

**THE SYNTHESIS OF POLYCARBOXYLATE
ETHER POLYMERS FOR USE AS ADDITIVE IN
TERNARY BLENDED CONCRETE**

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**THE SYNTHESIS OF POLYCARBOXYLATE
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TERNARY BLENDED CONCRETE**

by

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TABLE OF CONTENTS

ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS.....	iii
LIST OF TABLES	ix
LIST OF FIGURES	xii
LIST OF ABBREVIATIONS	xvi
ABSTRAK	xvii
ABSTRACT	xix
CHAPTER 1 INTRODUCTION.....	1
1.1 Study Background	1
1.2 Problem Statements.....	4
1.3 Research Objectives	5
1.4 Research Significance	5
1.5 Study Scope.....	6
1.6 Thesis Layout	7
CHAPTER 2 LITERATURE REVIEW.....	9
2.1 Introduction	9
2.2 Background of Current Issues	9
2.3 Supplementary Cementitious Materials (SCM) for Concrete Applications	12
2.3.1 Ground Granulated Blast Furnace Slag (GGBS)	16
2.3.2 Pulverized Fly Ash (PFA).....	18
2.4 GGBS-PFA Ternary Blended Cement Concrete.....	21
2.5 Introduction of Super-Plasticizers (SP).....	24
2.5.1 Development Background of SP	26
2.6 Synthesis Process of Polycarboxylate Ether (PCE) Polymers	30

2.6.1	Esterification	30
2.6.2	Free Radical Polymerization.....	32
2.6.3	Reversible Addition-Fragmentation Chain-Transfer (RAFT) Polymerization	34
2.7	Molecular Structure of PCEs.....	36
2.8	Working Mechanism of PCEs in Cementitious Systems	38
2.9	The Influence of Molecular Structure Design of PCE Polymers on Cementitious Systems	42
2.9.1	Main Chain Structure of PCE Polymers	42
2.9.2	Side Chain Structure of PCE Polymers.....	44
2.9.3	Molar Ratio of Side Chain to Main Chain (SC/MC)	48
2.9.4	Molecular Weight of PCE Polymers.....	48
2.9.5	Supplementary Factors.....	50
2.10	The Effect of the Application of PCE polymers on Cementitious Paste	51
2.10.1	Fluidity of Cementitious Systems	51
2.10.2	Workability of Cementitious Composites.....	53
2.10.3	Setting Time of Cementitious Paste.....	55
2.10.4	Hydrophile-Lipophile Balance (HLB) Value of Cementitious Composites.....	56
2.10.5	Zeta Potential of Cementitious Systems	57
2.10.6	Adsorption Isotherm of Cementitious Mixtures	59
2.10.7	Adsorption Capability of PCE Polymers in Cementitious Composites.....	61
2.10.8	Rate of Hydration of the Cementitious System	63
2.10.9	Heat Evolution of Cementitious composites.....	64
2.11	The Effects of PCEs on the Mechanical Properties and Durability Performance of Mortar and/or Concrete	66
2.11.1	Strength Development.....	66
2.11.1	Improvements in Intrinsic Air Permeability	67

2.11.2	Changes in Total Porosity	68
2.11.3	Drying Shrinkage Assessment	69
2.11.4	Carbonation Resistance.....	69
2.11.5	Chloride Binding Property	70
2.12	Knowledge Gap Analysis.....	71
2.13	Critical Summary of Literature Review	74
CHAPTER 3	METHODOLOGY.....	76
3.1	Introduction	76
3.2	Research Methodology.....	76
3.3	Materials.....	79
3.3.1	Binder Materials.....	79
3.3.1(a)	Ordinary Portland Cement (OPC)	79
3.3.1(b)	Ground Granulated Blast Furnace Slag (GGBS).....	80
3.3.1(c)	Pulverised Fly Ash (PFA).....	81
3.3.2	Aggregates	82
3.3.2(a)	Coarse Aggregate.....	82
3.3.2(b)	Fine Aggregate	82
3.3.3	Polycarboxylate Polymers (PCEs).....	83
3.4	The Characteristics Analyses of Synthesized PCE Polymers	84
3.4.1	Fourier Transform Infrared Spectroscopy (FTIR) Analysis	84
3.4.2	Nuclear Magnetic Resonance (NMR) Analysis.....	85
3.5	Manufacturing Parameter Optimizations for Cementitious Composites	85
3.5.1	Binder Composition Optimization.....	85
3.5.2	Coarse Aggregate to Fine Aggregate Ratio (CA/FA).....	88
3.5.3	PCE Solution Dosage.....	89
3.5.4	Water-Binder (w/b) Ratio	92
3.6	The Test Analyses on GGBS-PFA Ternary Blended Cement Paste.....	93

3.6.1	Mix Design of Cementitious Paste.....	93
3.6.2	Standard Consistency	94
3.6.3	Initial and Final Setting Time	95
3.6.4	Le Chatelier Soundness Test.....	96
3.6.5	Thermogravimetric Analysis (TGA).....	97
3.6.6	Microstructure Study.....	97
3.7	The Mix Design of GGBS-PFA Cementitious Concrete	98
3.8	The GGBS-PFA Ternary Blended Cement Concrete Fabrication Process.....	99
3.8.1	Mixing Method	99
3.8.2	Curing Method	99
3.9	The Test Method on the Rheological Properties of GGBS-PFA Ternary Blended Cement Concrete.....	100
3.9.1	Flow Table Test	100
3.10	The Assessments on the Engineering Properties of GGBS-PFA Ternary Blended Cement Concrete.....	101
3.10.1	Flexural Strength.....	101
3.10.2	Compressive Strength	102
3.10.3	Ultrasonic Pulse Velocity (UPV).....	103
3.11	The Assessments on Durability Performance of GGBS-PFA Ternary Blended Cement Concrete.....	104
3.11.1	Water Absorption.....	104
3.11.2	Intrinsic Air Permeability.....	105
3.11.3	Total Porosity	107
3.11.4	Capillary Sorptivity.....	108
3.11.5	Drying Shrinkage	109
3.11.6	Carbonation Resistance.....	111
3.11.7	Chloride Diffusivity	112
3.12	Summary	114

CHAPTER 4	RESULTS AND DISCUSSIONS	116
4.1	Introduction	116
4.2	The Characteristic Properties of Synthesized PCE Polymers	116
4.2.1	Fourier Transform Infrared Spectroscopy (FTIR) Analysis	116
4.2.2	Nuclear Magnetic Resonance (NMR) Analysis	118
4.3	The Properties of GGBS-PFA Ternary Blended Cement Paste	125
4.3.1	Standard Consistency	126
4.3.2	Initial and Final Setting Time	127
4.3.3	Le Chatelier Soundness Test.....	129
4.3.4	Thermogravimetric Analysis (TGA).....	130
4.3.5	Microstructure Study.....	133
4.4	The Rheological Properties of GGBS-PFA Ternary Blended Cement Concrete	149
4.4.1	Flow Table Test	150
4.5	The Engineering Properties of GGBS-PFA Ternary Blended Cement Concrete	153
4.5.1	Flexural Strength.....	153
4.5.2	Compressive Strength	155
4.5.3	Ultrasonic Pulse Velocity (UPV).....	157
4.6	The Durability Performance of GGBS-PFA Ternary Blended Cement Concrete	159
4.6.1	Water Absorption.....	160
4.6.2	Intrinsic Air Permeability.....	161
4.6.3	Total Porosity	163
4.6.4	Capillary Sorptivity.....	165
4.6.5	Drying Shrinkage	167
4.6.6	Carbonation Resistance.....	169
4.6.7	Chloride Diffusivity	172

CHAPTER 5	CONCLUSIONS AND FUTURE RECOMMENDATIONS .	175
5.1	Overview	175
5.2	The Effect of M-PEG PCE Polymers with Different Main Chain and Side Chain Densities on GGBS-PFA Ternary Blended Cement Paste	175
5.3	The Correlations between Molecular Structure of M-PEG PCE Polymers and Water-Reducing Property on GGBS-PFA Ternary Blended Cement Concrete.....	176
5.4	The Engineering Properties and Durability Performance of GGBS-PFA Ternary Blended Cement Concrete	176
5.5	Research Contributions	177
5.6	Recommendations for Future Research	178
REFERENCES.....		179
LIST OF INTERNATIONAL STANDARDS		197

