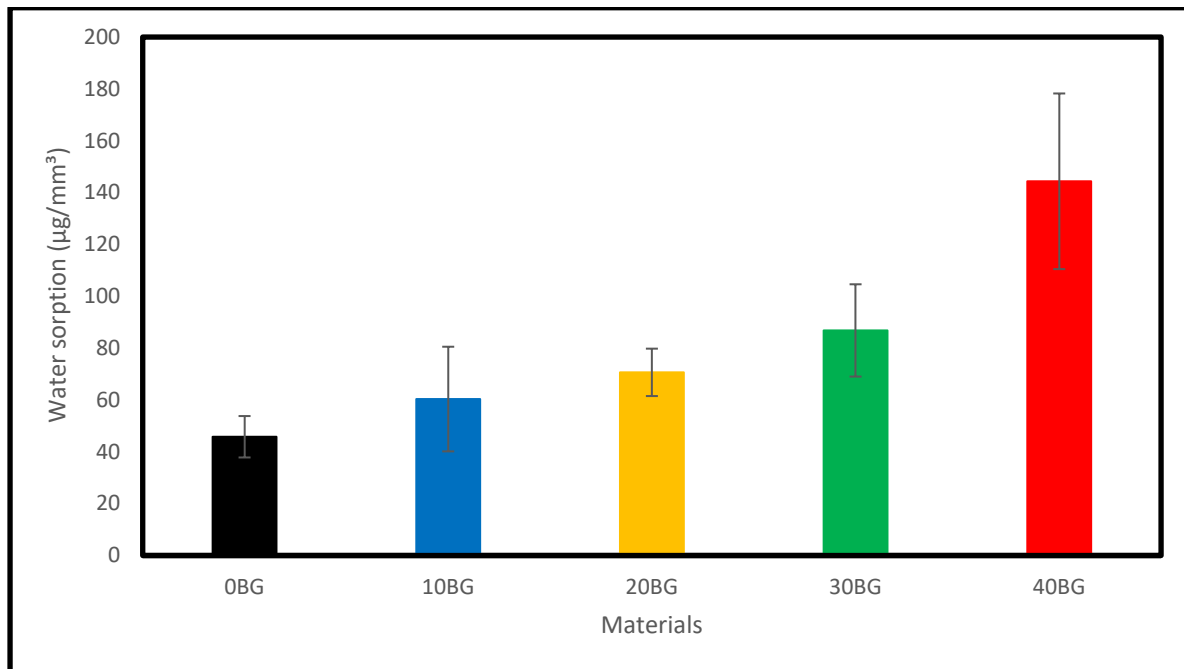
Days	100U-BG		75:25 UT-BG		50:50 UH-BG		75:25 UH-BG		75:12.5:12.5 UTH-BG		50:30:20 UTH-BG		50:40:10 UTH-BG	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	9	1.	8.8	0.7	3.8	0.5	7	0.9	5.6	1.2	5.4	1.4	5.5	1.1
7	9.1	1.3	6.8	0.7	1.3	0.2	4.7	0.3	5	0.7	4.5	0.7	5	0.8
14	5.1	1.1	7.2	0.7	1.6	0.3	4.8	0.7	4.9	1.1	4.7	0.9	5.6	1.0
28	4.3	0.8	4.9	1.1	1.5	0.2	3.6	0.5	4.4	0.9	3.7	0.8	3.5	0.4

Appendix 3

Appendix A: The DOC (%) of the five experimental composites, the F-BAGs-Free (0BG), and the F-BAGs composites (10BG, 20BG, 30BG and 40BG).

