BIO STABILIZATION FOR GEOPOLYMER ENHANCEMENT AND MINE TAILINGS DUST CONTROL

By

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DEDICATION

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ABSTRACT

The first part of the thesis investigates the enhancement of fly ash-based geopolymer with alkali pretreated sweet sorghum fiber. The unconfined compression, splitting tensile and flexural tests were conducted to investigate the mechanical properties of geopolymer composite. The results indicate that the inclusion of sweet sorghum fiber slightly decreases the unconfined compressive strength (UCS), however, the splitting tensile and flexural strengths as well as the post-peak toughness increase with the fiber content up to 2% and then decrease thereafter. A durability test program containing 10 wet/dry cycles was performed to evaluate the long-term performance of the geopolymer composite related to wet/dry cycling. The results indicate that both the UCS and the splitting tensile strength of the geopolymer composite progressively decrease with the number of wet/dry cycles.

The second part of the thesis investigates the utilization of biopolymers to stabilize MT for dust control. First, a fall cone method was adopted to evaluate the Atterberg limits and undrained shear strength of MT stabilized with biopolymers. The results indicate that the inclusion of biopolymers increases both the liquid limit and the undriained shear strength of MT. Two new equations are proposed for predicting the undrained shear strength of MT based on liquid limit and water content, and liquidity index. Second, an experimental program including moisture retention, wind tunnel and surface strength tests was performed to evaluate the effectiveness of biopolymer stabilization for dust control. The results indicate that biopolymers are effective in enhancing the moisture retention capacity, improving the dust resistance, and increasing

the surface strength of MT. Third, a durability test program containing 10 wet/dry cycles was applied to MT samples treated with biopolymer solutions of different concentrations. The results show that the dust resistance of MT samples progressively decreases with the number of wet/dry cycles. Finally, experimental and numerical studies on the unconfined compressive strength (UCS) of MT stabilized with biopolymer were carried out. It is found that inclusion of biopolymer into MT favors the increase of adhesion between MT particles and thus the increase of the UCS of MT.

CHAPTER 1
INTRODUCTION

1.1 GENERAL

Growing environmental concerns and the awareness to ensure sustainability have stimulated the interest of using biomaterials in civil engineering. For example, extensive research has been conducted on utilization of different kinds of natural fibers to reinforce cement based materials in recent decades. Some natural fiber-cement composites are considered excellent alternatives to hazardous asbestos and have found practical applications (Jarabo et al. 2013). Another bio-application in civil engineering is the use of microorganisms-induced bio-cementation and bio-plugging to improve problematic soils for engineering purpose (Ivanov and Chu 2008). The use of biomaterials in civil engineering is expected to improve environmental friendliness with less energy consumption and carbon dioxide neutrality. This thesis investigates the utilization of biomaterials in civil engineering with focus on two topics: natural fiber enhancement of geopolymer and biopolymer stabilization of mine tailings (MT) for dust control.

1.2 SCOPE AND OBJECTIVE OF RESERACH

The main objective of this research is to study the feasibility of using (1) natural fiber to enhance fly ash-based geopolymer, and (2) biopolymer to mitigate MT dust, with

the aim to promote sustainability and environmentally benign practice. The research takes a multi-scale and multi-disciplinary approach.

For the enhancement of geopolymer with natural fiber, the research includes:

(1) Treatment of natural fiber, sweet sorghum bagasse, to improve its effectiveness in enhancing the geopolymer.

(2) Unconfined compression, splitting tensile and flexural tests to investigate the mechanical properties of sweet sorghum fiber enhanced geopolymer.

(3) Durability tests to study the durability of sweet sorghum fiber enhanced geopolymer.

The research on biopolymer stabilization of MT for dust control includes:

(1) Fall cone test to evaluate the increase of undrained shear strength (s_u) of MT due to biopolymer stabilization.

(2) Moisture retention test to evaluate the enhancement of water retention capacity of MT after biopolymer stabilization.

(3) Wind tunnel test to study the increase of dust resistance of MT after biopolymer stabilization.

(4) Penetration test to evaluate the increase of surface strength of MT after biopolymer treatment.

(5) Durability test to study the long-term effectiveness of biopolymer stabilization of MT.

(6) Micro/nano-scale and chemical investigations to study the evolvement of microstructure and chemical composition of biopolymer stabilized MT.

(7) Numerical modeling to link macro-scale properties and micro/nano-scale characteristics to better understand the stabilization of MT with biopolymer.

1.3 ORGANIZATION OF THE THESIS

The research presented in this thesis starts with **Chapter 1**, the Introduction to the research project, followed by two major parts. The first part presents the investigation of bio-stabilization for geopolymer enhancement and includes **Chapters 2** and **3**. The second part presents the study of biopolymer stabilization for MT dust control and includes **Chapters 4**, **5**, and **6**. The final chapter of this thesis presents the major conclusions and describes the future work.

Chapter 2 is a literature review of natural fiber enhancement of cementitious materials. Special attention is paid to studies of fiber reinforced geopolymer and the pretreatment of natural fiber to enhance the durability of natural fiber reinforced composites.

Chapter 3 presents a study of utilizing sweet sorghum fiber to enhance the mechanical properties of fly ash-based geopolymer. The effects of incorporation of sweet sorghum fiber on the unit weight, unconfined compression strength, splitting tensile strength, flexural strength and post-peak toughness of fly ash-based geopolymer are

presented and discussed. The durability of the sweet sorghum fiber reinforced geopolymer related to wet/dry cycles is also presented in this chapter.

Chapter 4 describes the study of using two natural biopolymers, xanthan gum and guar gum, to enhance the undrained shear strength of MT. A fall cone method was adopted in this study to investigate the effect of biopolymers on the Atterberg limits and undrained shear strength of MT. The underlying mechanisms of how biopolymers improve the undrained shear strength of MT are also discussed based on SEM images. Two new equations for predicting the undrained shear strength of MT are proposed.

Chapter 5 presents an extensive experimental program to evaluate the performance of biopolymer stabilization for MT dust control, including moisture retention, wind tunnel, surface strength and durability (wet/dry cycling) tests, and SEM imaging.

Chapter 6 describes the experimental and numerical studies of the UCS of MT stabilized with biopolymer solutions of different concentrations.

Chapter 7 summarizes the conclusions of all the carried out studies. Recommendations for future work are also presented.

PART I

BIO-STABILIZATION FOR GEOPOLYMER ENHANCEMENT

The utilization of different types of manmade fibers to reinforce brittle cementitious materials has been of great interest for a long time. However, the manmade fibers are either derived from petroleum-based sources or produced by energy intensive processes with high cost and low environmental compatibility. Natural fibers appear to be a great replacement to the manmade fibers in reinforcing cementitious materials. In **Chapter 2**, the use of different types of natural fibers to reinforce cement based materials is reviewed, with a focus on the enhancement of geopolymer, an emerging cementitious material with superior properties to cement. In **Chapter 3**, an experimental study on utilization of sweet sorghum fiber to enhance fly ash-based geopolymer is presented.

CHAPTER 2

NATURAL FIBER ENHANCEMETN OF CEMENTITOUS MATERIALS – A REVIEW

2.1 INTRODUCTION

Cement based construction materials are widely used worldwide, which are well-known for their high compressive strength and low tensile strength. The brittleness makes the cementitious materials very sensitive to crack initiation and propagation. This disadvantage can be overcome by incorporation of fiber reinforcement, which can bridge across the cracks, if any, providing enhanced tensile strength and post-peak toughness. The use of dispersed fibers to strengthen brittle building materials can be dated back to 2000 B.C., when horse hair, straw or other organic materials were used to reinforce the clay sun-dry bricks, called Adobe (Brandt 2008; Galán-Marín et al. 2010). Modern concept of fiber reinforced concrete (FRC) developed in the 1960s and 1970s has brought great research interests worldwide (ACI 1996; Romualdi and Batson 1963; Romualdi and Mandel 1964). Cementitious materials reinforced with manmade fibers such as steel fiber, glass fiber, and synthetic fibers including carbon fiber and polyvinyl alcohol (PVA) fiber, have been intensively investigated and promising results have been obtained (Brena et al. 2003; Mangat 1976; Shah et al. 1988; Swamy and Mangat 1975; Wang et al. 1990; Zollo 1997). However, these fibers are derived from either petroleum-based sources or

produced by a highly energy intensive process with high cost and low environmental compatibility. Besides, how to deal with these fibers at the end of their life cycles is seriously concerned because they are stable within the matrix and are non-degradable (Herrmann et al. 1998; Pacheco-Torgal and Jalali 2011). Growing environmental awareness and the interest to ensure long-term sustainability are the driving force for seeking environmentally benign alternatives to manmade fibers. Recent years have witnessed a growing interest in the use of natural fibers as reinforcements in cemetitious materials because they are abundantly available, renewable, and environmentally friendly. Compared to the traditional manmade reinforcing fibers, natural fibers have advantages such as low density, high specific strength, low cost, biodegradability, enhanced energy recovery, and CO_2 neutrality (Chen et al. 2014; Faruk et al. 2014). Although the natural fibers can be subdivided into plant, animal and mineral fibers, this study mainly focuses on the plant fiber and its composite. Hereafter, the term natural fiber used in this thesis is only limited to plant fiber. So far researchers have studied sisal, cotton stalk, coconut, bamboo, Caesar weed, banana and rice straw fibers, just list a few, to reinforce cementitious materials and very promising results have been obtained – see next section for more detailed review.

2.2 LITERATURE REVIEW

2.2.1 Reinforcement of cement based materials with natural fibers

Researchers have studied the utilization of different natural fibers to reinforce cement based cementitious materials. Pacheco-Torgal and Jalali (2011) did an excellent review of the related research. Mansur and Aziz (1982) conducted an investigation on the mechanical properties of cement paste and mortar reinforced with jute fiber. The experimental results showed that inclusion of jute fiber in cement-based composite imparted significant increase in flexural toughness, tensile, flexural and impact strengths, but had very little influence on the compression strength. In a separate study (Mansur and Aziz 1983) they found that the inclusion of bamboo mesh also significantly increased the ductility, toughness, and tensile, flexural and impact strengths of cement mortar. Utilization of water sealing agent could effectively overcome the high water absorption of bamboo and improve the bonding strength. Al-Oraimi and Seibi (1995) conducted an experimental study on high strength concrete reinforced respectively with glass fibers and natural fibers extracted from palm tree leaves. The natural fibers used in this study were not pretreated. The results showed that the incorporation of fibers into plain concrete marginally decreased the compressive, flexural and split tensile strengths but improved the toughness and impact resistance. The natural fibers were comparable with the glass fibers in enhancing the performance of plain concrete. Yue et al. (2000) studied the properties and microstructure of cotton stalk reinforced cement/steel slag composites. The results indicated that the mechanical properties of the composites were effectively

improved by including the cotton stalk fibers pretreated with urea-formaldehyde resin. Savastano Jr et al. (2003b) performed an investigation on both OPC- and granulated blast furnace slag (BSF)-based composites reinforced respectively with Eucalyptus grandis kraft pulp, sisal, and banana fibers. The sisal and banana fibers were pretreated using mechanical and kraft pulping procedures. The results indicated that the fracture toughness of both the OPC- and BSF-based composites increased with the inclusion of fibers. The water absorption also increased with the inclusion of fibers. Ramakrishna and Sundararajan (2005) investigated the impact behavior of cement mortar slab reinforced with four different natural fibers, namely coir, sisal, jute, and hibiscus cannebinus, using a simple projectile test. No treatment of the fiber was reported in the study. The experimental results revealed that the presence of the natural fibers increased the impact resistance 3-18 times compared to the plain cement mortar slabs. Kriker et al. (2005) carried out a study on the mechanical properties and microstructure of date palm fiber-reinforced concrete cured in water and in a hot-dry climate. It was found that the increase of the length and volume fraction of fibers in both water and hot-dry climate favored the increase of the post-crack flexural strength and the toughness coefficients, but decreased the first crack and compressive strength. They also found that water curing helped to decrease the global degree of the voids and crack with aging while hot-dry climate increased it. Reis (2006) conducted a series of comparative experiments on epoxy polymer concrete reinforced with coconut, sugar cane bagasse, and banana fibers. The fibers were used as recycled waste without any kind of pre-treatment. The results showed that the coconut and sugar cane bagasse increased both fracture toughness and fracture

energy of the polymer concrete, but the banana pseudostem only increased the fracture energy. Li et al. (2004) and Li et al. (2006) studied four variables that influenced the mechanical properties of hemp fiber reinforced concrete, which were (1) mixing methods (dry and wet), (2) fiber content by weight, (3) aggregate size, and (4) fiber length. The hemp fiber was retted using NaOH solution at 120 ℃ for 40 minutes and was followed by a fresh bath rinse. The results showed that the fiber content had the largest effect. Under the optimum conditions, the compressive strength increased by 4%, the flexural strength increased by 9%, the flexural toughness increased by 144%, and the flexural toughness index increased by 214%. Peters et al. (2010) conducted a study on cellulose fiber reinforced concrete using splitting tensile and notched-beam tests. The cellulose fibers were pretreated using a chemical pulping process. It was reported that 3% microcellulose by weight of cement provided the greatest increase of fracture toughness.

The fiber cement composites invented by the so called Hatscheck technology in the late 19^{th} century have been commercially used as construction materials for non-structural purposes such as roofing, fencing, decking, etc. Initially, the fiber used in those composites was asbestos, which was prohibited in the 1980s due to its great threat to human health. Natural fibers, great alternatives to asbestos, which are abundantly available in many developing countries, have led to burgeoning research interests in development of low cost cement fiber composites. Cook et al. (1978) reported the use of randomly distributed short coir fiber reinforced cement composite for roofing and pointed out that the composite had adequate short term durability, but information was required to evaluate its long term performance. The authors concluded that the composite could be a

low cost alternative to asbestos cement sheet on a material cost basis. Savastano Jr et al. (1999) investigated the composites of blast furnace slag (BFS)-based cement mortar reinforced with vegetable fibers for producing roofing components. The results indicated that the composites reinforced with eucalyptus pulp, coir or eucalyptus pulp combined with sisal fibers showed desirable physical and mechanical performance. Mansour et al. (2007) reported an effort in development of straw-cement composite material for low-cost housing in Egypt. The authors concluded that, instead of burning the straw that would induce serious air pollution and respiratory and cardio-vascular illnesses, recycling it with a mixture of cement could not only produce a low cost building material achieving sustainable development, but reduce air pollution. Roma Jr et al. (2008) evaluated the mechanical, physical and thermal performance of cement-based tiles reinforced with sisal and eucalyptus fibers. They pointed out that the mechanical properties of the composites experienced a severe reduction after exposure to tropical climate. After four months of age under weathering, the toughness of the composites retained only 53-68% of the original. Khorami and Ganjian (2011) carried out a study of utilization of agricultural waster fibers included bagasse, wheat and eucalyptus fibers to produce fiber cement boards. It was found that the maximum flexural strength increased with increasing fiber content from 2% to 4% by weight of cement. The reinforced fibers showed a satisfactory consistency with cement paste. Jarabo et al. (2013) performed an investigation of using corn stalk as reinforcement to produce fiber-cement for roofing using a NaOH-anthraquinone technique. It was found that the best pulping process was cooking the corn

stalk in 10% NaOH solution at 140^{o}C for 30 minutes, resulting in final products with improved mechanical properties.

2.2.2 Natural fiber enhancement of geopolymer

Currently, the mainly used cementitious material is ordinary Portland cement (OPC). Every year more than 1 m^3 of concrete is produced per person in the world (Scrivener and Kirkpatrick 2008). However, the utilization of OPC imposes an enormous impact on the environment. The manufacturing of OPC not only consumes significant amount of natural materials and energy but also releases substantial quantity of greenhouse gases. To produce 1 ton of OPC, about 1.5 tons of raw materials is needed and 1 ton of CO_2 is released into the atmosphere (Davidovits 1994). Worldwide, the cement industry alone is estimated to be responsible for about 5-8% of all CO_2 generated (Huntzinger and Eatmon 2009; Scrivener and Kirkpatrick 2008). Another drawback of OPC is that it may not provide the required properties for specific applications, such as rapid development of mechanical strength and high resistance to chemical attack (Davidovits 2008).

Recently, a new type of “cement”, called geopolymer or inorganic polymer, has attracted the attention of many research groups. Geopolymer is a type of cementitious material which is generated from solid aluminosilicate oxides in chemical reaction with an alkali metal solution at ambient or slightly elevated temperatures. The raw material used to produce geopolymer can be obtained from natural sources such as kaolin and volcanic ash or from industrial by-products such as fly ash, blast furnace slag and mine

tailings. Geopolymer not only provides performance comparable to OPC in many applications, but has many additional advantages, including rapid curing, high acid resistance, excellent adherence to aggregates, immobilization of toxic and hazardous materials, and significantly reduced energy usage and greenhouse gas emissions. These characteristics have made geopolymer of great research interest as an ideal material for sustainable development (Ahmari and Zhang 2012,2013; Bakharev et al. 2003; Davidovits 2008; Duxson et al. 2007; Shi and Fernandez-Jimenez 2006; Van Jaarsveld et al. 1997; Zhang 2013; Zhang et al. 2011).

As OPC, however, geopolymer exhibits brittle behavior with low tensile strength and is sensitive to cracking (Zhang et al. 2010; Zhao et al. 2007). These shortcomings not only impose constraints in structural design, but also affect the long term durability of structures (Pernica et al. 2010; Zhao et al. 2007). To overcome the aforementioned disadvantages, different micro- and macro-fibers have been used to reinforce geopolymer cementitious materials. For example, Zhao et al. (2007) used plain woven stainless steel mesh to reinforce geopolymer and showed that the failure mode of the steel fiber reinforced composite could shift from brittle to ductile. Sun and Wu (2008) studied the mechanical behavior of PVA fiber reinforced fly ash geopolymer by investigating its splitting tensile strength, and demonstrated that 1% of fibers was the optimum fiber content that can significantly improve the ductility of the composite. He et al. (2010) investigated the thermal and mechanical properties of carbon fiber reinforced geopolymer and found that the mechanical properties of the reinforced composite had great improvement when heated at a temperature from 1100 to 1300 ℃. Li and Xu (2009a,b)

investigated the impact mechanical properties of basalt fiber reinforced geopolymer concrete using a 100 mm-diameter splitting Hopkinson pressure bar system. They revealed that the addition of basalt fiber can significantly improve the deformation and energy absorption properties of geopolymer concrete. However, as mentioned before, these currently studied fibers are all produced by a high energy-consuming process and there is serious concern about how to do with these materials at the end of their life cycle (Herrmann et al. 1998; Pacheco-Torgal and Jalali 2011).

To date, very little research has been conducted on utilization of natural fibers to reinforce geopolymer. Teixeira-Pinto et al. (2007) studied the utilization of jute fiber to reinforce metakaolin-based geopolymer. The results indicate that raw jute fabric, without any chemical treatment, can be used together with the geopolymer to produce a composite with good mechanical and fire resistance properties. Alomayri et al. (2013) studied the physical, mechanical and fracture behavior of fly-ash based geopolymer reinforced with cotton fibers. The results show that the appropriate addition of cotton fibers can improve the mechanical properties of geopolymer composites. Alzeer and MacKenzie (2012) investigated metakaolin-based geopolymer reinforced with unidirectional natural protein-based fibers (carpet and Merino wool). They found that the presence of fibers increased the flexural strength of the composites by approximately 40% compared to the unreinforced matrix. A recent study also by Alzeer and MacKenzie (2013) on metakaolin-based geopolymer reinforced with natural cellulose-based fibers showed that the flexural strength of plain matrix dramatically increased from 5.8 MPa to about 70MPa with 10 vol.% fiber reinforcement.

2.2.3 Pretreatment of natural fiber to improve durability of natural fiber-reinforced composites

The structure of a single fiber is similar to a microscopic tube, in which several cell walls surround a central lumen (Thomas et al. 2011). The lumen is believed to be responsible for the high water absorption behavior of natural fibers. The cell walls of a single natural fiber mainly comprise cellulose, hemicellulose, lignin, pectins, and waxes. Cellulose which provides mechanical strength to the fiber is resistant to strong alkali. The tensile strength and Young's modulus of natural fibers are believed to increase with increase of the cellulose content (John and Thomas 2008). The hemicellulose is the cementing matrix that binds the cellulose microfibrils together resulting in a cellulose/hemicellulose network, which is considered to be the major structural component of the fiber cell (Thomas et al. 2011). Hemicellulose is very hydrophilic and can be easily dissolved in alkali (John and Thomas 2008). Lignin is also a cementing agent binding the cellulose microfibrils, which provides rigidity to the fiber. Lignin is naturally hydrophobic but it is soluble in hot alkali (Mishra et al. 2004).

Although it is very promising for utilization of natural fibers to enhance cementitious materials, a major concern is the durability. The alkaline pore water in the cementitious composite could dissolve the lignin and hemicellulose of the natural fiber, and weaken the individual fiber cell (Gram 1984). Another problem is the poor interface quality between the fiber and the matrix of the cementitious material. The performance of the composite depends not only on those individual components, but also on their interfacial compatibility (Mishra et al. 2004). Surface modification of the natural fiber is

essential to achieve good performance of the composites. Different methods have been proposed to pretreat the natural fiber used for reinforcement in order to enhance the durability of the composite and improve the interfacial condition. Sealing the matrix pores, impregnation of natural fiber with blocking agents or water-repellent agents, and partial replacement of cement with low alkaline binders, like silica fume, fly ash, and metakaolin, provided some promising results (Bergström and Gram 1984; Canovas et al. 1992; De Gutiérrez et al. 2005; Gram 1984; Toledo Filho et al. 2003). The embrittlement tendency of the composites could also be slowed down by using the aforementioned methods, although could not be completely avoided. Pulping, either from chemical or mechanical process, is another fiber pretreatment method that can effectively improve the durability of the composite and the adhesion between the fiber and the matrix (Savastano Jr et al. 2003a; Tonoli et al. 2007).

To enhance the adhesion between the two components, alkaline solutions are often applied to pre-treat the natural fibers. The alkali treatment gives rise to fiber fibrillation by breaking down fiber bundle into smaller fibrils thereby improving the effective surface area contacting with the matrix. It also improves the cohesion between the fiber and the matrix by removing the surface debris and irregularities (Mishra et al. 2004). Alkali treatment affects both the fiber strength and the fiber-matrix adhesion in a positive way (Rong et al. 2001; Sedan et al. 2008). Cao et al. (2006) studied the mechanical properties of aliphatic polyester composite reinforced with bagasse fiber before and after alkali treatment. It was found that 1% NaOH treated bagasse fiber composite exhibited increase of respectively 13% in tensile strength, 14% in flexural

strength and 30% in impact strength. SEM imaging of the fracture surface showed that fiber after alkali treatment became finer because of the dissolution of the hemicellulose. Li et al. (2004, 2006) found that the pretreatment of hemp fibers in NaOH solution at 120℃ for 40 minutes favored the increase of compressive and flexural strengths as well as flexural toughness of the hemp fiber reinforced cement composite. Sedan et al. (2008) also found that the flexural strength of hemp fiber reinforced cement composite could be significantly improved by pretreating the hemp fiber with NaOH solution. Gomes et al. (2007) reported that alkali-treated natural fiber reinforced composites showed twice to three times increase in fracture strain compared to untreated fiber reinforced composites, without significant loss in strength. Van de Weyenberg et al. (2006) studied the effect of alkali-treatment of flax fiber on the mechanical properties of the composite and claimed that alkalization of flax fibers was a simple and effective method to enhance the adhesion between the fiber and the matrix. Alkaline treatment seems to be a good method to pretreat natural fibers for geopolymer enhancement because of its compatibility with the alkaline environment in geopolymer.

2.3 SUMMARY AND COMMENTS

a) Natural fibers have been excellent replacements to manmade fibers as reinforcements to enhance cementitious materials and promising resutls have been obtained.
b) Geopolymer emerging as an ideal cementitious material for sustainable development has comparable performance to OPC with additional advantages, but

shows the same sensitivity to crakcing as OPC. Although studies have been carried out to enhance geopolymer with fibers of different nature, the utilization of natural fibers to reinforce geopolymer is rarely explored.

c) Different methods have been attempted to treat natural fibers in order to improve the durability of reinforced composites. Alkaline treatment seems to be a good method to pretreat natural fibers for enhancement of geopolymer because of its compatibility with the alkaline environment in geopolymer.

CHAPTER 3
UTILIZATION OF SWEET SORGHUM FIBER TO ENHANCE FLY ASH-BASED GEOPOLYMER

3.1 INTRODUCTION

The annual production of agricultural crop residues such as straw, corn stalk, bagasse, etc. is estimated to be billions of tonnes worldwide, only a small portion of which is reused for animal feed or biofuel production, with the major portion burned in the field or disposed of in landfill causing environmental issues (Thomas et al. 2011). Environmental concerns and the concept of sustainability have led to an increasing interest of using the agricultural waste and turning them into value-added biocomposites. Recent years have seen the application of natural fibers reinforced composites in many industrial fields including construction, automotive, packaging, and electronics, etc.

Sweet sorghum has become an important crop for research and development given its potential as a feedstock for large-scale bio-ethanol production. Sweet sorghum is especially suitable to be grown in arid areas because compared with corn it requires less fertilizer, water, and pesticides and is cheaper to grow (Bennett and Anex 2009; Goshadrou et al. 2011; Ottman 2008; Wu et al. 2010). After the juice is extracted from sweet sorghum stalks during the process of ethanol production, a large amount of bagasse (residue) is left behind. It is a great challenge to handle the significant amount of bagasse. Because the bagasse contains a large amount of fibers, 37% acid detergent fiber (ADF),

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56% neutral detergent fiber (NDF) and 3.8% protein based on the measurements by Ottman (2008), it has a great potential to be used as a reinforcing fiber of cementitious materials.

This part of thesis studies the feasibility of utilizing sweet sorghum fiber to reinforce geopolymer cementitious material. Specifically, the unit weight of fly ash-based geopolymer specimens containing different content of sweet sorghum fibers was measured. Unconfined compression, splitting tensile and flexural tests were conducted to evaluate the effect of inclusion of sweet sorghum fiber on the compressive, tensile and flexural strength of geopolymer paste. Based on the splitting tensile tests, the post-peak toughness was also evaluated. In addition, scanning electron microscopy (SEM) imaging was performed to study the distribution of sweet sorghum fibers in the geopolymer paste in order to better understand how they reinforce the geopolymer cementitious material.

A major concern of natural fiber reinforced geopolymer composite is the durability. The hydrophilic property and the special structure of natural fibers enable them a large capacity of moisture absorption, which may induce volumetric change and reduction in strength and toughness when using in humid environment (Melo Filho et al. 2013). Therefore, the effect of wet/dry cycling on the mechanical performance of geopolymer composite must be understood. The mechanical properties of natural fiber reinforced geopolymer composites after experiencing a specific number of wet/dry cycles were investigated using unconfined compression and splitting tensile tests.

3.2 MATERIALS AND METHODS

3.2.1 Materials

The sweet sorghum bagasse was provided by the Campus Agriculture Center (CAC), University of Arizona. The sorghum bagasse was harvested in October 2010. Leaves and husks were stripped from the fresh stalks, then juice was squeezed from the stalks for ethanol production, and bagasse was produced.

Class F fly ash and sodium hydroxide solution were used to produce the geopolymer paste. The paste specimens were used so that the reinforcement effect of sweet sorghum fibers could be better studied with no need to consider the effect of the presence of aggregate. The fly ash was provided by Salt River Materials Group (SRMG) in Phoenix, Arizona. The fly ash contains about 57% (weight percentage) SiO_2, 29% Al_2O_3 and 6.1% CaO and has 71% particles passing #325 (44 μm) sieve. The specific gravity of the fly ash is 1.97. The sodium hydroxide (NaOH) solution was prepared by dissolving NaOH flakes in deionized water. The NaOH flakes were obtained from Alfa Aesar in Ward Hill, Massachusetts.