LIST OF TABLES

	Page
Table 2.1 A summary of reported studies on GGBS-PFA ternary blended cement composites	22
Table 2.2 The previous studies related to PCE polymers main chain structures	44
Table 2.3 The previous studies related to PCE polymers side chain structures	47
Table 2.4 The previous studies related to PCE polymers molecular weights	50
Table 2.5 The previous studies related to supplementary factors of PCE polymers	51
Table 2.6 The previous studies related to cementitious system fluidity with PCE polymers	53
Table 2.7 The previous studies related to workability of cementitious composites with PCE polymers	54
Table 2.8 The previous studies related to setting time of cementitious paste with PCE polymers	56
Table 2.9 The previous studies related to adsorption isotherm of cementitious mixtures with PCE polymers	61
Table 2.10 The previous studies related to adsorption capability of cementitious composites with PCE polymers	63
Table 2.11 The previous studies on the inclusion of PCE polymers into cementitious composites in terms of hydration rate and heat evolution	65
Table 2.12 The previous studies related to the effect of PCE polymers on strength development of cementitious composites	66
Table 2.13 The previous studies related to the effect of PCE polymers on total porosity of cementitious composites	68

Table 2.14	The previous studies related to the effect of PCE polymers on carbonation resistance of cementitious composites	70
Table 2.15	The knowledge gap analysis on the literature studies.....	72
Table 3.1	The chemical compositions of OPC used	80
Table 3.2	The chemical compositions of GGBS used	80
Table 3.3	The chemical compositions of PFA used.....	82
Table 3.4	The design details for M-PEG PCE polymers in 1 litre volume.....	84
Table 3.5	The mix design details of cementitious mortars in 1 m ³ volume.....	86
Table 3.6	The mix design details of GGBS-PFA ternary blended cement concrete for 1 m ³ volume	88
Table 3.7	The mix designs of GGBS-PFA ternary blended cement pastes for 1 ℓ volume of materials	90
Table 3.8	The mix designs of GGBS-PFA ternary blended cement paste for 1 ℓ volume of materials.....	92
Table 3.9	The mix designs of GGBS-PFA ternary blended cement paste for 1 ℓ volume of materials.....	94
Table 3.10	The mix designs of GGBS-PFA ternary blended cement concrete for 1 m ³ volume of materials.....	99
Table 4.1	The significance stretching vibration peak for each PCE polymers	117
Table 4.2	The chemical shift of synthesized PCE polymers via ¹ H NMR.....	122
Table 4.3	The chemical shift of synthesized PCE polymers via ¹³ C NMR	123
Table 4.4	The setting time of GGBS-PFA ternary blended cement paste with synthesized M-PEG PCE polymers	128
Table 4.5	A general descriptions for EDX analysis.....	133
Table 4.6	The elemental compositions of reference GGBS-PFA ternary blended cement paste upon 7 days of curing ages	135
Table 4.7	The elemental compositions of GGBS-PFA ternary blended cement paste with PCE (1:4) upon 7 days of curing ages.....	137

Table 4.8	The elemental compositions of GGBS-PFA ternary blended cement paste with PCE (1:16) upon 7 days of curing ages.....	138
Table 4.9	The elemental compositions of reference GGBS-PFA ternary blended cement paste upon 28 days of curing ages	141
Table 4.10	The elemental compositions of GGBS-PFA ternary blended cement paste with PCE (1:4) upon 28 days of curing ages.....	142
Table 4.11	The elemental compositions of GGBS-PFA ternary blended cement paste with PCE (1:16) upon 28 days of curing ages.....	144
Table 4.12	The elemental compositions of reference GGBS-PFA ternary blended cement paste upon 90 days of curing ages	146
Table 4.13	The elemental compositions of GGBS-PFA ternary blended cement paste with PCE (1:4) upon 90 days of curing ages.....	147
Table 4.14	The elemental compositions of GGBS-PFA ternary blended cement paste with PCE (1:16) upon 90 days of curing ages.....	149
Table 4.15	The final w/b ratio used for GGBS-PFA ternary blended cement concrete mixtures	150
Table 4.16	The velocity of propagation of UPV value and the normalized UPV value to the reference concrete at various ages.....	158
Table 4.17	Concrete Quality Classification based on UPV value.....	159
Table 4.18	The concentration of chloride ion in GGBS-PFA ternary blended cement concrete with a range of penetration depth at various testing ages	173

LIST OF FIGURES

	Page
Figure 2.1 The adsorption amount of NSF and PCE super-plasticizers on the surface of cement grains in function of dosage.....	29
Figure 2.2 The general mechanism of the esterification process	31
Figure 2.3 The mechanism of the esterification process under high temperature.....	32
Figure 2.4 The synthesis of the methoxy terminated M-PEG macromonomer...	33
Figure 2.5 Mechanism of RAFT polymerization	36
Figure 2.6 The chemical structure of the polycarboxylate (PCE) polymer.....	36
Figure 2.7 A model interface among C ₃ S and C-S-H.....	59
Figure 2.8 The adsorption models of chloride ions on cement hydrates surface	71
Figure 3.1 The experimental programme for the research study.....	77
Figure 3.2 SEM image of GGBS at magnification of 3 000 times.....	81
Figure 3.3 The compressive strength of mortars on 7 days and 28 days.....	87
Figure 3.4 The concrete flow and compressive strength of GGBS-PFA ternary blended cement concrete with various curing ages	89
Figure 3.5 The flow time of marsh cone with varied dosage of chemical admixture.....	91
Figure 3.6 The flow time of marsh cone with varied w/b ratio	93
Figure 3.7 The setup for standard consistency test.....	95
Figure 3.8 The water bath and Le Chatelier mould used for soundness test.....	96
Figure 3.9 The concrete spread of mixture during flow table test.....	101
Figure 3.10 The three-point bending testing setup for flexural strength test	102
Figure 3.11 The Leeds permeameter Cell	106

Figure 3.12	The measurement setup for drying shrinkage assessment	110
Figure 3.13	The colour change of tested sample after 3 hours.....	112
Figure 3.14	The marking position of the samples to be cored for each testing ages and the label for the immersion depth on the cored- cylindrical samples.....	113
Figure 3.15	The first permanent red colour solution obtained after testing	114
Figure 3.16	A flow diagram to summarize phase of works and test methods used	115
Figure 4.1	The FTIR spectra for synthesized PCE polymers	117
Figure 4.2	The ^1H NMR spectra for synthesized PCE polymers	119
Figure 4.3	The ^{13}C NMR spectra for synthesized PCE polymers	120
Figure 4.4	The standard consistency of GGBS-PFA ternary blended cement paste with synthesized M-PEG PCE polymers	126
Figure 4.5	The expansion variation of Le Chatelier soundness with varied PCE polymers	129
Figure 4.6	The TGA curve of GGBS-PFA ternary blended cement paste with various PCE polymers.....	131
Figure 4.7	The TGA curve of GGBS-PFA ternary blended cement paste with various PCE polymers.....	132
Figure 4.8	The micrograph of reference GGBS-PFA ternary blended cement paste upon 7 days of curing ages (1 000x magnification).....	134
Figure 4.9	The micrograph of reference GGBS-PFA ternary blended cement paste upon 7 days of curing ages (5 000x magnification).....	135
Figure 4.10	The micrograph of GGBS-PFA ternary blended cement paste with PCE (1:4) upon 7 days of moist curing (1 000x magnification)	136
Figure 4.11	The micrograph of GGBS-PFA ternary blended cement paste with PCE (1:4) upon 7 days of moist curing (5 000x magnification)	136

Figure 4.12	The micrograph of GGBS-PFA ternary blended cement paste with PCE (1:16) upon 7 days of curing ages (1 000x magnification)	137
Figure 4.13	The micrograph of GGBS-PFA ternary blended cement paste with PCE (1:16) upon 7 days of curing ages (5 000x magnification)	138
Figure 4.14	The micrograph of reference GGBS-PFA ternary blended cement paste upon 28 days of curing ages (1 000x magnification).....	140
Figure 4.15	The micrograph of reference GGBS-PFA ternary blended cement paste upon 28 days of curing ages (5 000x magnification).....	140
Figure 4.16	The micrograph of GGBS-PFA ternary blended cement paste with PCE (1:4) upon 28 days of curing ages (1 000x magnification)	141
Figure 4.17	The micrograph of GGBS-PFA ternary blended cement paste with PCE (1:4) upon 28 days of curing ages (5 000x magnification)	142
Figure 4.18	The micrograph of GGBS-PFA ternary blended cement paste with PCE (1:16) upon 28 days of curing ages (1 000x magnification)	143
Figure 4.19	The micrograph of GGBS-PFA ternary blended cement paste with PCE (1:16) upon 28 days of curing ages (5 000x magnification)	143
Figure 4.20	The micrograph of reference GGBS-PFA ternary blended cement paste upon 90 days of curing ages (1 000x magnification).....	145
Figure 4.21	The micrograph of reference GGBS-PFA ternary blended cement paste upon 90 days of curing ages (5 000x magnification).....	145
Figure 4.22	The micrograph of GGBS-PFA ternary blended cement paste with PCE (1:4) upon 90 days of curing ages (1 000x magnification)	146