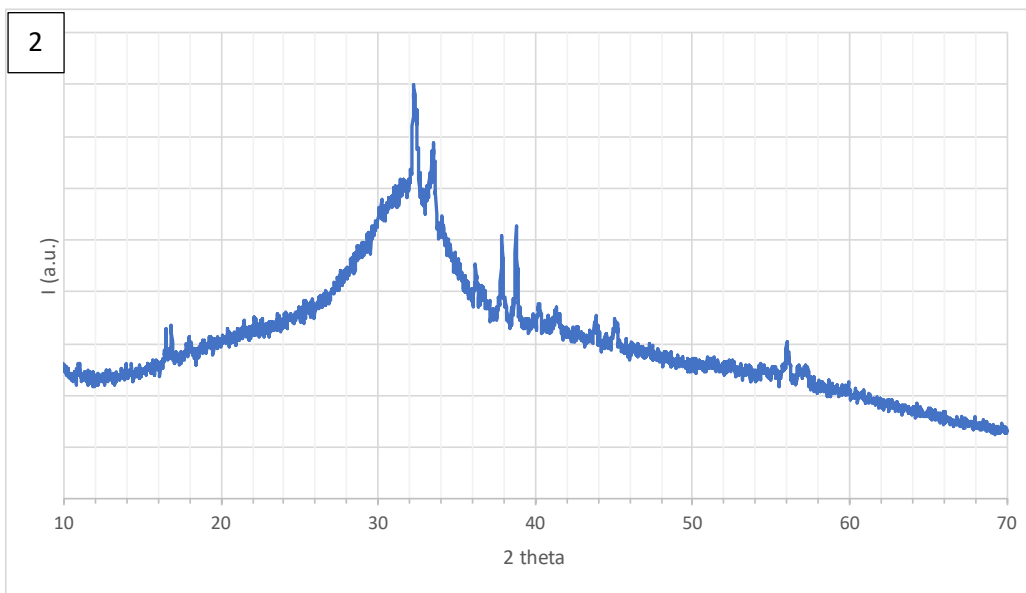
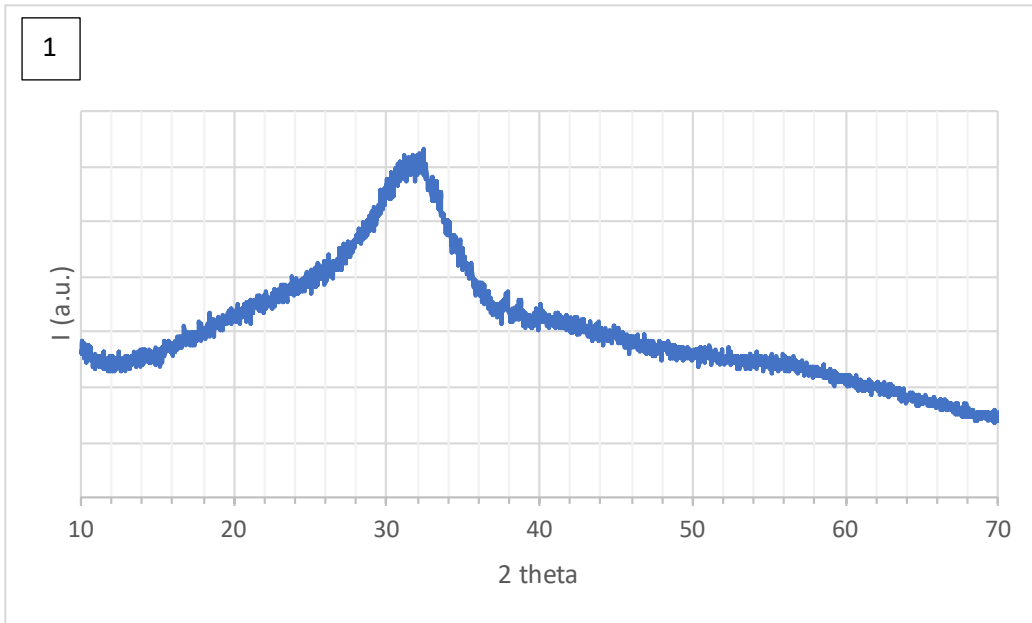
Time (sec)	0BG		10BG		20BG		30BG		40BG	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
10	66.04	3.87	69.57	4.67	67.40	3.17	69.78	0.51	70.19	3.67
20	67.65	2.15	69.57	2.84	70.92	1.37	71.85	1.42	72.50	1.63
30	70.08	4.98	69.07	2.36	63.11	6.16	70.11	2.50	73.01	2.42
40	69.80	4.27	69.81	2.51	70.04	2.28	69.82	1.49	64.55	1.81
60	70.53	2.52	70.19	2.36	69.31	2.68	69.02	2.47	70.28	2.57

Appendix B: The water sorption ($\mu\text{g}/\text{mm}^3$) of the five experimental F-BAGs composites after 28 days of storage. Increase the concentration of the F-BAGs fillers led to increase in the water sorption.

