PARTICLE SIZE EFFECT OF ACACIA MODESTA GUM POWDER ON THE PROPERTIES OF SELF-COMPACTING PASTE SYSTEMS

MS STRUCTURES DISSERTATION

BY

MUHAMMAD WAQAS MALIK
MS-Structures 2015
00000118413

MS THESIS ADVISOR

Prof. Dr. Syed Ali Rizwan

NUST Institute of Civil Engineering (NICE)
School of Civil & Environmental Engineering (SCEE)
National University of Sciences and Technology (NUST), Islamabad, Pakistan

July, 2017

THESIS ACCEPTANCE CERTIFICATE

Certified that final copy of MS thesis written by Mr. Muhammad Waqas Malik, Registration No. 00000118413, of MS Structural Engineering 2015 Batch (NICE), has been vetted by undersigned, found completed in all respects as per NUST Statutes/Regulations, is free of plagiarism, errors, and mistakes and is accepted as partial fulfillment for award of MS degree. It is further certified that necessary amendments as pointed out by GEC members of the scholar have been incorporated in the said thesis.

Signature:______________________________

Name of Supervisor: Dr. Syed Ali Rizwan

Date: ________________________________

Signature: ______________________________

Head of Department: Dr. Syed Hassan Farooq

Date: ________________________________

Signature: ______________________________

Dean: Dr. Syed Muhammad Jamil

Date: ________________________________

Dedication

I dedicate this Research to

Prof. Dr. Syed Ali Rizwan, my mentor

And

To my parents

ACKNOWLEDGEMENTS

I am thankful to Allah Almighty, The Most Gracious and The Most Bountiful, who gave me the strength to complete this dissertation. After that, I would like to express sincere gratitude to my mentor and advisor Prof. Dr. Syed Ali Rizwan for his continuous support, guidance and valuable discussions on the topic throughout the research phase. His doors were always remains open for me and he guided me towards the right path whenever I stuck at any phase of the research.

I am thankful to Prof. Dr. Ibrahim Qazi, HOD, Materials Science, Institute of Space Technology (IST) Islamabad for his corporation in the PSD and SEM test. I am also indebted to all the faculty members of NUST Institute of Civil Engineering (NICE) for their knowledgeable suggestions.

My profound thanks are due to my class fellows and Structures lab staff for their help and co-operation in the experimental lab work. Thanks are also due to my senior, Miss Neha Mahmood who always responded positively whenever I called her for the help.

Last but not the least; I would also like to thank my parents as this research work would not have been completed without their constant support and prayers.

ABSTRACT

Particle size of powdered Acacia Modesta (AM) gum affects the fresh and hardened properties of self-compacting paste (SCP) systems and this aspect has not been researched so far. This study focuses on the effect of particle size of botanical Acacia Modesta (AM) gum powder incorporated in self-compacting paste systems (SCPs). Powdered Acacia Modesta gum with an average particle size (D50) of 307 microns, 135 microns and 47.5 microns were used with variable Acacia Modesta (AM) gum dosages in the range of 0.25% to 1% by weight of the dry cement. The results show that with the decrease in the average particle size of AM gum powder, the water demand, viscosity, yield stress, Vicat setting times, water absorption capacity, air content and maximum shrinkage values of SCPs were reduced while super-plasticizer (SP) demand, compressive strength, fresh and harden cement paste densities got increased. Scanning Electron Microscopy (SEM) technique has been used for microstructural studies which complement the findings of the experimental work.

The effect of both air and water curing has been studied and results shows about 12% and 13% improvement in compressive strength for average particle size of 47.5 microns for air cured and water cured samples respectively as compare to OPC. While in comparison to average particle size of 307 microns, this improvement goes up to 20% and 25 % for air cured and water cured samples respectively. Improvement in compressive strength at smaller sizes was due to improvement in fresh paste and hardens densities of SCPs containing smaller sizes of AM gum particles. It was also observed that retardation effect of AM gum powder in SCPs is independent of average particle size of AM gum at constant w/c ratio of 27%. About 25% maximum shrinkage of SCPs got reduced by with average particle size of 47.5 microns of AM gum powder as compare to OPC. This can be either due to internal curing property of AM gum powder or due to higher ettringite growth at smaller sizes of AM gum powder.

TABLE OF CONTENTS

THESIS ACCEPTANCE CERTIFICATE……………..……............................. i

DEDICATION……………………………………………………………………. ii

ACKNOWLEDGEMENTS……………………………………………………... iii

ABSTRACT……………………………………………………………………… Iv

TABLE OF CONTENTS……………………………………………………... v

LIST OF FIGURES…………………………..…………………………….. viii

LIST OF TABLES…………………………..………………………….. X

LIST OF NOTATIONS/ABBREVIATIONS…………………………………….. xi

CHAPTER 1 – INTRODUCTION

1.1 Problem Statement………………………………………………………….. 1

1.2 Research Objectives……………………………………….……………... 2

1.3 Research Significance……………………………………….…………... 2

1.4 Research Methodology……………………………...…………………………… 2

1.5 Research Scope...……………………………………………….……………….. 3

1.6 Thesis Organization………………………………………………………………… 3

CHAPTER 2 - LITERATURE REVIEW

2.1 Introduction ………………………………………………………………………… 4

2.2 Self-Compacting Cementitious Systems (SCCS)……………….………………….. 4

2.3 Advantages of Self-Compacting Cementitious Systems ……….….………………. 5

2.4 Self-Compacting Paste Systems…………………………………………………….. 5

2.5 Acacia Modesta (AM) gum as admixture in SCPs…………………………………. 5

2.6 Composition of Acacia Modesta Gum Powder…………………………………..…. 6

2.7 Nuclear Magnetic Resonance (NMR)……………………………………..………… 6

2.8 Fourier Transform Infrared Spectroscopy (FTIR)………………………………... 7

2.9 Internal Curing – A specialty of AM gum powder...……………………………….. 7

2.10 Particle Size effect of AM Gum Powder – A novel idea…………………………. 7
2.11 Findings of Researchers Regarding Acacia gums ………………………………… 8
2.12 Super Plasticizer – Melflux 2651F ……………………………………………….. 8

CHAPTER 3 - EXPERIMENTAL PROGRAM

3.1 Introduction ………………………………………………………………….. 10
3.2 Research Materials…………………………………………………………………. 10
3.2.1 Cement ………………………………………………………………… 10
3.2.2 Acacia Modesta Gum Powder …………………………………………….. 10
3.3 Physical and Chemical Characterization of Powdered AM Gum ………………… 11
3.3.1 X-Ray Diffraction (XRD) of AM Gum Powder …………………………… 11
3.3.2 Scanning Electron Microscopy (SEM) of AM Gum Powder ……………… 12
3.3.3 NMR Characterization of AM Gum Powder ………………………………. 12
3.3.4 FTIR Characterization of AM Gum Powder ……………………………….. 12
3.1.5 X-Ray Fluorescence (XRF) analysis of OPC ……………………………….. 12
3.4 Formulations and Mixing Regime ………………………………………………… 12
3.5 Water demand ………………………………………………………………. 14
3.6 Super-Plasticizer demand …………………….. …………………………………..... 14
3.7 Viscosity and Yield Stress …………………… ….………………………..….. 15
3.8 Rheometric investigation …………………….. …………………….…………….… 15
3.9 Air Content measurement ……………………..…….. …………………………...... 15
3.10 Initial and Final Setting times …………………….... …………………………… 16
3.11 Fresh and Harden paste densities ……………………...………………………..... 16
3.12 Absorption capacity ………………………………………………………….... 17
3.13 Shrinkage Response ……………………………………………………….... 17
3.14 Compressive Strength ……………………………………………………… 17
3.15 Scanning Electron Microscopy of SCPs ………………………………………… 18

CHAPTER 4 - RESULTS AND DISCUSSION

4.1 Introduction ………………………………………………………………….. 19

4.2 Physical and Chemical Characterization of Powdered AM gum…………………. 19

4.2.1 X-Ray Diffraction (XRD) of AM Gum Powder …………………………… 20

4.2.2 Scanning Electron Microscopy (SEM) of AM Gum Powder ……………… 21

4.2.3 NMR Characterization of AM Gum Powder ………………………………. 21

4.2.4 FTIR Characterization of AM Gum Powder ……………………………….. 22

4.2.5 X-Ray Fluorescence (XRF) analysis of OPC ……………………………….. 22

4.3 Water demands ………………………………….……………………….…….. 23

4.4 Super-Plasticizer demands …………………….. ……………………..……...... 24

4.5 Viscosity and Yield Stress …………………. …….………………………..….. 25

4.6 Rheometric investigation …………………….. ……………….………………. 26

4.7 Initial and Final Setting times …………………….. ………………………....... 27

4.8 Compressive Strength ……………………………………………………… 28

4.9 Densities of SCPs and their Relevance with Compressive Strength…………… 30

4.10 Air content measurement …………………... …………………………….…… 32

4.11 Absorption capacity ………………………………………………………….... 32

4.12 Shrinkage Response …………………………………………………………... 33

4.13 Scanning Electron Microscopy of SCPs ………………………………………… 34

CHAPTER 5 – CONCLUSIONS AND RECOMMENDATIONS

5.1 Concluding Remarks...……………………………………………………... 37

5.2 Recommendations ……………………………………………………..... 38

REFERENCES……………………………………………………………… 39

APPENDIX…..……………………………………………………………… 42

LIST OF FIGURES

Fig 3.1 AM gum in un-grinded form……………………………………......... 10

Fig 3.2 AM gum in Three different powdered forms………………………… 11

Fig 3.3 Particle size analysizer, Mastersizer 3000 …………………………… 11

Fig 3.4 Hagerman’s mini-cone slump apparatus..……………………………. 15

Fig 3.5 Orthogonal diameter measurement…………………………...…….. 15

Fig 3.6 Programmable Rheometer………………………………...…….. 16

Fig 3.7 Air content meter……………………….………………..…...….. 16

Fig 3.8 Initial set determination..……………….……………………...…….. 16

Fig 3.9 Final set determination...………………….………………...…….. 16

Fig 3.10 German Schwindrine apparatus……….………………...…….. 17

Fig 3.11 Samples wrapped in conductive tape apparatus……………..…….. 18

Fig 3.12 Sputter coater for carbon coating of the samples……………..…….. 18

Fig 3.13 Samples placement in SEM chamber…………………….…..…….. 18

Fig 4.1 Average particle size of AM gum and OPC…………………..…….. 19

Fig 4.2 XRD of Powdered AM gum…………………………………..…….. 20

Fig 4.3 SEM of AM gum powder…………………………………..……... 21

Fig 4.4 SEM of AM gum powder…………………………………..…….. 21

Fig 4.5 NMR pattern of AM gum powder…….……………………...…….. 21

Fig 4.6 FTIR characterization of AM gum powder..…………………..…….. 22

Fig 4.7 Water demands of SCPs formulations..……………………...…….. 24

Fig 4.8 SP demands of SCPs formulations...……………….……...…….. 25

Fig 4.9 T25 and T30 cm flow Time of SCPs ……………..…………....…….. 26

Fig 4.10 Apparent viscosities of SCPs at varying shear rate.………………… 27

Fig 4.11 Vicat setting times of SCPs formulations..…………...……………. 28

Fig 4.12 Compressive strength of SCPs subjected to air curing……...…….. 29

Fig 4.13 Compressive strength of SCPs subjected to water curing……...…. 29

Fig 4.14 Fresh Paste densities of SCPs ……………….………...…….. 30

Fig 4.15 Harden densities of SCPs ……………….……..……...…….. 30

Fig 4.16 Air content of SCPs ……………….……..……...…….. 32

Fig 4.17 Water absorption capacities of SCPs ……………….…………... 33

Fig 4.18 Shrinkage Response of SCPs ……………….………...…….. 34

Fig 4.19 SEM of formulation A1 at 28 days……………….………...… 35

Fig 4.20 SEM of formulation A4 at 28 days……………….………...… 35

Fig 4.21 SEM of formulation C1 at 28 days……………….………...… 35

Fig 4.22 SEM of formulation C4 at 28 days……………….………...… 35

LIST OF TABLES

Table 3.1 List of SCP formulations studied …………..................................... 13

Table 3.2 No. of samples tested for each test ………………………………… 14

Table 4.1 Physical properties of AM gum and OPC ………….......................... 20

Table 4.2 XRF Analysis of OPC…………………………………………….. 23

Table 4.3 Mineral Composition of OPC…………………………………….. 23

Table A-1: Water Demand of SCPs…………………………………………. 42

Table A-2: SP demand, Viscosity and Yield Stress of SCPs………………... 42

Table A-3: Setting Times of SCPs………………………………………….. 42

Table A-4: Air Content measurement of SCPs……………………………… 43

Table A-5: Rheological Properties (Viscosity in cP)……………………….. 43

Table A-6: Fresh Paste Densities of SCPs………………………………….. 43

Table A-7: Harden Densities of SCPs at age of 28 Days…………………… 44

Table A-8: Absorption capacity of SCP s at age of 28 Days………………. 44

Table A-9: Compressive Strength of SCPs………………………………… 45

LIST OF NOTATIONS/ABBREVIATIONS

ACI	American Concrete Institution
AM	Acacia Modesta
ASTM	American Society of Testing Of Materials
SCCS	Self-Compacting Cementitious Systems
SCP	Self-Compacting Paste
SCM	Self-Compacting Mortar
SCC	Self-Compacting Concrete
SCPs	Self-Compacting Paste Systems
SP	Super plasticizer
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infra-Red
NMR	Nuclear Magnetic Resonance
SRM	Secondary Raw Material
W/C	Water to Cement Ratio
OPC	Ordinary Portland Cement
FA	Fly Ash
LSP	Lime Stone Powder

CHAPTER 1

INTRODUCTION

Self-compacting concrete (SCC) is defined by ACI 237R-07 as *a highly flow-able, non-segregating concrete that can spread into place, fill the formwork, and encapsulate the reinforcement without any mechanical consolidation* [1]. The properties of Self-Compacting Concrete (SCC) mainly depend upon the properties of cement paste phase. This study mainly focuses on the properties of self-compacting cement paste systems containing powdered Acacia Modesta (AM) gum powder with varying particle sizes. Very little published literature exists on use of acacia gum in self-compacting cementitious systems [7] and no previous work has reported the effect of different particle sizes of AM gum powder on the response differences of self-compacting cementitious systems (SCCs).