Figure 4.23	The micrograph of GGBS-PFA ternary blended cement paste with PCE (1:4) upon 90 days of curing ages (5 000x magnification)	147
Figure 4.24	The micrograph of GGBS-PFA ternary blended cement paste with PCE (1:16) upon 90 days of curing ages (1 000x magnification)	148
Figure 4.25	The micrograph of GGBS-PFA ternary blended cement paste with PCE (1:16) upon 90 days of curing ages (5 000x magnification)	148
Figure 4.26	The flexural strength of GGBS-PFA ternary blended cement concrete at various curing ages	154
Figure 4.27	The compressive strength of GGBS-PFA ternary blended cement concrete at various ages	156
Figure 4.28	The water absorption of GGBS-PFA ternary blended cement concrete at various curing ages	160
Figure 4.29	The intrinsic air permeability of GGBS-PFA ternary blended cement concrete at various curing ages.....	162
Figure 4.30	The total porosity of GGBS-PFA ternary blended cement concrete at various curing ages	164
Figure 4.31	The capillary sorptivity of GGBS-PFA ternary blended cement concrete against square root of time duration	166
Figure 4.32	The length change of GGBS-PFA ternary blended cement concrete over exposure duration	168
Figure 4.33	The carbonation depth in GGBS-PFA ternary blended cement concrete at various testing ages.....	170

LIST OF ABBREVIATIONS

C-S-H	Calcium-Silicate Hydrate
EDX	Energy-Dispersive X-ray
FTIR	Fourier Transform Infrared Spectroscopy
GGBS	Ground Granulated Blast Furnace Slag
HLB	Hydrophile-Lipophile Balance
MAA	Methacrylic acid solution
M-PEG	α -methoxy- ω -hydroxy-poly(ethylene glycol)
NMR	Nuclear Magnetic Resonance
OPC	Ordinary Portland Cement
PCE	Polycarboxylate
PCEs	Polycarboxylate super-plasticizer
PEG	Poly(ethylene glycol)
PEO	Polyethylene oxide
PFA	Pulverized Fly Ash
RAFT	Reversible Addition-Fragmentation Chain Transfer
SCM	Supplementary Cementitious Materials
SEM	Scanning Electron Microscope
SNF	Sulfonated Naphthalene Formaldehyde
SP	Super-plasticizers
TGA	Thermogravimetric Analysis
UPV	Ultrasonic Pulse Velocity
w/b	Water-Binder Ratio
XRD	X-ray Powder Diffraction
XRF	X-ray Fluorescence

PENSINTESISAN POLIMER POLIKARBOKSILAT UNTUK DIAPLIKASIKAN KEPADA KONKRIT ADUNAN TERNER

ABSTRAK

Penggunaan campuran simen konkrit dengan sanga terkisar relau-letupan (GGBS) dan abu arang batu (PFA) semakin meningkat dalam pengeluaran konkrit pada hari ini. Walau bagaimanapun, satu isu berkenaan ketidakserasian campuran konkrit ini dengan polimer polikarboksilat (PCE) telah dilaporkan dalam kajian terdahulu. Kejadian ini telah terbukti dengan kesan pemisahan agregat (apabila simen dan agregat mula terpisah) dan pengeluaran lebihan air semasa proses pembuatan konkrit GGBS-PFA dengan polimer PCE. Oleh itu, nisbah polimer polikarboksilat (M-PEG: MAA) diubah untuk mengurangkan kegunaan air dalam campuran konkrit GGBS-PFA ini supaya kesan pemisahan agregat dan pengeluaran lebihan air dapat dikurangkan. Sehubungan ini, kajian ini dijalankan untuk mengkaji hubungan antara ketumpatan rantaian utama (M-PEG) dan rantaian sampingan (MAA) dalam polimer PCE dengan prestasi campuran konkrit ini. Untuk tujuan ini, lima polimer PCE telah disediakan dengan ketumpatan rantaian utama (M-PEG) dan rantaian sampingan (MAA) yang berlainan. Sebelum itu, beberapa parameter campuran konkrit GGBS-PFA ini telah dioptimumkan sebelum pembuatan konkrit dijalankan seperti pengubahan pengikat, nisbah batuan baur kasar dengan batuan baur kecil (CA/FA), sukatan polikarboksilat polimer dan juga pemberian jumlah air (w/b). Campuran konkrit ini telah diuji dari aspek kebolehtkerjaan, kekuatan dan ketahananlasakan sedangkan ciri-ciri campuran terhidrat GGBS-PFA dengan polimer PCE tersebut juga dipastikan pada masa yang sama. Selain itu, ciri-ciri polimer PCE ini juga diuji dengan spektroskopi inframerah transformasi Fourier (FTIR) dan resonans magnetik

nuklear (NMR). Berdasarkan keputusan yang diperolehi, perbezaan kecil telah diperhatikan dalam unit berulang daripada struktur molekul polimer PCE. Kapasiti pengurangan air polimer PCE ini telah dipengaruhi oleh ketumpatan rantaian utama dan rantaian sampingan dalam polimer PCE. Walaupun ciri kecairan campuran simen boleh diperbaiki dengan polimer PCE yang mempunyai ketumpatan rantaian utama yang lebih tinggi, kesan aglomerasi boleh didapati dengan polimer PCE yang mempunyai ketumpatan rantaian utama yang terlalu tinggi. Kesimpulannya, keputusan optimum dari segi kekuatan dan ketahananlaksakan yang dicapai oleh campuran konkrit dengan polimer PCE yang bernisbah 1:8 untuk M-PEG: MAA. Hal ini demikian disebabkan keseimbangan antara daya elektrostatik dan halangan sterik telah dicapai untuk konkrit GGBS-PFA dengan nisbah 5: 4: 1 (OPC: GGBS: PFA).

THE SYNTHESIS OF POLYCARBOXYLATE ETHER POLYMERS FOR USE AS ADDITIVE IN TERNARY BLENDED CONCRETE

ABSTRACT

Ground granulated blast furnace slag–pulverized fly ash (GGBS-PFA) cement concrete is widely used in the contemporary concrete industry. But both GGBS and PFA are incompatible with polycarboxylate (PCE) polymers as reported in previous studies. It can be seen by the segregation effect and bleeding of ternary blended cement concrete containing PCE in its fresh state. As such, the ratio of α -methoxy- ω -hydroxy-poly(ethylene glycol) (M-PEG) to methacrylic acid (MAA) was adjusted to reduce the water demand of the GGBS-PFA ternary blended cement concrete while maintaining favorable segregation and bleeding resistance. This study was conducted to investigate the effect of PCE polymers with varying main chain densities (M-PEG) and side chain densities (MAA) on fresh and hardened of GGBS-PFA ternary blended cementitious composite properties. A total of five PCE polymers were designed and synthesized with various main chain densities (M-PEG) and side chain densities (MAA) for use in concrete fabrication. Before concrete fabrication, the mix design parameters for the concrete fabrication were optimized with respect to binder compositions, ratio of coarse aggregates to fine aggregates (CA/FA), PCE polymers dosage and the designed water-binder (w/b) ratio. The fabricated concrete was tested in terms of workability, strength development and durability performance while the properties of the GGBS-PFA cement paste with the synthesized PCE were accessed. Furthermore, an analysis of PCE polymer characteristics was carried out using Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR). From the results, these PCE

polymers possessed small differences in MAA repeating unit molecular structure. The water reducing capacity of the PCE polymers in GGBS-PFA concrete was mainly influenced by main chain and side chain densities. Although the dispersibility ability of the cementitious mixture was improved by incorporating a PCE polymer with higher main chain density and/or lower side chain density, an agglomeration issue was created by further increase in main chain density. In conclusion, optimum strength and durability performance were obtained by the concrete mixture with M-PEG: MAA ratio of 1:8. This is because equilibrium condition was achieved for the electrostatic force and steric hindrance effect with a ratio of 5: 4: 1 (OPC: GGBS: PFA) for GGBS-PFA ternary blended cement concrete.