3.2.2 Pre-treatment of sweet sorghum fiber

In this research, the received sweet sorghum bagasse [see Fig. 3.1(a)] was pre-treated using an alkaline solution as follows. The alkali method was selected for pretreating the sweet sorghum fiber based on the compatibility of the alkaline pretreatment solution and the alkaline environment of geopolymer.

1) Remove the soft inner portion of the bagasse (referred to as “depithing”).

2) Cut the bagasse into smaller than 5cm lengths.

3) Dissolve NaOH flakes in water to produce NaOH solution of 2 M concentration.

4) Submerge the bagasse in the NaOH solution for 12 hours.

5) Wash the bagasse thoroughly until the slippery texture is removed.

6) Dry the washed bagasse in a 90^{o}C oven for 24 hours.

7) Grind the dried bagasse to pass #20 (840 μm) sieve screen.

Fig. 3.1 (b) shows the bagasse after treatment.

Figure 3.1. Sweet sorghum bagasse: (a) As received; and (b) After treatment.

3.2.3 Specimen preparation

First the fly ash and the treated sweet sorghum fibers at a specified weight percentage were dry mixed to ensure uniform fiber distribution. The geopolymer matrix was produced by mixing NaOH, fly ash and de-ionized water to give the molar ratios SiO_2/Al_2O_3 = 3.35 and H_2O/Na_2O=11.1. The fiber content of 1, 2 and 3% by weight of fly ash were used to evaluate the effect of fiber on the mechanical properties of

geopolymer, and 0% was also considered as a control. Then the NaOH solution at a concentration of 10 M was slowly added and the mixing was continued for about ten minutes to ensure sufficient dissolution of silica and alumina in the alkaline solution. The NaOH solution was prepared by dissolving NaOH flakes in de-ionized water and stirring for about ten minutes. Considering the generated heat, enough time was allowed for the NaOH solution to cool down before it was used. Some additional water was added to the geopolymer paste with 2% and 3% of fibers to improve the workability. The resulted geopolymer-fiber paste was then placed in cylindrical Plexiglas molds of 35 mm inner diameter and 70 mm length to make unconfined compression and splitting tensile test specimens, and in wood molds of 360 mm × 60 mm × 25 mm to make flexural test specimens. The mold was shaken by a vibrator during the casting to release the trapped air bubbles. Then, the mold was capped and placed in oven for curing at 60 ° C. The specimens were de-molded after 3 hours and placed back in the oven for prolonged curing of 7 days before tested.

3.2.4 Measurement of unit weight

Before conducting the mechanical (unconfined compression, splitting tensile and flexural) tests, the unit weight of the geopolymer paste specimens containing different content of sweet sorghum fibers was determined by weighing and sizing the cured cylindrical specimens.

3.2.5 Unconfined compression tests

Unconfined compression tests were performed on the 7-day cured cylindrical specimens with an ELE Tri Flex 2 loading machine at a constant loading rate of 0.1 mm/min following ASTM C39. The tests were performed to measure the unconfined compressive strength (UCS) of geopolymer specimens containing different content of sweet sorghum fibers. For each condition, three specimens were tested and the average of the measured UCS values was used for the analysis. Before conducting the compression test, the end surfaces of the specimens were polished to make sure they are accurately flat and parallel. In addition, the end surfaces were lubricated to minimize the friction between the specimen and the steel platens.

3.2.6 Splitting tensile tests

The splitting tensile tests were conducted to measure the tensile strength of the geopolymer paste specimens containing different content of sweet sorghum fibers following ASTM C496. The same specimen size as in the unconfined compression tests was used. Based on the test, the splitting tensile strength was determined as follows:

$$\sigma_t = \frac{2P}{\pi DL} \tag{3.1}$$

where σ_t is the splitting tensile strength (MPa); P is the maximum load on the specimen (N); D is the diameter of the specimen (mm); and L is the length of the specimen (mm). Again, for each condition, three specimens were tested and the average of the measured values was used.

Using the force-displacement curves obtained from the splitting tensile tests, the effect of sweet sorghum fibers on the toughness of geopolymer was also evaluated. In this paper, the toughness is simply defined as the post-peak toughness or the area under the force-displacement curve beyond the peak (see Fig. 3.2).

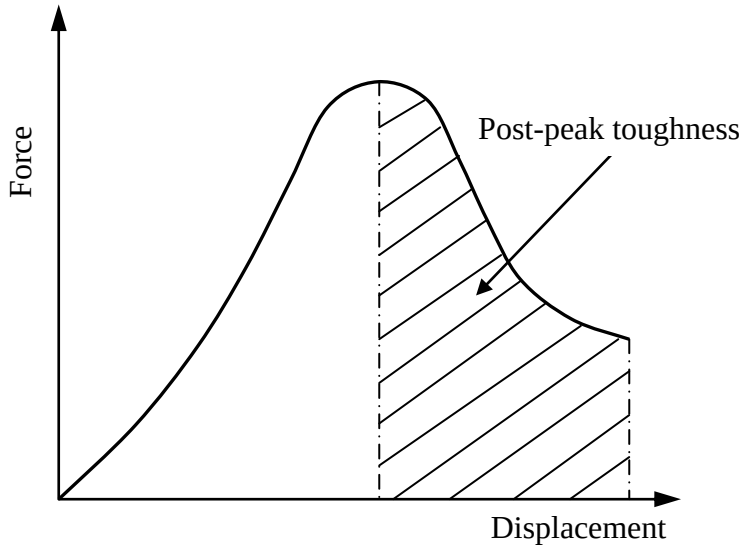


Figure 3.2. Definition of post-peak toughness.

3.2.7 Flexural tests

A three-point bending setup with a loading span of 320 mm was used to measure the flexural strength of the sweet sorghum fiber reinforced geopolymer following ASTM C1609. The flexural strength was calculated using the following equation:

$$\sigma_f = \frac{3P_m L}{2bd^2} \tag{3.2}$$

where σ_f is the flexural strength (MPa); P_m is the maximum load (N); L is the loading span of the specimen (mm); b is the width of the specimen (mm); and d is the thickness of the specimen (mm). For each condition, three specimens were tested.

3.2.8 Scanning electron microscopy (SEM) characterization

To better understand the effects of sweet sorghum fibers on the microstructure and mechanical performance of the geopolymer-fiber composites, SEM imaging characterization was also performed. The SEM imaging was performed in SE conventional mode using the FEI INSPEC-S50/Thermo-Fisher Noran 6 microscope. The freshly failed surfaces from the splitting tensile tests, without polishing to keep the fractured surface "un-contaminated", were used for the SEM imaging.

3.3 RESULTS AND DISCUSSION

3.3.1 Unit weight

The effect of fiber content on the unit weight of sweet sorghum fiber reinforced geopolymer is shown in Fig. 3.3. As expected, the unit weight decreased as the fiber content increased, from 15.4 kN/m^3 at 0% fiber content to 14.4 kN/m^3 at 3% fiber content. Since the fiber content was low, the values of unit weight were still within the range of reported values for fly ash-based geopolymer in the literature, 14.5–17.1 kN/m^3 (Andini et al. 2008) and 11.8–15.7 kN/m^3 (Cioffi et al. 2003).

3.3.2 Unconfined compressive strength (UCS)

The effect of fiber content on the UCS of sweet sorghum fiber reinforced geopolymer is presented in Fig. 3.4. The UCS slightly decreased with higher content of fibers included. The UCS decreased from 27.7 MPa with no fiber to 25.1, 22.9 and 20.4 MPa respective at 1, 2 and 3% of fibers.

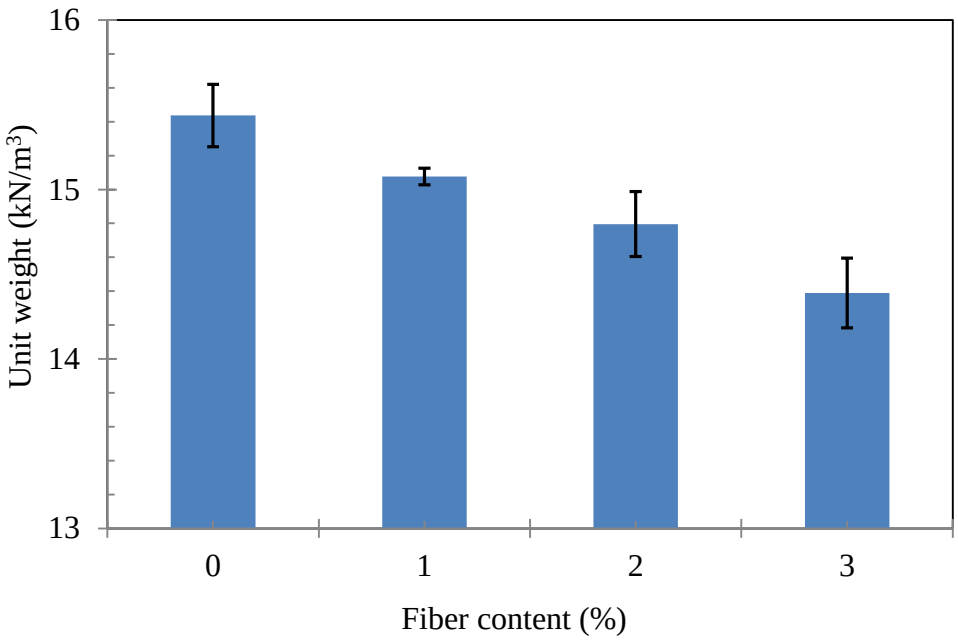


Figure 3.3. Unit weight versus fiber content for sweet sorghum reinforced geopolymer.

The trend is in agreement with the results by other researchers. For example, the research by Al-Oraimi and Seibi (1995) showed the decrease of UCS for natural fiber reinforced concrete. Kriker et al. (2005), Li et al. (2006), and De Gutiérrez et al. (2005) also reported that the incorporation of natural fiber in cement mortar and concrete caused decrease in UCS. This is in agreement with the general concept that the main function of fiber is not to increase the compressive strength (sometimes it may decrease the compressive strength); but to control the cracking of the reinforced composite by bridging across the cracks and providing post-cracking ductility (Bentur and Mindess 2006).

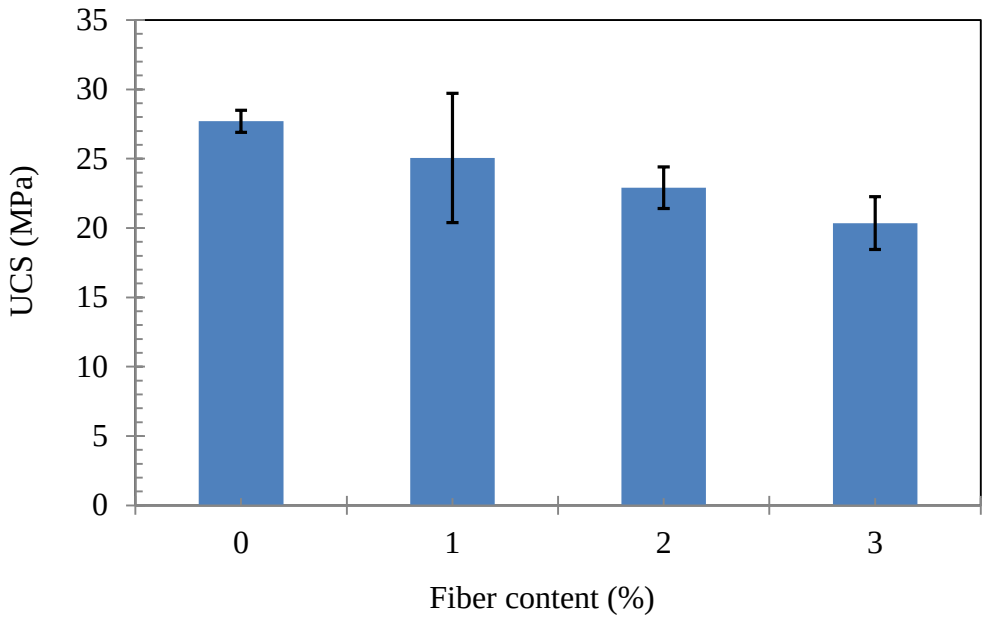


Figure 3.4. Effect of fiber content on the UCS of geopolymer paste.

3.3.3 Splitting tensile strength

Fig.3.5 shows the typical splitting tensile test load and displacement curves of geopolymer paste specimens containing different content of sweet sorghum fibers. The plain geopolymer paste specimens failed suddenly at the peak load, whereas the incorporation of fiber improved the post-peak ductility significantly. The load at the peak increased with the content of sweet sorghum fibers up to 2% and then decreased.

Fig.3.6 shows the tensile strength versus the content of sweet sorghum fibers included in the geopolymer paste. The tensile strength increased about 36% when 2% sweet sorghum fibers were utilized. Further increase of the fiber content, however, led to decrease of the tensile strength. Similar trend was also reported by Mansur and Aziz (1982) for the jute fiber reinforced cement paste.

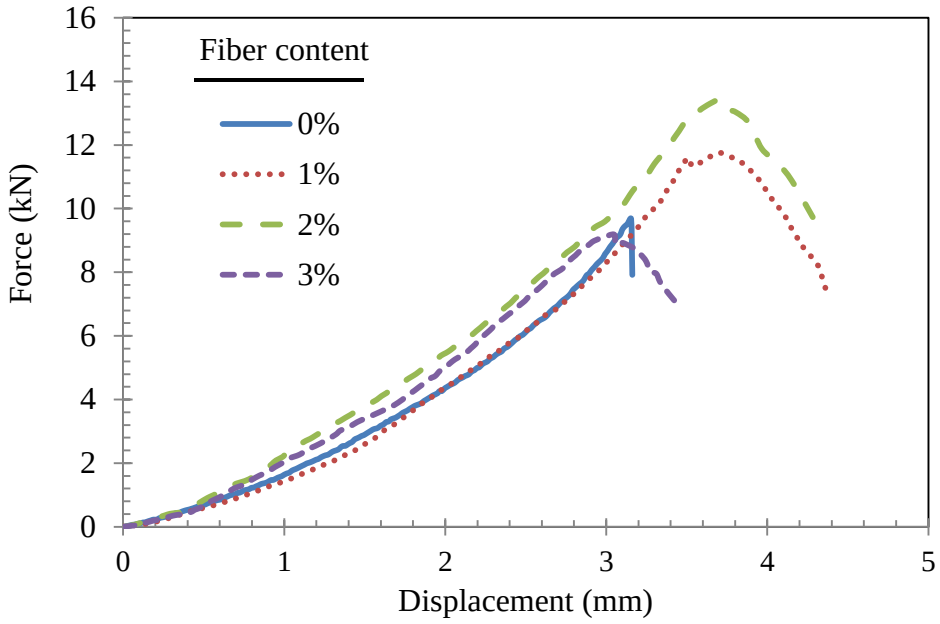


Figure 3.5. Splitting tensile test load and displacement curves of geopolymer paste specimens containing different amount of sweet sorghum fibers.

The enhanced ductility comes from the de-bonding and pull-out of fibers that bridge across the cracks, which can carry large amount of loads. The fibers transfer loads back to the uncracked parts of the specimen, which permits multiple cracking of the specimen (Sun and Wu 2008). Fig. 3.7 shows the direct comparison of the failure modes between two specimens during and after the splitting tensile tests, one containing no fibers and the other 1% sweet sorghum fibers. One can clearly see the brittle failure of the plain specimen and the "ductile" failure of the specimen containing sweet sorghum fibers. The same behavior was also reported for other natural fiber reinforced cement composites (Mansur and Aziz 1982). The pulling out of these fibers during the loading process absorbs energy and thus improves the tensile behavior of geopolymer paste.

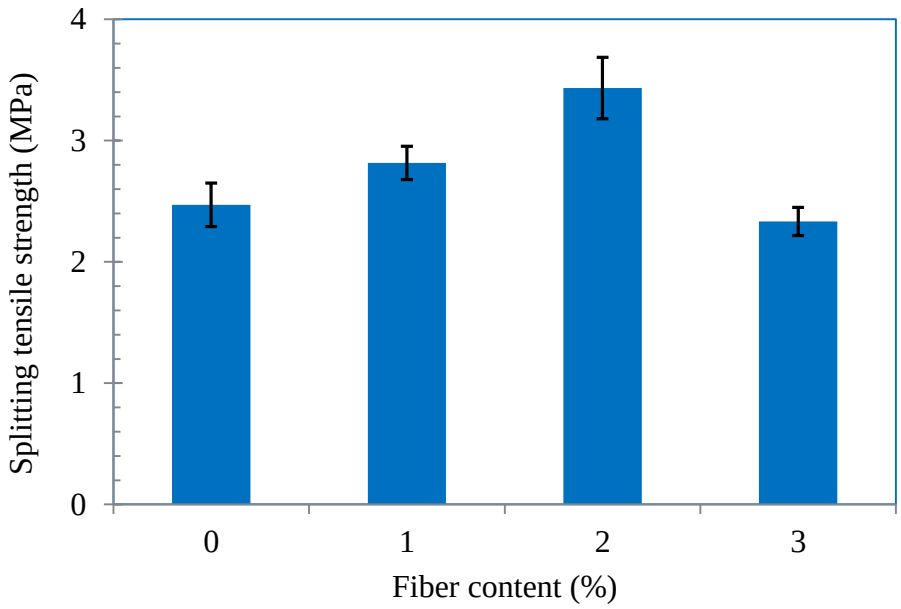
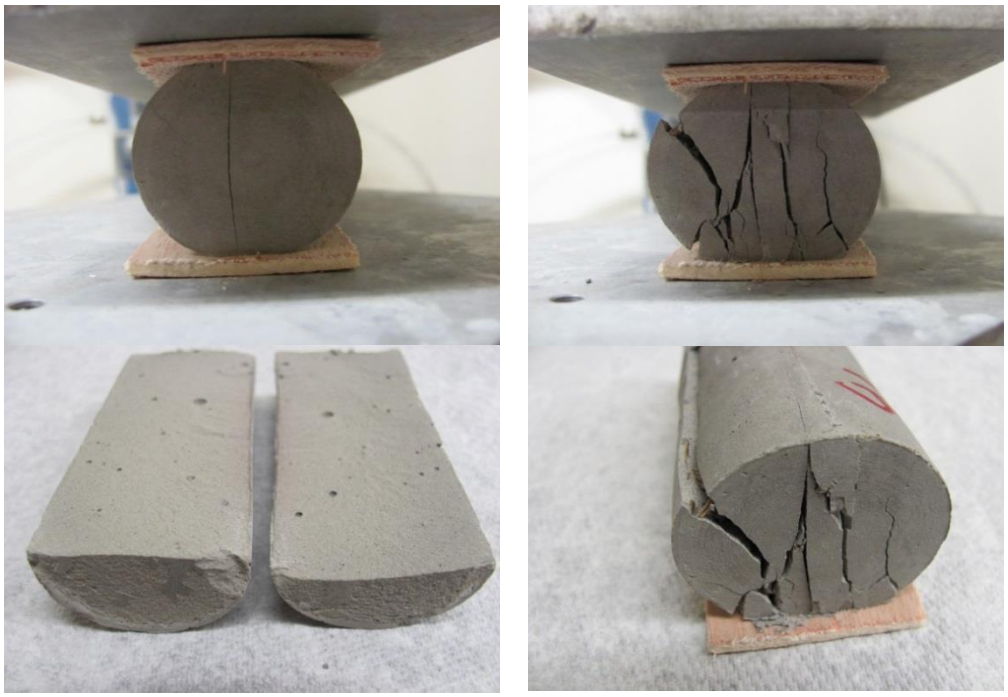


Figure 3.6. Effect of fiber content on tensile strength of geopolymer paste.



(a) (b)

Figure 3.7. Different failure modes of geopolymer paste specimens containing (a) no fibers; and (b) 1% sweet sorghum fibers.

Fig. 3.8 presents the comparison of the splitting tensile strength (T) versus the UCS of current study with those available in the literature (Hardjito and Rangan 2005; Joseph and Mathew 2012; Kumar et al. 2013; Mishra et al. 2008; Olivia and Nikraz 2012; Parmar et al. 2013; Ryu et al. 2013; Sofi et al. 2007; Vijai et al. 2012).

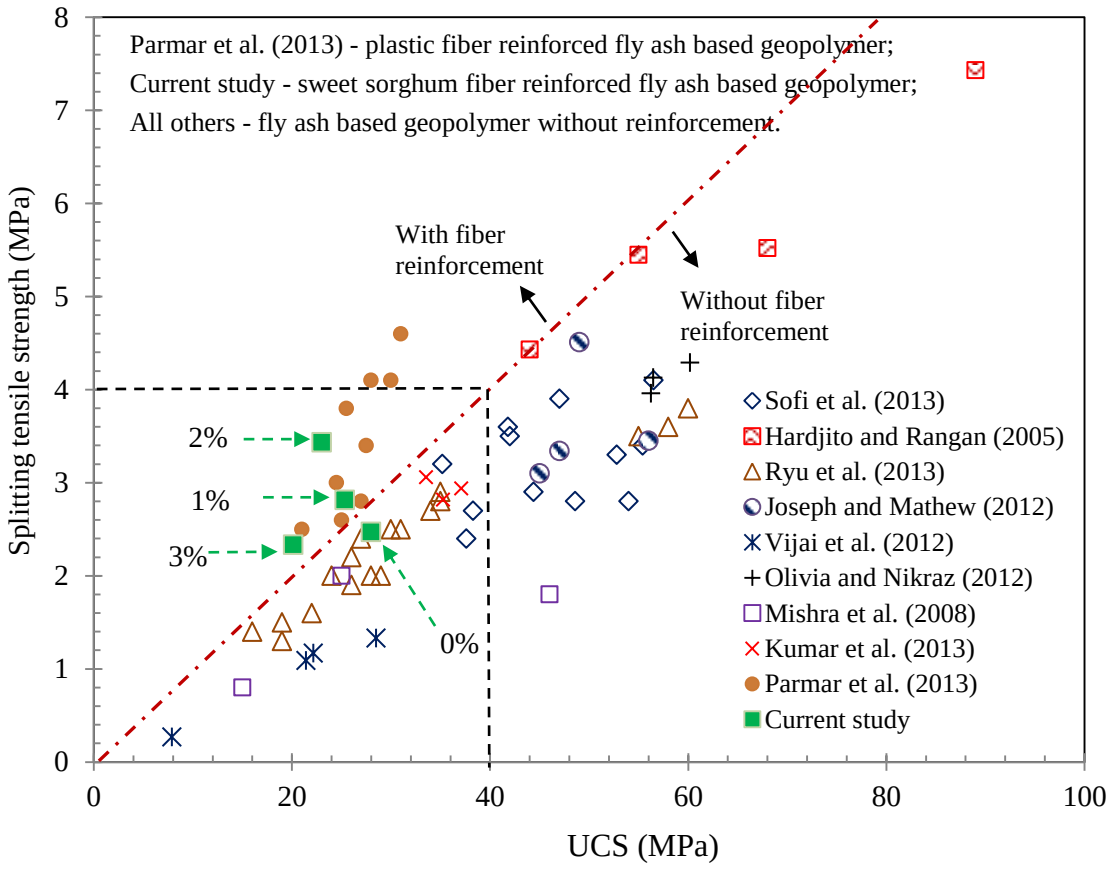


Figure 3.8. Comparison of splitting tensile strength vs. UCS relationship of current study with those in the literature.

The comparison is limited to fly ash based geopolymer (paste, mortar and concrete), with and without fiber reinforcement. The fly ash based geopolymer has a wide range of UCS values, between approximately 10 and 90 MPa, and splitting tensile strength values, between approximately 0.25 and 7.5 MPa with most of the values

ranging from 1 to 5 MPa. It is interesting to note that all of the data points for unreinforced geopolymer are on or below the T:UCS = 1:10 line while those for reinforced geopolymer are above the line. This can be more clearly seen in Fig. 3.9 which shows the T/UCS ratio versus UCS. The fiber reinforcement with sweet sorghum fiber in the current study and metalized plastic waste fiber in Parmar et al. (2013), effectively increases the T/UCS value.

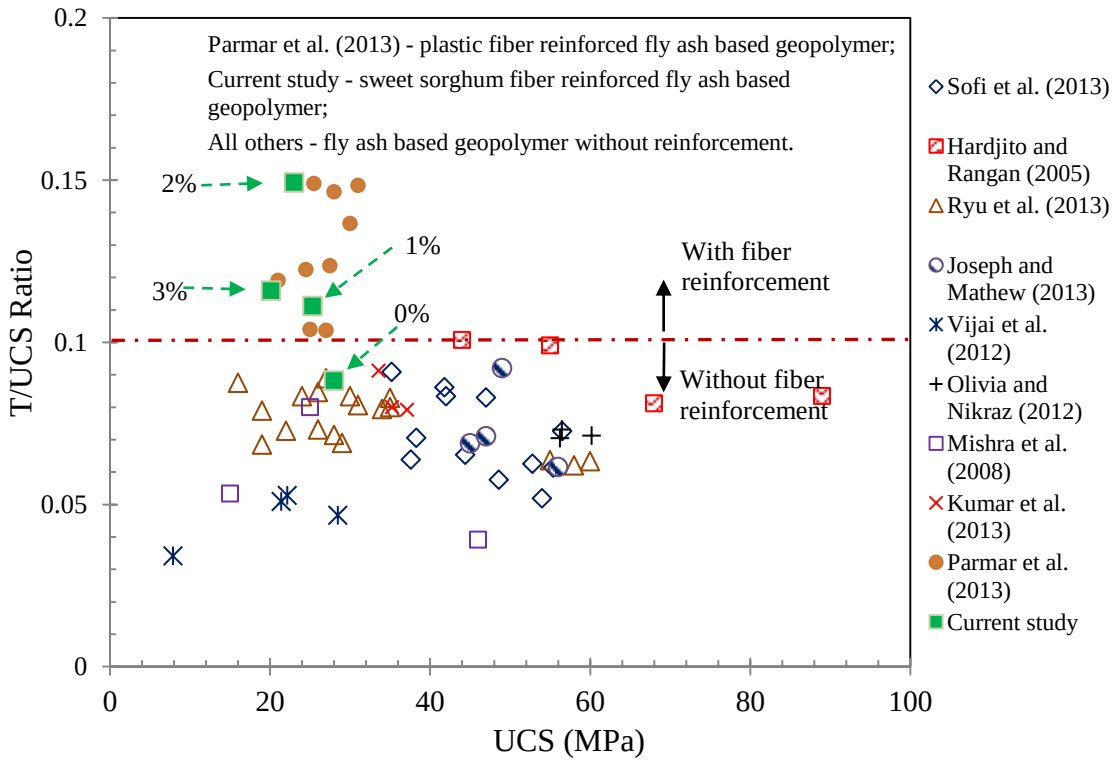


Figure 3.9. Comparison of splitting tensile strength over UCS (T/UCS) ratio vs. UCS relationship of current study with those in the literature.

3.3.4 Flexural strength

The effect of sweet sorghum fiber content on the flexural strength of geopolymer is presented in Fig. 3.10. It can be seen that the flexural strength of the fiber-reinforced geopolymer shows a similar trend to that of the tensile strength, which increases with higher fiber content up to 2% and then decreases thereafter.