Self-compacting paste system acts as a vehicle for the transport of the aggregate phase in self-compacting mortar (SCM) and self-compacting concrete (SCC) systems as SCC generally requires 34-40% paste content [2] which plays a vital role in determining the over-all properties of SCC system. The addition of suitable admixtures to self-compacting paste systems can lead to an improved response. Botanical Acacia Modesta (AM) gum is a natural organic ooze-out of Acacia Modesta trees, locally known as "*Phulai*" and has been added in self-compacting paste systems (SCPs) during mixing stage as an admixture [3, 4]. Acacia Modesta gum powder of different sizes was used to study the effect on water demand, super-plasticizer demand, viscosity, yield stress, Vicat setting times, compressive strength, fresh paste densities, harden densities, air content and linear shrinkage values of SCPs.

1.1 Problem Statement

Different type of acacia gums are available in the world namely acacia Nilotica, acacia Modesta, acacia Senyal, acacia Senegal, gum Arabic karoo, etc. These acacia gums have been used in self-compacting cementitious systems (SCCs) to improve their responses. Result of the relevant studies shows that that incorporation of these gums degrades the compressive strength of self-compacting cementitious systems. Strength degradation can be encountered by either using supplementary Raw Materials (SRMs) or by reducing the particle size of acacia gums. So this study was conducted with the view to study the particle size effect of Acacia Modesta (AM) gum on the response differences of self-compacting cementitious systems (SCCs).

1.2 Research Objectives

There are two objectives of the research:

1. To explore the particle size effect of botanical Acacia Modesta (AM) gum powder on the response differences of self-compacting cementitious systems (SCCs).
2. To offset the strength reduction caused by the incorporation of Acacia Gums in self-compacting paste systems.

1.3 Research Significance

Acacia gum or Gum Arabic have recently found it's uses in self-compacting cementitious paste systems [7] but the effect of particle size of Acacia gum in self-compacting cementitious paste systems has not been investigated so far. This innovative research explores this aspect and reports response modifications of SCPs and especially offsets the strength reduction caused by the incorporation of acacia gum powders in self-compacting paste systems reported earlier [7].

1.4 Research Methodology

The methodology adopted to study the effect of particle size of Acacia Modesta (AM) gum in Self-compacting paste systems is given below:

1. Literature review has been carried out on the subject topic.
2. For characterization and composition of AM gum, Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques were utilized.
3. SCP formulations were prepared by varying the AM gum content and AM average particle size.
4. Laboratory tests were performed. These include tests for water demand, flow, setting times, fresh paste density, hard paste density, viscosity, total shrinkage, air contents, absorption capacity and the compressive strength.

5. To have insight into the effect of particle size of AM gum powder in SCPs based formulations, Scanning Electron Microscopy test was conducted at the age of 28 days.
6. Finally the discussions were made on the topic with the help of relevant literature and supervisor's guidance.

1.5 Research Scope

Scope of the research was limited to evaluate the response of Acacia Modesta Gum powder in self-compacting paste (SCP) systems at three different particle sizes while each particle size contain four varying dosages of Acacia Modesta Gum powder by the dry weight of the cement. This research investigated the response of self-compacting paste (SCP) systems considering the particle size effect of the AM gum at average particle sizes of 307 microns, 135 microns and 47.5 microns. AM gum powder dosage varied in each particle size from 0% to 1% by the dry weight of the cement with an interval of 0.25.

1.6 Thesis organization

The first chapter gives an introduction to the thesis topic. The next chapter presents the literature review. The third chapter presents various methods employed for the characterization of AM gum. It also deals with the standard methods and apparatuses employed for conduction of laboratory tests. The fourth chapter presents discussions and reasoning of the performed tests. Finally the fifth chapter gives conclusions and recommendations. References and appendices are attached at the end of this thesis.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter gives information about self-compacting cementitious systems, advantages of self-compacting cementitious systems with special focus on importance of self-compacting paste systems. It also deals with the studies which were already carried out on the use of acacia gums in self-compacting cementitious systems and discusses about the techniques employed for the composition and characterization of Acacia Modesta gum powder. At the end, it discusses about the findings of studies already carried out on the usage of acacia gums in self-compacting cementitious systems.

2.2 Self-Compacting Cementitious Systems

Self-consolidating cementitious systems (SCCS) include self-compacting pastes (SCP), self-compacting mortars (SCM) and self-compacting concrete (SCC). Self-compacting concrete technology was introduced by the Japanese researchers to tackle the shortage of skilled labours in 1980s. After then, SCC was being successfully used in different parts of the world for construction of high rise buildings, bridges, etc. Self-compacting concrete (SCC) is defined by ACI 237R-07 as

"A highly flow-able, non-segregating concrete that can spread into place, fill the formwork, and encapsulate the reinforcement without any mechanical consolidation" [1]

The basic criteria for achieving self-compaction are high deformability, high passing ability and high resistance to segregation. A super-plasticizer may be used for achieving high flow and a viscosity enhancing agent may be used in the mix with low or moderate water-powder ratio to obtain higher resistance to segregation.

The self-compaction of self-compacting concrete (SCC) mainly depends upon the cement paste content [2], thus this study is mainly focused on the properties of self-compacting cement paste systems containing powdered Acacia Modesta (AM) gum as an admixture with variable particle size of the AM gum powder. Admixture is defined as a material added in small quantities, during the mixing process, to modify the properties of cementitious systems in the fresh and/or hardened state [3, 4, 5].

2.3 Advantages of Self-Compacting Cementitious Systems

Self-Compacting concrete is used in the construction industry nowadays due to a number of advantages it presents over the conventional high slump concrete.

- SCC reduces construction time and manpower requirements due to its ability to compact under its own weight, thereby eliminating the requirement for manual vibration which is time consuming and results in differential compaction of concrete which leads to different durability.
- SCC results in an overall better finished surface and better homogeneity and self-compaction of the concrete mix.
- Absence of mechanical compaction eliminates the possibility of worker error.
- SCC also improves the workplace environment by reducing noise pollution and eliminates health related problems.

2.4 Self-compacting Paste Systems

Self-compacting paste systems acts as a vehicle for the transport of the aggregate in self-compacting concrete (SCC) systems as SCC generally requires 34-40% paste content [27] and play a vital role in determining the over-all properties of a system. The higher amount of paste normally has detrimental effects on the properties of SCC in terms of higher heat of hydration and higher shrinkage etc. Therefore the addition of suitable admixtures to a paste can offset these issues and could lead to better, improved and durable structure.

2.5 Acacia Modesta (AM) gum as admixture in SCPs

Different species of acacia gums are available in the world. A specie of genus Acacia namely Acacia Modesta, mostly found in the tropical countries of the world has been used for this study. The selection of Acacia Modesta (AM) gum, locally obtained from tree known as “Phulai”, was made to explore the possibilities of using it in self-compacting cementitious systems.

Recently Acacia Modesta Gum has been used as an admixture for modifying the properties of self-compacted paste systems [7] especially to reduce early-age shrinkage and to minimize the need for curing. Acacia Modesta gum is found mainly in the tropical countries of the world [28]. In Pakistan it can be found in the northern areas of the country. Its gum emanates from the mature trees of Acacia Modesta that are injured and exists in the form of non-viscous liquid which is rich in soluble fibers and composed mainly of carbohydrates and proteins [29].

In the ancient times, acacia gum was used as ink and adhesive agent. In modern world, it is being used in medicine, textile and food, cosmetics, glue and printing industry and has many other industrial applications. It is also used as an antioxidant agent and a cure for many diseases including digestion of lipids [8, 31].

2.6 Composition of Acacia Modesta gum powder

The chemical composition of acacia gum varies with origin, source, age of the tree, harvesting season, climatic conditions and processing conditions [8]. For characterization and composition of AM gum, Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques were used. Characterization tests revealed that AM gum is largely composed of hydrophobic components and therefore it behaves as a nearly inert material in SCPs.

Chemically AM gum consists of small amount of proteins and highly branched polysaccharides (97%) that contains carbohydrates in the form of Galactose, Rhamnose and Arabinose [7, 8]. Silicates present in the cement matrix do not seem to react with carbohydrates [9], therefore AM powder particles remain as almost unreacted particles within the cement matrix and are responsible for prolonged setting times of SCP systems using AM gum powder. This non-reactiveness nature of AM makes it a kind of inert material in SCPs.

2.7 Nuclear Magnetic Resonance (NMR)

NMR technique was used for structural determination of molecules of AM gum powder. It uses a large magnet to probe the intrinsic spin properties of atomic nuclei. Like all spectroscopies, NMR uses a component of electromagnetic radiation (radio frequency waves) to promote transitions between nuclear energy levels (Resonance). Upon absorption of the frequencies, the nuclei resonate and different atoms within a molecule resonate at different frequencies. This observation allows a detailed analysis of the structure of a molecule, especially of organic origin.

2.8 Fourier Transform Infrared Spectroscopy (FTIR)

The preferred method of infrared spectroscopy is Fourier Transform Infra-Red (FTIR) spectroscopy in which IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum may be direct indication of the amount of material present. This makes infrared spectroscopy useful for several types of analysis. [13]

2.9 Internal Curing- A specialty of AM gum powder

Curing, a process of maintaining sufficient moisture content inside the matrix helps in strength gain, durability, serviceability and resistance to wear and abrasion. Conventional curing methods ensure that the mixture stays moist and warm at the surface. This makes possible continued and complete hydration of a typical cement mix having w/c ratio more than 0.42 [30]. With the advent of high rise buildings and long spanned bridges, production of high strength concrete with limited w/c ratio is in high demand. Such mixtures have insufficient free water content which might result in self-desiccation of cement matrix [31]. Therefore it is recommended to have a material that plays the role of internal curing inside the matrix. Acacia Modesta gum powder is of those materials. AM gum powder basically adsorbs the water on its surface and releases it back to the system when the relative humidity drops ensuring crack-free structure.

2.10 Particle Size effect of AM gum powder – A Novel idea

No published literature exists in any form that discusses the effect of particle size of AM gum powder, so this is a novel idea to explore the effect of AM gum powder particles in Self-Compacting Paste Systems (SCPs). Apart from particle size effect, a limited literature is available that addresses the response of Acacia Modesta gum in SCP systems. Acacia gum has been recently found its uses in Self-Compacting Paste Systems (SCPs). The limited literature available on the use of Acacia gums in SCC or SCPs is listed below along with the key findings and highlights of the relevant paper.

2.11 Findings of Researchers Regarding Acacia Gums

Very little published literature exists on use of acacia gum in self-compacting cementitious systems [7, 27] and no previous work has reported the effect of different particle sizes of AM gum powder on the response differences of self-compacting cementitious systems (SCCs). S.A. Rizwan et al. investigated the response of Acacia Nilotica gum in the self-compacting paste systems. They used locally available Acacia Nilotica gum and incorporated it self-compacting paste systems with varying water-cement ratio. They reported that Acacia Nilotica Gum increases the viscosity of SCPs. They also concluded that the acacia nilotica degrades the strength of SCPs, which they offset with Fly Ash (FA) and Limestone Powder (LSP) added as SRMs. They also reported that insulation properties and freeze-thaw resistance got improved with addition of acacia nilotica gum in SCPs.