CHAPTER 1

INTRODUCTION

1.1 Study Background

In modern concrete technology, chemical admixtures are important concrete mixture components that reduce water content and improve general properties. Most chemical admixtures are categorized using expected functionalities, such as retarder, accelerator, water reducer, super-plasticizer, air entrainer, corrosion inhibitor, shrinkage controller, and water proofing (Özbay *et al.*, 2016). Commonly, chemical admixtures are added to a concrete mix in a quantity no more than 5 % by weight of cement (bwoc) (Wiliński *et al.*, 2016). This is because a high concentration of polymer can form film layers inside the hardening cement paste, with deleterious effects (Liu *et al.*, 2014a; Wiliński *et al.*, 2016). At the same time, the utilization of chemical admixtures in concrete production enables the manufacture of special concretes such as high fluidity concrete, high strength concrete, underwater concrete, and sprayed concrete (Plank *et al.*, 2015).

Super-plasticizer (SP) is added to concrete mixtures to reduce water-cement ratios while achieving a given workability to improve strength and durability (Winnefeld *et al.*, 2007; Zingg *et al.*, 2009; Huang *et al.*, 2016; Kong *et al.*, 2016; Russo *et al.*, 2017). SP creates a repulsion force that disperses flocculated cement grains so that entrapped water can be released (Zhang *et al.*, 2015; Shui *et al.*, 2016). With this, the surface of heterogeneous charged cement grains adsorbs charged super-plasticizer molecules through electrostatic interaction between the cement surface and super-plasticizer (Zhang *et al.*, 2015; Akhlaghi *et al.*, 2017; Yang *et al.*, 2019). However, workability properties of the concretes are significantly influenced by the chemical composition and the molecular structure of a chemical admixture, especially

in terms of yield stress, viscosity and concrete slump (Winnefeld *et al.*, 2007; Kashani *et al.*, 2014).

Polycarboxylate super-plasticizers (PCEs) are a new generation of super-plasticizer polymers. They have been widely used in concrete production due to their superior water reducing rate and good slump retention capability compared to previous generations of water reducers (Shui *et al.*, 2016; Chen *et al.*, 2018). In terms of molecular structural, PCEs have a comb-like copolymer that consists of one main lateral chain composed of anionic groups with grafted long side chains (Norachai and Veera, 2011). The molecular structure of polycarboxylate super-plasticizers can be adjusted by selecting appropriate response monomers to adjust main chain and side chain length, types, and groups proportion to fulfill necessary technical requirements (Gui *et al.*, 2011). Therefore, structure design for PCE polymers has become a popular method of tailoring molecular structures to obtain target materials. This had led to the development of molecular structure diversification (Fiat *et al.*, 2012; Toledano-Prados *et al.*, 2013; Li *et al.*, 2014b).

Nevertheless, concrete production process and formulation must be improved to address global issues and ecological conservation. This is because concrete production is one of the most significant contributors to global energy demand and ecological degradation (Yaphary *et al.*, 2017). This is due to the utilization of Portland cement as the main binder component in concrete production, which has serious environmental effects (Imbabi *et al.*, 2012; Pacheco Torgal *et al.*, 2012; Yang *et al.*, 2015). Indeed, the main issue is related to the production of clinker, which is the main component of Portland cements. Its production releases an amount of carbon dioxide (CO₂) approximately equivalent to the amount of clinker produced. This is worsened by the high amount of energy used during clinker production sintering process

(Marchon *et al.*, 2013; Rashad, 2015). For example, 5 % to 8 % of man-made CO₂ emission are produced by the cement industry with an annual total production of 3.5 billion tonnes worldwide (Suhendro, 2014; Paris *et al.*, 2016; Akhlaghi *et al.*, 2017; Kim *et al.*, 2018; Shubbar *et al.*, 2018; Ustabaş and Kaya, 2018). In addition, modern concrete technology aims towards minimizing cement content in concrete without sacrificing the important engineering properties of hardened concrete (Shi *et al.*, 2015). In such cement, part of the clinker is replaced by Supplementary Cementitious Materials (SCM) with a lower carbon footprint to reduce CO₂ emissions. Common SCMs include Ground Granulated Blast-Furnace Slag (GGBS), Pulverized Fly Ash (PFA), Rice Husk Ash (RHA), and Silica Fumes (SF). Such utilization offers two-fold advantages. First, it provides an avenue for recycling industrial by-product solving waste management problems (Paris *et al.*, 2016; Shubbar *et al.*, 2018; Vishwakarma and Ramachandran, 2018). Second, it reduces the cement content in concrete while maintaining or improving engineering performance of concrete produced. Apart from its environmental impact, the application of the SCM has reduced material cost of concrete production and subsequent reduced construction cost (Samad and Shah, 2017).

There are a number of studies related to the structural design of the PCE polymers in terms of functional group, main chain and also side chain configurations (Winnefeld *et al.*, 2007; Gui *et al.*, 2011; Marchon *et al.*, 2013; Shu *et al.*, 2016). However, most previous studies on concrete mixes only used ordinary Portland cement as a constituent binder. Few studies have been done on the effect of polycarboxylate (PCE) polymers with different main chain and side chain densities on the fresh and hardened properties of ternary blended cement concrete. GGBS-PFA ternary blended cement concrete has been increasingly used for construction and

infrastructure in recent years, making a thorough understanding of this subject matter crucial. Hence, this study investigated the effect of main and side chain densities of PCE polymers on ternary blended cement systems using OPC, GGBS, and PFA.

1.2 Problem Statements

The challenges related to the synthesis of methoxy-poly(ethylene glycol) (M-PEG) PCE polymers for the concrete applications are as follows:

- i. A lower carbon footprint binder system can be developed by utilizing of cement blended systems with Supplementary Cementitious Materials (SCM). However, the effect of PCE polymers on these blended systems has not been well established.
- ii. Previous studies on PCE polymers were carried out on cement paste, in terms of fluidity, workability, setting time, hydrophile-lipophile (HLB) value, zeta potential, adsorption isotherm, adsorption capability, hydration rate and heat evolution. Most previous studies were only conducted on ordinary Portland cement paste. Few studies have been done on the effect of PCE polymer with different main chain and side chain densities on ternary blended cementitious composites.
- iii. Previous studies on the structural design of the PCE polymers were done using functional groups, main chain and side chain structure, and molecular weight. Previous studies have been mostly concerned with the fresh properties of ordinary Portland cement paste, with the mechanical and durability performance of the concrete not being well established.
- iv. Few studies have been done on the application of PCE polymers for mortar and concrete applications, in terms of compressive strength, flexural strength, total porosity, drying shrinkage, carbonation resistance, and chloride binding

properties. Moreover, most of previous studies compared between mixtures with and without PCE polymers while the main and side chain densities of the PCE polymers were not considered in detail.

1.3 Research Objectives

The study developed framework for the influence of M-PEG PCE polymers chain densities on the fresh and hardened properties of GGBS-PFA ternary blended cementitious composites. The objectives of this research work are as follows:

- i. To investigate the effect of M-PEG PCE polymers with different main chain and side chain densities on GGBS-PFA ternary blended cement paste
- ii. To examine correlations between the molecular structure of M-PEG PCE polymers and the water reducing property on GGBS-PFA ternary blended cement concretes
- iii. To study the engineering and durability performance of GGBS-PFA ternary blended cement concrete that incorporated M-PEG PCE polymers with different main chain and side chain densities

1.4 Research Significance

The application of GGBS-PFA ternary blended cement concrete has become widespread in the concrete industry, to reduce carbon footprints and binder phase energy use. Nonetheless, numerous issues have been reported regarding the incompatibility of these materials with conventional PCEs. Some common issues were the segregation and bleeding of GGBS-PFA ternary blended cement concrete, which were seen clearly in the initial mixing stage and fresh concrete compaction into the structural formwork. As such, the time-based uniformity of the produced fresh concrete was seriously impaired with chronic phase separation between paste and

aggregates. This resulted in subsequent hardened concrete serviceability issues, which were largely attributed to plastic shrinkage and surface crack development during hardening. Therefore, this study focused on incorporating synthesized PCEs with different main chain and side chain densities into the GGBS-PFA cement concrete mixtures, which has been scarcely explored by previous researchers.

1.5 Study Scope

This research studies the mechanical and durability performance of GGBS-PFA ternary blended cement concrete with M-PEG PCE polymers. M-PEG PCE polymers with different main and side chain densities were examined. This study covers the characteristics of M-PEG PCE polymers to examine the correlations between PCE polymer molecular structure and the workability of cementitious concrete with GGBS-PFA ternary blended cement system.

This study investigated the effect of main chain and side chain densities of the PCE polymers on the engineering properties and durability performance of GGBS-PFA ternary blended cement concretes. The engineering properties of concrete are composed of flexural strength, compressive strength, and Ultrasonic Pulse Velocity (UPV). Meanwhile, durability performance was investigated using water absorption, intrinsic air permeability, total porosity, capillary sorptivity, drying shrinkage, carbonation resistance, and chloride diffusivity assessment.