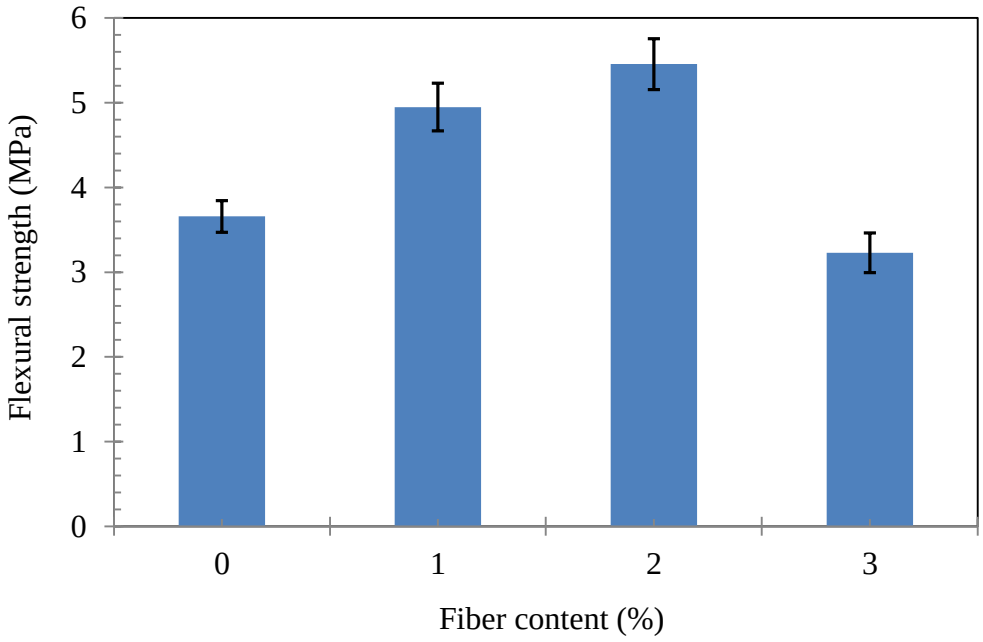


Figure 3.10. Effect of fiber content on flexural strength of geopolymer paste

The presence of fiber at the optimum content can effectively carry more tensile load and thus delay the growth of micro cracks and increase the flexural strength. However, further increase of the fiber content induces poor workability and fiber agglomeration, resulting in increase of air bubbles entrapped in the composite and nonuniform fiber dispersion. These flaws may lead to stress concentrations and degrade the flexural strength. Similar trend was also reported by Alomayri et al. (2013) for fly-ash based geopolymer reinforced with cotton fibers.

3.3.5 Post-peak toughness

Fig. 3.11 shows the effect of sweet sorghum fiber content on the post-peak toughness of geopolymer paste specimens. It can be seen the post-peak toughness reaches the highest at fiber content of 2%. Beyond 2%, the post-peak toughness decreases gradually, but is still higher than that of the plain geopolymer paste. The de-bonding, sliding and pull-out of fibers dissipate significant amount of energy that would otherwise be used to propagate the cracks. Hence, the post-peak toughness of the composite increases considerably due to the incorporation of sweet sorghum fibers.

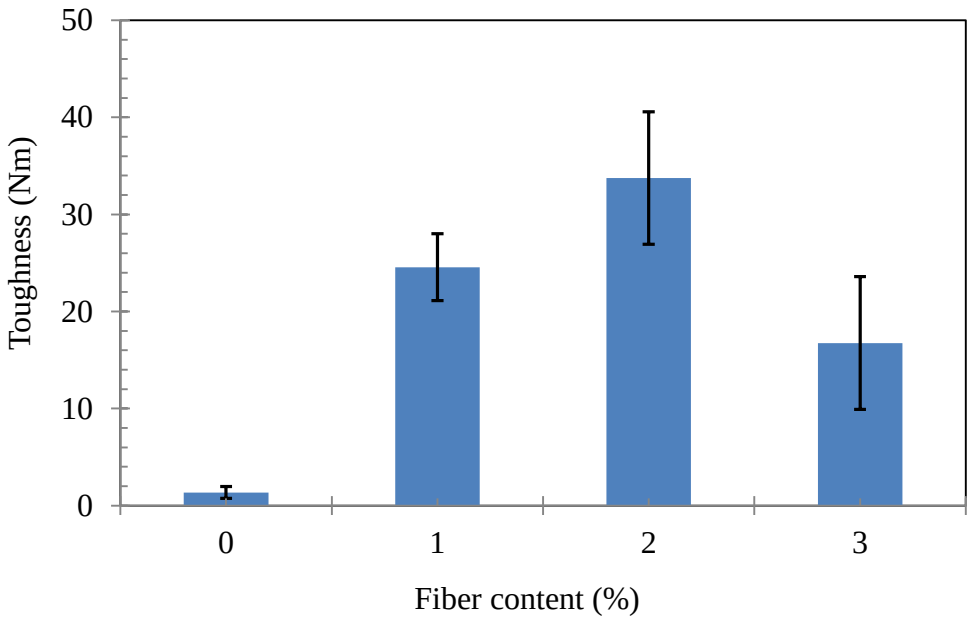


Figure 3.11. Effect of fiber content on post-peak toughness of geopolymer paste.

Fig. 3.12 presents the splitting tensile strength, the flexural strength, and the post-peak toughness in the same figure. One can see that they follow essentially the same trend when the fiber content increases and have the same optimum fiber content of 2 %.

This is not surprising because they are all related to the improvement of the tensile behavior of the geopolymer reinforced with sweet sorghum fibers.

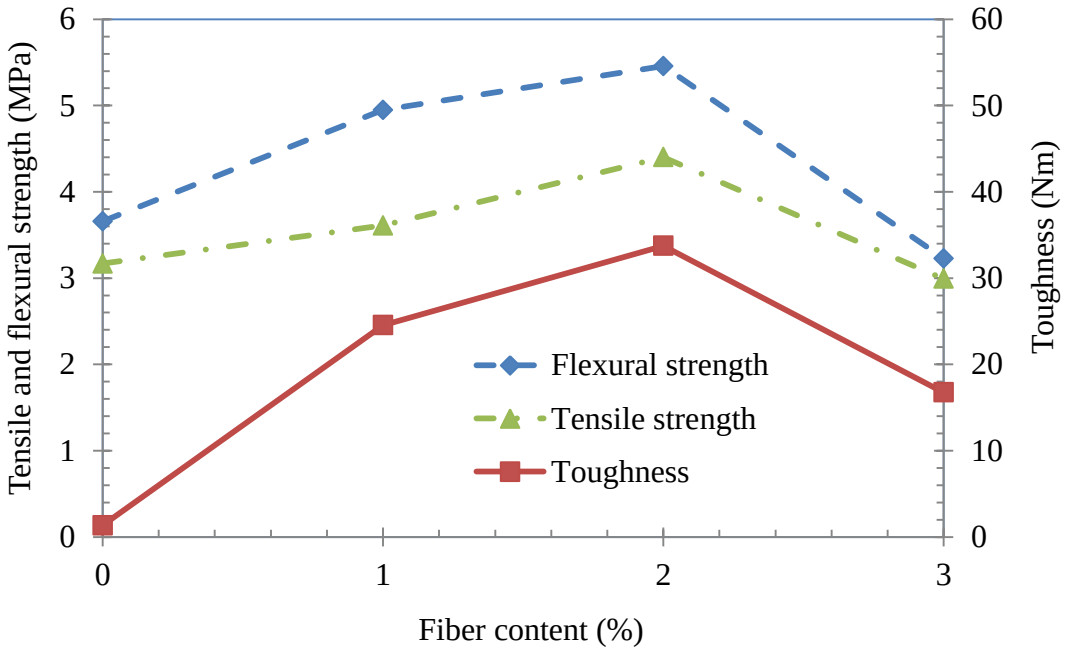


Figure 3.12. Splitting tensile strength, flexural strength, and post-peak toughness of geopolymer paste versus fiber content.

3.3.6 SEM

Fig. 3.13 shows the representative SEM images for sweet sorghum fiber reinforced geopolymer specimens tested after 7-days curing. It is evidently noticeable that fiber pull-out and fracture (Figs. 3.13a and b) are the main mechanisms that lead to the enhanced tensile and flexural strength and ductility, which is in accordance with the description by Savastano Jr et al. (2005) for cement-fiber composites. Closer inspection shows that some fibers have good bonding with the matrix (Fig. 3.13c), but some do not (Fig. 3.13d).

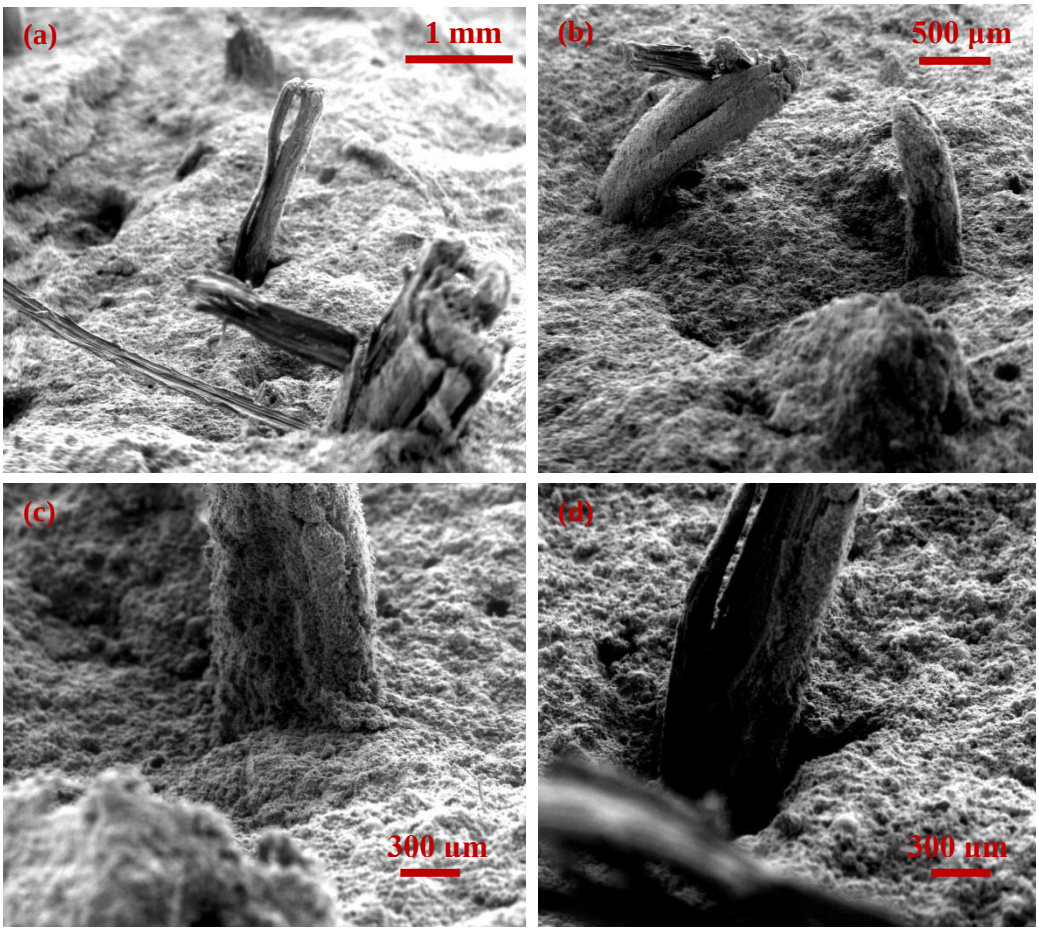


Figure 3.13. SEM images of the failed surface of a splitting tensile test specimen.

Fibers with good bonding with the surrounding matrix tend to fracture rather than pull out at the failed surface (Soroushian and Marikunte 1992). Fibers poorly bonded to the matrix contribute little to the improvement of the tensile and flexural strength, ductility and toughness; sometimes they may act as flaw or crack initiation deteriorating the mechanical performance of the composite. Further research should be conducted to ensure all fibers are in good contact with the geopolymer matrix so that the effectiveness of sweet sorghum fibers in reinforcing the geopolymer is maximized.

3.4 DURABILITY TEST

3.4.1 Experimental detail

Previous experimental results have showed that 2% sweet sorghum fiber by weight of fly ash incorporation into the plain geopolymer yields the optimum tensile strength, flexural strength and post-peak toughness. Therefore, all samples were prepared at this optimum condition to evaluate the durability of the geopolymer composite related to wet/dry cycling. To eliminate the effects of aging on matrix strength, Mohr et al. (2005) suggested that all specimens should be tested at the same age, regardless of the number of wet/dry cycles. This study follows this suggestion and uses unconfined compression and splitting tensile tests to evaluate the mechanical performance of the geopolymer composites after experiencing a specific number of wet/dry cycles.

Previous studies (Claramunt et al. 2011; Mohr et al. 2005) have revealed that it was important to determine the time to reach full saturation and drying for the investigation of durability with respect to wet/dry cycling. A 72-h soaking/48-h drying cycle length is appropriate to achieve saturated and dry conditions in the fiber reinforced geopolymer specimens. In this study, the wet/dry cycle was determined as 71 h soaking in water plus 1 h air drying at room temperature (23 $\mp$ 2 ^{o}C) and 47 h drying in an oven at 60^{o}C plus 1 h air drying at 23 $\mp$ 2 ^{o}C. The 1-h air drying of specimens was allowed between saturation and drying in order to avoid thermal shock and subsequent micro-cracking (Mohr et al. 2005). All specimens were cured at 60 ^{o}C oven for 7 days before exposure to the wet/dry cycling. The specimens exposed to 0, 1, 2, 5, and 10 cycles were

tested. All specimens were tested at 57 days, regardless of the number of wet/dry cycles, which means all specimens remained in the curing environment for at least 7 days before tested, with those subjected to fewer or no wet/dry cycles remaining in the curing oven for longer periods until wet/dry cycling or mechanical testing. For each wet/dry cycling condition, two specimens were prepared respectively for unconfined compression and splitting tensile tests.

3.4.2 Durability test results

The results of the unconfined compression and splitting tensile tests of geopolymer composites subjected to different number of wet/dry cycles are shown respectively in Figs. 3.14 and 3.15, in which a progressive reduction in both UCS and tensile strength is observed with increasing the number of wet/dry cycles. After experiencing 10 wet/dry cycles, there is an approximately 50% loss in both UCS and tensile strength.

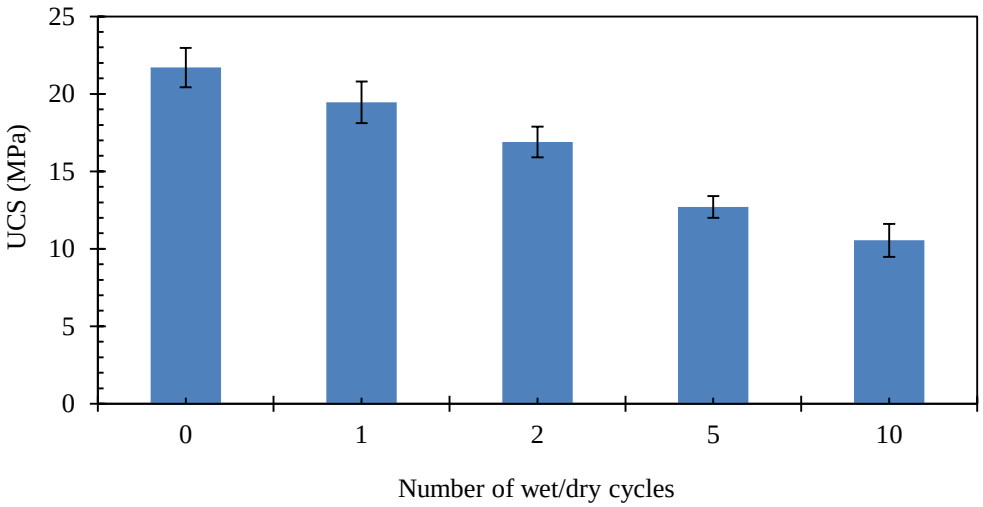


Figure 3.14. The UCS of geopolymer composites versus the number of wet/dry cycles.

The major strength loss occurs within the first five wet/dry cycles. Typical splitting tensile test force and displacement curves of geopolymer composites subjected to different number of wet/dry cycles are presented in Fig. 3.16. It can be seen that the maximum load decreases with the number of wet/dry cycles, indicating a significant loss of tensile strength.

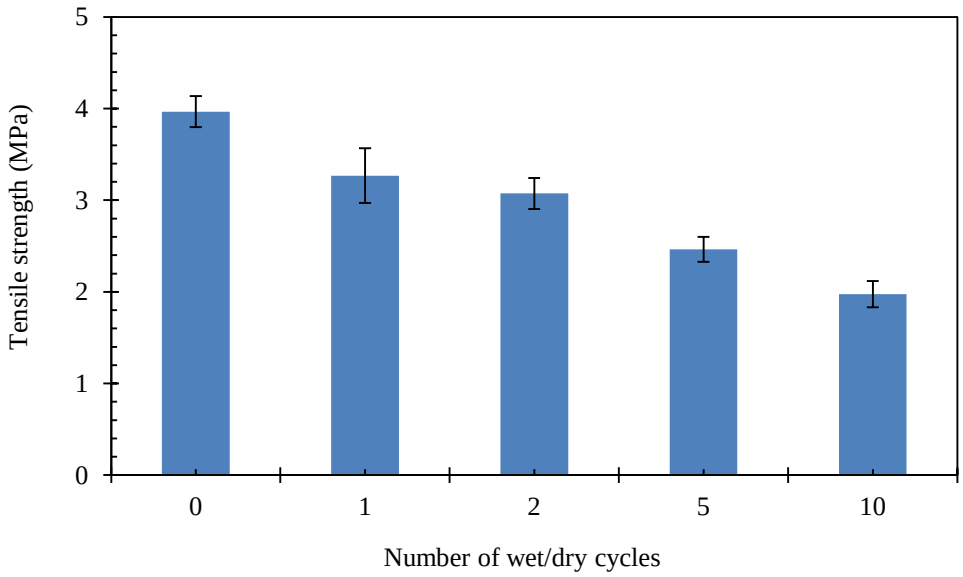


Figure 3.15. The splitting tensile strength of geopolymer composites versus the number of wet/dry cycles.

There are three possible mechanisms for explaining the weakening effect by the wet/dry cycling on the geopolymer composite. First, the swelling/shrinking of the natural fiber leads to fiber-geopolymer debonding and formation of microcracks. Initially, all samples were free of cracks after 7-day curing. However, microcracks were observed in samples exposed to wet/dry cycling. Since care was taken to minimize the effect of thermal shocks during wetting and drying, the development of microcracks may be attributed to the swelling and shrinking of the natural fiber within the geopolymer matrix.

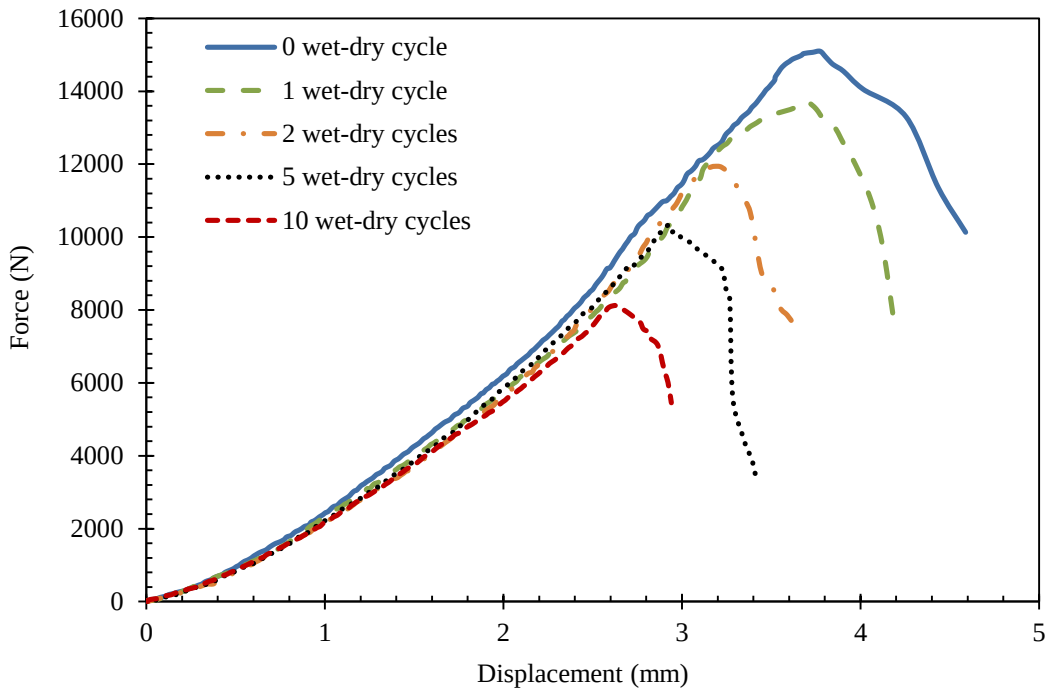


Figure 3.16. Typical splitting tensile test load and displacement curves of geopolymer composites exposure to 0, 1, 2, 5, and 10 wet/dry cycles.

The lumen in the center of a single fiber is capable of holding water during the wetting process and giving it up during the drying process. Consequently, the sweet sorghum fiber swells with increasing water content and shrinks upon water losing. The swelling/shrinking can cause volumetric change leading to fiber-geopolymer debonding and formation of microcracks, and as a result, decreasing the strength of the geopolymer composite. Second, the intrusion of water causes hydration of some Si-O-Si bonds into Si-OH bond in the geopolymer matrix weakening the composite (Lemougna et al. 2013). Third, the deposition of geopolymer gel in the surface and cell of sweet sorghum fiber causes fiber mineralization, which may gradually reduce the amount of cellulose in the fiber causing fiber degradation (Melo Filho et al. 2013). The degraded fiber exhibits

decreasing strength and rigidity with time, which may act as flaw or crack initiation degrading the strength of composite.

3.5 CONCLUSIONS

The feasibility of using alkali pretreated sweet sorghum fiber to improve the mechanical behavior of fly ash-based geopolymer was studied. Based on the results, the following conclusions can be drawn.

a) The unit weight of geopolymer paste decreases with higher sweet sorghum fiber content.

b) The inclusion of sweet sorghum fibers in geopolymer paste slightly decreases the UCS.

c) The tensile and flexural strengths both increase with the content of sweet sorghum fibers up to 2% and then decrease to be lower than that of the plain geopolymer paste.

d) The post-peak toughness increases significantly with the content of sweet sorghum fibers up to 2% and then slightly decreases but is still much higher than that of the plain geopolymer paste.

e) There is a clear transition from the brittle failure of the plain geopolymer paste specimen to the “ductile” failure of the geopolymer paste specimen containing sweet sorghum fiber.

f) The UCS and tensile strength of 2% sweet sorghum fiber reinforced geopolymer composite progressively decrease with increasing the number

of wet/dry cycles. The degradation of sweet sorghum fiber reinforced geopolymer composite may attribute to (1) fiber-geopolymer debonding and formation of microcracks caused by swelling/shrinking of sweet sorghum; (2) hydration of geopolymer matrix; and (3) sweet sorghum fiber degradation due to fiber mineralization.

PART II
BIOPOLYMER STABILIZATION OF MINE TAILINGS FOR DUST CONTROL

The second part of the thesis investigates the utilization of two natural biopolymers, xanthan gum and guar gum, to stabilize mine tailings so that their mechanical properties and resistance to wind erosion can be improved. The Part II includes **Chapters 4**, **5** and **6**. In **Chapter 4**, the Atterberg limits and undrained shear strength of mine tailings stabilized with biopolymer solutions of different concentrations are investigated using a fall cone method. In **Chapter 5**, an extensive experimental study on utilization of biopolymers for mine tailings dust control is presented. **Chapter 6** presents experimental and numerical studies of the UCS of MT stabilized with biopolymer solutions of different concentrations.

CHAPTER 4
UTILIZATION OF BIOPOLYMER TO STRENGTHEN MINE TAILINGS

4.1 INTRODUCTION

The mining industry produces significant amount of mine tailings every year, accounting for nearly half of all solid waste generated in the United States (Collins and Ciesielski 1994; TFHRC 2009). Mine tailings (MT) are large piles of grinded rocks left over after the minerals of economic interest such as copper, zinc, molybdenum, and gold have been extracted from ore. Most of the MT are disposed of in on-site impoundments behind engineered earth and rock dams, which lead to different environmental and safety concerns (U.S.EPA 2004). Mine tailings, generally classified as loose sandy silts or silty sands, are far from being ideal materials for embankment construction and are highly vulnerable to liquefaction (Pépin et al. 2012; Wijewickreme et al. 2005). The failure of tailing dams or impoundments can cause large amount of contaminated liquid and slurry released into the environment, resulting in pollution and loss of lives and properties (Macklin et al. 2003; Rico et al. 2008). During the period 2001 to 2008 in China, it was reported that tailings dam accidents resulted in 1892 deaths, ranking five in all types of accidents (Zhang 2010). Tailings are also quite susceptible to wind erosion, especially in arid and semiarid regions. Wind can disperse fines of mine tailings far away from the impoundments (Blight 2008). The fugitive dust

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from mine tailings can reduce the visibility along nearby roads, degrade air quality in the vicinity, and contaminate soils and surface water. The MT usually contain trace quantities of toxic minerals such as arsenic, cadmium, lead and, if not managed properly, may adversely affect surrounding ecosystems and human health. Recent studies have revealed that oxidation of metal-bearing MT when subjected to oxygen and moisture leads to metal dissolution and mobilization. The released metals can be dispersed into the surrounding environment by water runoff or miles downstream by wind (Hayes et al. 2012; Meza-Figueroa and Maier 2009). Some trace metals in MT, such as lead and cadmium are extremely poisonous and, even inhaled in very low amounts, can trigger many diseases (Meza-Figueroa et al. 2009). According to U.S.EPA (2006), short-term exposure to fine particles ($PM_{2.5}$) can result in premature death in people with heart and lung disease, lung function changes, and changes in heart rate variability. Long-term exposure to fine particles can cause death from lung cancer, reduction in lung function and development of chronic respiratory disease in children.

Different methods have been attempted to stabilize MT in order to improve the impoundment stability and the erosion resistance. Ordinary Portland cement (OPC) has been used to stabilize MT dams (Blight and Caldwell 1984; Rankhododo 2006). However, OPC is an energy-intensive material and its production generates significant amount of carbon dioxide (CO_2). Recent studies have revealed that the OPC industry is responsible for approximately 5-8% of the total CO_2 generated in the world (Huntzinger and Eatmon 2009; Scrivener and Kirkpatrick 2008). Therefore, wide application of OPC is running counter to sustainable and environmentally benign practice. The synthetic or

petroleum-based additives are widely used in construction site or tailings impoundments for wind erosion mitigation, which, however, are based on a depleting natural source with growing manufacturing cost and a great potential of leaching toxic products into the environment (Larson et al. 2012).

At the University of Arizona, an extensive research program is being conducted on the utilization of biopolymers to stabilize MT so that the impoundment stability and the erosion resistance can be improved. Biopolymers are characterized as polymers of natural origin produced by biological systems such as microorganisms, plants and animals or synthesized chemically but originated from biological starting materials such as amino acids, sugars, natural fats or oils (U.S. Congress Office of Technology Assessment (COTA) 1993). They are derived from natural renewable resources and can be biodegraded without negative impact on the environment. Their unique properties and the growing consciousness of sustainability have made them increasingly popular in various industrial applications including food processing, packaging, cosmetics, medicine and pharmacy, aerospace, electronics, photonics, construction engineering, wastewater treatment, soil stabilization and contaminant encapsulation. This part of the thesis presents the results of a study that focuses on the improvement of the undrained shear strength of MT by incorporation of xanthan gum and guar gum, two natural biopolymers. The undrained shear strength of MT is an important parameter related to the impoundment stability and the erosion resistance. A fall cone test method (British Standards Institution 1990) was adopted to evaluate the undrained shear strength of MT stabilized with xanthan gum or guar gum solution of different concentrations. Scanning

electron microscopy (SEM) imaging characterization was also conducted on the microstructure of the biopolymer-MT system in order to better understand how the biopolymers improve the undrained shear strength of the MT.

4.2 LITERATURE REVIEW

4.2.1 Application of biopolymer in soil improvement and stabilization

This section provides a brief review of the applications of biopolymers in soil improvement and stabilization because they are more related to the stabilization of MT addressed in this thesis. Researchers have investigated the application of biopolymers for hydraulic barriers, contaminant adsorption and soil stabilization.