R. Mbugua, R. Salim and J. Ndambuki in their paper titled "effect of Gum Arabic karroo as a Water-Reducing admixture in Concrete" investigated the effect of hum Arabic karroo in conventional concrete and reported that gum Arabic karroo increases the slump which resulted in decreased water-to-binder (w/b) ratio. Morover, they also concluded that compressive strength decreases with the addition of gum Arabic karoo and it can be used as super-plasticizer agent as they achieved the same flow with lesser water to cement ratio for samples containing gum Arabic karroo.

The most relevant research to the topic was carried out by Neha Mahmood during her MS degree on the topic "Response of self-compacting paste systems containing Acacia Modesta gum". She used a constant water to cement ratio of 27% and AM gum was varied from 0.25% to 1% by weight of the cement. She concluded that AM gum acts as internal curing agent during to its property to retain water on its surface and due to this property it reduces the total shrinkage of the sytem. She also reported that strength of AM gum containing SCP samples degraded with addition of AM gum powder in them for which she recommended SRMs.

2.12 Super Plasticizer – Melflux 2651F

A super plasticizer may decrease the water demand up to 30% without causing excessive retardation in setting times and ensures easy placement and consolidation of concrete by helping in achieving a highly flowable concrete at a lower water-cementitious material (w/cm) ratios. Melflux 2651F manufactured by BASF Germany, a third generation high-performance poly-carboxylate ether (PCE) based super-plasticizer was used in cement based mixes for current research. Apart from reducing the water to cement ratio, it helps in preventing bleeding and segregation and ensures high early strength development. It also acts as a retarder in SCP based formulations [7].

CHAPTER 3

EXPERIMENTAL PROGRAM

3.1 Introduction

This chapter focuses on the materials used in this research. It also discusses about the procedure employed for physical and chemical characterization of Acacia Modesta gum and ordinary Portland cement. Moreover, the different SCP formulation studied also form a part of this chapter. At the end, it discusses about the procedure and method of different tests like water demand, super-plasticizer demand, viscosity and yield stress, rheological measurement, air content, setting times, compressive strength, fresh and harden paste densities, absorption capacities, linear shrinkage response and scanning electron microscopy.

3.2 Research Materials

The following materials were used during the research. All the research materials were stored in sealed container prior to use in order to avoid contact with the moisture.

3.2.1 Cement

Locally manufactured Bestway Type I Ordinary Portland Cement (OPC) of grade 53, conforming to ASTM standard C150-04, was used.

3.2.2 Acacia Modesta Gum Powder

Acacia Modesta gum was obtained from a local retailer store in Rawalpindi in the form shown in fig. 3.1. Then it was grounded to three different average particle sizes namely 307 microns, 135 microns and 47.5 microns with the help of a grinder.

Figure 3.1 AM Gum in un-grinded form

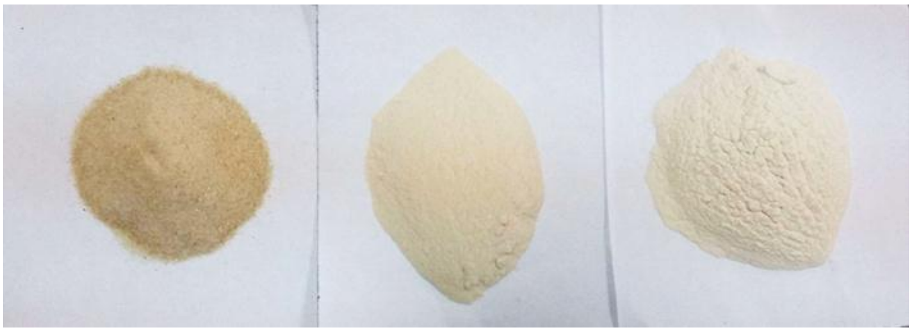

Figure 3.2 AM gum in Three different powdered forms

3.3 Physical and chemical characterization of powdered AM gum

The average particle size (D50) of AM gum and OPC was found using laser diffraction particle size analysizer, Mastersizer 3000. Fig. 3.2 showed three different sizes of AM gum obtained after grinding to different scales and then these were used to determine D50 with the help of Mastersizer 3000. Fig. 3.3 showed a typical laser diffraction particle size analysizer, Mastersizer 3000.

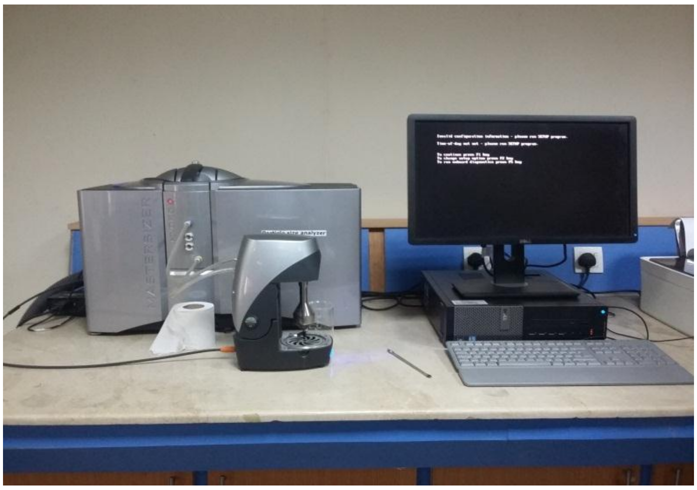

Figure 3.3 Particle size analyzer, Mastersizer 3000

3.3.1 X-Ray Diffraction (XRD) of AM Gum Powder

XRD was performed on the AM gum in powdered form using PANalytical - X'Pert³ Powder. The values of 2θ ranged from 10 to 60 degrees in the XRD test. XRD test was helpful in determining the nature of the AM gum.

3.3.2 Scanning Electron Microscopy (SEM) of AM Gum Powder

Scanning Electron Microscopy of Acacia Modesta Gum powder was performed on SEM JSM-6490 to study their microstructure, shape and interfacial transition zone (ITZ).

3.3.3 NMR Characterization of AM Gum Powder

Nuclear Magnetic Resonance (NMR) of AM gum powder was conducted using Proton 1H NMR on 300 MHz AVANCE Series Swiss spectrometer. 20 mg of AM gum powder was dissolved in 0.5ml DMSO (Dimethyl sulfoxide) to generate NMR pattern of the powdered AM gum. NMR pattern helps in identifying the various chemical compounds present in the Acacia Modesta gum powder.

3.3.4 FTIR Characterization of AM Gum Powder

Fourier Transform Infra-Red (FTIR) test of AM gum powder was conducted using Bruker Optics FT-IR Tensor 27 with standard KBr beam splitter technology in the scanning range of 500–4000 cm^{-1}. The FTIR spectrum provided wavelength absorbance peaks for the corresponding functional groups and helped in determining the various functional groups present in the Acacia Modesta Gum powder.

3.3.5 X-Ray Fluorescence (XRF) Analysis of OPC

Chemical composition of Ordinary Portland Cement (OPC) was determined by X-Ray Fluorescence (XRF) analysis using pressed pellet procedure in Axias Advanced WD-XRF PaNalytical machine. Using the results of XRF, Bough's potential were calculated to determine the mineral composition of OPC.

3.4 Formulations and Mixing Regime

After characterizing the AM gum powder, it was incorporated in cement matrices to obtain SCPs which were studied in fresh and hardened states. Table 1 gives the thirteen different SCP formulations studied by varying both Acacia Modesta gum powder content and average particle size. Each formulation was tested at a constant water-cement ratio of 27%, which is demand of the neat cement paste determined through consistency test while super-plasticizer (SP) demand of each formulation was measured by Hagerman's cone measuring 10x7x6 cm3 for the target flow of 30±1 cm. The formulations tested were as follows.

Table 3.1 List of SCP formulations studied

AM (%)	D50 (µm)	SP (%)	Formulation Name	Formulation ID
0.00	28.3	0.19	0.00AM-0.19SP-28.3	OPC
0.25	307	0.32	0.25AM-0.32SP-307	A1
0.50	307	0.38	0.50AM-0.38SP-307	A2
0.75	307	0.48	0.75AM-0.48SP-307	A3
1.00	307	0.57	1.00AM-0.57SP-307	A4
0.25	135	0.35	0.25AM-0.35SP-135	B1
0.50	135	0.43	0.50AM-0.43SP-135	B2
0.75	135	0.53	0.75AM-0.53SP-135	B3
1.00	135	0.66	1.00AM-0.66SP-135	B4
0.25	47.5	0.37	0.25AM-0.37SP-47.5	C1
0.50	47.5	0.45	0.50AM-0.45SP-47.5	C2
0.75	47.5	0.56	0.75AM-0.56SP-47.5	C3
1.00	47.5	0.70	1.00AM-0.70SP-47.5	C4

*All formulations were prepared using CEM-1 type cement at constant water demand of 27% by the dry weight of the cement.

A typical formulation of, for instance formulation A1(0.25AM-0.32SP-307), consists of CEM 1 type cement, 0.25 % Acacia Modesta (AM) gum, 0.32 % super plasticizer (SP) dose needed for target flow at 27 % mixing water content having mixing water temperature of 20±2 ºC and the AM gum used has an average particle size of 307 Micron. All other formulations should be read accordingly. Moreover all percentages in the formulation nomenclature are with respect to the dry weight of the cement and prepared at surrounding temperature of 25 ºC with 55 % relative humidity (RH) in the control chamber of the laboratory.

Mixing regime pertaining to DIN-196-3 [12] was followed to ensure uniformity in the preparation of respective formulation. Initially, the dry contents (cement, SP, AM) were first mixed manually for 30 seconds before adding into the mixer bowl containing the mixing water. Then slow mixing was carried out at 145 rpm for 30 seconds followed by 30 seconds break for cleaning the sides and edges of the bowl. Afterwards fast mixing was carried out at 285 rpm for 150 seconds. Total mixing time was 3 minutes.

Table 3.2 No. of samples tested for each Test

Test Name	Samples per formulation	Total Samples Tested	Mould Dimensions
Water Demand	2	26	10 cm height
SP Demand	2	26	10x6x7 cm^3
viscosity and yield stress	2	26	10x6x7 cm^3
Rheometric investigation	2	26	SC 4-27 spindle
Air Content	2	26	2 litre capacity
Initial and Final Setting Times	2	26	10 cm height
Fresh Paste Density	2	26	4x4x16 cm^3
and Harden Density	2	26	4x4x16 cm^3
Absorption Capacity	2	26	4x4x16 cm^3
Shrinkage Response	1	13	4x6x25 cm^3
Compressive Strength	6	78	4x4x16 cm^3
SEM	1	13	Resolution of 2µm

3.5 Water demands of SCPs formulations

Despite of the fact that a constant water demand of 27% was used for all SCPs formulations as indicated in Table 1, the respective water demands of all SCPs formulations was determined using Vicat apparatus in accordance with DIN-196-3 [12] to access the behavior of AM gum towards mixing water content. The zero error was eliminated by setting the bottom-top scale to zero over the base plate. Water demand is defined as the minimum water content required for lubricating the particles of the mix.

3.6 Super-Plasticizer demand of SCPs formulations

Different trials of flow tests were conducted to determine the required super-plasticizer demand of various SCP formulations with respect to cement content with the help of Hagerman's mini-cone slump apparatus having 10x7x6 cm3 dimensions to achieve a target flow of 30±1 cm. Orthogonal diameters were measured to get average flow of flow. Hagerman's mini-cone slump test of a typical formulation and measurement of orthogonal diameter is shown in fig 3.4

Figure 3.4 Hagerman's mini-cone slump apparatus

Figure 3.5 Orthogonal Diameter measurement

3.7 Viscosity and Yield Stress of SCPs Formulations

T25 cm and T30 cm flow time was also measured in a Hagerman's mini-cone slump test. T25 cm flow time is a measure of viscosity of the system while T30 cm flow time is a function of yield stress of the SCP systems.