This study investigated the setting properties of GGBS-PFA ternary blended cement paste using standard consistency, initial setting time, final setting time, and Le Chatelier soundness. At the same time, thermal decomposition analysis was conducted using Thermogravimetric Analysis (TGA) to determine the hydration process. Meanwhile, an inspection of the morphological and microstructure development of GGBS-PFA ternary blended cement paste with PCE polymers using Scanning

Electron Microscopy (SEM) and Energy-Dispersive X-ray (EDX) techniques was conducted.

The analyses results were used to propose the PCE polymer optimum molecular structures for GGBS-PFA ternary blended cement system. The study scope was as follows:

- i. To optimize the manufacturing parameters, in terms of binder ratio, ratio of coarse aggregate to fine aggregates, water-binder ratio and chemical admixture dosage.
- ii. To assess the characteristic properties of M-PEG PCE polymers.
- iii. To evaluate the properties of GGBS-PFA ternary blended cement paste samples.
- iv. To correlate the molecular structure of M-PEG PCE polymers with the corresponding workability performance of GGBS-PFA ternary cement concrete.
- v. To review the mechanical and durability performance of the GGBS-PFA ternary blended cement concrete with PCE polymers with different main chain and side chain densities.

1.6 Thesis Layout

A total of five chapters are included in this thesis, including introduction, literature review, research methodology, results and discussion and conclusion.

Chapter one introduced the study background. Next, a list of problem statement was enumerated, which was followed by the research objectives. After this, the research significance and scope were clarified.

Previous knowledge related to this study was covered in Chapter 2. This chapter started with a discussion on the background of the current issue as well as a

brief introduction on the adoption of supplementary cementitious materials in concrete technology. In addition, information related to PCE polymers were discussed in this chapter. At the end of this chapter, a critical summary was outlined along with the identified knowledge gap.

Chapter 3 explained the methods used to conduct this research in depth. With this, an experimental program was showed the overall research flow. The testing methods for each test were listed according to the appropriate standards. Meanwhile, the materials used for concrete fabrication were discussed in this chapter. In addition, the manufacturing parameters for concrete were optimized before mix design.

Chapter 4 discusses the obtained results obtained. It was categorized into the characteristics properties of synthesized PCE polymers, the properties of the GGBS-PFA ternary blended cement paste, and the properties of the GGBS-PFA ternary blended cement concrete. The properties of the GGBS-PFA ternary blended cement concrete were separated in terms of rheological, engineering, and durability performance.

An overall conclusion was generated based on the results in the last chapter of the thesis. Moreover, recommendations for further research were provided.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, a critical review summarizes knowledge related to the synthesis and use of PCE polymers for concrete applications. It begins with current issues related to the use of PCE polymers in concrete production, which is followed by an overview of Supplementary Cementitious Material (SCM) use in concrete fabrication. Next, the introduction of super-plasticizers (SP) was drawn up, followed by a review of Polycarboxylate Super-Plasticizer (PCEs) synthesis methods. Then, the function of each PCE chemical structure was analyzed and the working mechanisms of PCEs on cement were discussed. The effect of PCE chemical structure and its effect on cement paste were studied. At last, a critical summary was presented to highlight knowledge gap and anticipated challenges to the future development of PCEs for concrete applications.

2.2 Background of Current Issues

In modern concrete technology, it is a common practice to increase the amount of water during concrete fabrication to maintain concrete liquidity but this generally impairs concrete performance (Bei *et al.*, 2017; Tramaux *et al.*, 2017). Furthermore, a high possibility remains of segregation effects and bleeding issues in the initial mixing stage with high amounts of mixing water (Goes *et al.*, 2016; Moreno-Juez *et al.*, 2018). With this, concrete uniformity can be seriously impaired, resulting in inconsistent strength performance for each batch of the concrete (Goes *et al.*, 2016; Tramaux *et al.*, 2017). In spite of this, a solution was developed through the inclusion of Polycarboxylate Super-Plasticizers (PCEs) as a water reducer in concrete production that maintained a desirable level of fresh mix workability (Shu *et al.*, 2016;

Akhlaghi *et al.*, 2017; Zhang *et al.*, 2017). This implementation of PCE as a concrete admixture not only reduced the water requirements of concrete mixture, but also maintained and/or increasing the strength of hardened concrete (Cheung *et al.*, 2016; Sun *et al.*, 2016; Bei *et al.*, 2017; Tramaux *et al.*, 2017). Moreover, some researchers found that certain PCE polymers formed a higher concrete spread with a lower water-cement ratio, at $0.30 < \kappa < 0.40$ (Chen *et al.*, 2012; Li *et al.*, 2014a; Lange and Plank, 2015; Kong *et al.*, 2016). This was due to different flow characteristics being induced by specific PCEs molecules, whereby the concrete attained a “water-like” consistency without segregation and bleeding (Lange and Plank, 2015).

To addition of most types of PCEs into high-strength concrete formed a fresh mixture with very high yield stress and cohesive consistency (Bei *et al.*, 2017; Huang *et al.*, 2018). As such, the mixture was hard to spread and possessed honey-like flow behaviour (Zingg *et al.*, 2009; Lange and Plank, 2015). This resulted from the extremely high solid volumetric content of the mixture. This kind of concrete mixture may still show a high final spread value but it may take a much longer time to reach final spread compared to a corresponding mix with lower yield stress (Lange and Plank, 2015; Antoni *et al.*, 2017). Hence, the produced concrete requires a longer time to be discharged from the concrete bin and to be fully spread into every corner of a formwork (Lange and Plank, 2015). Therefore, the concrete placement process was slowed down by concrete creeping behaviors. The poor flowability of the fresh concrete mix may result in a large region of the formwork being insufficiently filled with concrete during compaction (Li *et al.*, 2014b; Shu *et al.*, 2016).

From practical engineering aspect, another outcome was proved that retarders such as sodium citrate and sucrose in a concrete mixture reduced the water-cement ratio necessary to achieving a given workability (Goes *et al.*, 2016). They mainly

worked to offset the accelerating effects of hot weather on setting times or to retard concrete settings when an abnormal placement conditions occurred (Khudhair *et al.*, 2018). As usual, the inclusion of these retarders improved on strength and durability aspects (Plank *et al.*, 2015; Sun *et al.*, 2016). Nonetheless, another obstacle was observed in slump loss, which impaired the operational performance of the water-reducing agent (Zingg *et al.*, 2009; Goes *et al.*, 2016). This problem can be seen clearly in very hot weather and/or during the long-time and long-distance transportation of fresh concrete (Goes *et al.*, 2016; Khudhair *et al.*, 2018), both of which create rapid water evaporation from the surface of the cementitious mixture, causing large differences in existing concrete raw materials (Cheung *et al.*, 2016). The initial slump level should be kept as high as possible to avoid re-dosing unnecessary water during concrete placement at construction sites (Felekoglu and Sarikahya, 2008). Therefore, some researchers have begun to study slow-release PCEs to overcome the slump loss issue since the molecular structure of PCEs can be easily designed and modified through optimal combinations of different functional monomer units (Lv *et al.*, 2014; Goes *et al.*, 2016; Qian *et al.*, 2018).

The current issue was generally points to the raw materials used in concrete production. Generally, concrete is predominantly utilized in the construction industry, making growing demands for cement and the main limitation for concrete production, especially in developing countries (Imbabi *et al.*, 2012; Gartner and Hirao, 2015; Vishwakarma and Ramachandran, 2018). The demand for housing and concrete is forecasted to grow to approximately 18 billion tons annually by 2050 (Imbabi *et al.*, 2012) as the world population is estimated to increase from 1.5 to 9.0 billion (Imbabi *et al.*, 2012; Shubbar *et al.*, 2018). The worldwide cement production figure was 3.6 billion tons in 2011 (Imbabi *et al.*, 2012; Marchon *et al.*, 2013; Juenger and Siddique,