Karimi (1998) performed hydraulic conductivity and consolidated-undrained (CU) triaxial strength tests on compacted specimens of Bonnie silt mixed with xanthan gum. Samples were prepared by mixing the Bonnie silt either with xanthan gum powder or its solution. The hydraulic conductivity test results showed that the permeability of Bonnie silt was reduced about 100-fold by the two mentioned treatment methods, and this effect in reducing the permeability lasted up to one year. The undrained shear strength from triaxial tests of the Bonnie silt increased 30% by mixing the silt with 2% xanthan gum solution at 14% moisture content. Khachatoorian et al. (2003) investigated the plugging effect of different biopolymers (xanthan gum, polyhydroxy butyrate (PHB), guar gum, polyglutamic acid (PGA) and chitosan) using a laboratory-pressurized pumping flow system. The results showed that all of the biopolymers exhibited positive plugging effects and the best plugging effect was obtained from PHB, followed by

chitosan and PGA. The authors concluded that the plugging effect was influenced by the structure of biopolymers. Etemadi et al. (2003) studied both the plugging effect and the metal (Cu) binding capacity of the same five different biopolymers, used alone or in combinations, in laboratory drainage flow systems. The experimental results indicated that all the biopolymers tested improved the sand characteristics by decreasing permeability and increasing shear strength, and had good metal uptake capacity. While biopolymers used alone were more efficient in metal uptake, the combination of two biopolymers (xanthan gum and chitosan) increased the plugging effect. Cabalar et al. (2009) performed hydraulic conductivity tests by using micro-organisms and direct shear tests by using xanthan gum on sandy soils. The hydraulic conductivity test results showed that the presence of micro-organisms decreased the hydraulic conductivity by two orders of magnitude. The direct shear tests indicated that 5% by weight of xanthan gum mixed with sandy soils significantly improved the shear strength of them. Ivanov and Chu (2008) did an excellent review of the applications of biopolymers for permeability reduction and strength improvement of soils in situ. They pointed out that biopolymers reduce the permeability of soils by filling the pores between soil particles and increase the strength of soils by forming cross-linking interpenetrating networks which interact with the soil matrix and bind the soil particles. Cabalar and Canakci (2011) carried out a series of direct shear tests to investigate the effect of incorporation of xanthan gum on the mechanical properties of sand. It was found that the peak shear stress and internal friction angle of sand significantly increased by inclusion of 3% and 5% xanthan gum, whereas decreased with incorporation of 1% xanthan gum, regardless of curing time. Chang and

Cho (2012) reported the application of a commercial biopolymer, named β-1,3/1,6-glucan polymer, to strengthen the Korean residual soil called *hwangtoh*. They prepared the β-1,3/1,6-glucan polymer solutions at different concentrations, mixed them with the soil and allowed the mixed soil to cure at different temperatures. The results showed that the β-1,3/1,6-glucan polymer increased the compressive strength of the *hwangtoh* more than 200% after curing at 20℃ for 28 days. A comparison of the compressive strength of the β-1,3/1,6-glucan polymer treated sample and that of a 10% cement-treated sample indicated that the β-1,3/1,6-glucan polymer treatment was comparable to the cement treatment in improving the compressive strength of the *hwangtoh*, but the β-1,3/1,6-glucan polymer treatment was much environmentally friendlier. A recent study by Khatami and O'Kelly (2012) showed that agar and modified starch, two biopolymers, were able to effectively improve the cohesion and stiffness of cohesionless soil without inducing environmental toxicity.

Researchers have also studied the utilization of biopolymers to reduce water and/or wind erosion of soils. Orts and Glenn (1999) explored a high molecular weight synthetic polymer called polyacrylamide (PMA) to reduce soil erosion during irrigation and found that the PMA was effective in reducing soil erosion due to (1) its high molecular weight, which enabled it to interact with soil particles and formed stable flocs with them; and (2) its charge affinity or Van der Waals attraction. However, the authors also stated several concerns about using PAM. First, the long-term environmental impact of PAM was unknown. PAM is a synthetic polymer that is non-biodegradable in the soil environment. Second, the monomer, called acrylamide, used to synthesize PAM is toxic.

Third, the use of PAM for erosion treatment was costly. And finally, the effectiveness of PAM varied depending on soil types. Based on the information from PAM, Orts and Glenn (1999) screened three types of biodegradable biopolymer, namely chitosan, starch xanthate, and acid-hydrolyzed cellulose micro-fibrils to reduce suspended solids in the run-off from tested soil. Experimental results indicated that the starch-based biopolymer worked as effectively as PAM after being modified. The cost of using starch xanthate was estimated roughly one-fifth the retail price of PAM. The effectiveness of cellulose microfibrils was comparable to PMA in reducing soil erosion because it had large size, surface charge and good water solubility, which enable it to create stable soil flocculation. Chitosan that has a net positive charge at neutral or acidic solution was as effective as PAM in reducing soil erosion. However, chitosan was more expensive than PAM. Kavazanjian Jr et al. (2009) investigated the application of biopolymers (xanthan and chitosan) as soil stabilizers to mitigate wind induced erosion, either by spraying biopolymer solutions at different concentrations on the surface of soil or mixing the solutions with soil prior to compaction. The results showed that both methods were effective in mitigating wind induced soil erosion. The enhanced wind erosion resistance by surface-spraying came from the formation of crust on the surface of treated soil. The mixing and compaction method could achieve similar improved resistance results but was more expensive. The effectiveness of the biopolymer treatment lasted for at least two weeks when exposed to sunlight and summer temperature. Larson et al. (2012) performed an investigation of using biopolymers derived from *Rhizobium tropici* as soil amendment to increase slope stability on earthen berms, control heavy metal leaching and abate

fugitive dust. It was found that the biopolymer amendment could effectively reduce surface runoff and maintain the slope stability; biopolymer mixed with contaminated soil showed a significant decrease in heavy metal transport in leachate; soil treated with 0.5% biopolymer showed a great reduction in fugitive dust generation.

Recently, the utilization of microorganisms induced calcite ($CaCO_3$) precipitation (MICP) to beneficially alter the engineering properties of soil has received increasing interests. Microorganisms with highly active urease enzyme consume urea, $CO(NH_2)_2$, as energy sources and produce ammonia, NH_3, which increases the pH level, leading to precipitation of calcite (DeJong et al. 2006; Whiffin et al. 2007). The bio-induced mineralization in soils may reduce the pore space of soil and strengthen the particle contacts, leading to increased strength and decreased permeability and compressibility (DeJong et al. 2010). This biotechnology has been explored to control fugitive dust. Meyer et al. (2011) reported the utilization of a natural soil microorganism, Sporosarcina pasteurii, induced calcium carbonate precipitation as suppressant to control airborne fugitive dust. The experimental results showed that a crust layer was formed on the surface of the treated sample which showed a significant reduction in mass loss. The MICP has also been applied to strengthen liquefiable soils. For example, Montoya et al. (2013) recently reported a study of using the MICP to improve the dynamic response of liquefiable sand. A soil bacterium, called *Sporosarcina pasteurii*, was used to facilitate chemical reactions and induce cementation. The centrifuge test results revealed that the MICP-treated sand showed an increase in resistance to liquefaction compared to

untreated sand by reducing pore pressure and the shaking-induced settlement. However, the maximum acceleration at the ground surface was amplified.

Inspired by the idea that incorporation of gas bubbles into saturated soils induces a decrease in the degree of saturation leading to increased liquefaction resistance, He et al. (2013) carried out a study of using microbial-generated biogas to mitigate the liquefaction potential of saturated sand. Denitrifying bacteria was cultivated to produce inert nitrogen (N_2) gas bubbles partially filling the pore of sand to reduce the degree of saturation down to 80%, 90% and 95%. The shaking table tests using a fully instrumented laminar box indicated that the pore water pressure generated in the sand treated with microbial-generated biogas was obviously smaller than that in the untreated sand, proving the effectiveness of using biogas to improve the liquefaction resistance of sand. Another study by He and Chu (2014) showed that inclusion of biogenic nitrogen gas into loose sand induced a slightly reduction in the degree of saturation, causing a significantly increase of the undrained shear strength and liquefaction resistance.

A detail review by DeJong et al. (2010) summarized the bio-mediated soil improvement methods with focus on bio-mediated calcite precipitation of sands.

4.2.2 Fall cone test to characterize soil

The fall cone test is often used to determine the liquid and plastic limits and undrained shear strength of soils. The liquid and plastic limits were originally proposed by Atterberg (1911) for agricultural purpose. These limits, well known as Atterberg limits, were standardized by Casagrande (1932,1958) and are used worldwide for classification of fine-grained soils. Casagrande (1932) assumed that the shearing

resistance at the liquid limit irrespective of the soil type must have a constant value and proposed the so called percussion cup method to determine the liquid limit. However, the percussion cup method has received considerable criticisms due to its high operator-dependency and poor repeatability and consistency. Hansho (1957) conducted experiments on several Swedish clays by using cones with different weights and geometries to investigate the relationship between cone penetration (h) and undrained shear strength (s_u). He proposed the following expression for quick and simple evaluation of the undrained shear strength of clays:

$$s_u = K\frac{W}{h^2} \tag{4.1}$$

where s_u = undrained shear strength, W = weight of cone, K = fall cone factor, and h = penetration of the cone into the soil. The fall cone factor K was found to depend on the cone apex angle, the cone surface roughness, the rate of shear strain during penetration (Houlsby 1982; Koumoto and Houlsby 2001), and soil texture (Towner 1973). Sherwood and Ryley (1970) proposed the utilization of the fall cone method to determine the liquid limit of soils. Wroth and Wood (1978) further proposed that the fall cone method could also be used to determine the plastic limit of soils based on the assumption that the undrained shear strength at plastic limit was 100-fold increase as compared to that at liquid limit. Since then, the fall cone test with its simplicity, reliability and repeatability has become a widely used method for determining the liquid and plastic limits of soils. For example, the British Standards Institution (1990) defines liquid limit as the water content at which a cone of apex angle of $30°$ and weight of 80 g, with its apex just touching the even surface of a soil sample, penetrates into a depth of 20 mm in 5 s. The

French Test Standard AFNOR (Association Francaise de Normalisation 1995) defines liquid limit using the same cone as BS 1377 but at a different penetration depth of 17 mm. In Canada, the standard the standard CAN/BNQ 2501-092-M-86 (Canadian Standards Association and Bereau de normalisation du Quebec 1986) describes the use of the Swedish 60 ° and 60 g cone method to determine liquid limit corresponding to a penetration depth of 10 mm. Similar methods proposed for determining liquid limit have been summarized and well documented in Budhu (1985), Leroueil and Bihan (1996), and Koumoto and Houlsby (2001). In the case of the plastic limit, Feng (2000) proposed that the best-fit straight line of a log-log plot of water contents (%) versus fall cone penetration (mm) be projected backwards to the water content axis (ordinate) at a depth of penetration of 1 mm. If the water content at the penetration depth of 1 mm is *C*, then the plastic limit (w_P) is

$$w_P = C(2)^m \tag{4.2}$$

where *m* is the absolute slope of the best-fit straight line.

Many attempts have been reported on using the fall cone method to determine the undrained shear strength of soils. Al-Durrah and Bradford (1981) studied the use of the fall cone method to measure the undrained shear strength of soils and concluded that the fall cone method was a rapid and inexpensive alternative over the unconfined compression test to measure the shear strength of soils. Bradford and Grossman (1982) investigated the utilization of a modified Swedish fall-cone device for in situ measurement of shear strength of soils near the surface. The results indicated that the shear strength of the near-surface soil decreased with depth within the 0-2 cm zone and a

heavier cone provided lower strength than a lighter one. Ekwue (1990) used the fall cone method to investigate the influence of organic matter on the shear strength of soils. Godwin et al. (1991) carried out a study of using a dynamic drop cone device for rapid assessment of soil strength, in which a cone with a weight of 2 kg and an apex angle of 30 ° was adopted. The cone was allowed to freely drop from a height of 1 m and its penetration into the soil was measured. The experimental results showed a linear relationship between the cone penetration and the vane shear strength for shear strengths exceeding 20 kPa. Zreik et al. (1995) reported a new fall cone device that was able to measure the undrained shear strength of extremely soft soils. This device was used to measure the undrained shear strength of Boston Blue Clay with different ages (Zreik et al. 1997,1998). Becher et al. (1997) proposed the utilization of an insensitivity index I to characterize hardsetting and non-hardsetting soils based on the measurements of fall-cone penetration at different water contents. Rajasekaran and Narasimha Rao (2004) used the fall cone method to measure the shear strength of lime treated marine clays based on Eq. (4.1) proposed by Hansbo (1957). Laboratory vane shear tests were carried out in order to validate the results of the fall cone test. The results showed a linear relationship between the measured shear strength values from the fall cone and laboratory shear tests respectively. The authors concluded that the fall cone method could be a good alternative to determine the shear strength of soils.

Although the fall cone method is gaining popularity as the preferred method to determine the liquid and plastic limits, and/or undrained shear strength of soils, few attempts have been devoted to the utilization of the fall cone method to determine the

liquid and plastic limits and/or undrained shear strength of mine tailings. Dimitrova and Yanful (2011) used an automated fall cone device to measure the undrained shear strength of mine tailings beds at different depths. The results showed that the undrained shear strength of the tailing beds varied between 0.008 and 0.975 kPa for effective stresses below 1.19 kPa and increased with depth.

4.3 MATERIALS AND METHODS

4.3.1 Materials

The MT were provided by a local mine company in Tucson, Arizona. The mineralogy analysis shows that the copper MT contain about 69% by weight of alumina silicate (including K-feldspar, plagioclase and muscovite), 30% quartz and 1% pyrite. Fig. 4.1 shows the grain size distribution of the MT. Based on the Unified Soil Classification System (ASTM 2006), the MT contain 5% clay, 28% of silt and 67% of fine and medium sand. The uniformity coefficient and the coefficient of curvature are respectively 33.9 and 1.82, indicating that the MT are well-graded.

The two biopolymers, xanthan gum and guar gum, were purchased from Gum Technology Corporation in Tucson, Arizona. These two biopolymers were chosen because they are commercially available at relatively low price, extensive literature is available on their chemical and physical properties, and studies have shown that they can stabilize soils and having outstanding characteristics of metal chelation (Kim et al. 2009).

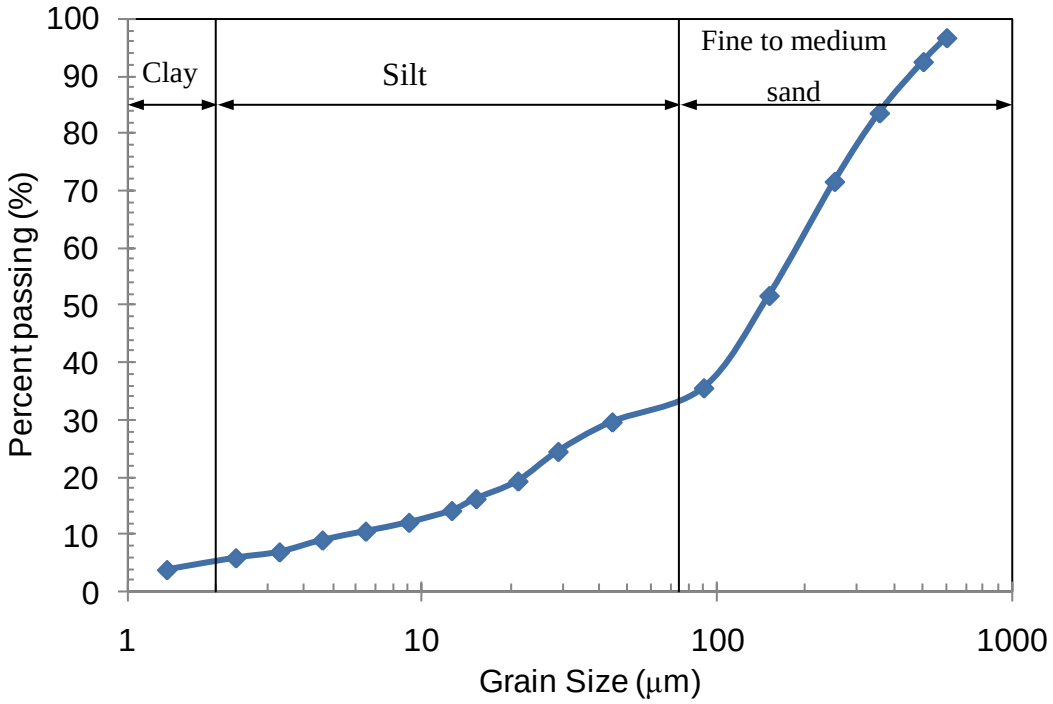


Figure 4.1. Grain size distribution of MT.

Xanthan gum is an extracellular polysaccharide produced by the bacterium called *Xanthomonas campestris*. Xanthan gum is an anionic polysaccharide whose backbone is similar to that of cellulose with a primary structure composing of repeated pentasaccharide units formed by two glucose units, two mannose units and one glucuronic acid unit (García-Ochoa et al. 2000). The toxicology and safety of xanthan gum has been extensively studied and has been approved by the United States Food and Drug Administration (FDA) as a food additive for use as a stabilizer and thickener (Barbara 1998). Xanthan gum is soluble in cold and hot water and is stable over a broad range of pH values (Barbara 1998). Because of its special properties, xanthan gum is widely used in many industrial areas such as salad dressing, cosmetics, drug delivery, etc.

Detail information of the application of xanthan gum can be referred to García-Ochoa et al. (2000).

Guar gum is a water soluble polysaccharide extracted from the cluster bean called *Cyamopsis tetragomolobus*. Guar gum molecule is lineal structure consisting of numerous hydroxyl groups which can induce cross linking of the molecules resulting in a three dimensional network (Chudzikowski 1971). The presence of hydroxyl groups in guar gum makes it easily hydrogen bond to hydrated mineral and organic surfaces (Chudzikowski 1971).

4.3.2 Preparation of biopolymer solutions

The biopolymer solutions were prepared by dissolving the biopolymer powder in deionized water at specified concentrations. The concentration is defined as the ratio in percentage of the dry weight of biopolymer to the total weight of the biopolymer solution. In order to prevent clumping, the biopolymer powder was slowly added into deionized water and a hand mixer was used to stir the solution for 10 minutes until a homogeneous solution was obtained. Xanthan gum solutions with concentrations of 1, 2 and 3% and guar gum solutions with concentrations of 0.5, 1 and 2% were used to investigate the effect of biopolymers on the liquid limit and undrained shear strength of MT.

4.3.3 Fall cone test

The fall cone test was performed following the British Standard BS 1377 (1990). The weight of the cone is 80 g and its apex angle is 30 °. First the MT were thoroughly

mixed with certain amount of biopolymer solution at a specified concentration until a homogeneous paste was formed. Next, the paste was carefully filled in a sample cup with a diameter of 55 mm and 40 mm deep, forming a smooth even surface without trapping any air bubbles. Then the cone was lowered until its tip just touched the sample surface. After that, the cone was released and allowed to penetrate into the sample for 5 seconds under its own weight. The penetration depth was measured by a dial gauge with an accuracy of 0.01 mm. After the measurement of the penetration depth, about 10 gram of sample was taken from the cup to measure the water content of the tested paste. For each biopolymer concentration, including the 0% one which was used as a control, six fall cone tests were conducted at different water contents. By plotting the water content versus the penetration in a log-log scale and finding the straight line best-fitting the data points, the liquid limit was determined as the water content corresponding to a penetration of 20 mm. The plastic limit was determined using Eq. (4.2). The undrained shear strength was also calculated using Eq. (4.1) by adopting a cone factor K value of 1.33 for the British fall cone used (Koumoto and Houlsby 2001; Mahajan and Budhu 2009).

4.3.4 Scanning electron microscopy (SEM) characterization

To better understand the effect of biopolymers on the microstructure and the physical and mechanical performance of MT, SEM imaging characterization was performed. The biopolymer-MT samples were observed and imaged using a Hitachi S-3400N Variable Pressure SEM under VP mode with an Environmental Secondary

Electron detector. The 2% xanthan gum and 1% guar gum- samples were used for the SEM imaging.

4.4 RESULTS AND DISCUSSION

4.4.1 Effect of biopolymer on undrained shear strength and liquid limit

Figs.4.2 and 4.3 show log-log plot of the cone penetration depth versus water content at different biopolymer concentrations respectively for MT mixed with xanthan gum and guar gum solutions. At a given water content, the cone penetration decreases as the biopolymer concentration increases, indicating that the inclusion of more biopolymer makes the MT even stronger. This is confirmed in Fig. 4.4 which shows the undrained shear strength calculated with Eq. (4.1) increases with higher biopolymer concentrations.

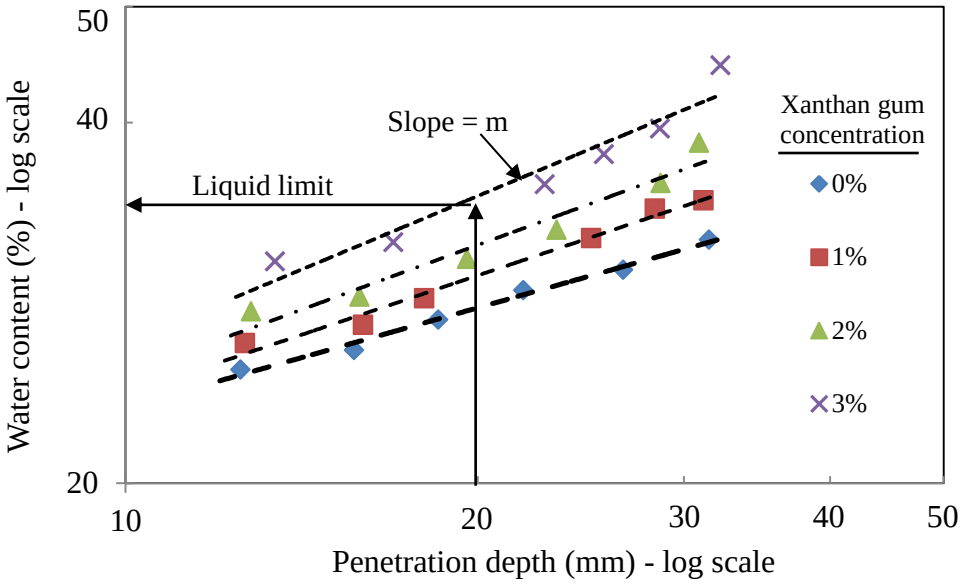


Figure 4.2. Log-log plot of penetration depth versus water content at different xanthan gum concentrations.

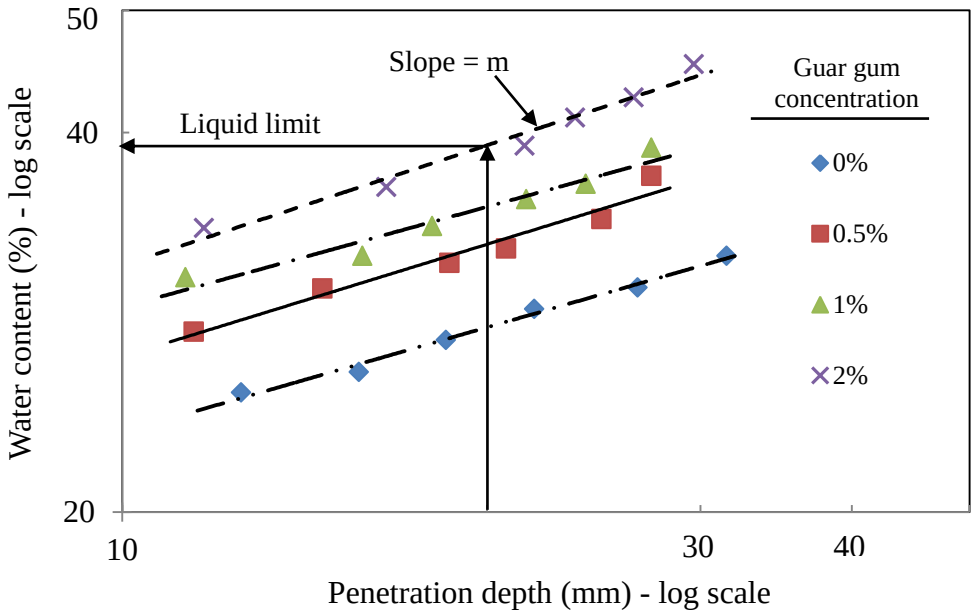


Figure 4.3. Log-log plot of penetration depth versus water content at different guar gum concentrations.

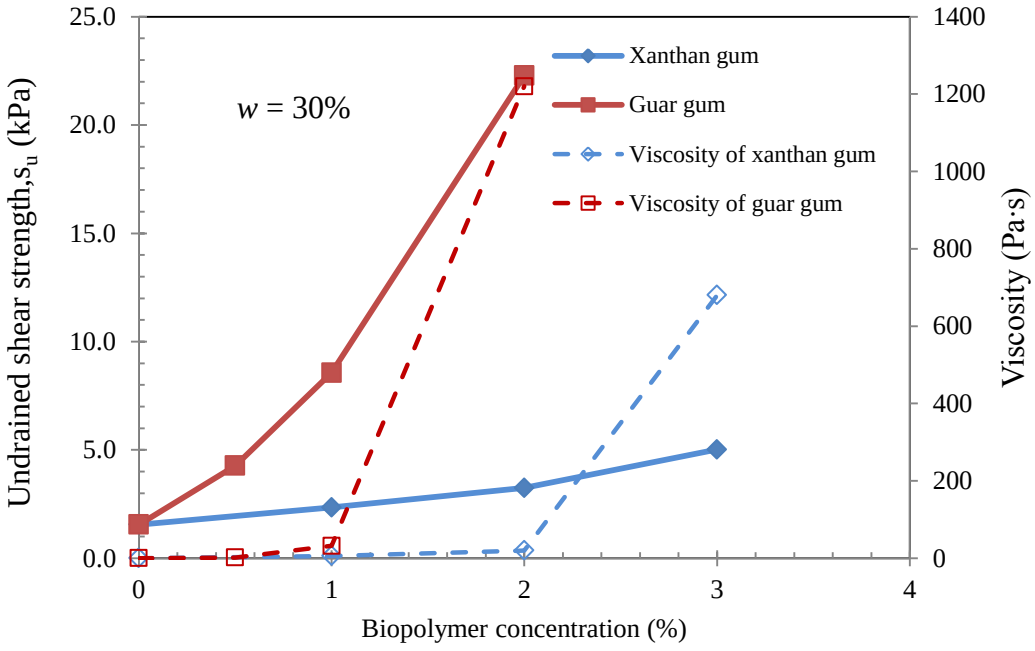


Figure 4.4. Biopolymer concentration versus undrained shear strength of MT at water content w = 30% and viscosity of biopolymer solution.

Also plotted in Fig. 4.4 are the room temperature zero-shear-rate dynamic viscosities of xanthan gum and guar gum solutions (García-Ochoa et al. 2000; Milas et al. 1985; Nugent et al. 2009; Whitcomb et al. 1980). Viscosity is a measure of the resistance of a fluid to shear stress. Water has nearly zero viscosity and contributes little to the ability of MT to resist shear stress. By including xanthan gum or guar gum, the viscosity of the pore fluid increases dramatically and thus the undrained shear strength of the MT increases. Guar gum is more effective than xanthan gum in increasing the viscosity of the pore fluid and thus more effective in increasing the undrained shear strength of MT. The viscosity of the guar gum solution increases from nearly zero at 0% concentration to 1200 Pa·s at 2% concentration, whereas the viscosity of the xanthan gum solution increases from nearly 0 to only 680 Pa·s even when the concentration increases from 0% to 3%.