3.8 Rheometric investigation of SCPs Formulations

To measure viscosities of specific SCPs formulations containing Acacia Modesta gum, Brookfield DV-III Ultra Programmable Rheometer with SC4-27 spindle was used. In order to get the readings in the viscometer range and to facilitate the spindle movement, w/c ratio was increased to 0.40 for this particular test while keeping the SP demand as determined through the flow test. Viscosities were measured for 2 minutes at shear rates of 20.4 s^{-1}, 27.2 s^{-1} and 34 s^{-1} corresponding to 60 rpm, 80 rpm and 100 rpm respectively. These shear rates are the same through which concrete passes during the processes of mixing, placing and casting [19]. It should be noted that the temperature during the test was kept constant at 30±1˚C. A typical rheometer is shown in fig. 3.6

3.9 Air content measurement of SCPs formulations

Air content of SCP formulations was measured in the fresh state within the fifteen minutes after mixing. The air contents of fresh SCPs determined using Luftgehaltspruefer Testing equipment having 1 liter capacity using the pressure method. Typical Air content meter is shown in Fig. 3.7

Figure 3.6 Programmable Rheometer *Figure 3.7 Air Content Meter*

3.10 Initial and Final Setting Times of SCPs formulations

Initial and final setting times of SCP systems were determined using Vicat apparatus following DIN 196-1 [10]. For initial setting times, the initial set needle was penetrated after every 15 minutes into the mould. Initial set was taken when the needle penetrated 5±1 mm from the bottom. For the final set, the larger ring impression of final set needle was observed until it vanishes on the paste surface. A typical Vicat apparatus while determining initial and final set is shown below.

Figure 3.8 Initial Set Determination *Figure 3.9 Final Set Determination*

3.11 Fresh and Harden paste densities of SCPs formulations

Fresh paste weight was measured using digital balance, divided by the volume of the cubical mould to get fresh paste densities as shown in Fig. 15 while prisms casted to check air cured strength of SCP formulations were used for measurement of harden stage densities. After demoulding prisms were marked, weighed and placed in open air for curing purposes. The samples were weighed again at respective test age and volume was determined by measuring dimensions with the help of Vernier caliper.

3.12 Absorption capacities of SCP formulations

Water absorption capacity of all the SCP formulations was determined using prisms casted for strength purposes. After demoulding prisms were marked, weighed and placed in water curing tank at laboratory temperature of 20±1 °C for curing. The samples were weighed again in SSD conditions at respective test age after removing from curing tank. The difference between the weights for each prism at a given age gave the water absorption in percent

3.13 Shrinkage Response of SCP formulations

Linear shrinkage response of 10 SCP formulations containing varying amount and particle size of AM gum were studied for the first 72 hours using modified German Schwindrine shrinkage apparatus of dimensions 4x6x25 cm^3 with a sensitivity of 0.31 microns.

Fig. 3.10 German Schwindrine apparatus

3.14 Compressive Strength of SCP Formulations

A total of seventy eight prisms, six prisms of each formulation, having cross sections of 40mm x 40mm and a length of 160 mm were casted. The casted samples were covered with plastic sheet and de-molded after their respective setting times. After demoulding, samples were placed for curing. Effect of both air curing and conventional water curing has been studied. The temperature of curing tank containing water cured samples was kept constant at 20+1 ºC as per DIN 196 standards. At the age of 7th, 14th and 28th days, respective formulations were tested for compression according to DIN-196 standard.

3.15 Scanning Electron Microscopy of SCP formulations

Scanning Electron Microscopy (SEM) was carried out for selected SCP formulations at the age of 28 days using MIRA3 TESCAN for ensuring minimal noise and high resolution imagery. The broken pieces of about 2-3 mm were obtained from 4x4x16 cm^3 prisms broken in compression. Hydration of these SCP samples was stopped by chemical injection method. Prior to samples placement inside SEM chamber, the samples were covered with conductive tape and then carbon coated in a sputter coater. SEM was performed to determine shape, morphology and microstructure of the SCP systems containing AM gum powder. The resolution of SEM images varied from 1 μm to 20 μm.

Figure 3.11 Samples wrapped in conductive tape

Figure 3.12 Sputter coater for carbon coating of the samples

Figure 3.13 Sample Placement in SEM chamber

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter deals with results and discussions of the results obtained from different test. It discuss about the results of physical and chemical characterization of Acacia Modesta gum powder along with ordinary Portland cement, their surface areas determination and density calculations of each particle size. The laboratory results that were discussed in detailed includes water demand, super-plasticizer demand, viscosity and yield stress, rheological measurement, air content, setting times, compressive strength (both air cured and water cured), fresh and harden paste densities, absorption capacities and linear shrinkage response. For microstructural studies, scanning electron microscopy (SEM) was discussed in detailed. All tests were discussed in two dimensions, one particle size effect of AM gum powder and other effect of AM gum powder dosage.

4.2 Physical and Chemical Characterization of Powdered AM gum

The average particle size (D50) of AM gum was found using a laser diffraction particle size analysizer, Mastersizer 3000. Fig. 4.1 showed the D50 of three different sizes of AM gum powder and cement used during this study.

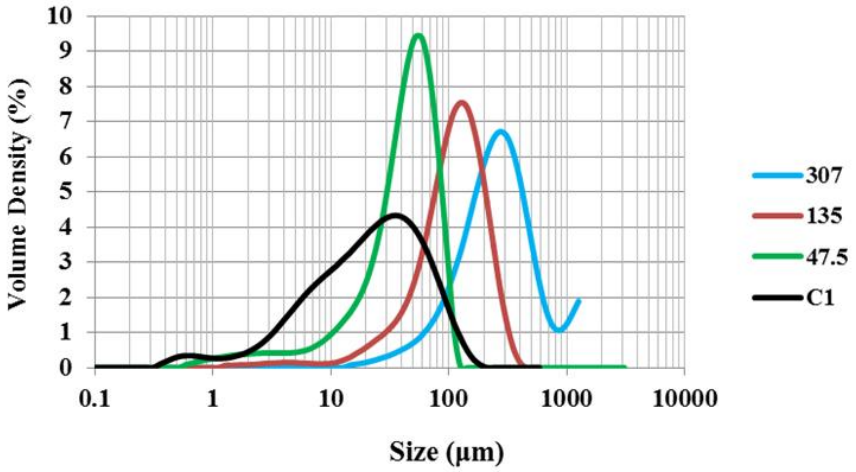

Figure 4.1 Average particle size of AM gum and OPC

The physical properties of three different sizes of AM gum powder and OPC were shown in Table 4.1. The specific gravity of AM gums was determined through volume displacement method by using Ethanol as liquid. D50 and specific surface area were evaluated using Mastersizer 3000 which is a particle size analysizer.

Table 4.1 Physical Properties of AM gum and OPC

Property	Size A	Size B	Size C	OPC
Average Particle Size (D_{50})	307 μm	135 μm	47.5 μm	28.3 μm
Specific Surface Area (m^2/kg)	19.08	60.40	258.8	402.4
Specific gravity of AM gum	1.48	1.63	1.80	3.15

4.2.1 X-Ray Diffraction (XRD) of AM gum powder

XRD was performed on the powder form of AM gum using PANalytical - X'Pert^3 Powder. The qualitative XRD of gum powder in Fig 4.2 shows that it is poorly crystalline. The values of 2θ ranged from 10 to 60 degrees in XRD test. The results of the XRD test were taken from the thesis titled "A study of self-compacting paste systems using Acacia Modesta gum as an admixture" written by Neha Mahmood, student of MS Structural Engineering, NICE, Batch 2014. [31]

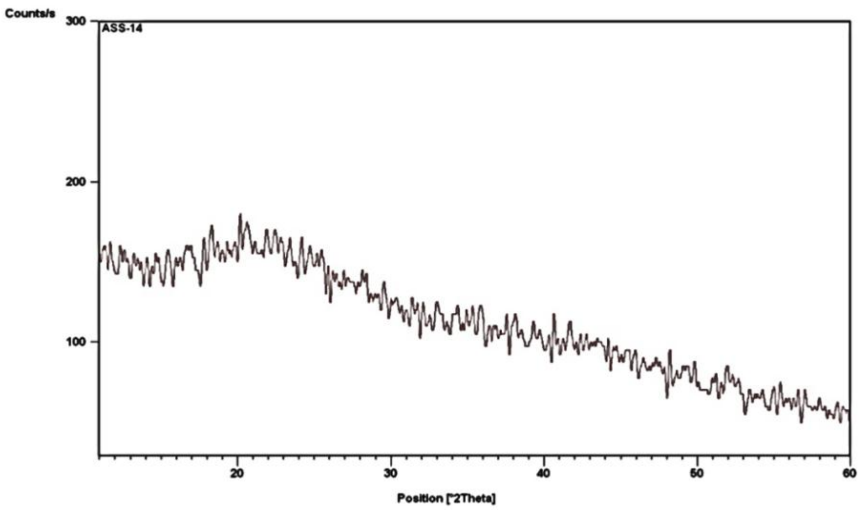

Fig 4.2 XRD of *powdered* AM gum

4.2.2 Scanning Electron Microscopy (SEM) of AM gum powder

Scanning Electron Microscopy of powdered Acacia Modesta Gum was performed on SEM JSM-6490 to study their microstructure, shape and interfacial transition zone (ITZ). Microscopy results depicted that Acacia Modesta gum powder possess poorly formed hexagonal crystals as shown in Fig. 4.3 and Fig. 4.4. SEM images were taken from the thesis titled "A study of self-compacting paste systems using Acacia Modesta gum as an admixture" written by Neha Mahmood, student of MS Structural Engineering, NICE, Batch 2014.[31]

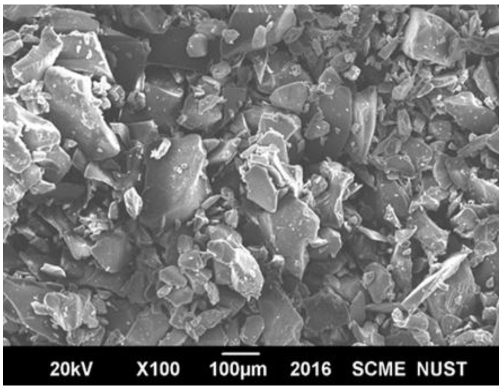

Figure 4.3 SEM of AM gum *powder*

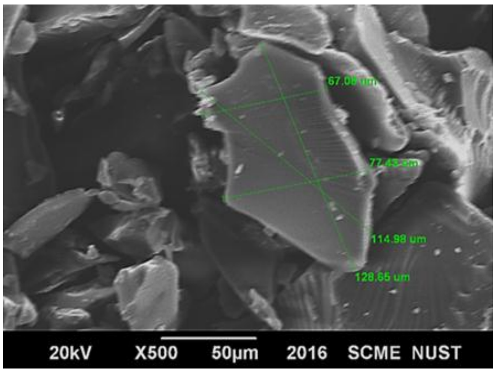

Figure 4.4 SEM of AM gum powder

4.2.3 NMR characterization of AM gum powder

Nuclear Magnetic Resonance (NMR) pattern of powdered AM gum was generated using Proton 1H NMR on 300 MHz AVANCE Series Swiss spectrometer.

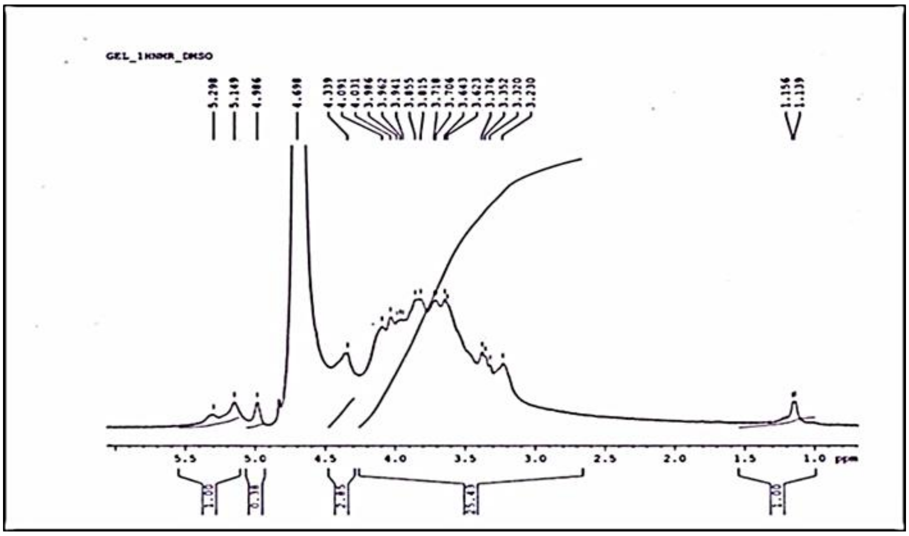

Figure 4.5 NMR pattern of AM *gum* powder

The peaks in NMR pattern correspond to the relative amounts of compounds present in the powdered Acacia Modesta (AM) gum [31]. Presence of amide group results in highest peak at 4.698 ppm which may be due to glycoproteins [7]. The series of peaks between 3.2 ppm and 4.3 ppm possibly represent halogenated hydrocarbons that are not capable to form intermolecular interactions with water and other polar compounds due to their non-polar nature [13, 31]. It shows that AM gum powder might act as inert material in SCPs and leads to flocculation in the matrix. Peaks at 1.156 and 1.139 ppm indicates the presence of long-chain hydrocarbons containing single and double bond and are hydrophobic in nature [14].