2015; Rashad, 2015). This number is forecasted to exceed 5.8 billion tons by 2050 (Juenger and Siddique, 2015; Rashad, 2015; Sun *et al.*, 2016; Shubbar *et al.*, 2018). This creates an environmental issue in that since the late 1990's (Yang *et al.*, 2015) cement production has involved serious environment impacts such as acid rain, greenhouse gas emissions, environmental pollution from dust, and enormous energy consumption from calcination temperatures over 1300 °C (Duan *et al.*, 2013; Rashad, 2015; Yang *et al.*, 2015; Samad and Shah, 2017; Ganesh and Murthy, 2019). Moreover, a few researchers have mentioned that cement production emits as much as 5 % - 8 % of CO₂ emissions around the world (Pacheco Torgal *et al.*, 2012; Kandasamy and Shehata, 2014; Gartner and Hirao, 2015; Yang *et al.*, 2015; Zhao *et al.*, 2015a; Morandea *et al.*, 2015; Paris *et al.*, 2016; Aprianti S, 2017; Samad and Shah, 2017; Golewski, 2018; Shubbar *et al.*, 2018). Therefore, a challenge was given to the cement industry over the past 10 years to effectively reduce and control CO₂ emission (Imbabi *et al.*, 2012; Yang *et al.*, 2015; Shubbar *et al.*, 2018; Ganesh and Murthy, 2019). For now, the utilization of Supplementary Cementitious Materials (SCM) in concrete production is a way to reduce environmental pollution while meeting rising demand (Gartner and Hirao, 2015; Part *et al.*, 2015; Hossain *et al.*, 2016; Aprianti S, 2017; Vishwakarma and Ramachandran, 2018; Ganesh and Murthy, 2019)

2.3 Supplementary Cementitious Materials (SCM) for Concrete Applications

To minimize CO₂ emissions from the cement industry, four alternative technologies have been introduced (Imbabi *et al.*, 2012; Gartner and Hirao, 2015; Yang *et al.*, 2015):

- i. Changes in fuels to alternatives with a lower carbon content, such as from coal to natural gas for the limestone calcination process.

- ii. Adding a chemical adsorption process that captures the CO₂ released from cement production kilns.
- iii. Changing the clinker manufacturing process to use efficient grinding techniques and to convert from a wet to dry grinding process
- iv. Adding high volumes of Supplementary Cementitious Materials (SCM) such as Ground Granulated Blast Furnace Slag (GGBS), Pulverized Fly Ash (PFA), and Silica Fume (SF)

Of all these technologies, the utilization of blended cement system containing SCM was established as the most practical and economical method. Furthermore, it was verified to have a lower carbon footprint binder system than conventional Portland cement (Gartner and Hirao, 2015; Cheah *et al.*, 2016; Mo *et al.*, 2017; Ganesh and Murthy, 2019). This approach caused an 22 % approximate reduction greenhouse gases (Yang *et al.*, 2015). At the same time, it contains an avenue for recycling SCM (Paris *et al.*, 2016). This is important for solving waste management problems related to material disposal (Rashad, 2015; Lu *et al.*, 2018; Ganesh and Murthy, 2019), which contributes to environmental protection by saving energy (Lothenbach *et al.*, 2011; Gartner and Hirao, 2015; Samad and Shah, 2017) and conserving natural resources (Yang *et al.*, 2015; Paris *et al.*, 2016; Aprianti S, 2017). Besides, the cost of construction materials can be indirectly reduced (Juenger and Siddique, 2015; Paris *et al.*, 2016; Samad and Shah, 2017; Kim *et al.*, 2018; Shubbar *et al.*, 2018). Nevertheless, there are a series of limitations that need to be solved for effective SCM used in concrete production. For example, a lower calcium hydroxide crystal (Ca(OH)₂) forms in SCM concrete mixtures, creating a more carbonation issues than concrete with only OPC (Ashraf, 2016; Mo *et al.*, 2017; Shah and Bishnoi,

2018) and compatibility issue with the water reducing chemicals used in concrete production (Burgos-Montes *et al.*, 2012; Li *et al.*, 2014b; Smirnova, 2016).

The utilization of SCM generally enhances concrete properties and performance through a filler effect and pozzolanic reaction (Benachour *et al.*, 2008; Megat Johari *et al.*, 2011; Mo *et al.*, 2017; Xu *et al.*, 2017). At the same time, greater cohesiveness is achieved from the use of fine mineral admixture particles to enhance grain size distribution and particle packing (Lothenbach *et al.*, 2011; Dadsetan and Bai, 2017; Samad and Shah, 2017; Shubbar *et al.*, 2018). SCM alters pore structures to lower concrete permeability, (Lothenbach *et al.*, 2011; Imbabi *et al.*, 2012; Borosnyói, 2016) improving its resistance against reinforcement corrosion (Imbabi *et al.*, 2012; Qian *et al.*, 2014; Paris *et al.*, 2016), acid attacks (Gruyaert *et al.*, 2012; Hossain *et al.*, 2016; Pu and Unluer, 2018) and sulphate attacks (Kandasamy and Shehata, 2014; Qian *et al.*, 2014; Juenger and Siddique, 2015; Paris *et al.*, 2016). Besides, dependence on SP can be reduced through the use of these materials while improving concrete fluidity (Uysal *et al.*, 2012; Mo *et al.*, 2017). Moreover, the fabrication of high-strength concrete and Self-Compacting Concrete (SCC) becomes easier with the adoption of SCM in blended cement systems (Dadsetan and Bai, 2017; Kim *et al.*, 2018).

Theoretically, the production of high strength and high performance concrete become easier when mineral admixtures, such as SF, GGBS and fly ash are used. Most of them have a smaller or the same size particles as Portland cement and they exhibit pozzolanic behavior after the primary hydration reaction (Megat Johari *et al.*, 2011; Ashraf, 2016; Borosnyói, 2016; Dadsetan and Bai, 2017; Xu *et al.*, 2017). The mineral admixtures normally used as filler fill voids by adsorbing water at filler particle surfaces (Lothenbach *et al.*, 2011; Megat Johari *et al.*, 2011; Lollini *et al.*,

2016; Dadsetan and Bai, 2017; Hu *et al.*, 2017), providing greater thickness to the water layer around particles, which improves flow properties and workability by reducing viscosity (Benachour *et al.*, 2008). This situation can be explained by the amount of free water being decreased in cement-based filler-added materials without the adoption of super-plasticizer, with most of the water being adsorbed on filler particle surfaces or entrapped inside particles flocks (Benachour *et al.*, 2008; Ma *et al.*, 2018). Therefore, the utilization of these mineral admixtures provides better engineering and performance properties.

There is a marked difference in the properties of both fresh and hardened concrete with different types of SCM. This is because they exhibited different particle characteristics with different chemical and mineralogical compositions. Thus, their water requirements, packing ability, and reactivity may vary from one type to another when blended with cement. For instance, the use of fly ash enhances concrete workability, but the early strength of concrete is reduced (Megat Johari *et al.*, 2011; Tkaczewska, 2014; Rashad, 2015). An increase in early-age strength can be compensated for through the inclusion of silica fumes (Aprianti S, 2017; Samad and Shah, 2017). However, fly ash retards the setting time of high-strength concretes with similar water-binder (w/b) ratios and constant SP dose (Megat Johari *et al.*, 2011; Zhao *et al.*, 2015a; Rashad, 2015; Ustabaş and Kaya, 2018). Moreover, chloride ion penetration was decreased with the use of GGBS or PFA (Rashad, 2015; Lollini *et al.*, 2016; Kim *et al.*, 2018; Pu and Unluer, 2018; Ganesh and Murthy, 2019) and increased with the addition of silica fume or limestone (Lollini *et al.*, 2016; Feng *et al.*, 2018b).

2.3.1 Ground Granulated Blast Furnace Slag (GGBS)

GGBS is a by-product of the iron smelting industry. It is the slag left-over on the top layer when pig iron is extracted from melted raw iron ore by coke and limestone at about $1\,350\text{ }^{\circ}\text{C} - 1\,550\text{ }^{\circ}\text{C}$. This molten iron slag is quickly quenched with water to form calcium-magnesium aluminosilicate granules, which is a glassy-sand like material that is known as granulated slag. The granulated slag is further grounded into a fine powder called Ground Granulated Blast Furnace Slag (GGBS) (Imbabi *et al.*, 2012; Cheah *et al.*, 2016; Samad and Shah, 2017). GGBS is a powder with an off-white colour and a bulk density of $1\,200\text{ kg/m}^3$ (Samad and Shah, 2017). The specific gravity of GGBS is $2.85 - 2.95$ (Zhao *et al.*, 2015b; Ouattara *et al.*, 2018) while the specific surface area is $400 - 600\text{ m}^2/\text{kg}$ (Kar *et al.*, 2012; Mo *et al.*, 2017).