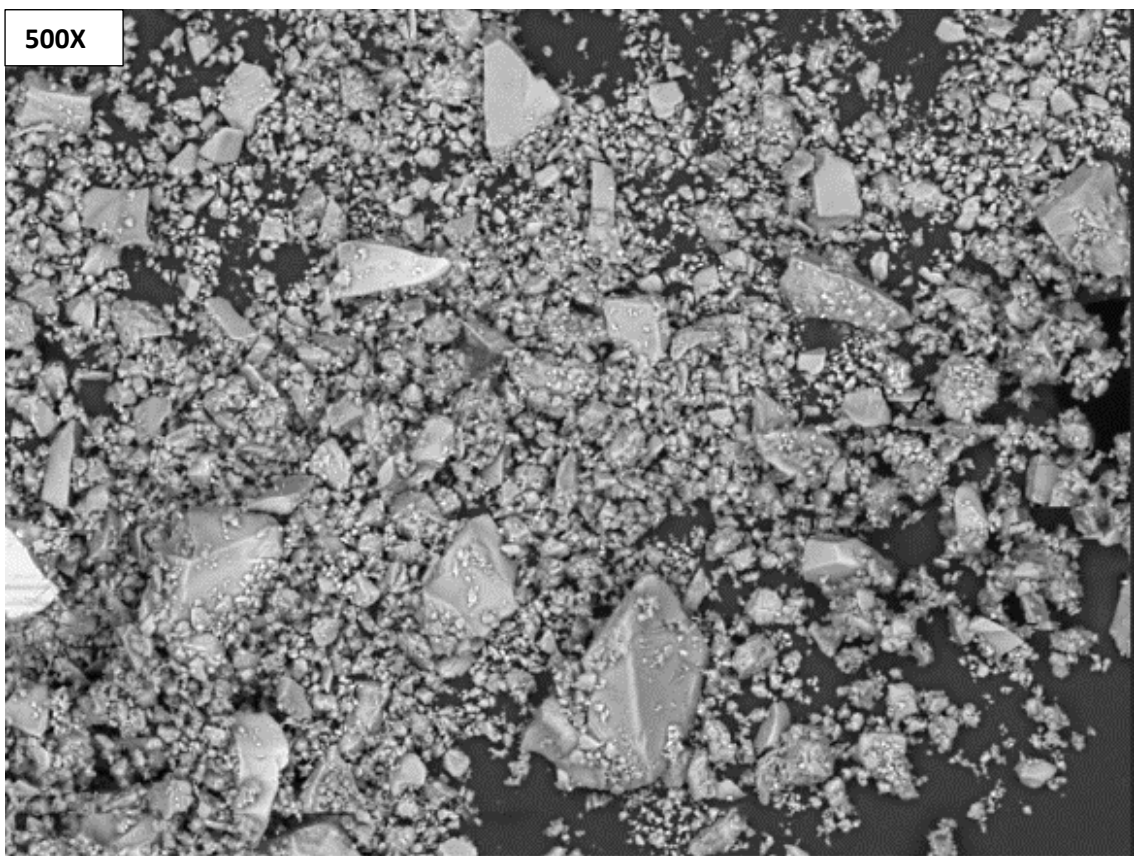
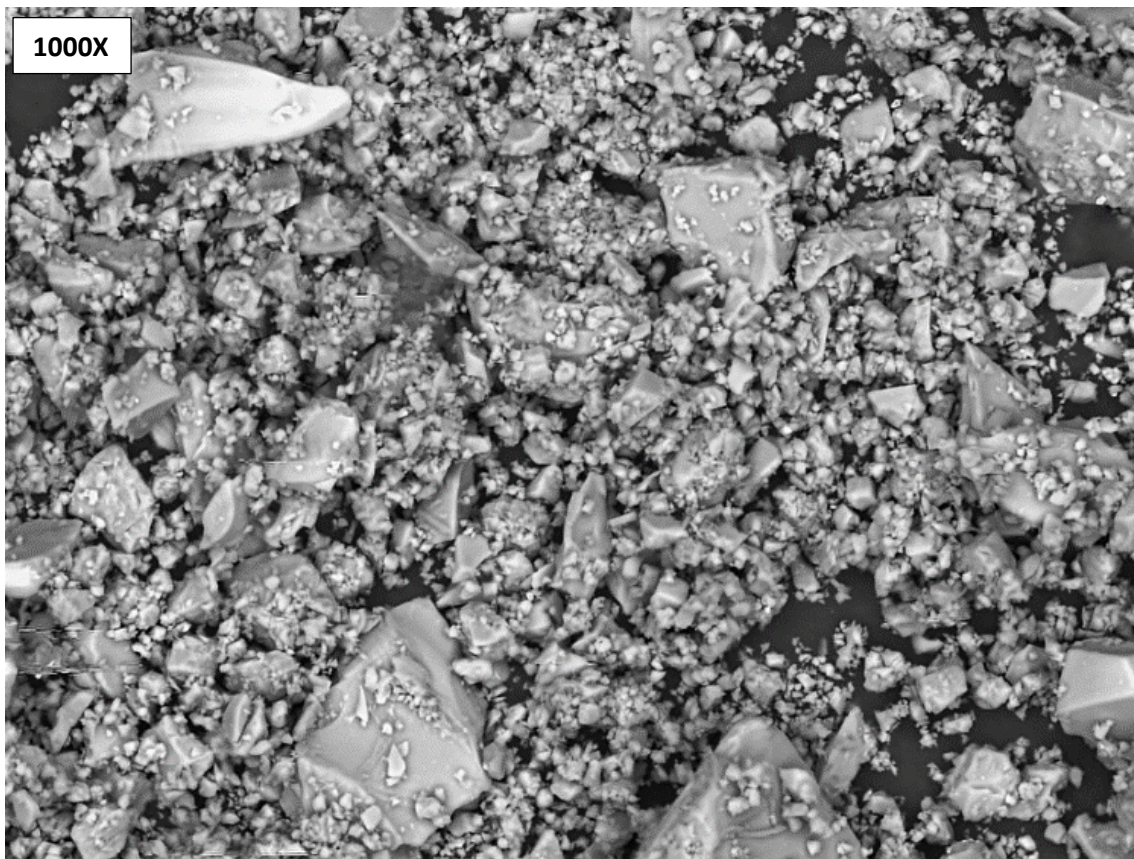