4.2.4 FTIR characterization of AM gum powder

FTIR results of powdered AM gum conducted on Bruker Optics FT-IR Tensor 27 with standard KBr beam splitter technology in the scanning range of 450–4000 cm^{-1} were shown in Fig. 4.6

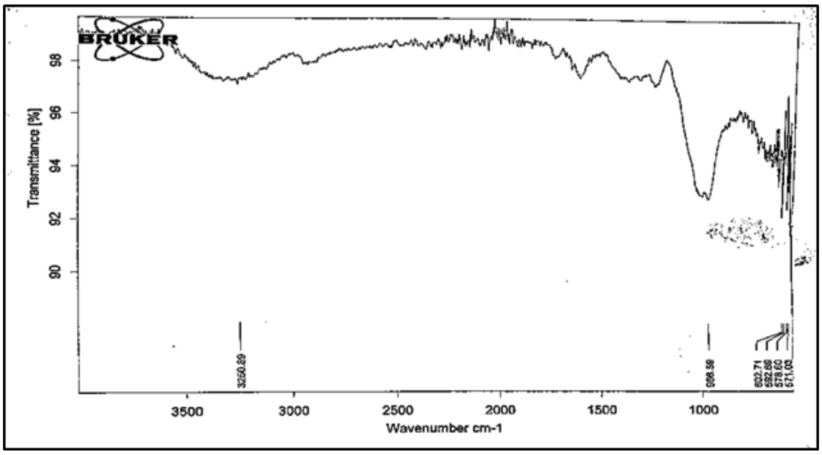

Figure 4.6 FTIR characterization of *AM* gum powder

The broad peak at 3250.89 cm-1 is possibly due to the presence of hydrocarbons in the AM gum powder containing single and double bond [31]. Peak at 966.59 cm-1 indicates the presence of aromatic amines. Peaks between 602.71 and 571.03 indicate the presence of alkyl halides in the AM gum powder [15].

4.2.5 X-Ray Fluorescence (XRF) analysis of OPC

AM gum powder being highly organic in nature was characterized using techniques mentioned in section 4 while Ordinary Portland Cement (OPC) has been characterized using X-Ray Fluorescence (XRF) analysis. Table 4.2 shows the chemical composition of

OPC determined by XRF analysis using pressed pellet procedure in Axias Advanced WD-XRF PaNalytical machine.

Table 4.2 XRF analysis of OPC

Oxides	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI
Amount (%)	19.19	0.29	4.97	3.27	2.23	61.8	0.57	0.51	0.68	3.78

Using XRF results and Bouges' equation, approximate amount of minerals content present in the cement clinker were determined. The amount of C_3S, C_2S, C_3A and C_4AF obtained is listed below.

Table 4.3 Mineral Composition of OPC

Mineral/Phase	**Abbreviation**	**Amount (%)**
Alite	C_3S	67.63
Belite	C_2S	4.0
Aluminate phase	C_3A	7.64
Ferrite phase	C_4AF	9.95

After characterizing the AM gum powder, it was incorporated in cement matrices to obtain SCPs which were studied in fresh and hardened states. Table 3.1 gives the SCP formulations investigated.

4.3 Water demand of SCPs containing AM gum

Although a constant water to cement ratio of 27% was used during this research which was the demand of the neat cement paste as indicated in Table 3.1 but to determine the response of AM gum towards mixing water content, Vicat apparatus was used to determine respective water demands of SCP formulations containing AM gum as per DIN 196-3 [12]. The results obtained were shown below in Fig. 4.7

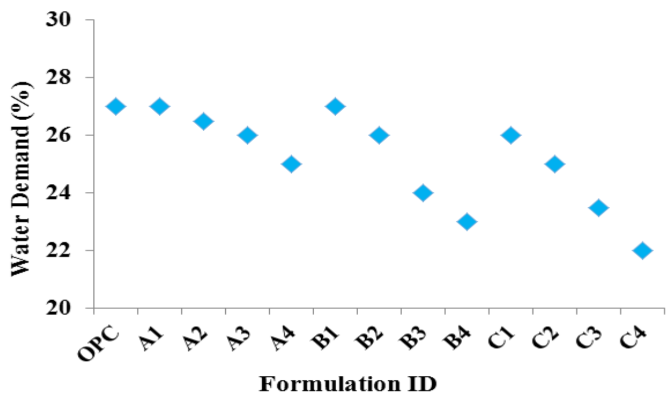

Figure 4.7 Water demands of SCPs *formulations*

From the Figure 4.7, it can be inferred that water demand decreases with the increase in the powdered AM gum content. This might be due to moisture adsorption by AM gum during dry mixing or during weighing the material before adding to Hobart mixer and AM gum releases this extra water back to the system during mixing in the Hobart mixer resulting in decrease of the water demand of the SCP system. Water demand of the SCP systems decreases at higher dosages of AM gum due to increase in water adsorption tendency of the AM gum powder.

Moreover, as particle size of AM gum decreases, the surface area of the AM gum powder increases, as mentioned in Table 3.2, which leads to further reduction in water demand of the SCP system due to increased adsorption of water molecules on the surface of the AM gum powder.

4.4 Super-Plasticizer demand of SCPs formulations

Different trials of flow tests were conducted using Hagerman's mini-cone slump apparatus having 10x7x6 cm^3 dimensions to achieve a target flow of 30±1 cm. Fig. 4.8 shows the SP demand of various SCP formulations with varying AM gum content in percentage on x-axis.

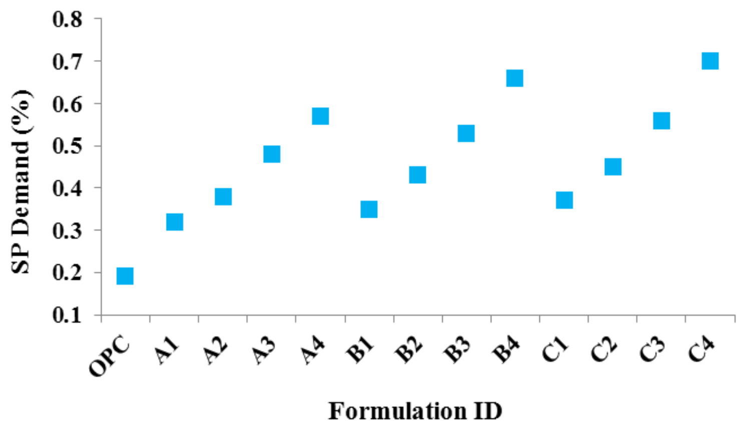

Figure 4.8 SP demand of SCP formulations

Super-plasticizer demands of the SCP systems containing AM gum powder increases with the decrease in the particle size of the AM gum as shown in Figure 4.8. This could be due to increased internal friction and increased surface area of AM gum powder. As the particle size of AM gum powder decreases, more SP dosage was needed to coat the periphery of the finer particles as compare to the larger particles in order to prevent water contact with AM gum particles. As AM gum adsorbs more water physically, so by reducing the size of AM gum, the surface area got increased which leads to more water adsorbtion through ionic attraction. So to overcome this ionic attraction, a higher SP dosage was needed to achieve the target flow.

Figure 4.8 shows that SP demand of SCPs containing AM gum powder got increased by increasing the AM gum content. This could possibly due to the anionic polysaccharides present in acacia gums [16]. The calcium ions (Ca2+) present in the cement paste or H+ ions present in mixing water may get adsorbed on the polysaccharides through ionic attraction causing an increased attraction between the cement grains and AM gum powder resulting in an enhanced viscosity [17] which ultimately increased the SP dosage to achieve the required target flow of 30+1 cm.

4.5 Viscosity and Yield Stress of SCPs formulations

Viscosity and Yield stress were measured indirectly with the help of Hagerman's mini-cone slump test. T25 cm time is a measure of viscosity of the system while T30 cm flow time is a function of yield stress of SCP systems. Fig. 4.9 depicts the viscosity and yield stress of the SCP system containing different dosages and different particle sizes of the AM gum powder.

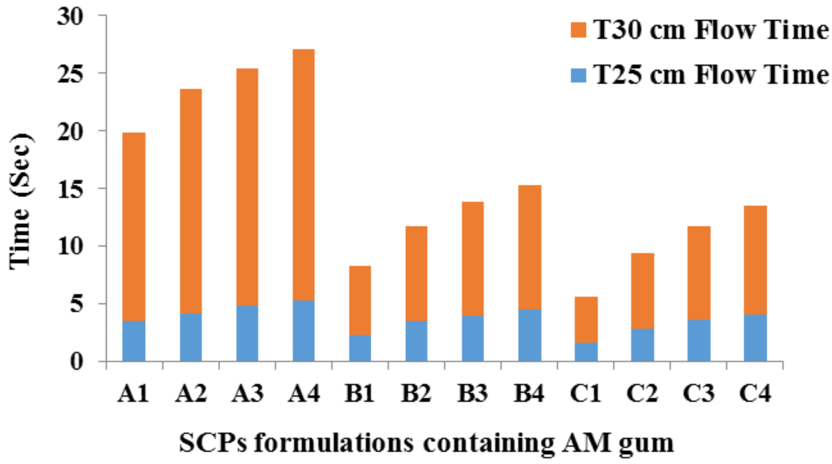

Figure 4.9 T25 cm and T30 cm flow time of SCPs

With the increase in AM gum content, the time required (T25 & T30) to reach the specific flow value (30±1cm) got increased indicating that the plastic viscosity and yield stress of the respective SCP system becomes higher with the incorporation of AM gum in SCP systems. This is in accordance with the literature postulate that acacia gums acts as viscosity enhancing agent [7].

With the decrease in the average particle size of AM gum powder, both viscosity and yield stress values got decreased. As mentioned in section 4.2, water demand of the SCPs containing AM gum powder got decreased with the decrease in AM gum particle size, hence more water was available in the matrix than the demand of the system which ultimately decreased the viscosity and yield stress. So, it can be concluded that AM gum powder can be used as a "flow enhancing agent" by decreasing the particle size of the AM gum powder.

4.6 Rheometric investigation of SCP systems

Viscosities of SCPs formulations containing Acacia Modesta gum powder were also measured using Brookfield DV-III Ultra Programmable Rheometer with SC4-27 spindle. Viscosities were measured for 2 minutes at shear rates of 20.4 s^{-1}, 27.2 s^{-1} and 34 s^{-1} corresponding to 60 rpm, 80 rpm and 100 rpm respectively. The shear rates selected were the same through which concrete passes during the processes of mixing, placing and casting [19].

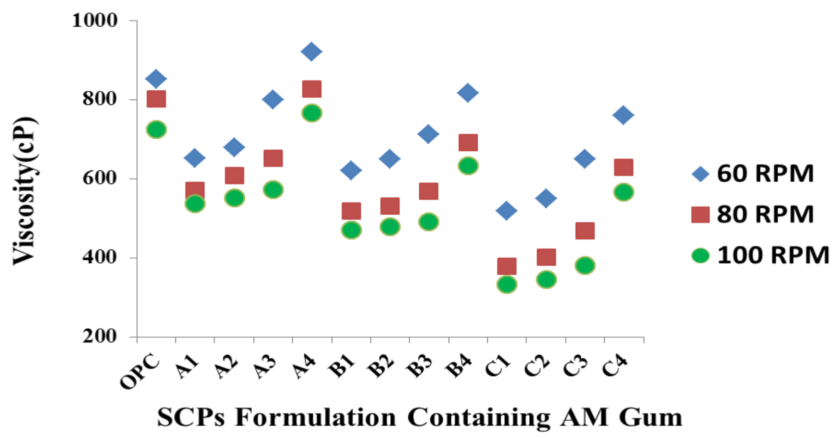

Figure 4.10 Apparent viscosities of SCP formulations at varying shear rates

The results obtained through rheometric investigation compliment the results obtained indirectly through mini-cone slump flow test by measuring T25cm and T30cm times. From figure 4.10, it can be seen that viscosity of the SCP systems increases with the increase in AM gum content and decreases with decrease in the average particle size of AM gum powder. Both these trends can be due to adsorption, association or intertwining as explained by K.H.Khayat [18]. Due to intertwining at smaller sizes of AM gum powder, the highly branched polysaccharides may break loose and align themself in the direction of flow, thereby decreasing viscosity of the SCP systems [18]. This property is known as shear thinning [31] and is more prominent for formulations containing either small sizes of AM gum powder or higher dosages of AM content.