Aggregation of MT particles due to the added biopolymer and the type of bonding between the biopolymer and MT particles also account for the difference between the effectiveness of xanthan gum and guar gum in increasing the undrained shear strength of MT. Xanthan gum is an anionic polysaccharide (Garcia-Ochoa et al. 2000) which interacts with the cations (Cu^{2+}, Na^{+}, Fe^{2+}) presented in the MT to form ionic bonding between xanthan gum and MT particles and induces high degree of aggregation. In contrast, guar gum is a neutrally charged polysaccharide (Chudzikowski 1971) with numerous hydroxyl (-OH) groups which form hydrogen bonds between guar gum and MT particles and only induce slight aggregation. Fig. 4.5 shows the SEM images of MT mixed respectively with 2% xanthan gum solution and 1% guar gum solution. The xanthan gum solution caused much higher level of aggregation and induced larger voids

filled with air or biopolymer gel than the guar gum solution. The smaller voids and stronger hydrogen bonding contribute to the higher undrained shear strength of MT mixed with the guar gum solution than with xanthan gum solution.

Figs. 4.6 and 4.7 plot the liquid limit against the biopolymer concentration respectively for the MT containing xanthan gum and guar gum solutions. Also plotted in these figures are the room temperature zero-shear-rate dynamic viscosities of xanthan gum and guar gum solutions at different concentrations.

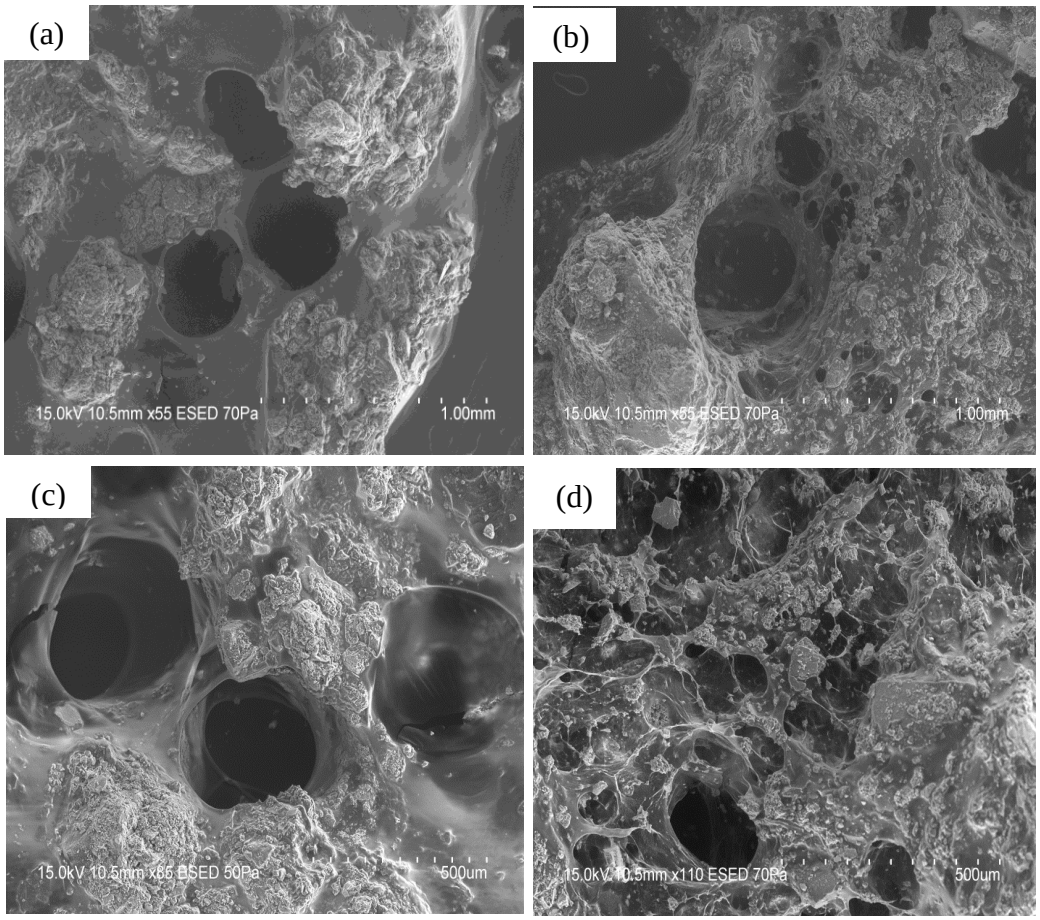


Figure 4.5. SEM images of MTmixed with 2% xanthan gum solution (a and c) and 1% guar gum solution (b and d).

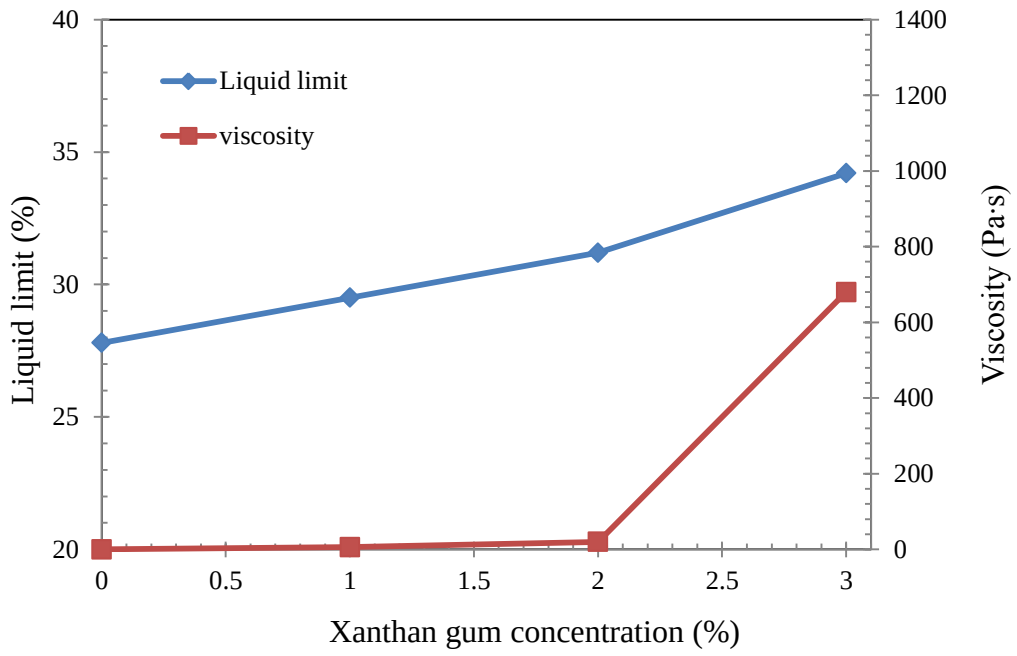


Figure 4.6. Xanthan gum concentration versus liquid limit of MT and viscosity of xanthan gum solution.

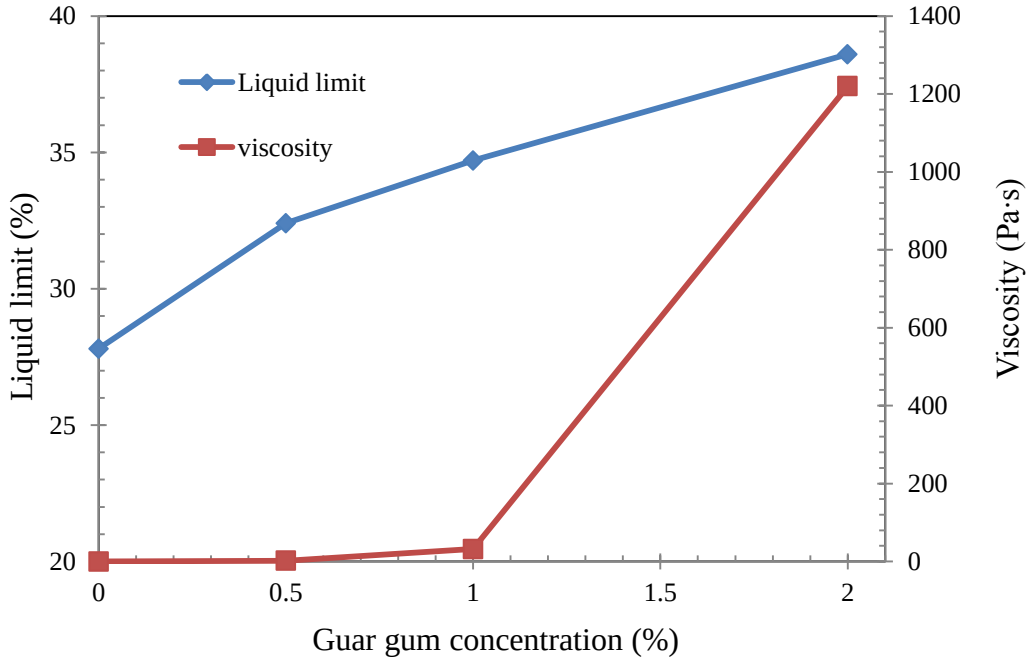


Figure 4.7. Guar gum concentration versus liquid limit of MT and viscosity of guar gum solution.

The liquid limit of MT increases with higher biopolymer concentration and guar gum is more effective than xanthan gum in increasing the liquid limit. For guar gum, the liquid limit increases from 27.8% to 38.6% when the concentration changes from 0 to 2%, but for xanthan gum, the liquid limit only increases from 27.8% to 34.2% even when the concentration changes from 0% to 3%. The liquid limit is a measure of how much fluid must be added to a soil to reduce its undrained shear strength to a specific threshold (~ 2 kPa). At higher biopolymer concentration, the higher viscosity of the pore fluid contributes to the shear resistance of the MT and thus more fluid is required in order for the undrained shear strength to reach the specific threshold and thus the liquid limit is higher (Nugent et al. 2009). The difference between the effectiveness of xanthan gum and guar gum in increasing the liquid limit of MT is also related to the different viscosities of xanthan gum and guar gum solutions and the different levels of aggregation of MT particles.

4.4.2 Comparison of unstrained shear strength from fall cone tests and those from empirical equations

It is well known that the undrained shear strength is a function of water content. Various empirical relations have been proposed for estimating the undrained shear strength based on liquid limit and water content. Federico (1983) proposed the following empirical equation for determining the undrained shear strength of remoulded clayey soils at high water content:

$$s_u = exp5.52\left(1 - \frac{w}{w_L}\right) \tag{4.3}$$

where s_u = undrained shear strength; w = water content, and w_L = liquid limit. Lee (2004) proposed an empirical equation for determining the undrained shear strength of dredged fine-grained material:

$$s_u = 182.93exp\left(-2.23714\frac{w}{w_L}\right) \quad (4.4)$$

A similar empirical equation was also proposed by Berilgen et al. (2007) for determining the undrained shear strength of dredged marine clay:

$$s_u = 145exp\left(-2.86\frac{w}{w_L}\right) \quad (4.5)$$

Figs. 4.8 and 4.9 show the s_u obtained from the fall cone test based on Eq. (4.1) and those from empirical equations (4.3) to (4.5) using the measured liquid limit values. In general, the undrained shear strength s_u decreases with higher water content, as indicated by both the fall cone test data and the empirical equations. The s_u obtained from the fall cone test fall between the upper bound set by Eq. (4.5) and the lower bound set by Eq. (4.4). Eq. (4.3) predicts the s_u from the fall cone test very well at the high water content range for each biopolymer concentration but under-predicts the s_u at the low water content range.

To improve the accuracy for predicting the undrained shear strength of MT, a new equation needs to be developed based on the test data. To be simple, the exponential equation is proposed to relate the undrained shear strength to the liquid limit and water content:

$$s_u = a\ exp\left(-b\frac{w}{w_L}\right) \quad (4.6)$$

Based on the best fitting of the test data of s_u versus w/w_L, a and b are obtained respectively as 1227 and 6.08 and Eq. (4. 6) can be rewritten as:

$$s_u = 1227\ exp\left(-6.08\frac{w}{w_L}\right) \tag{4.7}$$

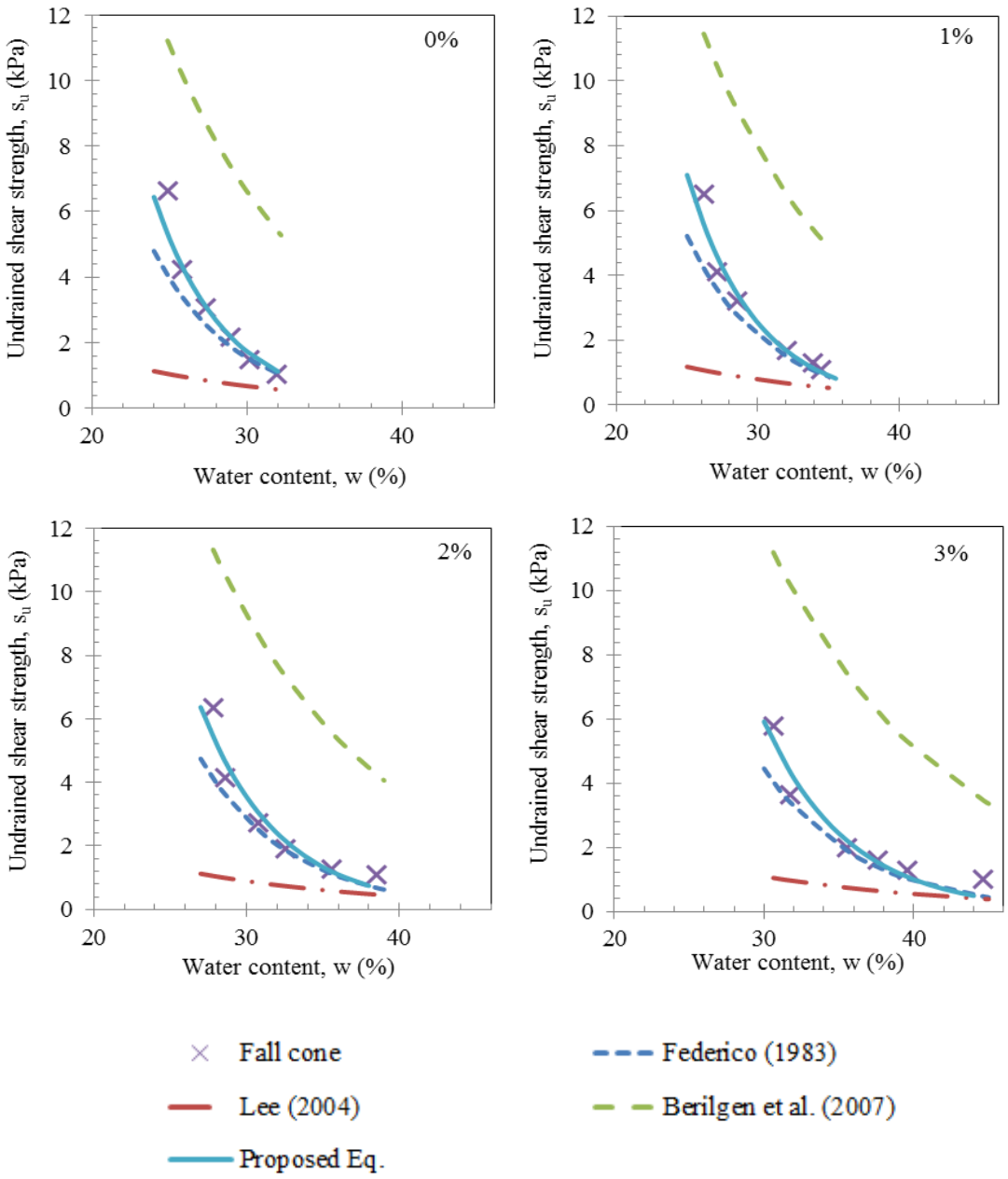


Figure 4.8. Water content versus undrained shear strength of MT mixed with xanthan gum solution at different concentrations.

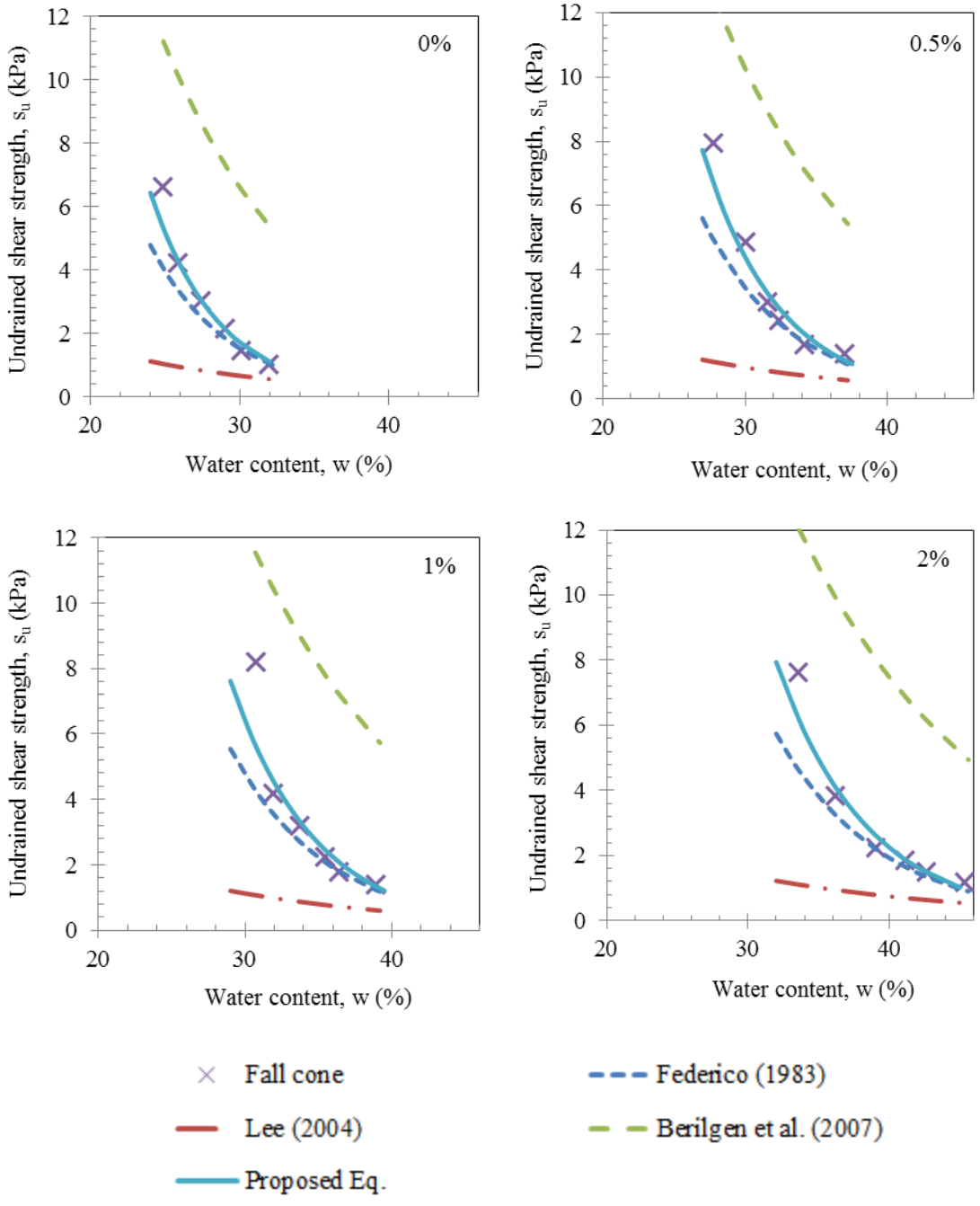


Figure 4.9. Water content versus undrained shear strength of MT mixed with guar gum solution at different concentrations.

The coefficient of determination R^2 = 0.9578. The predictions from Eq. (4.7) are also plotted in Figs. 4.8 and 4.9. It can be seen that the predictions are now in good agreement with the test values.

Researchers have also proposed many empirical equations relating the undrained shear strength to the liquidity index (*LI*):

$$LI = \frac{w - w_P}{w_L - w_P} \tag{4.8}$$

For example, Schofield and Wroth (1968) proposed the following equation for estimating the undrained shear strength of clay:

$$s_u = 170 exp(-4.6LI) \tag{4.9}$$

Whyte (1982) proposed a similar empirical equation to estimate the undrained shear strength of clay based on critical state theory:

$$s_u = 1.6\ exp 4.23(1 - LI) \tag{4.10}$$

Berilgen et al. (2007) related the undrained shear strength to the liquidity index of dredged marine clay as follows:

$$s_u = 28\ exp(-1.33LI) \tag{4.11}$$

Figs. 4.10 and 4.11 present the s_u obtained from the fall cone test based on Eq. (4.1) and those from Eqs. (9) to (11) using the test liquidity index values. Eqs. (4.9) and (4.10) slightly underestimate the undrained shear strength whereas Eq. (4.11) significantly overestimates the undrained shear strength.

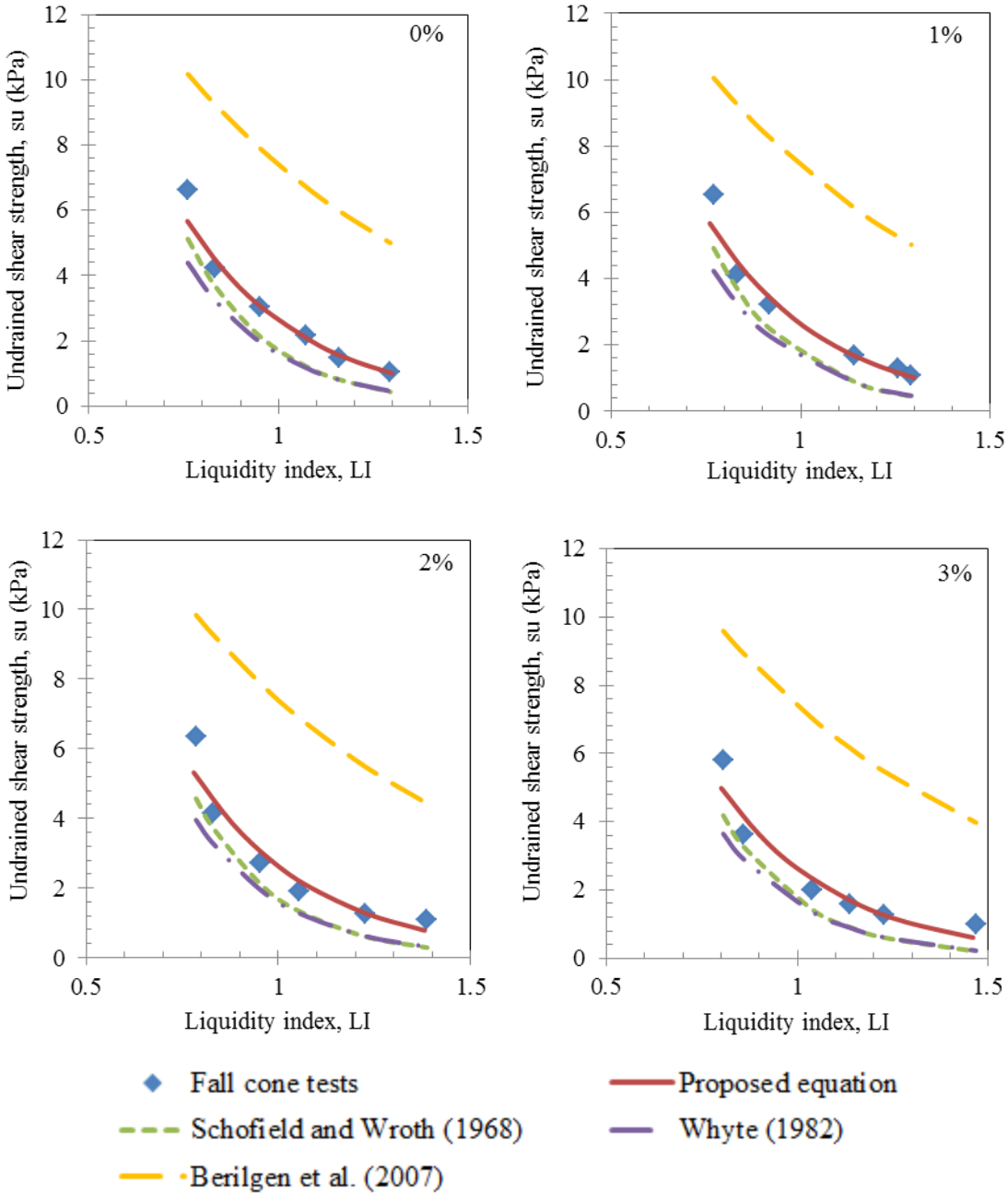


Figure 4.10. Liquidity index versus undrained shear strength of MT mixed with xanthan gum solution at different concentrations.

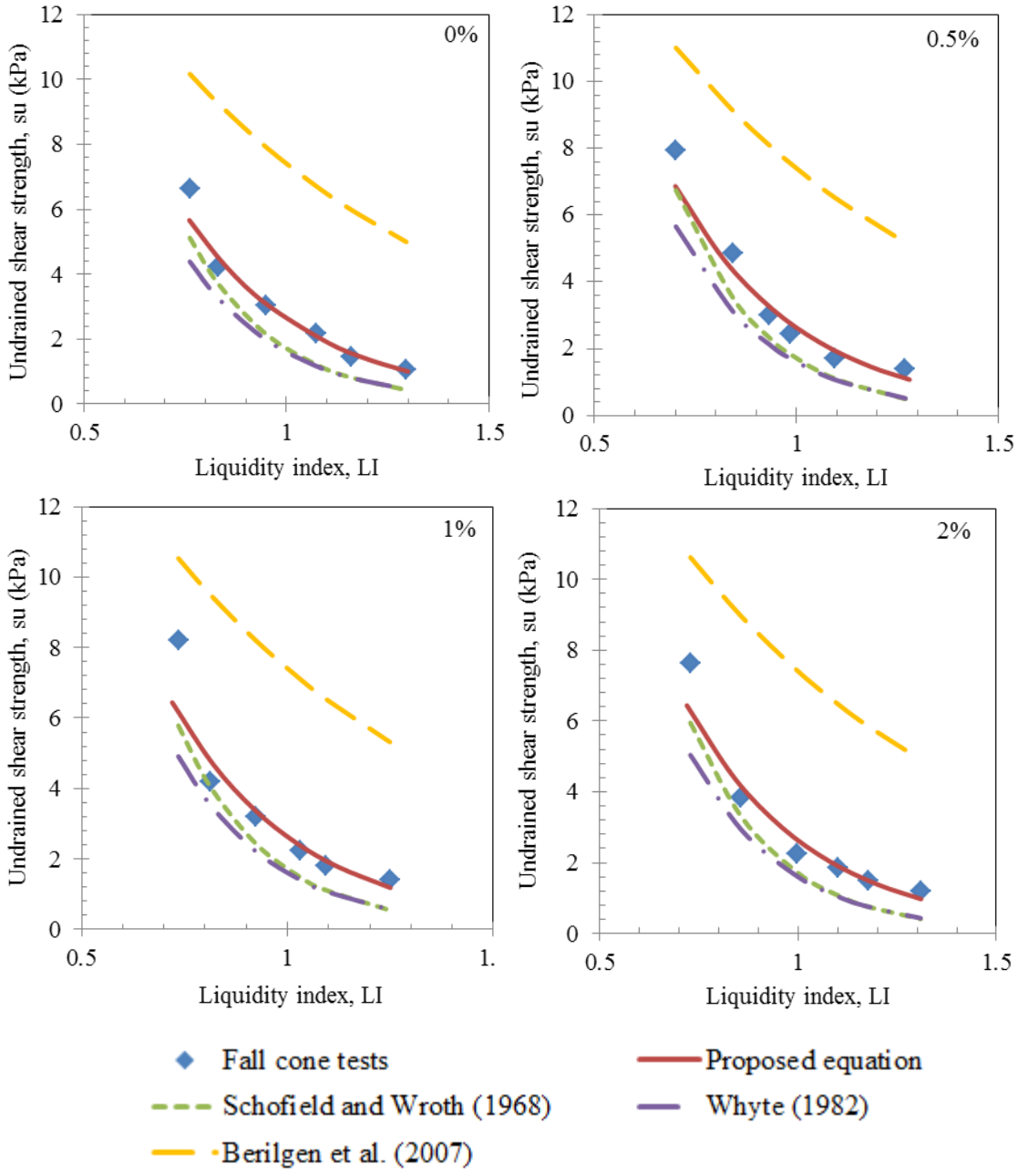


Figure 4.11. Liquidity index versus undrained shear strength of MT mixed with guar gum solution at different concentrations.