Appendix 4:

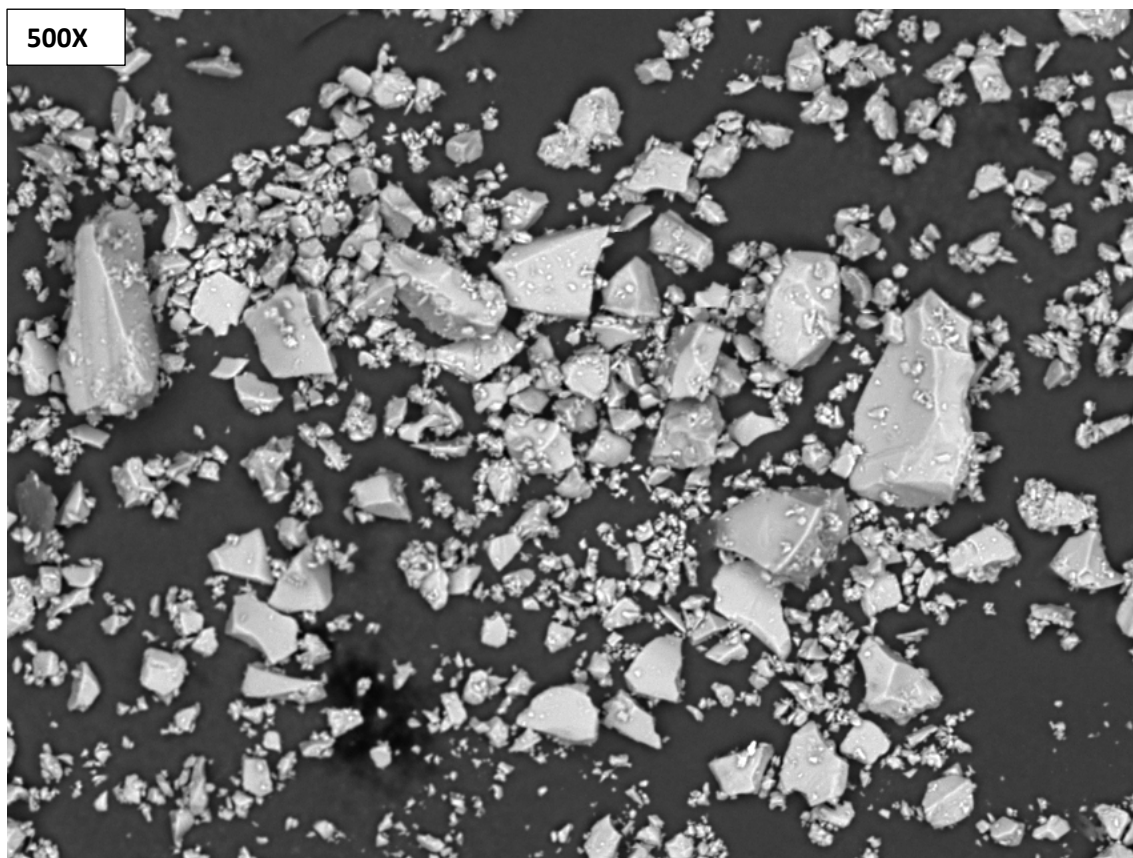
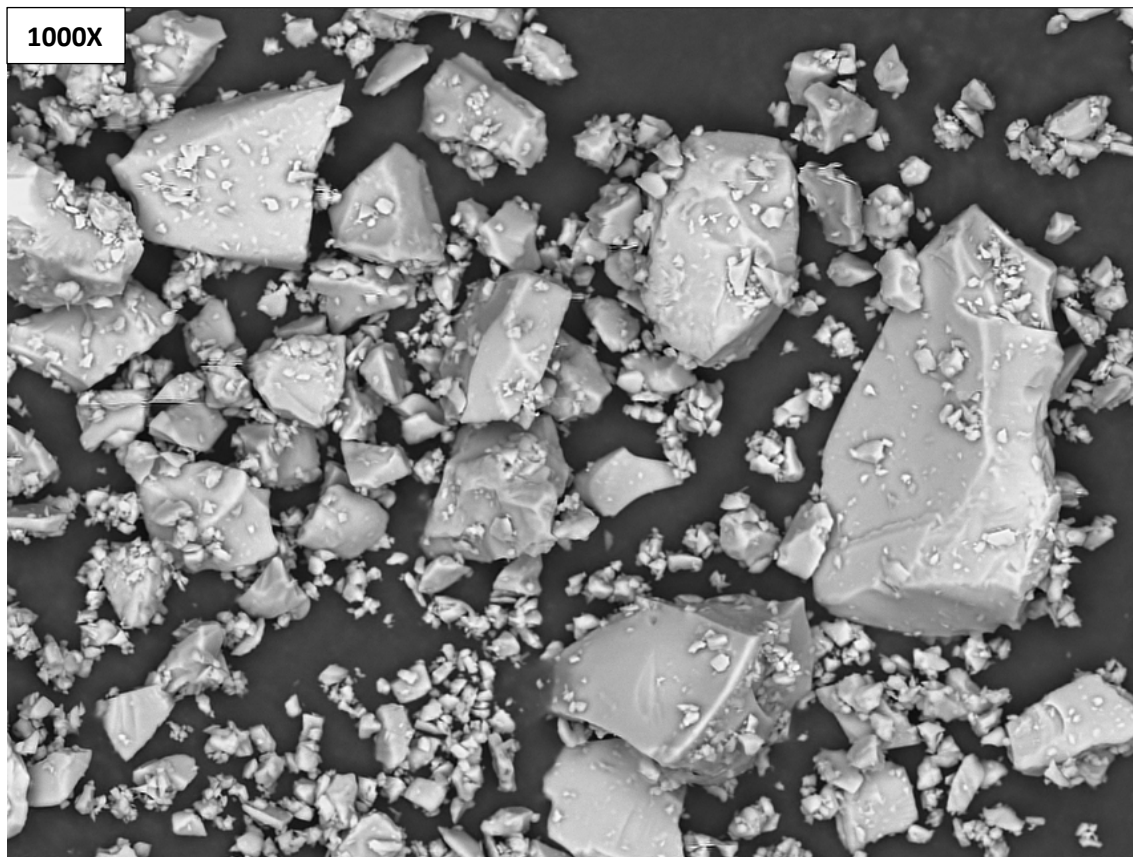
A: 1- XRD spectra of the GTS glass, 2- XRD spectra of the lab-made glass



B: SEM images of the lab-made glass at 500X and 1000X magnification



C: SEM images of the GTS glass at 500X and 1000X magnification



Appendix 5: IADR interactive talk presentation (Bogota, Colombia from 21st-24th of June 2023)

Increased scale novel glass production effect on composite flexural properties

Abdulaziz Algadhi, Dr.Oana Bretcanu, Dr.Matthew German

Introduction

When developing new glasses for resin composites it is important to confirm that scaling up from lab-scale to industrial-scale does not deleteriously effect properties (Figure 1). Here, we compare a lab-made glass with an industrially made glass in terms of composite flexural properties.



Figure 1: GTS1, GTS2, GTS3 and the lab-made glass.