Due to association [18] the adjacent polysaccharide chains gets adsorbs on the surface of cement particles and starts developing an attraction that constrains the motion of water molecules in between and formed a gel-like structure that increases the viscosity of the SCP systems. A constant water demand of 27% was used in the study which was more than the Vicat water demand of SCP formulations. This excess of water aligned the AM gum powder particles in the direction of the motion which resulted in the decrease of the viscosity of SCP systems with decrease in particle size of AM gum powder.

4.7 Initial and Final Setting Times of SCPs formulations

Initial and final setting times of SCP systems were determined using Vicat apparatus following DIN 196-1 [10]. Result shows that both Initial and final setting times got increased with increase in AM gum content as shown in Fig 4.11

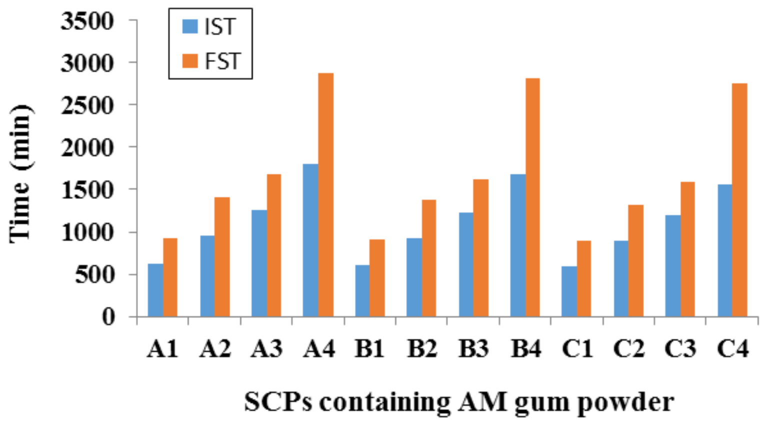

Figure 4.11 Vicat Setting Times of SCPs

Setting times of SCPs containing AM gum powder seems to be independent of the particle size of the AM gum powder. Though literature says that smaller particles required less time to set due to its increased hydration rate [22], the availability of water more than water demand in the matrix at smaller sizes due to decreasing water demand trend of AM gum powder prevents the early stiffening of the paste and it seems that setting times of AM gum powders are independent of the particle size of the AM gum powder at constant water to cement ratio of 27%.

Setting times also got delayed due to the carbohydrates content present in the AM gum in the form of polysaccharides for the particular size of AM gum powder. Carbohydrates are the main ingredients that retard the settings of cement paste by forming layer around the cement grains which results in slowing down the hydration process by preventing the contact of cement grains with the added water [20, 21]. Setting times might also be increased due to the nature of the SP which acts as retarder [7] and ultimately resulted in prolonged setting times.

4.8 Compressive Strength of SCP formulations

A total of seventy eight prisms, six prisms of each SCP formulation, having cross sections of 40mm x 40mm and a length of 160 mm were casted. The detailed dprocedure was mentioned in chapeter 3. The compressive strength was taken as the average of the two prisms at the respective test age. Fig. 4.12 showed the compressive strength of SCP samples subjected to air curing while Fig. 4.13 showed the compressive strength of SCP samples at the age of 7, 14 and 28 days after casting subjected to conventional water curing.

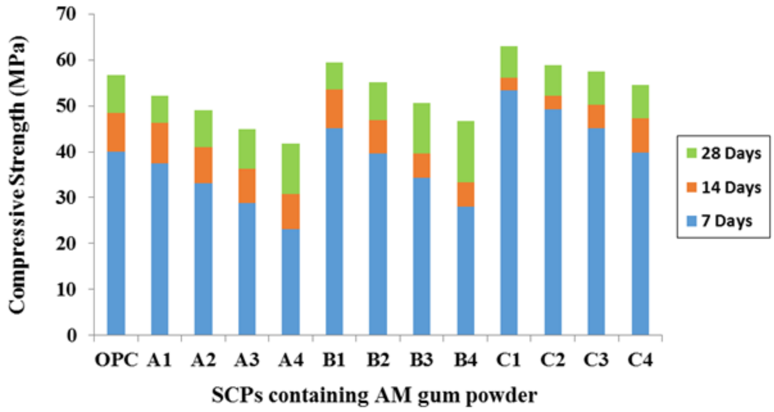

Figure 4.12 Compressive Strength of SCPs Subjected to Air Curing

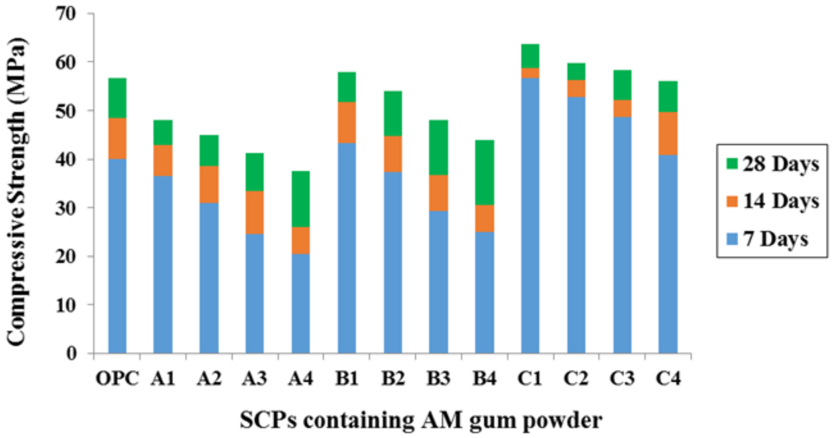

Figure 4.13 Compressive Strength of SCPs Subjected to Water Curing

Following observation can be made from the compressive strength figures.

1. Compressive strength decreases as the AM gum content increases for a particular average particle size (D50) of AM gum. Strength degradation can be associated with the air content which increases with increase in AM gum dosage resulting in weaker SCP matrix by enhancing the porosity of the system.
2. For average particle size of 307 micron, compressive strength of SCPs reduces about 8% for air cured samples and about 15% for water cured samples at the

age of 28 days, which was in accordance with the literature that AM reduces the strength of SCPs. [7, 31]

3. For average particle size of 135 micron, compressive strength of 0.25% AM content exceeds the compressive strength of OPC by 5% and 2.5% for air cured samples and water cured samples respctively.
4. For average particle size of 47.5 micron, OPC strength lacks behind for 0.25%, 0.5% and 0.75% AM dosage in SCP systems while at 1.0% AM dosage, it is almost equal for both air and water curing. About 12% and 13% stregth improvement was noted for air cured and water cured samples respectively containing 0.25% AM dosage as compare to control specimen at the age of 28 days. This might be due to improvement in fresh and harden paste densities of SCP systems containing AM gum powder.
5. It was also visible that air curing gives higher compressive strength as compare to water curing regime for particle sizes of 307 microns and 135 microns. The reason being the nature of AM gum which adsorbed water on its surface and releases it back to the cementitious matrix with the drop in relative humidity [31]. In this way, the internal relative humidity was maintained which leads to higher compressive strength.
6. Water curing regime gives almost the same compressive strength for average particle size of 47.5 micron due to drastic decrease in absorption capacity and air content of the AM gum. Water curing prevents the early escape of water from the matrix and ultimately leads to enhanced compressive strength of SCP systems.

4.9 Densities of SCPs and their Relevance with Compressive Strength

Both fresh and harden paste densities of the SCP formulations containing AM gum were measured. Fresh paste densities were measured within fifteen minutes after mixing while harden densities were measured at an age of 28 days with the help of prisms casted for determination of compressive strength. The fresh paste and harden densities at 28 days which are related to 28 days air cured compressive strength of SCPs and are shown in the Fig.4.14 and Fig. 4.15 respectively.

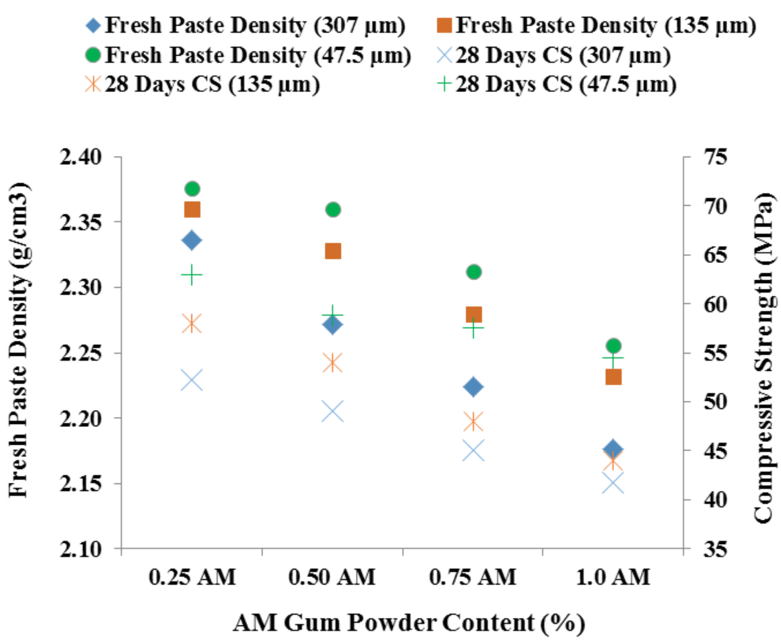

Figure 4.14 Fresh SCP densities and 28 Days Compressive strength of SCPs

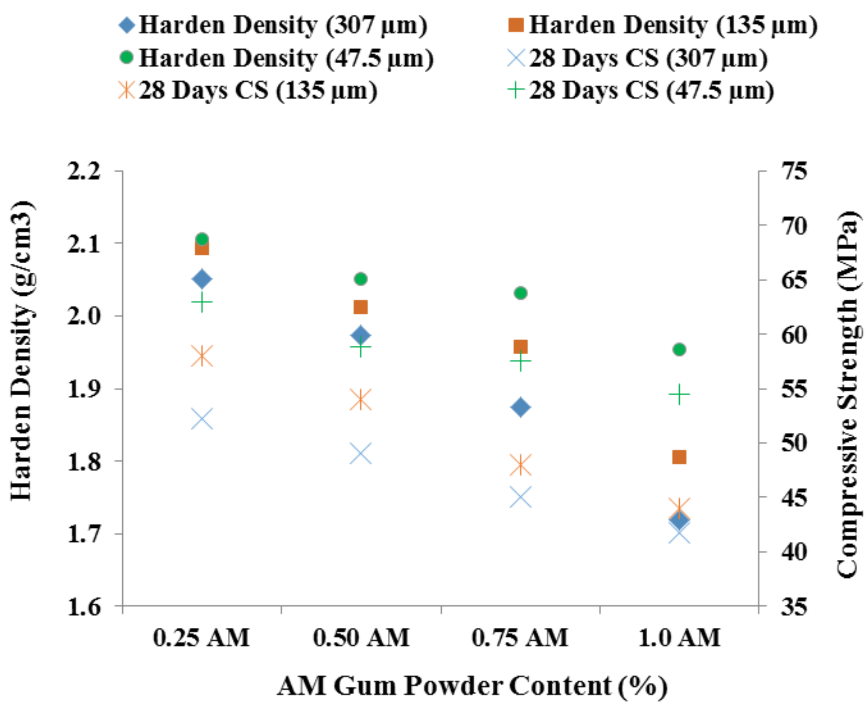

Figure 4.15 Harden SCP densities and compressive strengths at 28 Days

The entrainment of air content resulted in reduction of both fresh and hardens densities with the increase in AM gum content. Both densities got increased with the decrease in average particle size of AM gum due to reduction in the porosity of the SCP system. From Fig. 4.14 and Fig. 4.15 as the fresh and harden densities decreases, the corresponding compressive strength values also decreases and vice versa. Maximum strength was attained when the fresh and harden densities were maximum irrespective of dosage and particle size of AM gum powder.

4.10 Air content measurement of SCPs formulations

The air content of fresh SCPs was determined in the fresh state using Luftgehaltspruefer Testing equipment having 1 liter capacity using the pressure method. The results obtained through air content meter are shown in Fig. 4.16

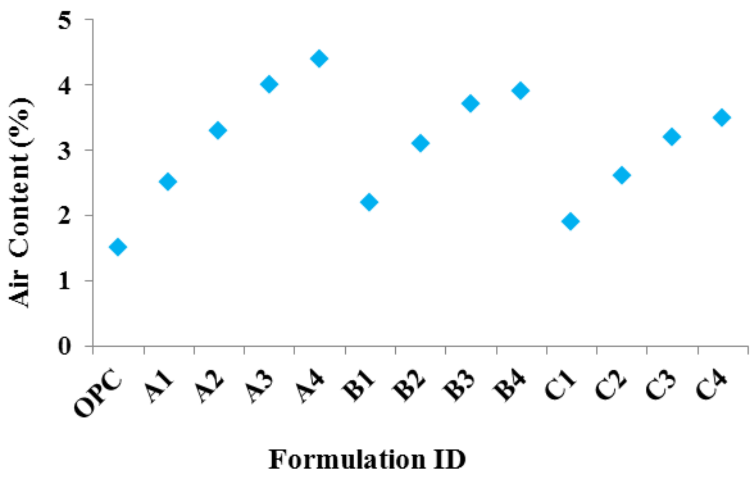

Figure 4.16 Air content of SCP formulations

Air content of the SCP formulations increases with the increase in the amount of AM gum which was in accordance with the postulate that most polysaccharide gums entrain air [23]. These air voids might be entrained during mixing process and were ultimately responsible for the reduction in the strength of SCPs.