GGBS generally contains calcium oxide (CaO) ($30 - 42\%$), silicone dioxide (SiO_2) ($35 - 38\%$), aluminium oxide (Al_2O_3) ($10 - 18\%$) and magnesium oxide (MgO) ($5 - 14\%$) (Megat Johari *et al.*, 2011; Samad and Shah, 2017). It is considered a latent hydraulic material (Kar *et al.*, 2012; Özbay *et al.*, 2016; Mo *et al.*, 2017) because GGBS develops a strong cementitious property when it comes into contact with alkali such as lime or Portland cement, which creates cementitious behaviour (latent hydraulic activity) and a certain pozzolanic characteristics (reaction with portlandite) (Özbay *et al.*, 2016). In fact, the formation of calcium-silicate-hydrate (C-S-H) gels is promoted with higher calcium and silica content (Ganesh and Murthy, 2019). Recently, GGBS was applied in the production of large quantities of site batched concrete for ready-mix concrete and also in manufacturing production products for precast concrete (Cheah *et al.*, 2017; Samad and Shah, 2017). Owing to its wide availability, it has become a common mineral addition for the replacement of clinkers in blended cement systems.

A lower hydration heat was provided through the use of GGBS in cement replacement, which indirectly contributes to environmental protection by minimizing cement content during concrete production (Yang *et al.*, 2015; Samad and Shah, 2017; Wu *et al.*, 2017; Ganesh and Murthy, 2019). When compared to conventional Portland cement concrete, concrete workability was improved with the use of GGBS cement replacement levels up to 40 % (Wu *et al.*, 2017; Ganesh and Murthy, 2019). Concrete with GGBS has a larger paste volume since GGBS has a lower specific gravity than OPC, improving segregation resistance and workability (Dadsetan and Bai, 2017; Ganesh and Murthy, 2019). However, the reduction of OPC decreased the tri-calcium aluminate (C_3A) content in the mixture (Jeong *et al.*, 2015). Hence, the setting time of GGBS-OPC concrete was prolonged with increased levels of GGBS (Zhao *et al.*, 2015a; Özbay *et al.*, 2016; Dave *et al.*, 2017; Samad and Shah, 2017).

The early strength of concrete with GGBS was lower than conventional Portland cement concrete due to the dilution effect and the slow reactivity of GGBS, but this can be improved with higher curing temperatures (Xu *et al.*, 2017; Ganesh and Murthy, 2019). Although the strength gain for GGBS-OPC concrete is slower than conventional OPC concrete, a slightly higher compressive strength can be achieved for long-term assessments (Liew *et al.*, 2017; Vollpracht *et al.*, 2018), where the pozzolanic reaction forms more C-S-H gels and portlandite during cement hydration (Ganesh and Murthy, 2019). Cheah *et al.* (2016) reported that the development of compressive strength can be accelerated by incorporating GGBS with greater fineness as this exposes a larger amorphous particles reactive surface (Cheah *et al.*, 2016; Ustabaş and Kaya, 2018).

In microstructures, the filling abilities of vacant pores was improved through the incorporation of GGBS into cementitious paste (Duan *et al.*, 2013; Hossain *et al.*,

2016; Pu and Unluer, 2018; Ganesh and Murthy, 2019). Meanwhile, capillary pore volume was reduced, causing capillary pore discontinuity to retard the water adsorption coefficient during the cement hydration process (Ganesh and Murthy, 2019). As such, the durability properties of cementitious concrete can be improved in terms of permeability, water absorption coefficient, resistance to chloride penetration, and sulphate attack (Dadsetan and Bai, 2017; Liew *et al.*, 2017; Samad and Shah, 2017; Pu and Unluer, 2018; Ganesh and Murthy, 2019).

2.3.2 Pulverized Fly Ash (PFA)

Pulverized fly ash (PFA) is a fine waste residue or the by-product collected from the combustion process of pulverized coal in thermal power plants (Imbabi *et al.*, 2012; Uysal *et al.*, 2012; Tkaczewska, 2014; Rashad, 2015; Samad and Shah, 2017; Lu *et al.*, 2018). Fine particulate residues are removed from combustion gases by dust collection systems before being discharged into the atmosphere and then recovered as fine particle fly ash (Tkaczewska, 2014; Zhao *et al.*, 2015a; Rashad, 2015; Samad and Shah, 2017; Ustabaş and Kaya, 2018; Ganesh and Murthy, 2019). PFA particles normally have a solid sphere shape (Rashad, 2015; Ramezaniapour *et al.*, 2016; Dadsetan and Bai, 2017) and a size from $< 1 \mu\text{m}$ to more than $100 \mu\text{m}$, with typical particle sizes measuring less than $20 \mu\text{m}$. Its surface area generally range between $300 - 500 \text{ m}^2/\text{kg}$ (Rashad, 2015; Mo *et al.*, 2017), but some particles can have a surface area as low as $200 \text{ m}^2/\text{kg}$ and as high as $700 \text{ m}^2/\text{kg}$ (Karahan and Atiş, 2011; Rashad, 2015; Mo *et al.*, 2017). The mass per unit volume can vary from 540 to 860 kg/m^3 , including air between particles and can reached 1 120 to $1\,500 \text{ kg/m}^3$ with regard to closed packed storage or vibration (Rashad, 2015). The specific gravity relative density of PFA stays between 1.9 to 2.8 (Karahan and Atiş, 2011; Rashad, 2015; Sonebi *et al.*, 2015; Mo *et al.*, 2017).

It is a beneficial to make use of PFA to generate cost-effective and green concrete structures, given that PFA mainly prevents toxic chemicals from contaminating natural resources (Pu and Unluer, 2018; Vishwakarma and Ramachandran, 2018). The effect of greenhouse gas emissions was minimized as CO₂ emissions were reduced (Paris *et al.*, 2016; Samad and Shah, 2017). At the same time, it has similar characteristics to pozzolanic materials in terms of silica (SiO₂) and alumina (Al₂O₃) (Rashad, 2015; Aprianti S, 2017). Therefore, it has been widely used in blended cement for concrete applications to reduce the heat hydration (Karahan and Atiş, 2011; Samad and Shah, 2017).

PFA is commonly added to concrete mixtures either as a binder replacement or additive to react to the Ca(OH)₂ produced by cement, to form a stronger and more durable compound (Vishwakarma and Ramachandran, 2018). Besides, concrete workability is increased due to its spherical shape, which reduces w/b ratio when compared to the normal cement concrete, while minimizing the bleeding effect and segregation issue (Uysal *et al.*, 2012; Dadsetan and Bai, 2017; Samad and Shah, 2017; Wu *et al.*, 2017; Vishwakarma and Ramachandran, 2018). It has also been reported that an optimum cement replacement by fly ash provides better slump flow due to PFAs particle shape, particle packing effect, particle size distribution, and smooth surface texture (Uysal *et al.*, 2012; Toledano-Prados *et al.*, 2013; Dadsetan and Bai, 2017). A 'ball-bearing effect' was attributed for the reduction in friction between the aggregate-paste interfaces at the point of contact on its spherical shape, which enhanced mixture plasticity and cohesiveness (Toledano-Prados *et al.*, 2013; Dadsetan and Bai, 2017; Mo *et al.*, 2017). Moreover, when C-S-H gels produced by the Ca(OH)₂ reacts with the SiO₂, Al₂O₃, iron (III) oxide (Fe₂O₃) in the fly ash during cement hydration, the fly ash acts as a good filler, which increases compressive

strength and bulk density while reducing alkali-aggregate reactions and corrosion (Liew *et al.*, 2017; Samad and Shah, 2017; Pu and Unluer, 2018; Vishwakarma and Ramachandran, 2018). At the same time, the drying shrinkage effect can be minimized and resistances to sulphate and acid attacks can be enhanced through lower permeability factors and reductions in total porosity (Hossain *et al.*, 2016; Liew *et al.*, 2017; Pu and Unluer, 2018; Vishwakarma and Ramachandran, 2018).

Although the early strength development for PFA concrete is slower due to its slower hydration reaction (Tkaczewska, 2014; Hu *et al.*, 2017; Samad and Shah, 2017), a better long-term strength development occurred due to the pozzolanic activity from fly ash employment (Karahan and Atiş, 2011; Zhao *et al.*, 2015b; Hossain *et al.*, 2016; Hsu *et al.*, 2018). Strength development is dependent on hydroxide ion (OH^-) acting as an activator for concrete with high fly ash replacements (Marchon *et al.*, 2013). However, a finer PFA particle increased concrete density by filling voids, although pozzolanic reaction was not affected (Hsu *et al.*, 2018). As well, it reduces capillary pores to improve the water absorption coefficient and total porosity (Hsu *et al.*, 2018; Yu *et al.*, 2018).

In addition, it has been reported that water requirements and setting time increases when fly ash content increases within the binder (Karahan and Atiş, 2011; Toledano-Prados *et al.*, 2013; Dave *et al.*, 2017; Liew *et al.*, 2017; Ustabaş and Kaya, 2018). Thus, it is not recommended for normal construction due to the delay in hydration process (Lothenbach *et al.*, 2011; Liew *et al.*, 2017). Furthermore, Liew *et al.* (2017) mentioned it is hard to use in cold weather since it has low resistance to deicer-salt scaling carbonation (Liew *et al.*, 2017).