A fluoride glass (37.5SiO₂:20.4 CaO:20.4:Na₂O:5P₂O₂:16.7 NaF, sieved particle size <45mm) was made at <50g scale in our lab and in three batches of 250g scale industrially (GTS, Glass Technology Services, UK) (Table 1). 50:50 urethane dimethacrylate: triethylene glycol dimethacrylate composites (Sigma Aldrich, UK) were made with 20v% our glass and 40v% barium-alumo-borosilicate glass (0.7 mm particle size, SCHOTT® UltraFine). Five composites were made, one for each batch and a fifth from the three GTS batches combined.

Glass oxides	SiO ₂	CaO	Na ₂ O	P ₂ O ₅	NaF
BG	45	24.5	24.5	6	-
NU Lab-made	37.5	20.4	20.4	5	16.7

Table 1: The composition of the fluoridated bio-active glass made at Newcastle University (Lab-made) compared with the conventional 45S5 Bioglass® made by Larry Hench

Degree of conversion (DC) was measured using ATR-FTIR (Spectrum One, Perkin Elmer) (n=5, 6×1mm) exposed to 40s of light (intensity=1000 mW/cm², Elipar DeepCure, 3M ESPE, UK).

Three-point bend test flexural strength (FS) and modulus (FM) specimens (n=10, 5 overlapping 20s light exposures, 25×2×2mm) were stored in distilled water at 37°C and properties measured at day 1, 7, 14 and 28 using a universal test machine (model 5567, Instron, UK).



Figure 2: one of the samples before, During and after applying the flexural test.

Results: No significant differences in DC were measured ($P > 0.05$, range = 60-69%) (Table 2). Similar behaviour was found for the FS and FM. Initially, all composites had FS above 80MPa and FM above 7.1GPa, with no significant difference measured ($P > 0.05$). Both parameters then decreased for all composites over time, significantly so for the lab-made glass composites ($P < 0.05$), while no significant differences were found for the scaled-up glass composites ($P > 0.05$).

Conclusion: All composites showed high DC% and good initial mechanical properties. While properties decreased over storage time, the scaled-up glass composites showed superior flexural properties to the lab-based glass composites, suggesting this glass could be suitable for use in an ion-release dental composite.

Materials	DOC (%)	SD
GTS1	69.77	2.83
GTS2	67.56	3.12
GTS3	66.81	3.33
GTS-mix	65.04	3.12
Lab-made	68.72	3.71

Table 2: DOC (%) of the tested composites with their standard

Day	Flexural Strength (MPa): Mean (SD)					Flexural Modulus (GPa): Mean (SD)				
	Lab	GTS1	GTS2	GTS3	GTSMIX	Lab	GTS1	GTS2	GTS3	GTSMIX
1	82 (9) ^{A,a}	89 (9) ^{A,e}	84 (5) ^{A,e}	87 (10) ^{A,e}	88 (10) ^{A,e}	7.1 (0.5) _{Z,z}	7.7 (1.5) _{Z^x}	7.6 (0.3) _{Z^x}	7.8 (0.4) _{Z^x}	8.1 (0.8) _{Z^x}
7	57 (5) ^{B,b}	69 (11) ^{C,e}	69 (7) ^{C,e}	70 (10) ^{C,e}	71 (9) ^{C,e}	5.7 (0.5) _{Y^y}	6.9 (0.3) _{X^x}	6.5 (0.9) _{X^x}	7.4 (0.4) _{X^x}	7.3 (0.4) _{X^x}
14	49 (5) ^{D,c}	67 (8) ^{E,e}	72 (7) ^{E,e}	74 (8) ^{E,e}	73 (6) ^{E,e}	5.7 (0.6) _{W^y}	7.5 (1.0) _{V^x}	7.1 (0.7) _{V^x}	7.0 (0.7) _{V^x}	7.4 (0.4) _{V^x}
28	41 (5) ^{F,d}	68 (9) ^{G,e}	69 (10) ^{G,e}	74 (8) ^{G,e}	70 (7) ^{G,e}	5.3 (0.6) _{U^y}	6.9 (1.2) _{T^x}	6.9 (1.2) _{T^x}	7.4 (1.0) _{T^x}	6.4 (2.4) _{T^x}

Table 3: Flexural strength and flexural modulus results with their standard deviation

Different superscript capital letters denote significant differences between materials

Different superscript lower case letters denote significant differences between time.

Appendix 5: Different classes of tooth preparation restored with the F-BAGs composites made in chapter 6 (10BG, 20BG, 30BG and 40BG composites)