Further, air content decreases with the decrease in the average particle size of AM gum, as shown in Fig. 4.16, due to better bonding with cement particles. Reduction in average particle size of AM gum powder brought it closer to the average particle size of cement which ultimately results in dense packed structure with minimum air entrapped in the matrix.

4.11 Absorption capacities of SCP formulations

Water absorption capacity of all the SCP formulations was determined using prisms casted for strength purposes. After demoulding prisms were marked, weighed and placed in water curing tank at laboratory temperature of 20±1 °C for curing. The samples were weighed again in SSD conditions after removing from curing tank at respective test age. The difference between the weights for each prism at a given age gave the water absorption in percent and that at 28 days was shown in the Fig.4.17.

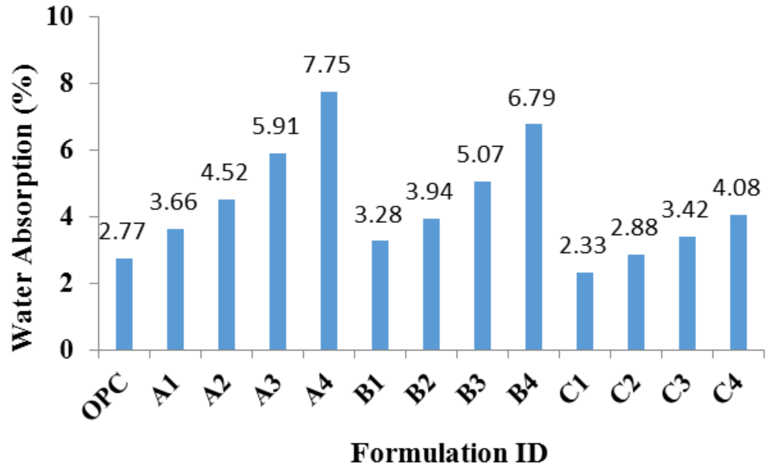

Figure 4.17 Water absorption capacities of SCPs

As the average particle size of AM gum decreased, water absorption capacity also decreased due to decrease in the internal voids and air content of SCP systems which resulted in denser packing of hydration products [24] as seen through SEM pictures. With the decrease in the size of AM gum, there will be fewer chances for the amides present in the AM gum powder to participate in hydrogen bonding with water which resulted in lesser solubility of AM gum powder as compared to the hydrocarbons [26].

Water absorption capacity also significantly increased at higher dosages of AM gum and can be indirectly related to the internal pore structure and to its connectivity. At higher dosages, AM gum powder entrains more air content [23] leading to loose packed matrix which resulted in increased water absorption of the SCP systems.

4.12 Shrinkage Response of SCP formulations

Linear shrinkage response of 10 SCP formulations having varying amount and particle size of AM gum powder were studied for the first 72 hours using modified German Schwindrine shrinkage apparatus of dimensions 4x6x25 cm^3 with a sensitivity of 0.31 microns. The recorded data of linear shrinkage is shown in Fig. 4.18.

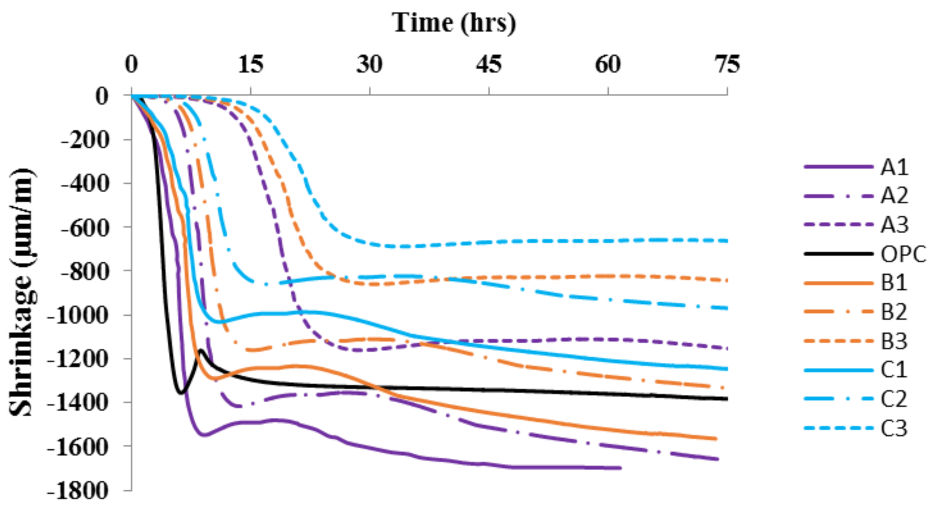

Figure 4.18 Shrinkage Response of SCPs formulations

Shrinkage at early ages affects the volume stability of cement based systems [25, 31]. Linear shrinkage reduced with a decrease in the particle size of the AM gum powder. It was observed that for average particle size of 307 microns, the peak shrinkage of AM gum powder based SCP formulations were about 14% higher as compared to control formulation. For average particle size of 135 microns, the peak shrinkage was about 7% lesser than control formulation while for average particle size of 47.5 microns; about 25% reduction in peak shrinkage was noted. The possible reasons for the reduction in shrinkage values could be the presence of water more than the Vicat demand of the SCP systems in the matrix and the internal curing nature of the AM gum powder. Higher growth of ettringite (hydration product) as seen through SEM images was also responsible for decrease in shrinkage of SCP systems.

It was also observed that shrinkage got reduced with the increase in AM gum content at particular size of AM gum powder in SCP systems and shrinkage peaks starts becoming flatter indicating that setting process got delayed [31]. The following could be the possible reasons for the reduction in shrinkage values.

- Presence of water more than the Vicat demand of the SCP systems.
- The internal curing nature of the AM gum powder.

4.13 Scanning Electron Microscopy of SCPs

Scanning Electron Microscopy (SEM) was carried out for the formulations A1 and A4 containing 0.25% and 1% AM with respect to weight of the cement at the age of 28 days for average particle size of 307 micron as shown in Fig. 4.19 and Fig. 4.20. SEM was also done for formulations C1 and C4 containing 0.25% and 1% AM with respect to weight of the cement at the age of 28 days for average particle size of 47.5 micron as shown in Fig. 4.21 and Fig. 4.22.

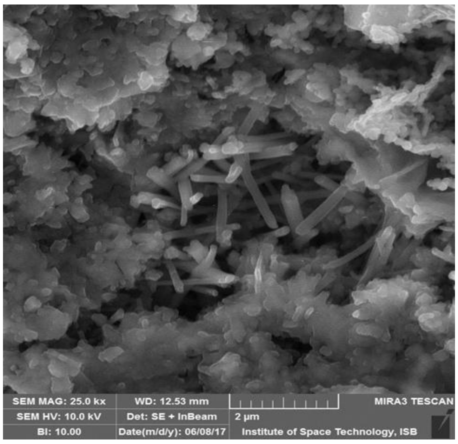

Figure 4.19 SEM imagery of formulation A1

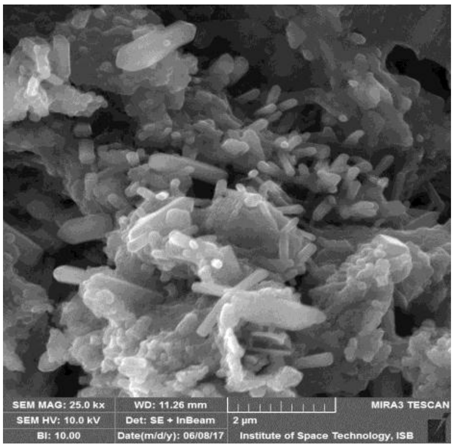

Figure 4.20 SEM imagery of formulation A4

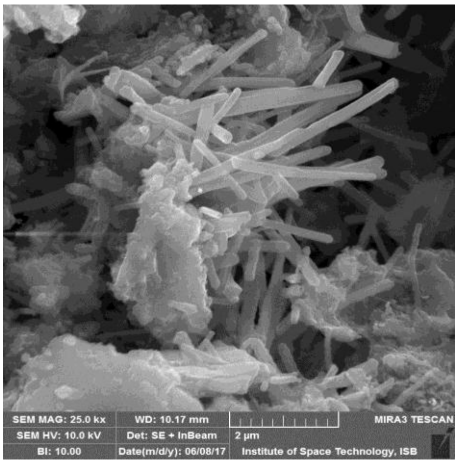

Figure 4.21 SEM imagery of Formulation C1

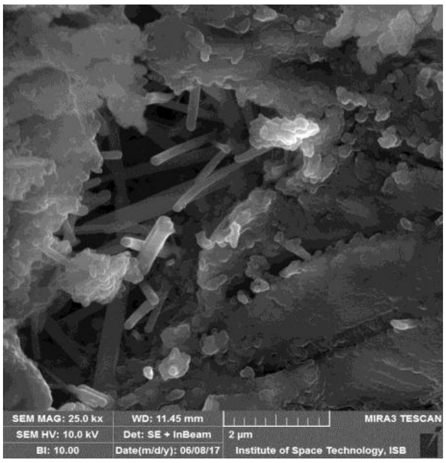

Figure 4.22 SEM imagery of formulation C4

From the SEM imagery, following observations can be made;

1. With the increase in the AM dosage for a particular size, the growth of hydration products was prevented, might be due to presence of polysaccrides that provide hindrance towards the growth of hydration products and hence responsible for the reduction in the compressive strength with the increase in the AM gum content.

2. Presence of black holes in SEM images shows that air content was more at higher dosages of AM gum and decreases with the decrease in the particle size of the AM gum powder .
3. Microstructure improved with the decrease in the average particle size of the AM gum powder which improves the densities of SCPs and ultimately results in higher compressive strength at 47.5 microns particle size as compare to particle size of 307 microns.
4. More ettringite growth was seen for average particle size of 47.5 microns as compare to 307 microns. This higher growth of hydration product was responsible for the reduction in the shrinkage of AM gum powder based SCP formulations with the decrease in average particle size of the AM gum powder.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Concluding Remarks

Average particle size of AM gum powder affects the fresh and hardens properties of SCPs to a great extent. With the decrease in the average particle size of AM gum powder, the water demand, viscosity, yield stress, Vicat setting times, water absorption capacity, air content and linear early shrinkage of SCPs were reduced while super-plasticizer (SP) demand, compressive strength, fresh and harden cement paste densities got increased. Water demand of SCPs containing AM gum powder decreases with decrease in particle size of AM gum powder due to increased filler effect while super-plasticizer demand increased due to increased internal friction and increased surface area of AM gum powder. Viscosities and yield stress of SCPs decreased with decrease in AM gum particle size because the highly branched polysaccharides may break loose and align themself in the direction of flow resulting in decreased viscosity and shear stress. Moreover higher void filling effect may produce slightly higher effective water content which may also be a reason. Strength degradation of AM gum powder based SCP formulations decreased by decreasing the particle size of the AM gum powder possibly due to enhanced confinement in the matrix. Almost 12% and 13% improvement in compressive strength was noted for average particle size of 47.5 microns for air cured and water cured samples respectively as compare to OPC based SCP system. While in comparison to average particle size of 307 microns, this improvement goes up to 20% and 25 % for air cured and water cured samples respectively. Improvement in compressive strength at smaller sizes was due to improvement in fresh paste and hardens densities of SCPs containing smaller sizes of AM gum particles. At particle size of 47.5 microns, both air and water curing regime gives almost similar compressive strength at 7, 14 and 28 days, so both curing regimes can be used at smaller particle sizes of AM gum powder. It was also observed that retardation effect of AM gum powder in SCPs is independent of average particle size of AM gum at constant w/c ratio of 27%. About 25% maximum shrinkage of SCPs got reduced by with average particle size of 47.5 microns of AM gum powder as compare to OPC. This can be either due to internal curing property of AM gum powder or due to higher ettringite growth at smaller sizes of AM gum powder.