Based on the best fitting of test data of s_u versus *LI*, the following exponential equation can be obtained for estimating the undrained shear strength from the liquidity index for biopolymer stabilized MT:

$$s_u = 64.5\, exp(-3.2LI) \tag{4.12}$$

The coefficient of determination R^2 = 0.9592 which is about the same as that for Eq. (8). So Eqs. (4.7) and (4.12) have about the same accuracy for predicting the undrained shear strength of biopolymer stabilized MT.

It needs to be noted that there are uncertainties associated with the determination of s_u from the fall cone test based on Eq. (4.1). The empirical correlations from Eqs.(4.7) and (4.12) should be validated using direct measurements of s_u before they are used in practice.

4.5 CONCLUSIONS

The feasibility of using two natural biopolymers, xanthan gum and guar gum, to stabilize MT was investigated. The following conclusions can be drawn based on the experimental results:

a) Inclusion of either xanthan gum or guar gum increases the liquid limit and undrained shear strength of MT, higher biopolymer concentration leading to greater increase. The increase is mainly due to the higher viscosity of the biopolymer pore fluid and the bonding between the biopolymer and the MT particles.
b) Guar gum is more effective than xanthan gum in increasing the liquid limit and undrained shear strength of MT because the guar gum solution is more viscous than the xanthan gum solution at the same concentration, the guar

gum-MT particle bonding is stronger than the xanthan gum-MT particle bonding, and guar gum causes less degree of aggregation of MT particles than xanthan gum.

c) For MT mixed with biopolymer solutions, the variation of undrained shear strength with water content follows the general trend of empirical equations for soils, although the magnitudes can be quite different. For better prediction of the undrained shear strength of MT, the two newly proposed equations can be used.

CHAPTER 5
BIOPOLYMER STABILIZATION OF MINE TAILINGS FOR DUST CONTROL

5.1 INTRODUCTION

The unconfined mine tailings in arid and semiarid areas have been a significant source of fugitive dust, which induce many environmental and safety concerns. In general, there are two methods commonly used to mitigate the generation of fugitive dust: the first one is to reduce the wind speed by creating physical barriers in the path of wind or by roughening the surface; and the second one is to create a more resistant surface by aggregating the soil particles or forming a crust using dust suppressants (Lyles 1988). With respect to the first method, vegetation is commonly introduced to reduce wind speed. Phytostabilization of MT is gaining increasing research interest for mitigation of MT dust recently (Haque et al. 2008; Mendez and Maier 2008; Zornoza et al. 2012). However, it has limitations. Additional soil is required to lay on the surface of MT to support plant growth since the MT usually show acidic pH and contain no organic matter. The plants suitable for phytostabilization should be of metal- and salt-tolerance and are usually expensive to obtain. Also, continuous irrigation may be required, especially in arid and semiarid regions, leading to increased water consumption and costs. In addition, the phytostabilization method is only applicable to MT impoundments after closure. A variety of dust suppressants are currently used in unpaved road, construction sites and MT impoundments for dust abatement, which can be subdivided into two

categories: physical covers such as topsoil or geotextile, and chemical dust suppressants (Piechota et al. 2004). The use of physical covers for dust mitigation is usually expensive due to the additional costs in transportation, installation and maintenance. Besides, the physical covers may experience cracking when subjected to wet/dry cycles in arid or semiarid areas, which adversely affects their effectiveness. Chemical dust suppressants are widely used to mitigate fugitive dust from MT. A chemical dust suppressant functions in one of the following ways: attracting and retaining moisture within soil mass; transforming smaller dust particles into larger ones; forming a protective crust on the soil; or working as adhesive to bind or agglomerate soil particles together (Pierce et al. 2007). A summary of currently used chemical dust suppressants with respect to their origin, functional mechanism, advantages and limitation of application, and environmental impacts is presented in Table 5.1. Intensive research has focused on evaluation of the effectiveness of the chemical dust suppressants; however, little is known about how the application of these chemicals for dust control affects human health and the environment (Pierce et al. 2007). There also exist gaps in understanding of the degradation, fate and toxicity of the chemical dust suppressants due to the exact formulation composition of the chemicals is vaguely or not provided for business confidentiality consideration (Piechota et al. 2004). Some of the chemical dust suppressants may have negative impact on the environment and human health (Piechota et al. 2004). For example, the oil containing dioxin used to suppress dust on unpaved roads in Times Beach, Missouri contaminated local homes and yards, and the cost to relocate the residents and clean up the polluted sites was estimated to be $80 million (U.S.EPA 1983). According to Piechota et al.

(2004), the potential environmental impacts of the chemical dust suppressants include deterioration of surface and ground water quality, contamination of topsoil, and toxicity to flora and fauna as well as human beings and animals. The aforementioned drawbacks of existing MT dust mitigation methods necessitate the pursuing of an environmentally friendly and cost-effective technology for MT dust mitigation both during the operation and after the closure of the MT impoundment.

This part of the thesis presents the results of a study on utilization of xanthan gum and guar gum to stabilize MT for (wind) dust control. Moisture retention tests, wind tunnel tests, and surface penetration tests were performed to evaluate respectively the enhancement of water retention capacity, the improvement of dust resistance, and the increase of surface strength (maximum penetration force) after MT were treated with biopolymer solutions of different concentrations. To better understand how biopolymer enhances the water retention capacity, improves the dust resistance and increases the surface strength of MT, scanning electron microscopy (SEM) imaging was also conducted to characterize the microstructure of biopolymer stabilized MT. For most biopolymers, water uptake induced passive hydrolysis is the most important mode of degradation (Göpferich 1996). Hence, it is of great importance to assess the long-term performance of biopolymer treatment related to wet/dry cycling. A durability test program containing 10 wet/dry cycles was applied to biopolymer treated MT samples and wind tunnel tests were conducted after the 1^{st}, 3^{rd}, 7^{th}, and 10^{th} wet/dry cycle respectively to evaluate the effect of wet/dry cycling on the performance of biopolymer treatment.

Table 5.1. Comparison of different types of dust suppressants (Bolander and Yamada 1999; Lima et al. 2003)

Dust suppressant	Origin	Functional mechanism	Advantages	Limitations	Environmental impact
Water	Surface or ground water sources	Wets and binds particles together, forming a protective crust on the surface	Readily available and easy to apply.	Frequent application to control dust, therefore it is the most expensive and labor intensive	None
Hydroscopic additives (e.g., calcium chloride, magnesium chloride, sodium chloride)	Derive from either the byproduct of ammonia-soda or naturally from salt brine	Attract and retain moisture in soil, increase surface tension, induce a hard crust	Reduce evaporation rate and detrimental effect of freeze-thaw cycles	Corrosive to vehicles; Limited effectiveness in arid and semi-arid regions due to low humidity	Have negative impact on the local vegetation and water system
Organic petroleum products (e.g., asphalt emulsions, crude oil)	Derive from industrial byproducts of petroleum, coal, and plastics	Form a protective crust against wind erosion	Waterproof the surface with long-term effectiveness	Adhesive to vehicles and hard to clear; some are difficult to maintain	Some are toxic to the environment and human beings
Organic non-petroleum products (e.g., vegetable oils, ligninsulfonate)	Mainly come from paper-making industrial byproducts; the composition depends on raw materials and chemicals	Binding particles together to form a protective crust against wind erosion	Increase dry strength of material and retain effectiveness after long dry periods	Corrosive to aluminum and its alloys; become slippery when wet and brittle when dry; crust could be easily damaged by rain	Leaching of lignin when subjected to moisture which has a high biological oxygen demand in aquatic systems, posing negative impact on aquatic ecosystem

Table 5.1. (Cont.) Comparison of different types of dust suppressants (Bolander and Yamada 1999; Lima et al. 2003)

Dust suppressant	Origin	Functional mechanism	Advantages	Limitations	Environmental impact
Electrochemical products (e.g., enzymes, ionic products)	Come from sulfonated oil, ammonium chloride enzyme, ionic products	Improve soil compaction by driving water out from voids of soil	Effective regardless of climatic conditions	The effectiveness depends on the clay fraction; limited life span; need time to react with the fines	Detail product-specific information is needed to do the analysis.
Synthetic polymer products (e.g., Soil-Sement, Envirotac II Soil Stabilizer)	Synthetic formulations contain polyvinyl acetate or vinyl acrylic	Work as a binding agent to agglomerate or aggregate soil particles	Applicable to most dust emission sources with good effectiveness	Take time to cure before used; may be degradable when subjected to sunlight.	Vinyl acetate is a potential carcinogen; little to no impact on the aquatic lives
Clay additives (e.g., bentonite, montmorillonite)	Derive from natural clay deposits	Transform the fine dust particles into larger one by agglomeration	Increase dry strength of materials; retain moisture; beneficial for vegetation.	Expensive to obtain; surface becomes slippery when wet	Impact to aquatic system is unknown

5.2 WIND EROSION OF SOIL

To better understand how to effectively control the generation of dust, it is necessary to understand the how the soil is eroded by wind. Wind erosion of soil includes initiation, transport, abrasion, sorting and deposition of soil aggregates (Lyles 1988). The movement of soil particles by wind consists of saltation, creep and suspension (Chepil 1945; Lyles 1988; Skidmore 1986). In saltation (hopping), the soil particles are lifted off the surface by wind, traveling 10-15 times of their height of rise, then returning with angular momentum impacting the surface, inducing dislodgement of other particles. It is reported that about 50%-70% of the weight of eroded soil is carried in saltation (Chepil 1945). The diameter of the saltating particles typically ranges from 0.1 to 0.5 mm. Soil particles with diameter larger than 0.5 mm are too large to be lifted off the surface by ordinary erosive wind. However, the energy from impact by saltating particles can push and roll these particles, the process of which is referred to as soil creep. 7-25% of total soil is transported through creep (Lyles 1988). Soil particles finer than about 0.1 mm can be easily entrained by airflow and become airborne traveling thousands of miles downwind for a long period of time. This process is called suspension. Soil suspension that is visible as dust makes up 3-38% of total soil transported.

Soil suspension is mainly attributed to saltation (Lyles 1988; Chepil 1945; Skidmore 1986). The wind induced shear stress is sometimes incapable of detaching fine particles off a soil surface because the fines of a soil are usually aggregated and finally crusted by bonding forces such as matric suction (Rice et al. 1997). Once a soil surface is

crusted due to aggregation, wind erosion of soil becomes difficult. Gillette et al. (1982) reported that even a weak crust can significantly increase wind erosion resistance. However, saltating particles can break the inter-particle bonding and disaggregate the surface crust, contributing to expose the fine particles beneath to wind entrainment and increase erosion rate. The saltating particles also potentially generate additional fines by abrasion and attrition of the crusted surface (Rice et al. 1997; Rice et al. 1996). The crust formed on the surface of a soil due to application of chemical dust suppressants is of great importance to mitigate dust emission. Therefore, the strength of the crust needs to be determined to assess its capacity of resisting impact and abrasion by saltation.

5.3 MATERIALS AND METHODS

5.3.1 Materials

MT were provided by a local mine company and guar gum and xanthan gum were the two biopolymers used in this study, the detail information of which can be referred to the **Chapter 4**.

5.3.2 Preparation of samples

The samples for water retention and wind tunnel tests were prepared using aluminum trays with a size of 11.75 inch × 9.25 inch × 2.5 inch. Each sample contained 2500 g of sun-dried MT treated with biopolymer solution at a specific concentration. First, the sun-dried MT were placed in the tray with slight compaction to achieve the approximate density of the field MT and a leveled surface. Then 520 ml of water was

gradually added to wet the MT. Finally, 130 ml of biopolymer solution at a specific concentration was sprayed on the MT surface to simulate the in situ application of dust suppressant. In practice, the typical application rate of dust suppressant varies greatly from 0.5 to 4.5 liter/m^2 depending on the dust suppressant used and the site conditions (Bolander and Yamada 1999). The application of 130 ml of biopolymer solution corresponded to a rate of 1.9 liter/m^2, which was determined based on the information from the literature and the application rate currently used by a local mining company. Biopolymer concentrations of respectively 0.6, 1.0 and 1.6% were used in this study. 0% (or just water) was also used as a control. Fig. 5.1 shows some of the MT samples treated with biopolymer solutions at different concentrations.

Figure 5.1. MT samples treated with biopolymer solutions of different concentrations.

The samples for surface strength measurements were prepared in the same way as the samples for moisture retention and wind tunnel tests but using steel trays with a size of 9.25 inch × 9.25 inch × 2.5 inch.

The samples for durability test were prepared using aluminum trays with a size of 8 inch × 8 inch × 1.63 inch. To be close to the real condition, the method used to prepare the samples for durability tests was slightly different from the previous. The sun-dried MT was first thoroughly mixed with water to obtain homogeneous slurry at a water content of 20%. Then each tray was filled with 2500 g wet MT. To achieve an application rate of 1.9 liter/m^2, 78 ml of biopolymer solutions at concentration of 0, 0.1, 0.3 and 0.5 were respectively sprayed on the surface of wet MT. Biopolymer solutions with lower concentrations were selected for durability tests because lowering the concentration induces decrease of the viscosity and dosage which would make the field application easier and more economical. Xanthan gum, guar gum and the combination of these two biopolymers (half and half) were used to evaluate the durability of biopolymer treatment. The combination of the two biopolymers was chosen because research has shown that additional guar gum to a xanthan gum solution at room temperature induces a synergistic increase in viscosity (García-Ochoa et al. 2000). Although it is not clearly understood, the interaction of the two biopolymers is expected to have better performance. Totally 10 groups of samples were prepared and each group had three samples at the same condition.

5.3.3 Moisture retention tests

The moisture retention tests were conducted to evaluate the enhancement of moisture retention capacity of MT after treatment with biopolymer solutions of different concentrations. The moisture benefits the development of inter-particle bonding force that mitigates the dust. The prepared samples were cured at atmospheric pressure and room temperature for one day and then exposed to sunshine. The weight of the samples was measured at end of every day. How fast the weight lost with time was then used to evaluate the moisture retention capacity of different samples. To evaluate the long-term performance of biopolymer stabilization related to sunlight exposure and wet-dry cycles, the dried samples were re-wetted with just water and then re-tested for a number of times.

5.3.4 Wind tunnel tests

An economic laboratory wind tunnel at a size of 450 cm × 60 cm × 60 cm was constructed using transparent PVC sheet so that the dust generation can be visually monitored (Fig. 5.2). An industrial fan was installed at one end of the tunnel to generate the wind. A rectangular frame at a size of 60 cm × 180 cm × 60 cm was installed at the other end of the wind tunnel to hold 5 pieces of air filters for capturing the fugitive dust. The dry samples after moisture retention tests, say after the first wet-dry cycle, were placed in the wind tunnel and the fan was run to generate a wind of 40 mph passing the sample for about 10 minutes. An anemometer was placed at 15 cm ahead and slightly above the tray to measure the wind speed. The weight of the tray sample was measured

before and after the wind tunnel test. The loss of the weight was used to evaluate the dust resistance of different samples.

Figure 5.2. Laboratory wind tunnel

5.3.5 Surface strength measurement

Wind dust (erosion) depends on how easy the particles can be detached from the surface and is thus closely related to the surface strength of MT. Researchers have used different methods to estimate the surface soil strength in order to evaluate the soil dust resistance, including the modulus of rupture method (Gillette et al. 1982; Richards 1953), the needle penetrometer method (Bengough and Mullins 1990; Rice et al. 1997), the fall cone or cone penetrometer (Bradford and Grossman 1982; Campbell and O'Sullivan 1991), the torvane method (Govers and Poesen 1986), and the aggregate stability method (Skidmore and Powers 1982). Rice et al. (1996) provided a brief review and evaluation of these different methods and recommended a simple flat-ended cylindrical penetrometer method for estimating the surface soil strength. This method was preferred to other

methods because it applies a load to an area encompassing many grains rather than just a few grains as with a needle penetrometer. It can also be easily adapted for use in the field.

In this study, the method recommended by Rice et al. (1996) was adopted to assess the surface strength of MT treated with biopolymer solutions of different concentrations. To do so, a flat-ended cylindrical penetrometer with a diameter of 6 mm was manufactured and attached to a loading machine so that the force-penetration curve can be obtained (Fig. 5.3). To do the penetration test, the sun-dried MT sample tray was placed on the loading platform and the penetrometer was then loaded to penetrate into the MT. For each sample, nine penetration tests were performed. A constant loading rate of 0.1 mm/min was used for all penetration tests and the test was stopped when the penetration depth reached 4.0 mm. The force and penetration were recorded during the penetration test and pictures were taken before and after the penetration test.

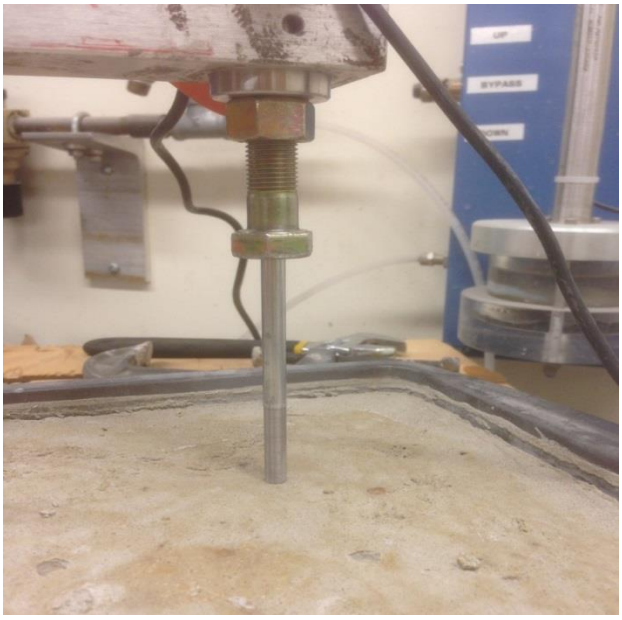


Figure 5.3. Penetrometer rests on a MT sample to be tested.

5.3.6 Scanning electron microscopy (SEM) characterization

SEM imaging was performed to investigate the development of micro-structure within the MT treated with biopolymer solutions of different concentrations – the aggregation of MT particles, the biopolymer coating on the particle surface and the biopolymer binding network between the encapsulated particles. It was also used to evaluate the evolvement of the micro-structure of MT samples after exposure to sunlight and wet-dry cycles. The imaging was performed using a Hitachi S-3400N Variable SEM under VP mode with an Environmental Secondary Electron detector.

5.3.7 Durability test program

After the wet MT samples were sprayed with biopolymer solutions of different concentrations, they were allowed to cure at room temperature for 24 hours before exposure to the sunlight. The weight of each sample was recorded at the end of each day. The moisture retention capacity of each sample was evaluated during each wet/dry cycle. The time when the weight of each sample reached constant was considered the end of a wet/dry cycle. After that, either re-wetting the samples using just water or wind tunnel test was performed. Wind tunnel tests were conducted on samples treated with biopolymer solutions of different concentrations after the 1^{st}, 3^{rd}, 7^{th}, and 10^{th} wet/dry cycle.

5.4 RESULTS AND DISCUSSION

5.4.1 Moisture retention tests

Fig. 5.4 shows the variation of total weight with time for MT samples treated with biopolymer solutions of different concentrations during the first wet-dry cycle. It can be clearly seen that the MT samples treated with biopolymer solutions exhibited higher moisture retention capacity (slower weight loss rate with time) than that treated with only water, higher biopolymer concentration leading to greater moisture retention capacity. The enhancement of moisture retention capacity is beneficial to MT dust mitigation because the moisture not only makes the MT particles heavier but benefits the development of inter-particle bonding force. The two biopolymers have long-chain polymer structure that enables them to absorb ample water molecules by hydrogen bonds and thus enhance the moisture retention capacity (Khayat 1998). However, the water-MT particle attraction is rather fragile because it is mainly through the weak van der Waals forces. This is why the water treated MT showed the lowest moisture retention capacity.

Fig. 5.5 shows the variation of total weight with time for MT samples treated with biopolymer solutions of different concentrations during the fifth wet-dry cycle. The biopolymer stabilization was still effective in enhancing the moisture retention capacity of MT during the fifth wet-dry cycle.

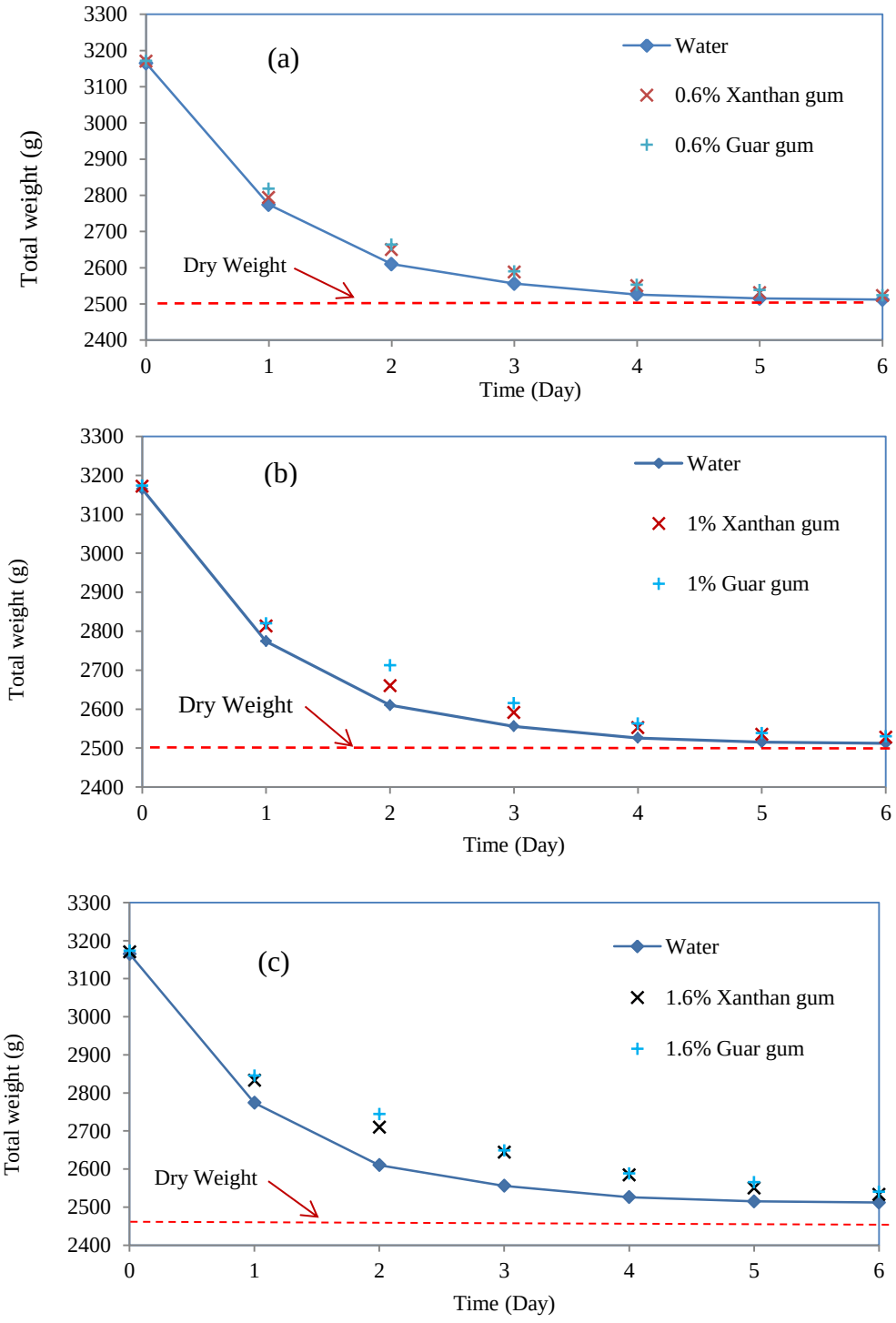


Figure 5.4. Variation of total weight with time during the first wet-dry cycle for MT samples treated with respectively water and biopolymer solutions at a concentration of (a) 0.6%, (b) 1.0%, and (c) 1.6%.

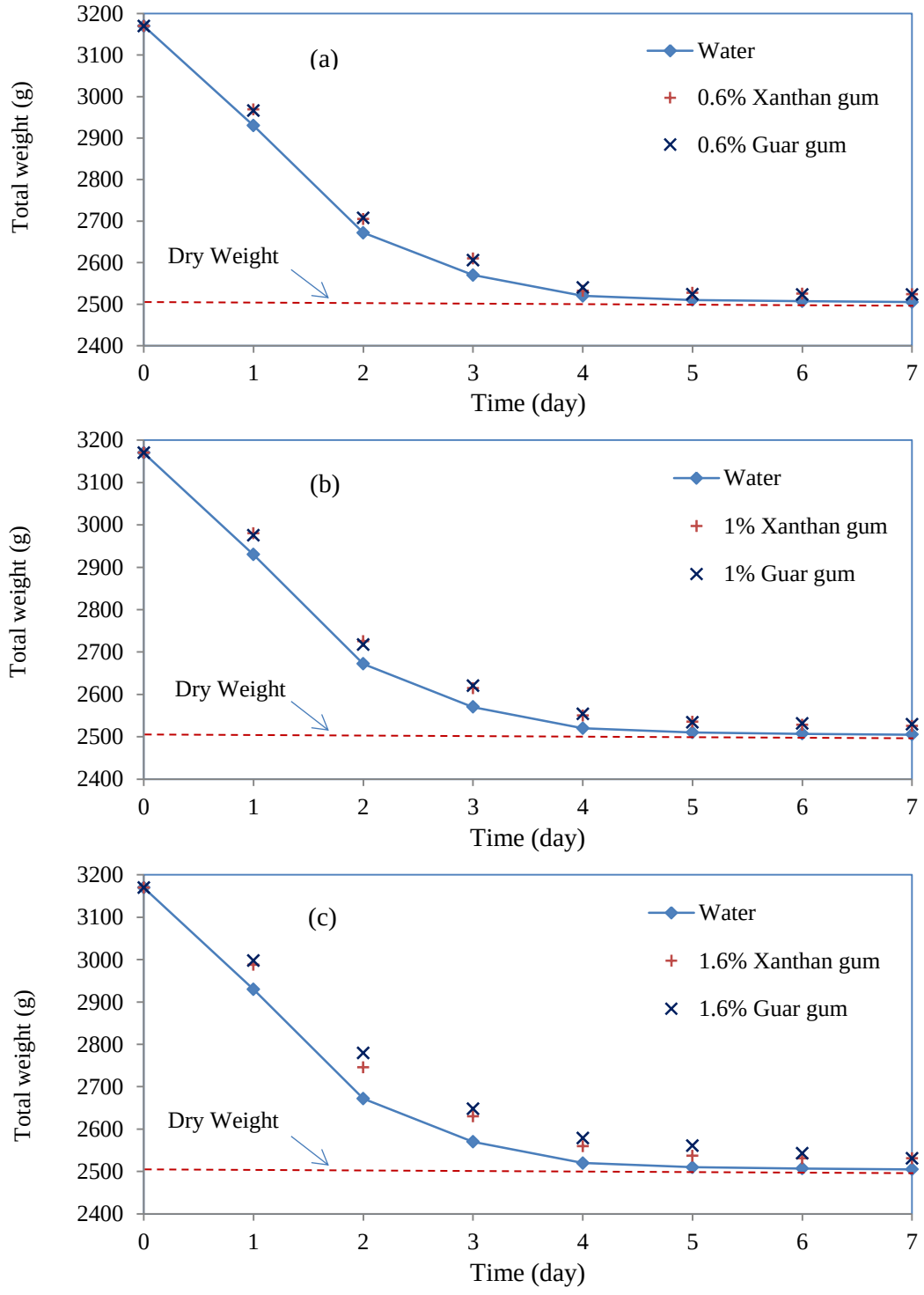


Figure 5.5. Variation of total weight with time during the fifth wet-dry cycle for MT samples treated with respectively water and biopolymer solutions at a concentration of (a) 0.6%, (b) 1.0%, and (c) 1.6%.