2.4 GGBS-PFA Ternary Blended Cement Concrete

GGBS-PFA cement concrete is commonly applied in construction nowadays, due to its costing considerations and environment degradation related to OPC production and disposal of GGBS and PFA. This concrete product can be observed in the construction of the Gwang-Ahn grand road and bridge in Busan, Korea (Jeong *et al.*, 2015).

In Jeong *et al.* (2015), the performance of OPC concrete was compared with GGBS-PFA ternary blended cement concrete. The results showed that a binder ratio of 4:4:2 and 3:5:2 (OPC-GGBS-PFA) reached up to 95 % of the compressive strength of OPC for a curing age of 90 days (Jeong *et al.*, 2015). Kuder *et al.* (2012) showed that a ratio of 40: 45: 15, 20: 60: 20, 40: 30: 30 and 20: 20: 60 (OPC-GGBS-PFA) gave a higher compressive strength than 100 % cement concrete for late curing ages (Kuder *et al.*, 2012). Nevertheless, most of them showed an approximately 50 % gain in compressive strength with 28 days of curing due to the slow hydration process of GGBS and PFA (Kuder *et al.*, 2012; Jeong *et al.*, 2015; Cheah *et al.*, 2016). Elastic modulus and splitting tensile strength tests gave a similar trend as compressive strength (Kuder *et al.*, 2012; Jeong *et al.*, 2015; Cheah *et al.*, 2016). For this, it was suggested that the higher fineness of GGBS and PFA improved the early-age strength development (Cheah *et al.*, 2016; Hu *et al.*, 2017) as the alkalinity environment of PFA enhanced the formation of C-S-H gels from the dissolution of GBS glassy phases (Shubbar *et al.*, 2018).

For durability performance, sulphate resistance can be enhanced from the use of an optimum cement replacement level for GGBS and PFA when compared to Portland cement concrete (Kandasamy and Shehata, 2014). This is due to the formation rate of ettringite being delayed due to low Ca(OH)_2 and C_3A content. Apart from that, a similar result was obtained for the autogenous shrinkage test (Hu *et al.*,

2017), drying shrinkage test (Kuder *et al.*, 2012; Jeong *et al.*, 2015), and adiabatic temperature rise (Jeong *et al.*, 2015). Apart from this, several studies have concluded that permeability and chloride resistance can be enhanced by the inclusion of GGBS and PFA into blended cement systems (Lollini *et al.*, 2016; Pu and Unluer, 2018; Shubbar *et al.*, 2018). This is mainly due to the well-known refinement of pore structure and densification in concrete microstructure.

Yang *et al.* (2015) mentioned that this GGBS-PFA ternary blended cement system had a lower carbon dioxide intensity of 12 % when concrete compressive strength reached 30 MPa. The intensity of CO₂ can be heightened nearly 48 % for concrete compressive strength of up to 100 MPa (Yang *et al.*, 2015). Table 2.1 presents some recent investigations on GGBS-PFA ternary blended cement composites.

Table 2.1 A summary of reported studies on GGBS-PFA ternary blended cement composites

References	Mix Design			Compressive Strength (MPa)			Flow (mm)
	Binder ratio (OPC: GGBS: PFA)	w/b ratio	SP dosage (%)	7 days	28 days	≥ 90 days	
Kuder <i>et al.</i> (2012)	100: 0: 0	0.40	0.40	51.9	67.3	74.3	700 ± 40 (SCC)
	40: 45: 15			30.9	54.2	75.3	
	20: 60: 20			30.5	63.0	76.8	
	10: 68: 22			25.8	47.2	68.6	
	40: 30: 30			34.0	56.0	84.5	
	20: 40: 40			20.6	41.4	74.1	
	10: 45: 45			11.5	33.0	60.3	
	40: 15: 45			25.4	49.0	68.3	
	20: 20: 60			14.3	28.0	76.8	
	10: 23: 68			11.3	32.0	61.9	
Jeong <i>et al.</i> (2015)	100: 0: 0	0.45	1.4	--	(100 %)	(100 %)	190
	40: 40: 20		0.8		(74 %)	(93 %)	190
	30: 50: 20		0.6		(69 %)	(95 %)	180

(Concrete)

Table 2.1 (continued) A summary of reported studies on GGBS-PFA ternary blended cement composites

References	Mix Design			Compressive Strength (MPa)			Flow (mm)
	Binder ratio (OPC: GGBS: PFA)	w/b ratio	SP dosage (%)	7 days	28 days	≥ 90 days	
Cheah <i>et al.</i> (2016)	100: 0: 0	---	---	34.21	35.70	35.95	145 ± 5 (Mortar)
	90: 8: 2			35.40	38.59	40.23	
	80: 16: 4			36.93	38.73	42.42	
	70: 24: 6			37.10	39.74	41.81	
	60: 32: 8			40.64	42.82	46.91	
	50: 40: 10			36.98	44.34	44.22	
	40: 48: 12			32.64	41.71	41.94	
	30: 56: 14			31.97	36.05	39.49	
	20: 64: 16			29.30	34.76	36.40	
	10: 72: 18			19.09	22.10	24.77	
	0: 80: 20			23.68	34.20	37.85	
Ma <i>et al.</i> (2018)	100: 0: 0	0.25	0.018	--	65.3	--	-- (Concrete)
	80: 10: 10				71.3		
	70: 15: 15				72.5		
	60: 20: 20				69.1		
	50: 25: 25				67.6		
	100: 0: 0	0.30	0.012	--	63.0	--	
	80: 10: 10				68.3		
	70: 15: 15				66.3		
	60: 20: 20				65.4		
	50: 25: 25				61.4		
	100: 0: 0	0.35	0.008	--	59.4	--	
	80: 10: 10				66.3		
	70: 15: 15				62.1		
	60: 20: 20				61.3		
	50: 25: 25				60.9		
	100: 0: 0	0.40	0.007	--	55.5	--	
	80: 10: 10				63.4		
	70: 15: 15				61.6		
	60: 20: 20				58.6		
	50: 25: 25				57.3		
Shubbar <i>et al.</i> (2018)	100: 0: 0	0.40	--	27	29	-- (Mortar)	
	50: 50: 10	0.40		22	33		
	42.5: 42.5: 15	0.40		21	30		
	40: 40: 20	0.40		18	28		
	37.5: 37.5: 25	0.45		17	27		
	35: 35: 30	0.50		18	27		
	32.5: 32.5: 35	0.55		15	23		
	30: 30: 40	0.55		13	21		
	27.5: 27.5: 45	0.55		11	19		
	25: 25: 50	0.55		9	15		

2.5 Introduction of Super-Plasticizers (SP)

Super-plasticizer (SP) is commonly applied in the concrete production industry due to its unique ability to improve the rheological properties of cement paste, mortars, and concrete (Norachai and Veera, 2011; Li *et al.*, 2014c; Khudhair *et al.*, 2018) by dispersing agglomerated hydrating cement particles (Boukendakdji *et al.*, 2012; Liu *et al.*, 2014b; Liu *et al.*, 2015). It is also a high-range water reducer because it can enhance the strength of concrete with either low cement content or low water-cement ratios. The addition of SP into cementitious mixtures improves mixture flowability (Norachai and Veera, 2011) while increasing bleeding and segregation effects past the optimum dosage (Antoni *et al.*, 2017).

SP promotes cement hydration and induces cement hydrate product crystallization when added to cement paste as a substituted mineral (Tkaczewska, 2014; Feng *et al.*, 2018a). This results from a reduction in cement paste water demand and an increase in the cement paste fluidity and mortar and/or concrete workability. At the same time, the mechanical properties of mortar and concrete were directly enhanced (Norachai and Veera, 2011; Boukendakdji *et al.*, 2012) by the dispersion effect on flocculated cement grains. With SP in a mixture, a charge repulsion force is created among cement particles that releases entrapped water, as proven by Derjaguin, Landau, Verwey, and Overbeek's (DLVO) theory and steric theory (Shu *et al.*, 2016; Shui *et al.*, 2016). However, cement paste fluidity was reduced with increased water demand when SP content exceed a certain reasonable value (Lv *et al.*, 2014; Antoni *et al.*, 2017; Feng *et al.*, 2018a).

When SP was added in the concrete mixture, SP molecules hindered water and calcium ion (Ca^{2+}) diffusion across the solution-cement interface due to their convergence on the cement surface (Zhang and Kong, 2015), decelerating the cement hydration rate and prolonging the hydration induction period (Tkaczewska, 2014;