5.2 Recommendations

- It is recommended to use AM gum powder in SCPs with particle size of 47.5µm for better workability, improved strength and reduced shrinkage.
- It is recommended not to use more than 0.5% dosage of AM gum powder in SCPs having particle size of more than 130µm. However, for particle size of around 50µm, one may use up to 1% AM dosage.
- AM gum powder is sensitive to mixing water temperature, so the effect of mixing water temperature should be evaluated to better understand the nature of the AM gum powder.
- Effect of particle size of AM gum powder should be studied for self-compacting mortar systems and self-compacting concrete systems.
- AM gum powder interaction with powdered super-plasticizer should be studied in detail to evaluate the mechanism of action of AM gum powder.
- SP were added in SCCs to improve packing, to reduce water demand, to increase flow, to reduce shrinkage and to increase durability. AM gum powder possess all these properties, so details studies should be carried to check whether AM can be used as a super-plasticizer.

REFERENCES

[1] ACI Committee 237, Self-Consolidating concrete, Farmington Hills, Mich, 2007.

[2] Mebrouki A. Belas N. Bouhamou N., Experimental Plans method to formulate a self-compacting cement paste. Materials and Technology, Volume 44, Pages 13-20, 2010

[3] Building code requirements for structural concrete (ACI 318-14) and commentary. Article 2.3, ACI, Farmington Hills, United States

[4] John Buekett, International Admixtures Standards, Cement and Concrete Composites, 20 (1998) 137 - 140, Elsevier.

[5] European Guidelines for Self-compacting Concrete , 2005

[6] Jilani, Seemal. Isolation and Structural studies of Acacia gum exudates from the species of Gummiferae. Diss. University of the Punjab, Lahore, 1997.

[7] S.A. Rizwan, Wajahat Latif, and Thomas A. Bier. Response of self-consolidating cement paste systems containing Acacia Nilotica Gum as an organic admixture. Construction and Building Materials 126 (2016): 768-776.

[8] M. A. Montenegro, M. L. Boiero, L. Valle and C. D. Borsarelli, "Gum Arabic: More than an edible emulsifier," in Products and Applications of Biopolymers, Dr. Johan Verbeek (Ed.), InTech, 2012, pp. 1-26.

[9] J.B. Lambert, S.A. Guruswamy-Thangavelu, The Role of Silicates in the Synthesis of Sugars Under Prebiotic Conditions, Bio-Inspired Silicon-Based Materials, Springer2014, pp. 19-25.

[10] DIN, EN. "196-1" Methods of testing Cement-Part 1, 2005.

[11] Cement, A. "ASTM C150, Type I-Normal Portland type. 1.", 2007.

[12] "DIN EN 196-3, Methods of testing cement - Part 3: Determination of setting time and soundness," CEN, Brussels, 2005.

[13] J. DeRuiter, Halogenated Hydrocarbon Structure and Chemistry, Principles Of Drug Action 1, (2005) 1-10.

[14] H. Warson, C.A. Finch, Applications of Synthetic Resin Latices, Latices in Diverse Applications, 3 (2001) 1667.

[15] A.E. Segneanu, I. Gozescu, A. Dabici, P. Sfirloaga, Z. Szabadai, "Organic Compounds FT-IR Spectroscopy", Edited by Jamal Uddin, (2012) 145-164.

[16] Y. Chang, Y. Hu and D. J. M., "Competitive adsorption and displacement of anionic polysaccharides (fucoidan and gum arabic) on the surface of protein-coated lipid droplets," Food Hydrocolloids, vol.52, pp. 820-826, 2016.

[17] R. Pei and S. W. Jun Liu, "Use of bacterial cell walls as a viscosity-modifying admixture of concrete," Cement & Concrete Composites, vol. 55, p. 186–195, 2015.

[18] K. H. Khayat, "Viscosity-Enhancing Admixtures for Cement-Based," Cement and Concrete Composites, vol. 20, pp. 171-188, 1998.

[19] A.W. Saak, H. Jennings. and S.P. Shah.," New methodology for designing self-compacting concrete," ACI materials journal, Vol. 98, no. 6, pp 429-439, 2001.

[20] Hasan Yildirim and Baris Altun, Usage of molasses in concrete as water reducing and retarding admixtures, Indian Journal of Engineering and Materials Science, Volume 19, Pages 421-426, December 2012.

[21] Maria C. Garci Juenger, Hamlin M. Jennings, New insights into the effects of sugar on the hydration and microstructure of cement pastes, Cement and Concrete Research, Volume 32, Issue 3, Pages 393– 399, March 2002.

[22] Bentz, Dale P., Edward J. Garboczi, Claus J. Haecker, and Ole M. Jensen. "Effects of cement particle size distribution on performance properties of Portland cement-based materials." Cement and Concrete Research 29, no. 10 pp 1663-1671, 1999

[23] R. Mbugua, R. Salim and J. Ndambuki, "Effect of Gum Arabic karroo as a Water-Reducing Admixture in Concrete," Materials, vol. 9, no. 80, 2016.

[24] L.Y. Cheng, X.Q. Chun, M.Z. Jin, H.X. Wang, Unusual Morphology of Calcium Carbonate controlled by Amino acids in Agrarose gel. J. Chil. Chem. Soc., Volume 55, 2010.

[25] S.A. Rizwan, High-performance mortars and concrete using secondary raw materials, Ph.D. Thesis Technical Universität Bergakademie Freiberg, Germany, (2006), pp. 161.

[26] J. DeRuiter, Amides and related functional groups, Principles of Drug Action, 1 (2005),pp 1-16.

[27] P. K. Mehta and P. J. M. Monteiro, "Concrete: microstructure, properties, and materials", 3rd Edition, Chapter 2, pp. 21-44, 2006.

[28] R.M. Daoub, A.H. Elmubarak, M. Misran, E.A. Hassan, M.E. Osman, Characterization and functional properties of some natural Acacia gums, Journal of the Saudi Society of Agricultural Sciences, (2016) 1-9.

[29] Afshan NAZ, Syed Ali Rizwan, Naveed Z. Ali, Thomas A. Bier and Hameed Ullah, "Using Carbon Nanotubes in Self-compacting Paste Systems", Construction Materials and Structures, p 40

[30] Anthony Babcock, Peter Taylor, "Impacts of Internal Curing on Concrete Properties", A report from National Concrete Pavement Technology Center, Iowa State University, 01-2015, p 1 – 3

[31] Neha Mahmood, "Response of self-Compacting Paste (SCP) systems containing Acacia Modesta Gum", MS-Structure Dissertation, NUST, (2017) pp 15-40

APPENDIX

Table A-1: Water Demand of SCPs

Water Demands				
Serial No.	AM (%)	307 µm (%)	135 µm (%)	47.5 µm (%)
1	0.0 AM	27	27	27
2	0.25 AM	27	27	26
3	0.50 AM	26.5	26	25
4	0.75 AM	26	24	23.5
5	1.0 AM	25	23	22

Table A-2: SP demand, Viscosity and Yield Stress of SCPs

AM (%)	307 µm			135 µm			47.5 µm		
	SP (%)	T25 (sec)	T30 (sec)	SP (%)	T25 (sec)	T30 (sec)	SP (%)	T25 (sec)	T30 (sec)
0.0 AM	0.19	2.89	11.49	0.19	2.89	11.49	0.19	2.89	11.49
0.25 AM	0.32	3.42	19.84	0.35	2.26	8.24	0.37	1.58	5.08
0.50 AM	0.38	4.12	23.65	0.43	3.42	11.67	0.45	2.82	9.11
0.75 AM	0.48	4.84	25.46	0.53	3.93	13.82	0.56	3.52	11.66
1.0 AM	0.57	5.28	27.12	0.66	4.48	15.24	0.70	3.98	13.52

Table A-3: Setting Times of SCPs

Setting Times							
Serial No.	AM (%)	307 µm		135 µm		47.5 µm	
		IST (hrs)	FST (hrs)	IST (hrs)	FST (hrs)	IST (hrs)	FST (hrs)
1	0.0 AM	180	300	180	300	180	300
2	0.25 AM	630	930	615	915	600	900
3	0.50 AM	960	1410	930	1380	900	1320
4	0.75 AM	1260	1680	1230	1620	1200	1590
5	1.0 AM	1800	2880	1680	2820	1560	2760

Table A-4: Air Content measurement of SCPs

Air Content				
Serial No.	AM (%)	307 µm (%)	135 µm (%)	47.5 µm (%)
1	0.0 AM	1.5	1.5	1.5
2	0.25 AM	2.5	2.2	1.9
3	0.50 AM	3.3	3.1	2.6
4	0.75 AM	4.0	3.7	3.2
5	1.0 AM	4.4	3.9	3.5

Table A-5: Rheological Properties (Viscosity in cP)

Rheological Properties (Viscosity in cP)										
Serial No.	AM (%)/Shear Rate	307 µm			135 µm			47.5 µm		
		20.4	27.2	34	20.4	27.2	34	20.4	27.2	34
1	0.0 AM	852	801	725	852	801	725	852	801	725
2	0.25 AM	652.7	570	537.5	621.5	519.5	470.8	518	378.1	332.1
3	0.50 AM	680	608	551	650	531.6	479.5	550	401.2	345.6
4	0.75 AM	800	652	573.5	712	568.1	491	649	468	380
5	1.0 AM	920	827.6	766.7	816	691	632.5	760	628.5	566.7

Table A-6: Fresh Paste Densities of SCPs

		307 µm		135 µm		47.5 µm	
AM (%)	Fresh paste volume	Fresh paste weight	Fresh Density	Fresh paste weight	Fresh Density	Fresh paste weight	Fresh Density
	(cm3)	(g)	(g/cm3)	(g)	(g/cm3)	(g)	(g/cm3)
0.00 AM	125	292	2.34	292	2.34	292	2.34
0.25 AM	125	292	2.34	295	2.36	297	2.38
0.50 AM	125	284	2.27	291	2.33	295	2.36
0.75 AM	125	278	2.22	285	2.28	289	2.31
1.00 AM	125	272	2.18	279	2.23	282	2.26

Table A-7: Harden Densities of SCPs at 28 Days

		307 µm		135 µm		47.5 µm	
	Harden volume (cm3)	Harden weight (g)	Harden Density (g/cm3)	Harden weight (g)	Harden Density (g/cm3)	Harden weight (g)	Harden Density (g/cm3)
0.00 AM	256	508	1.98	508	1.98	508	1.98
0.25 AM	256	525	2.05	536	2.09	539	2.11
0.50 AM	256	505	1.97	515	2.01	525	2.05
0.75 AM	256	480	1.88	501	1.96	520	2.03
1.00 AM	256	440	1.72	462	1.80	500	1.95

Table A-8: Absorption capacity of SCPs at 28 Days

	307 µm			135 µm			47.5 µm		
	Demoulding weight (g)	SSD weight (g)	Absorption capacity (%)	Demoulding weight (g)	SSD weight	Absorption capacity (%)	Demoulding weight (g)	SSD weight	Absorption capacity (%)
0.00 AM	505	519	2.77	505	519	2.77	505	519	2.77
0.25 AM	519	538	3.66	518	535	3.28	557	570	2.33
0.50 AM	509	532	4.52	507	527	3.94	556	572	2.88
0.75 AM	508	538	5.91	493	518	5.07	555	574	3.42
1.00 AM	503	542	7.75	501	535	6.79	515	536	4.08

Table A-9: Compressive Strength of SCPs

		307 µm		135 µm		47.5 µm	
		AC (Mpa)	WC (Mpa)	AC (Mpa)	WC (Mpa)	AC (Mpa)	WC (Mpa)
7 Days	0.00 AM	---	40.0	---	40.0	---	40.0
	0.25 AM	37.5	36.6	45.2	43.4	53.3	56.7
	0.50 AM	33.2	30.9	39.6	37.3	49.3	52.8
	0.75 AM	28.8	24.7	34.4	29.3	45.2	48.8
	1.00 AM	23.1	20.4	28.0	25.0	39.8	40.9
14 Days	0.00 AM	---	48.5	---	48.5	---	48.5
	0.25 AM	46.3	43.0	53.5	51.7	56.1	58.8
	0.50 AM	41.1	38.7	46.9	44.8	52.3	56.2
	0.75 AM	36.4	33.4	39.6	36.8	50.2	52.2
	1.00 AM	30.8	26.0	33.3	30.6	47.2	49.6
28 Days	0.00 AM	---	56.6	---	56.6	---	56.6
	0.25 AM	52.3	48.1	59.5	58.0	61.0	63.6
	0.50 AM	49.0	44.9	55.1	54.1	58.8	59.7
	0.75 AM	45.0	41.2	50.6	48.0	57.5	58.3
	1.00 AM	41.8	37.6	46.8	44.0	54.5	56.0