5.4.2 Wind tunnel tests

Fig. 5.6 plots the weight loss of MT samples treated with biopolymer solutions of different concentrations after wind tunnel test, respectively after the first wet-dry cycle and the fifth wet-dry cycle. One can see that the MT samples treated with just water had the largest weight loss and the MT samples treated with biopolymer solutions showed significant reduction in weight loss. For both xanthan gum and guar gum, higher biopolymer concentration led to greater decrease of weight loss of treated MT samples. For all MT samples either treated with just water or biopolymer solution of different concentrations, the weight loss after the fifth wet-dry cycle was larger than that after the first wet-dry cycle. This may be attributed to the damage of microstructure, creation of cracks and degradation of biopolymer macromolecules caused by sunlight exposure, wet-dry cycles and spray caused disturbance. However, at the high concentrations (1.0 and 1.6%), the increase of weight loss after five wet-dry cycles was small, showing the promise of biopolymer stabilization for long-term MT dust mitigation.

5.4.3 Surface strength tests

Fig. 5.7 shows the typical penetration force (resistance) versus penetration depth curves for MT samples treated with respectively xanthan gum and guar gum solutions at concentrations of 0, 0.6, 1.0, and 1.6% and after the first wet-dry cycle. The penetration force generally peaked before the penetrometer reached the maximum penetration depth of 4.0 mm.

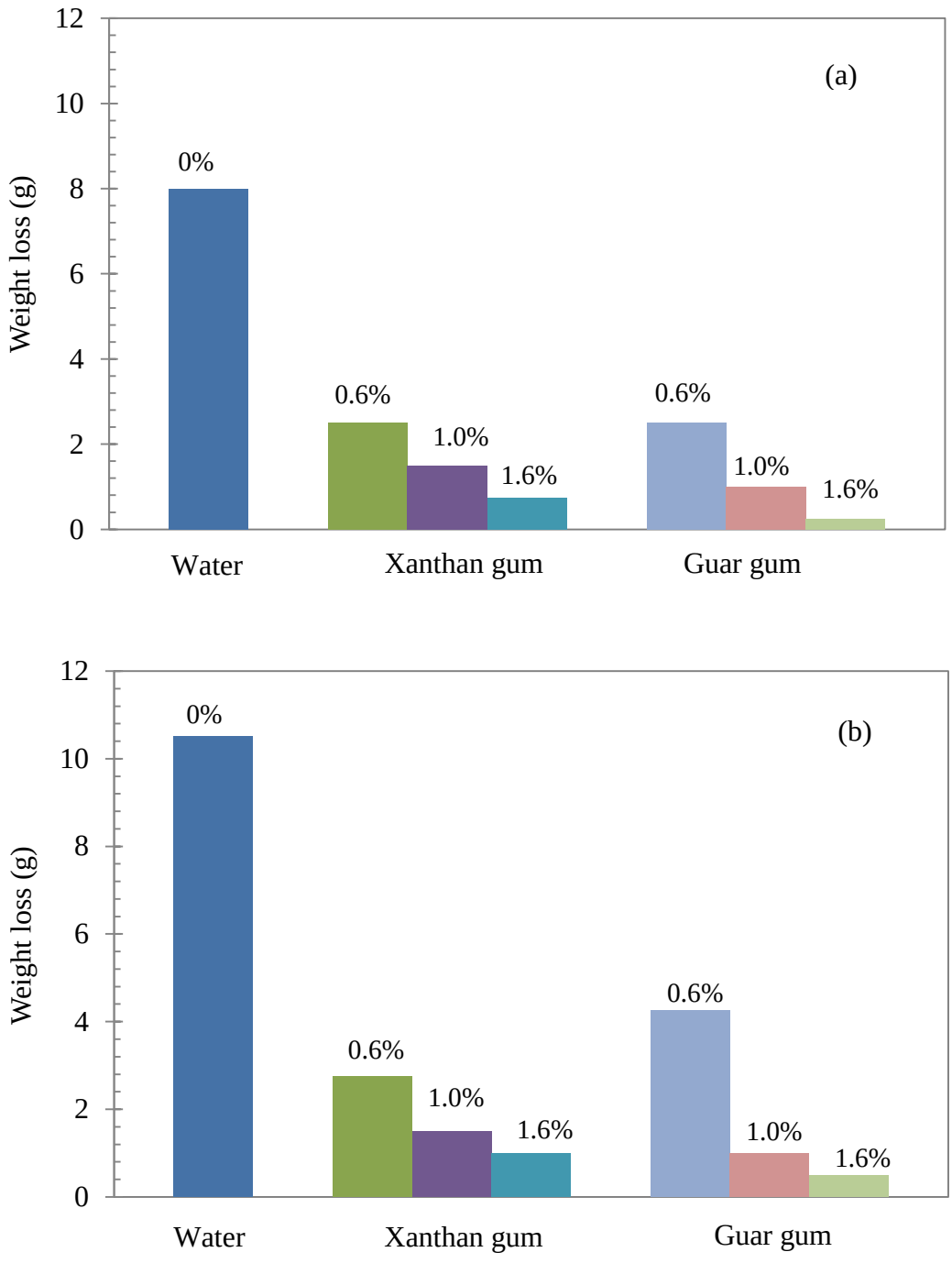


Figure 5.6. Wind tunnel test results of MT samples treated with biopolymer solutions of different concentrations: (a) tested after the 1st wet-dry cycle; and (b) tested after the 5th wet-dry cycle.

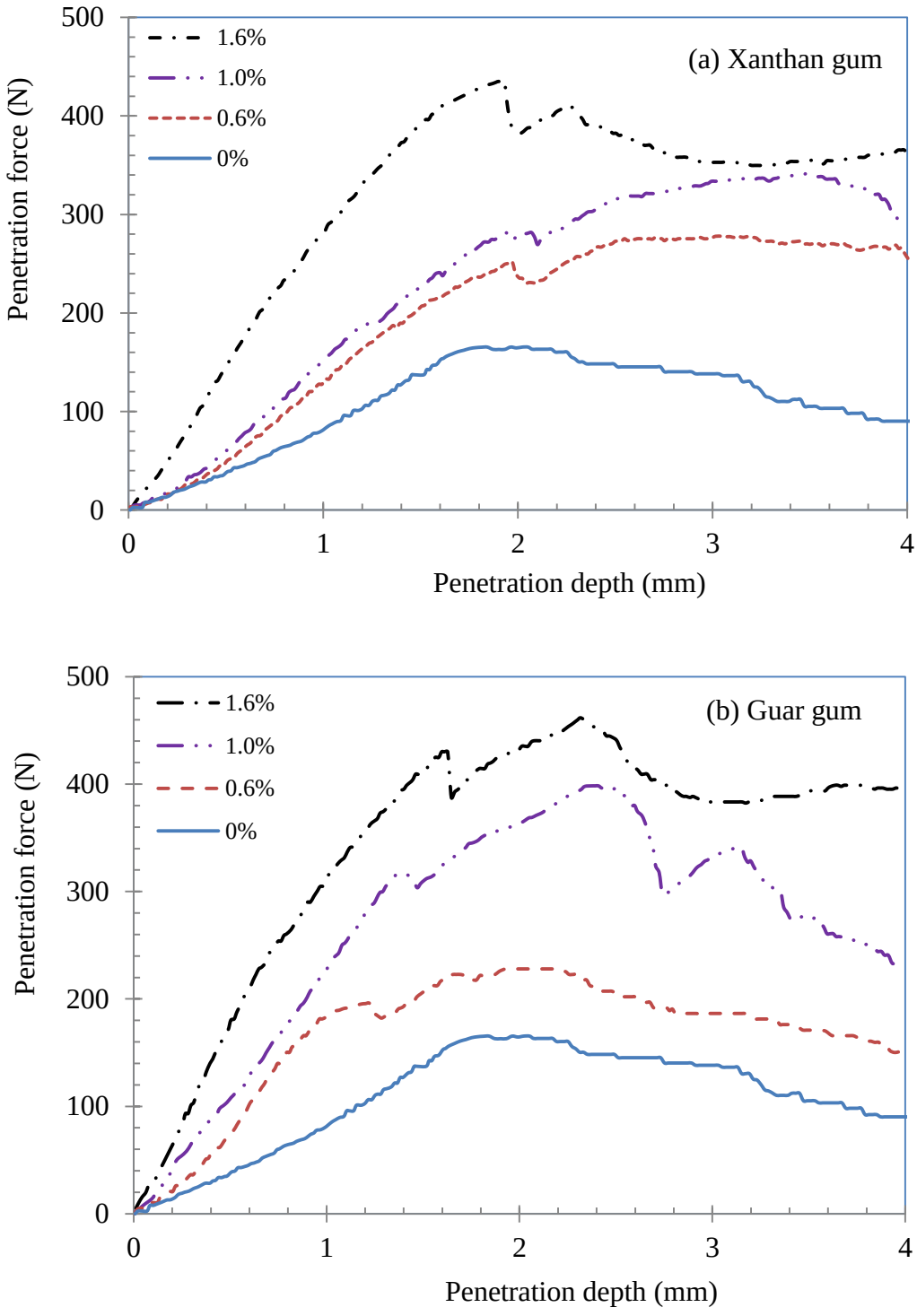


Figure 5.7. Typical penetration force versus penetration depth curves for MT samples treated with (a) xanthan gum and (b) guar gum solutions of different concentrations.

It can be seen that the MT samples treated with biopolymer solutions exhibited higher surface strength (greater maximum penetration force) than that treated with only water, higher biopolymer concentration leading to larger increase of surface strength. The average, standard deviation (STD), and coefficient of variation (COV) of the 9 measured maximum penetration forces for each condition are summarized in Table 5.2 and plotted in Fig. 5.8, which again clearly show the increase of the surface strength of MT samples with higher biopolymer concentration. It is also noted that the COV values at different conditions are all around 20%, indicating that the penetrometer test method is quite reliable.

The increase of the MT surface strength after biopolymer stabilization is due to the coating and bonding of MT particles by the biopolymer and the formation of a denser and stronger crust. Fig. 5.9 shows the surface of MT samples treated with respectively water and 1.0% guar gum solution and after penetration tests. An "intact" crust can be clearly seen in the penetration hole of the guar gum solution treated MT sample but not the water treated MT sample. The penetrations also created cracks on the water treated MT sample but not on the guar gum solution treated MT sample, indicating that the biopolymer stabilization significantly increased the tensile strength of MT (or the bonding strength between MT particles). This is similar to the increase of cohesion of sand after biopolymer treatment found by Khatami and O'Kelly (2012)

Table 5.2 and Fig. 5.8 show that guar gum is more effective than xanthan gum in increasing the surface strength of MT samples. This can be explained by the aggregation

of MT particles due to the added biopolymer and the type of bonding between the biopolymer and MT particles (Chen et al. 2013). Xanthan gum is an anionic polysaccharide (García-Ochoa et al. 2000) which interacts with the cations (Cu^{2+}, Na^{+}, Fe^{2+}) present in the MT to form ionic bonding between xanthan gum and MT particles and induces a high degree of aggregation. In contrast, guar gum is a neutrally charged polysaccharide (Chudzikowski 1971) with numerous hydroxyl (-OH) groups which form hydrogen bonds between guar gum and MT particles and only induce slight aggregation. This can be clearly seen from the SEM images (Figs. 5.12 and 5.13) to be discussed in next section. The xanthan gum caused much higher level of aggregation and thus induced larger voids than the guar gum. The smaller voids and stronger hydrogen bonding contribute to the higher surface strength of MT treated with guar gum than with xanthan gum.

Table 5.2. The average, standard deviation (STD) and coefficients of variation (COV) of measured maximum penetration forces, respectively for xanthan gum and guar gum treated MT samples.

Concentration (%)	Xanthan gum			Guar gum		
	Average (N)	STD (N)	COV (%)	Average (N)	STD (N)	COV (%)
0.0	212.8	43.6	20.5	212.8	43.6	20.5
0.6	250.8	56.3	22.5	263.0	66.6	25.3
1.0	304.5	68.4	22.5	358.8	67.6	18.9
1.6	340.6	68.9	20.2	428.0	73.1	17.1

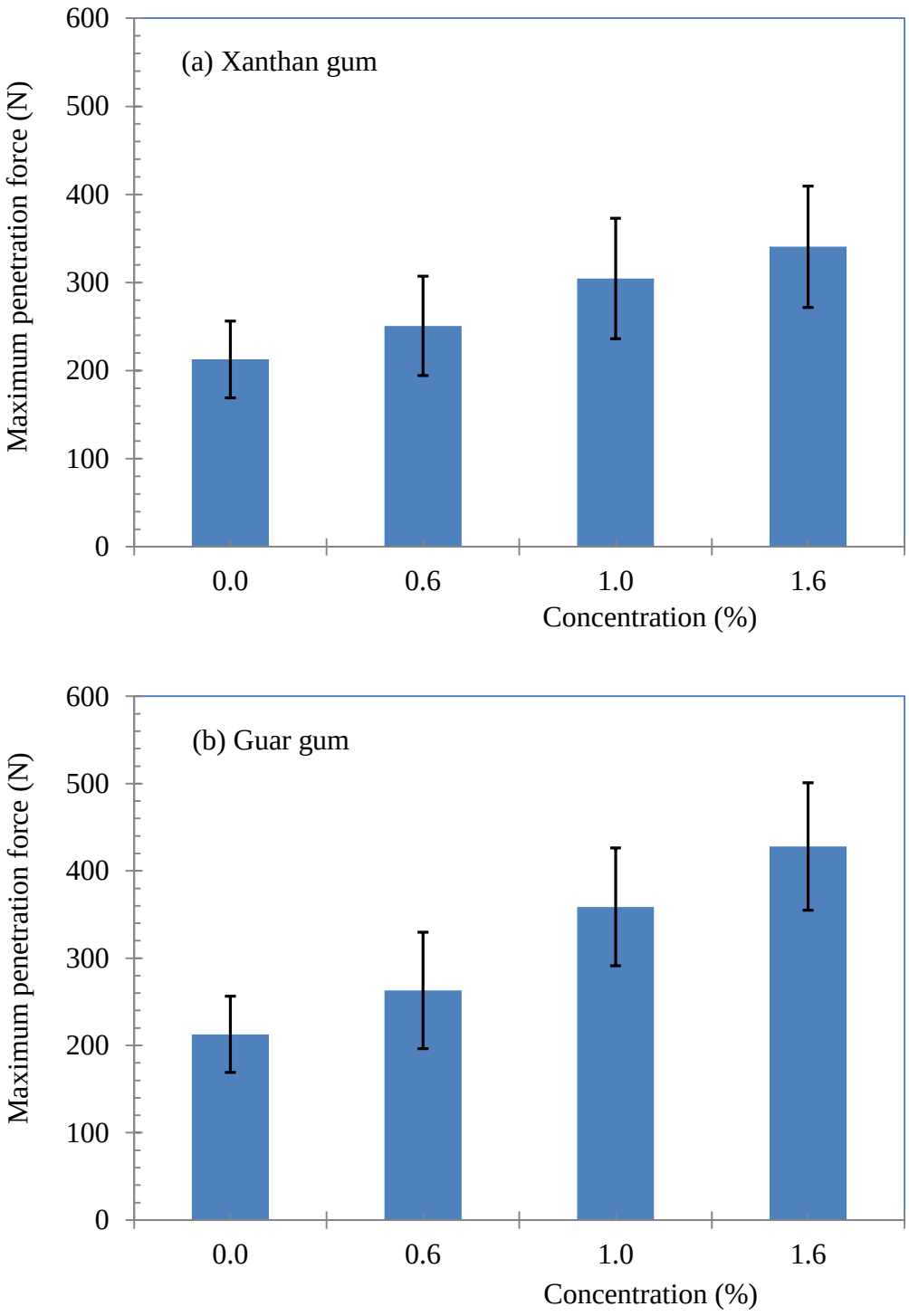


Figure 5.8. The average maximum penetration force for MT samples treated with (a) xanthan gum and (b) guar gum solutions at concentrations of respectively 0, 0.6, 1.0, and 1.6%.

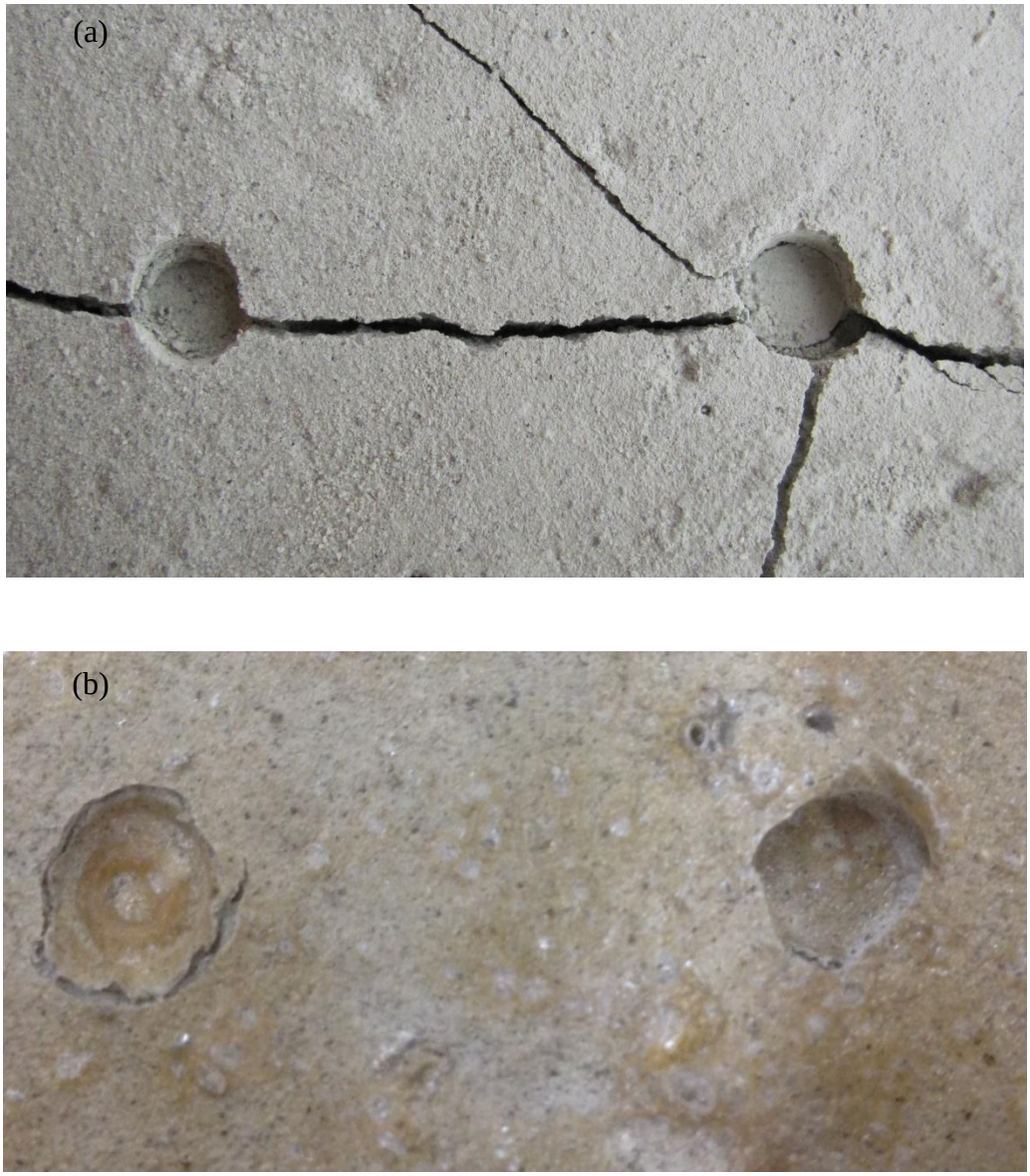


Figure 5.9. Surface of (a) water and (b) 1.0% guar gum solution treated MT samples after penetration tests.

Fig. 5.10 shows the weight loss of MT samples after wind tunnel test versus the maximum penetration force (surface strength), both for samples after the first wet-dry cycle. It can be seen that a strong relation exists between the weight loss, W_L, and the maximum penetration force, F_P, although the data are for MT samples treated with two

different types of biopolymers. Based on best fitting analysis, the relationship between W_L and F_P can be obtained as follows:

$$W_L = 3 \times 10^{11}(F_P)^{-4.576} \quad (1)$$

The coefficient of determination, r^2, is 0.965. The strong relationship between W_L and F_P indicates that the maximum penetration force (surface strength) is a good indicator of the weight loss (dust resistance). So the penetrometer test method is a promising technique for characterizing the dust resistance of MT.

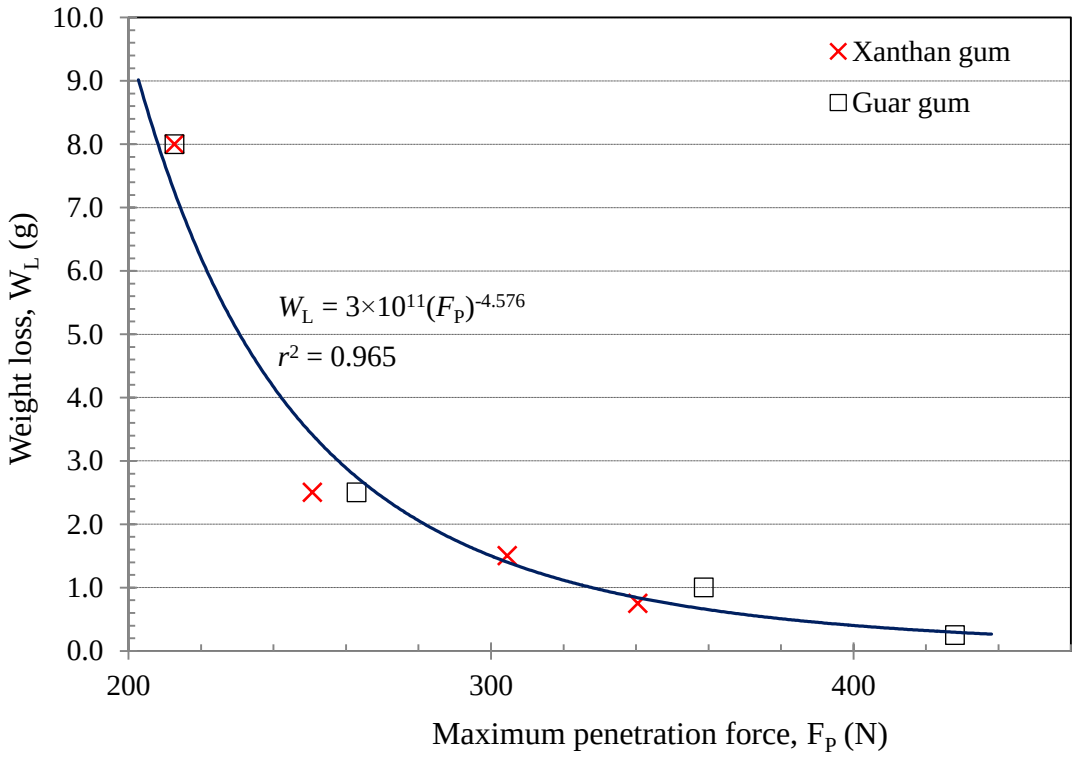


Figure 5.10. Weight loss of MT samples after wind tunnel test versus maximum penetration force (surface strength of MT samples).

5.4.4 SEM imaging

Fig. 5.11 shows the SEM images of the surface of wind tunnel tested MT samples treated with respectively just water and two biopolymer solutions. One can clearly see the voids between the particles in the MT sample treated with just water but the biopolymer gels coating and binding the particles in the samples treated with biopolymer solution.

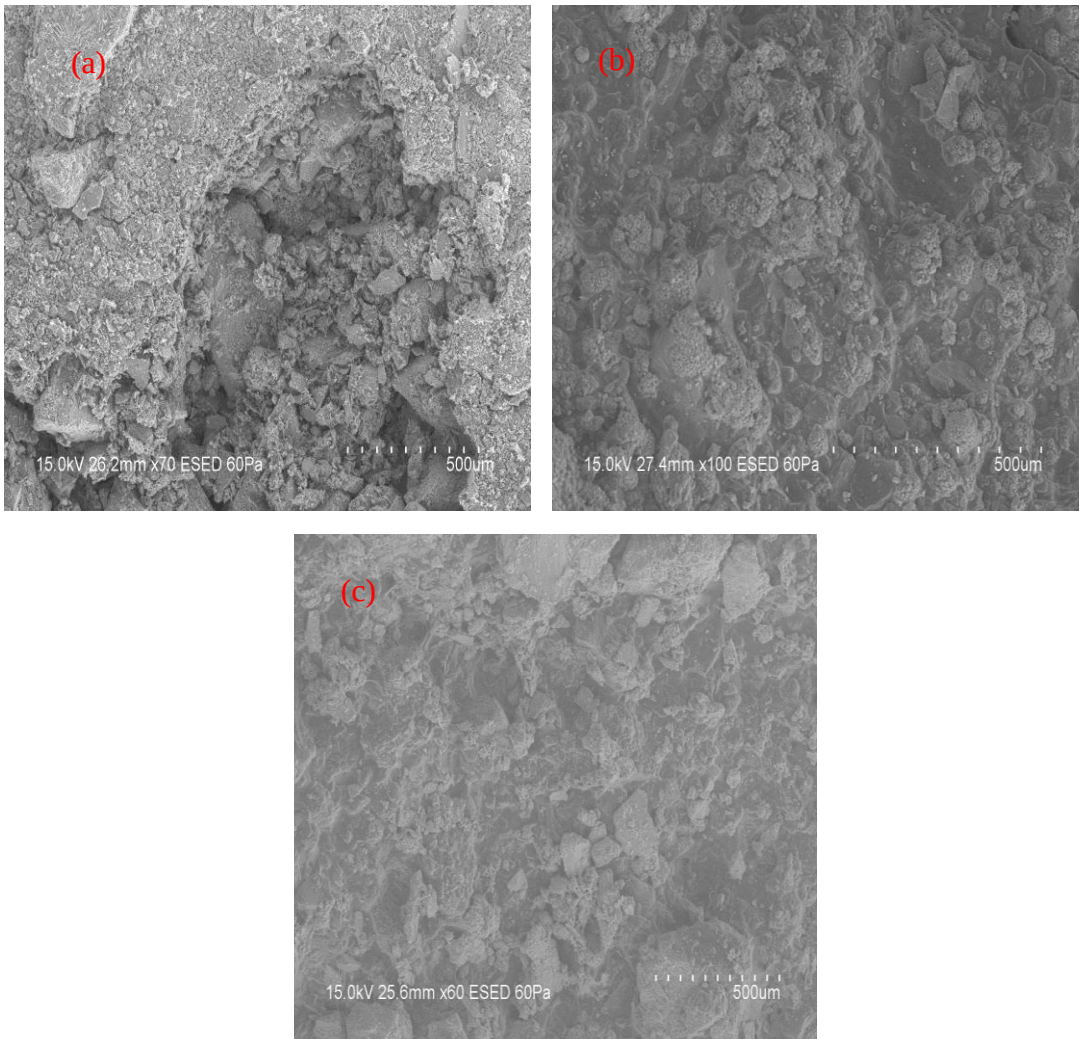


Figure 5.11. SEM images of the surface of MT samples treated with: (a) water, (b) 1.6% xanthan gum solution, and (c) 1.6% guar gum solution.

Fig. 5.12 shows the SEM images of the close to surface vertical cross-section of wind tunnel tested MT samples treated with respectively just water and two biopolymer solutions. Again the water treated MT sample exhibited a loose structure with empty voids while the biopolymer solution treated MT samples had a denser structure with voids filled with biopolymer gels coating and binding the particles.

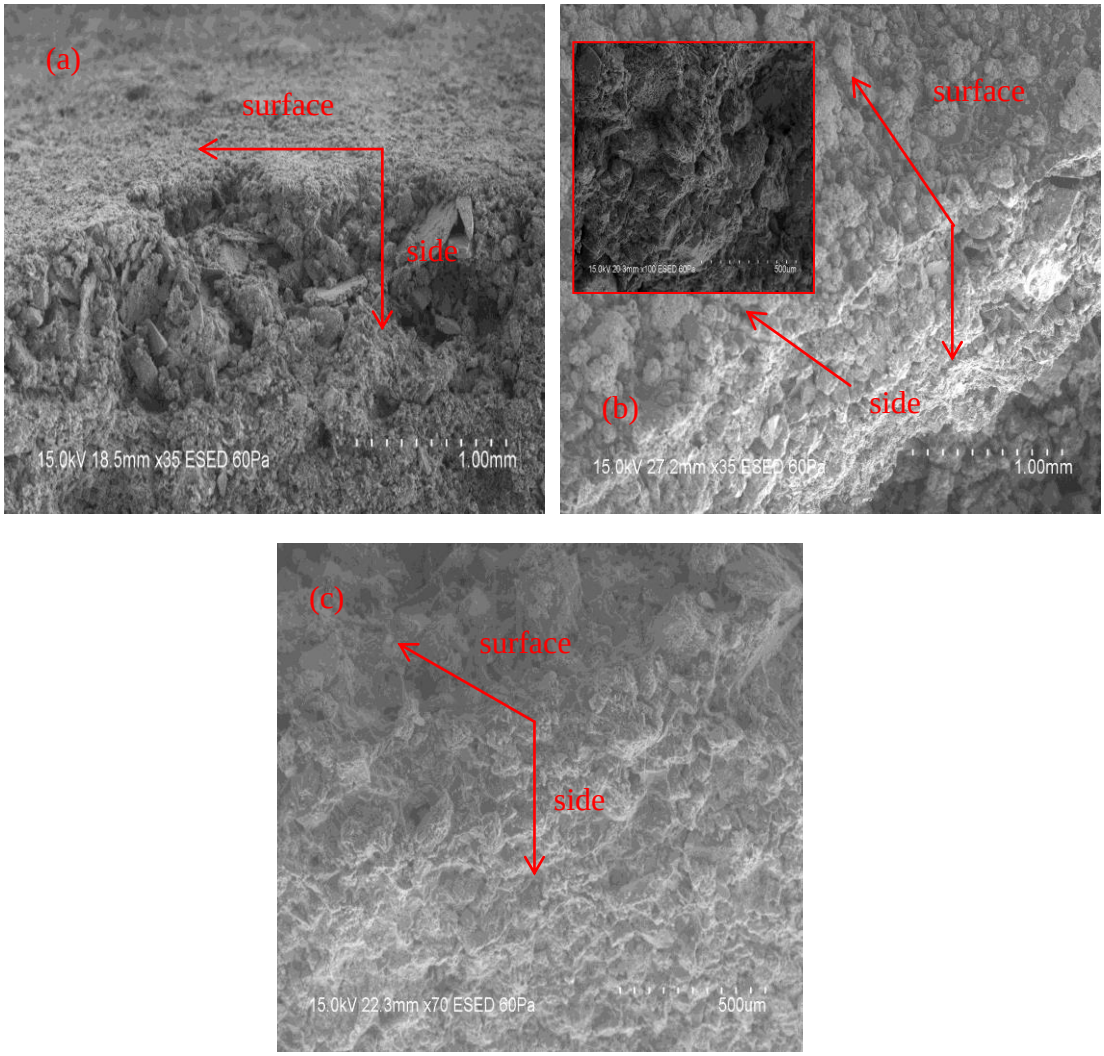


Figure 5.12. SEM images of the vertical side of MT samples treated with: (a) water, (b) 1.6% xanthan gum solution, and (c) 1.6% guar gum solution.

The denser structure and the biopolymer gels coating and binding the particles can explain the enhancement of water retention capacity, the improvement of dust resistance and the increase of surface strength (maximum penetration force) after MT are treated with biopolymer solution. Figs. 5.11 and 5.12 also show that the MT sample treated with guar gum solution has a denser structure than that treated with xanthan gum solution, which is due to the reasons described above.

5.4.5 Durability test results

The weight of each sample recorded at the end of each day during the water retention tests was normalized to its weight before testing and the normalized weight loss with time was used to compare the water retention capacity of different samples.

The water retention test results during the first and the second wet/dry cycle are respectively presented in Fig. 5.13. It can be seen the water retention capacity of MT samples treated with biopolymer solutions of low concentrations do not show improved water retention capacity compared to that treated with only water. The biopolymer solution of low concentration forms a thin layer of coating on the MT surface, which may have limited capacity to retain large amount of water via hydrogen bonding. Therefore, no improvement in water retention capacity is observed.

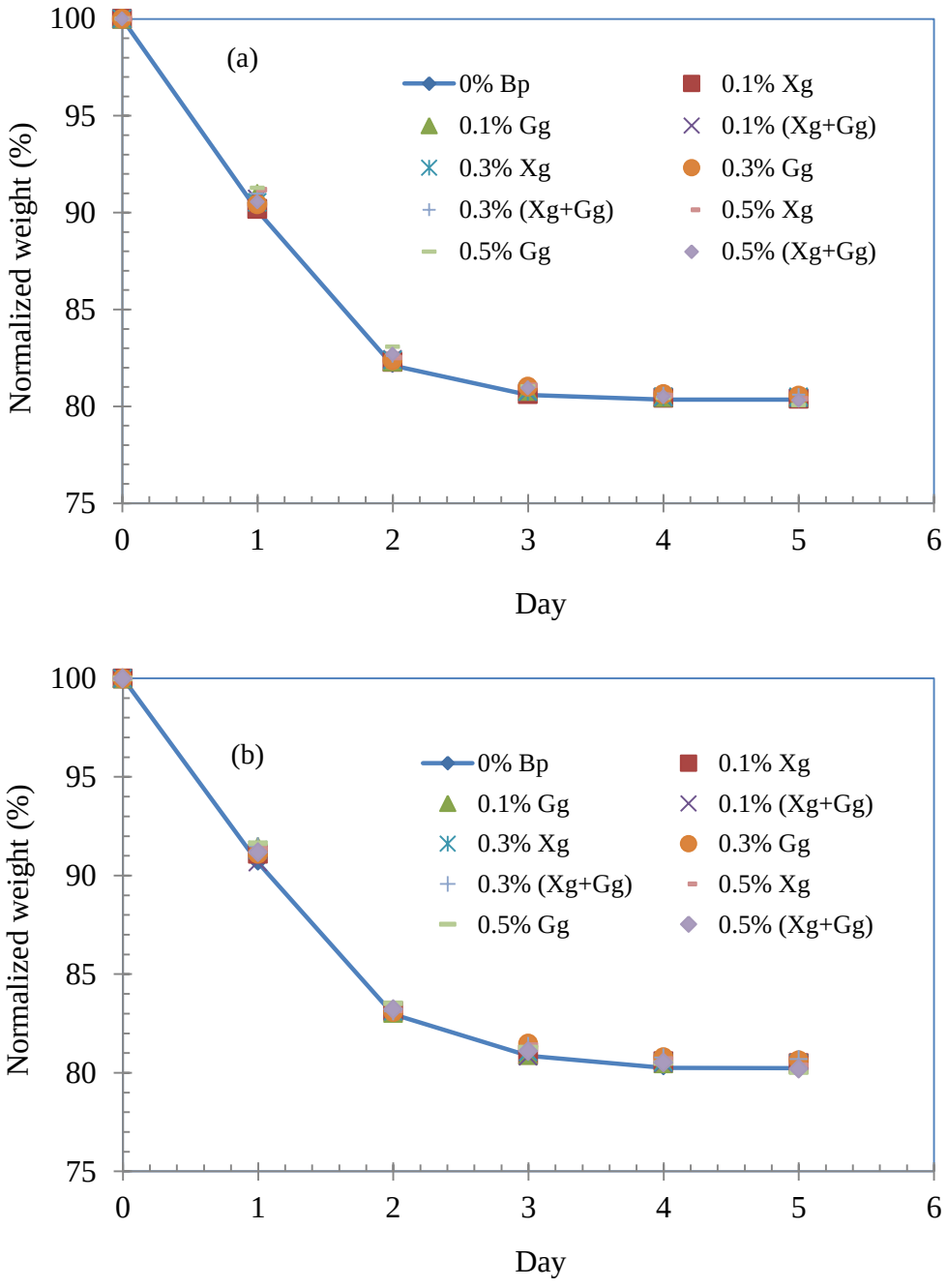


Figure 5.13. The normalized weight versus time during (a) the first and (b) the second wet-dry cycle respectively for MT samples treated with biopolymer solutions of concentrations of 0, 0.1, 0.3 and 0.5% (Xg, Gg and Xg+Gg indicate xanthan gum, guar gum and the combination of the two).

Figs. 5.14 and 5.15 shows the wind tunnel test results of MT samples treated with biopolymer solutions of different concentrations after the 1st, 3rd, 7th, and 10th wet/dry cycle, respectively. The weight loss of each sample was normalized to its weight before testing and the normalized weight loss was used to compare the dust resistance of different samples. Generally, it can be observed an increase in effectiveness of dust control with increasing the concentration of biopolymer solution, regardless of the type of biopolymer used, which is in good agreement with the previous finding that higher biopolymer concentration leads to greater dust resistance. Specifically, after experienced one wet/dry cycle, MT samples treated with only water showed the greatest weight loss, whereas the MT samples treated with 0.1, 0.3 and 0.5% biopolymer solutions showed slight or no weight loss after wind blowing. After three wet/dry cycles, the weight loss slightly increased after wind tunnel tests for MT samples treated with water, 0.1, and 0.3% biopolymer solutions, while those treated with 0.5% biopolymer solutions showed no weight loss. The results of wind tunnel tests after the 7th wet/dry cycle showed that all MT samples showed an obvious increase in the weight loss. However, the weight losses of 0.5% biopolymer solutions treated MT samples were only about one fourth that of the water treated samples, showing a good durability of biopolymer treatment. After 10 wet/dry cycles, a great weight loss was observed for all samples after wind blowing. The 0.1% biopolymer treatment completely lost its function in dust control. The 0.3 and 0.5% biopolymer treatments also experienced a significant loss of effectiveness for dust control. MT samples treated with the biopolymer solutions of combination of xanthan gum and guar gum did not show obvious improvement in dust resistance as expected.

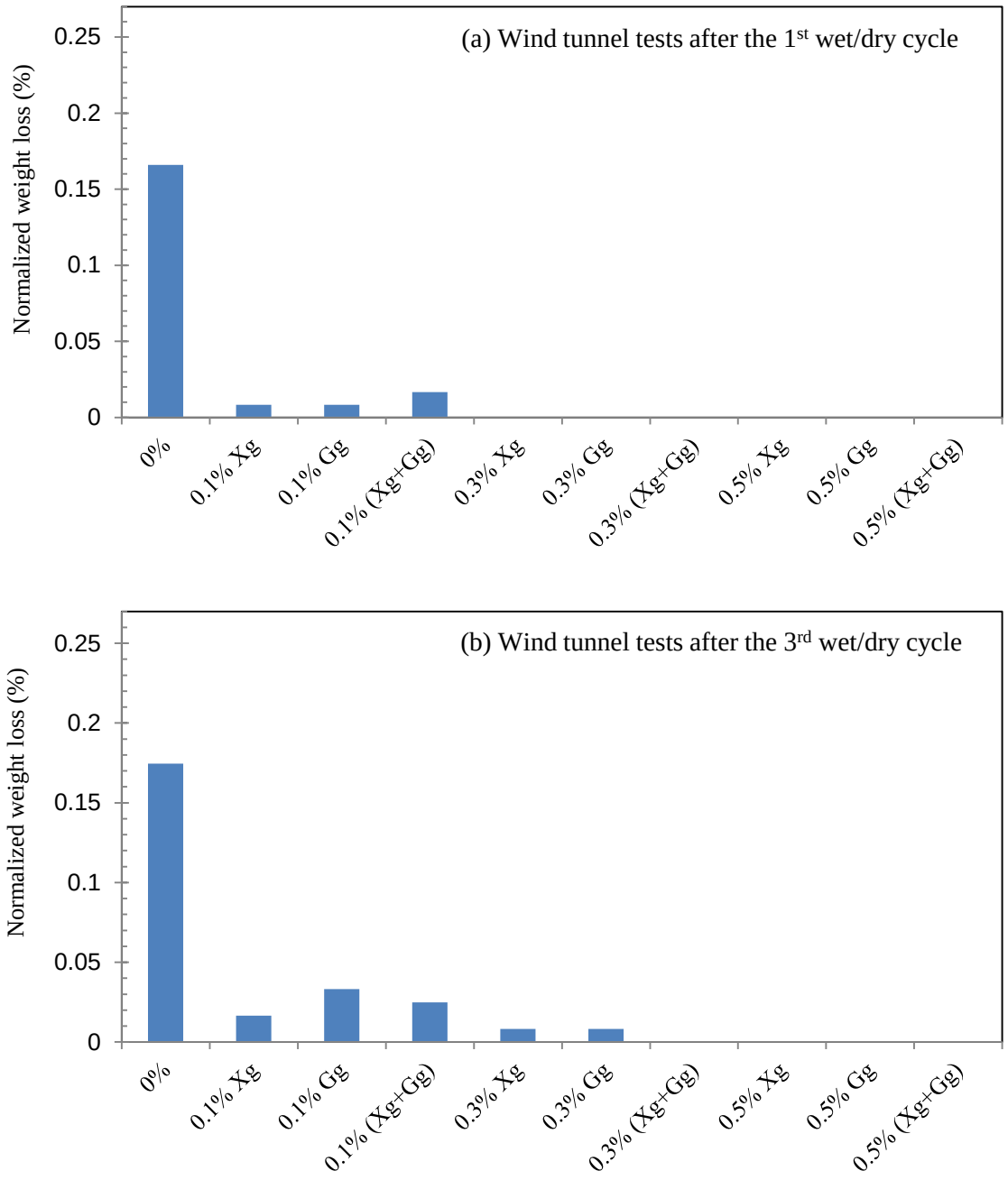


Figure 5.14. Wind tunnel test results of MT samples treated with biopolymer solutions of different concentrations: (a) tested after the 1st wet/dry cycle; and (b) tested after the 3rd wet/dry cycle.

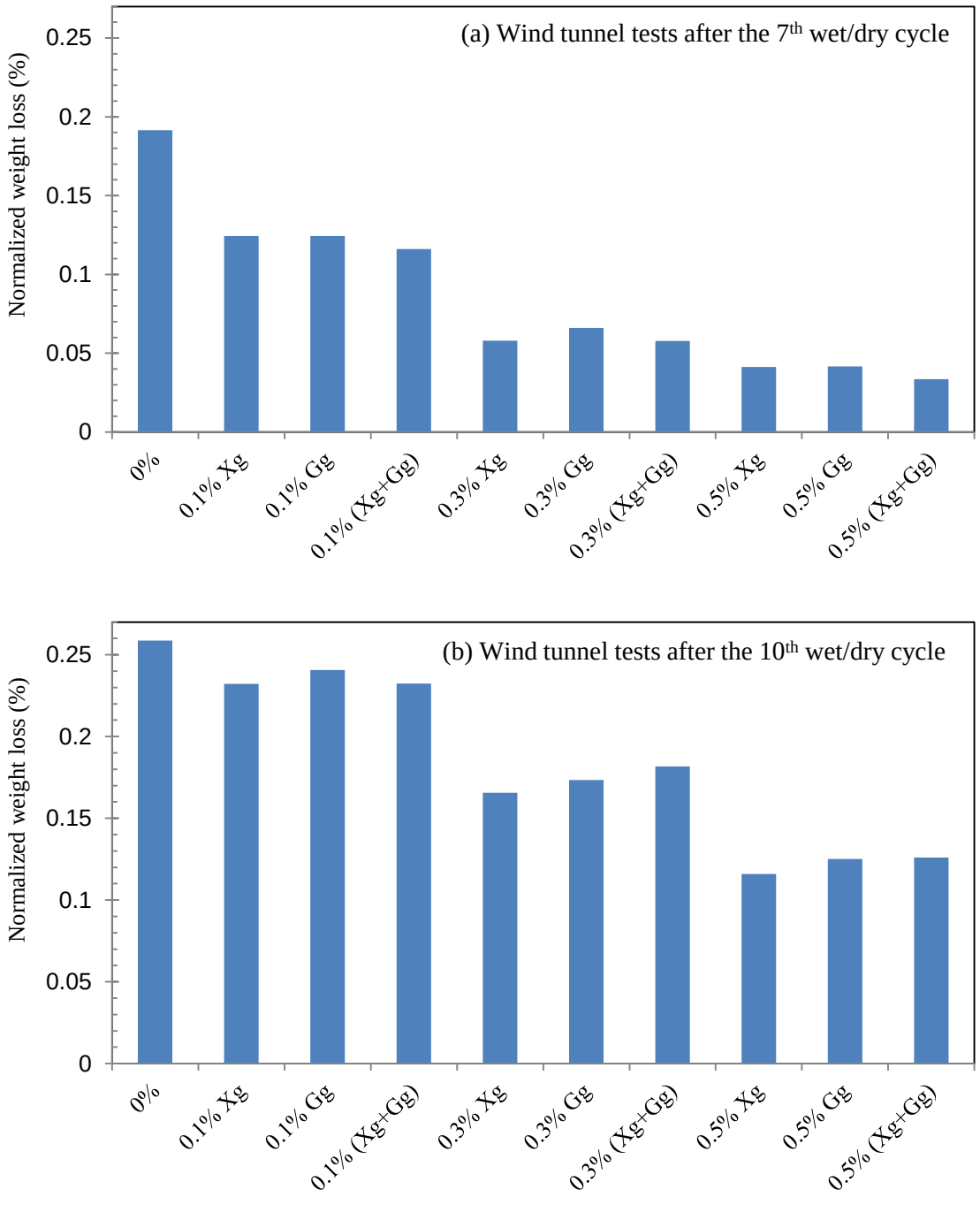


Figure 5.15. Wind tunnel test results of MT samples treated with biopolymer solutions of different concentrations: (a) tested after the 7th wet/dry cycle; and (b) tested after the 10th wet/dry cycle.

Fig. 5.16 shows the effect of the number of wet/dry cycles on the performance of biopolymer treatments of different concentrations on dust control. It can be clearly seen the weight loss of all samples gradually increases with the number of wet/dry cycles, regardless of the type of applied treatment, indicating that the treatment progressively loses its function in dust control with increasing the number of the wet/dry cycles. Water treated MT samples after wind blowing always showed the largest weight loss at the same wet/dry cycle condition, higher biopolymer concentration leading to greater stabilizing effect.

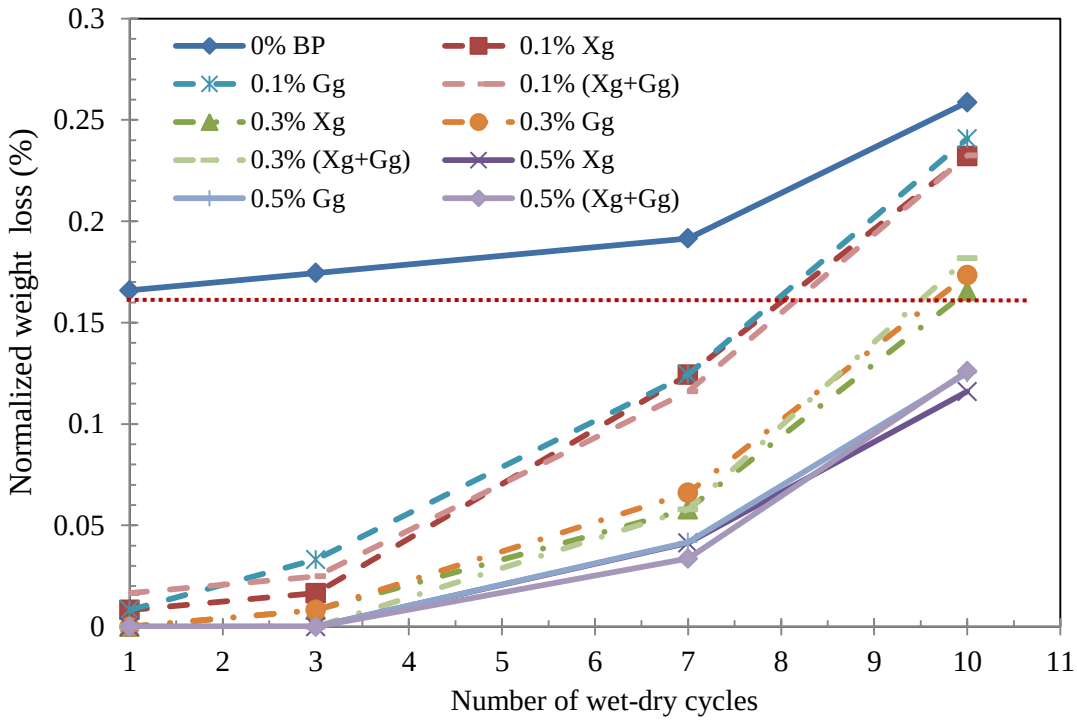


Figure 5.16. The effect of the number of wet/dry cycles on the performance of biopolymer treatments of different concentrations on dust control.

A horizontal boundary line was set at the normalized weight loss of water treated MT samples after the first wet/dry cycle and wind tunnel test. If the normalized weight

loss was above this boundary line, then the biopolymer treatment is considered ineffective. Based on this definition, one can see that biopolymer treatment is still effective in mitigating MT dust up to the 7 wet/dry cycles. After 10 wet/dry cycles, biopolymer treatment of 0.5% was still effective in abating MT dust whereas those of concentrations of 0.1 and 0.3% were completely ineffective.

The dust resistance mainly comes from the crusted layer on the surface of MT, which is formed either by water induced agglomeration of fine particles or by the biopolymer crosslinking network. Water can agglomerate fine particles in the MT forming a weak crusted layer which can effectively improve the wind erosion resistance (Gillette et al. 1982). However, this weak crusted layer is rather fragile and may experience cracking during the wetting and drying processes, leading to loss of wind erosion resistance. Besides, the wet/dry cycles may cause disturbance to the weak crusted layer making the fines be easily entrained by wind. Therefore, water treatment is ineffective in long-term dust control. The biopolymer gels can coat and bind the MT particles forming a protective crust, which leads to improve of dust resistance. Although the biopolymer crust may also experience cracking and disturbance during the wet/dry cycling, the most important factor contributing to the loss of dust resistance may be the degradation of biopolymer. There are many factors contributing to the degradation of biopolymer. The dragging force by wind and the impact force by saltating particles can induce mechanical degradation of biopolymer. Although the mechanical degradation is not the predominant factor leading the final degradation of biopolymer, it could be a catalyst activating or accelerating it (Briassoulis 2005). The sunlight induced heat and

radiation can potentially change the biopolymer structure by photoionization and chain scission, leading to degradation (Lucas et al. 2008). Most importantly, the chemical degradation caused by oxygen and water is the dominant factor provoking the degradation of biopolymer. Oxygen attacks the covalent bonds in the biopolymer, which can be accelerated by the aid of sunlight (Lucas et al. 2008). Intrusion of water into the biopolymer structure leads to swelling and release of oligomers and monomers, causing weight and mechanical strength losses (Göpferich 1996). The degradation of biopolymer induces the alteration of the polymer structure leading to deterioration of the integrity of biopolymer and finally to loss of its functionality (Kumar et al. 2009).

5.5 CONCLUSIONS

The feasibility of using two biopolymers, xanthan gum and guar gum, to stabilize MT for dust control was studied. The following conclusions can be drawn from the experimental results:

a) MT treated with biopolymer solution show higher moisture retention capacity than MT treated with just water, higher biopolymer concentration leading to greater increase of moisture retention capacity. The biopolymer stabilization is still effective for water retention capacity enhancement after five wet-dry cycles.
b) MT treated with biopolymer solution show greater dust resistance than MT treated with just water, higher biopolymer concentration leading to greater increase of dust resistance. The biopolymer stabilization is still effective for dust resistance improvement after five wet-dry cycles.

c) MT treated with biopolymer solution show increased surface strength (maximum penetration force), higher biopolymer concentration leading to greater increase of the surface strength.

d) Biopolymer forms coating on the MT particle surface, generates cross-linking network between MT particles and leads to a denser structure of MT, thus increasing the surface strength, enhancing the moisture retention capacity and improving the dust resistance.

e) There is a strong relationship between the dust resistance and the surface strength (maximum penetration force), indicating that penetrometer test method is a promising technique for characterizing the dust resistance of MT.

f) MT treated with biopolymer solutions of low biopolymer concentrations (0.1, 0.3, and 0.5%) do not show improved water retention capacity but show improved dust resistance compared to MT treated with water. MT treated with biopolymer solutions of low concentrations progressively lose the dust resistance with increasing the number of wet/dry cycles. The biopolymer treatment of 0.5% concentration is still effective for dust control after 10 wet/dry cycles. The loss of dust resistance for biopolymer treatments may attribute to the degradation of biopolymer including: mechanical degradation induced by wind dragging and saltating particles' impact; photodegradation caused by sunlight; and most importantly the chemical degradation caused by water and oxygen.

CHAPTER 6
NUMERICAL SIMULATION OF BIOPOLYMER ENHANCEMENT OF MINE TAILINGS USING PFC3D

6.1 INTRODUCTION

Numerical methods have been widely used in geotechnical engineering to investigate the response of soil or rock to loadings. Traditional numerical methods based on continuum theory, such as finite element or finite differences, have two major drawbacks: first, the currently available stress-strain laws may not be appropriate for some geo-materials; and second, the continuum assumption is not suitable for modeling geo-materials containing localized features such as cracks and shear bands (Cundall 2001). These drawbacks can be overcome by using discrete element method (DEM), the new idea of which is to replace the continuum with an assembly of circular (2-D) or sphere (3-D) particles. It is of great advantage to simulate discontinuous rock mass and soil using DEM because fractures are naturally formed at discrete points (Cundall 2001). One can also have direct insight into the experimental results by observing the particle velocities, displacements, stresses and so on, which are inaccessible in physical laboratory tests (Evans and Frost 2010). The DEM proposed by Cundall (1971; 1974) was originally used for analysis of rock mechanics problems and later on was extended to investigate the mechanical behavior of soil (Cundall and Strack 1979).

Researchers have used the DEM to model the mechanical behaviors of granular soils under different loading conditions. For example, Liu (2006) performed a two-dimensional (2D) DEM simulation using software GRADIA to investigate the drawbacks of traditional direct shear box test from a microscopic point of view. Yan and Ji (2010) conducted a 3D DEM simulation of direct shear test of irregular limestone rubble using a mixture of clumps to resemble the real shape of granular materials. The modeling results showed a good agreement with that in the laboratory tests. Hu et al. (2010) carried out DEM simulations to understand the stress-induced anisotropy in sand under cyclic loading using two-dimensional particle flow code (PFC2D).

Forces between granular particles are purely mechanical. The DEM is particularly appropriate to simulate granular materials because it repeatedly applies the Newton's laws to the particles in the assembly, simulating the interaction between them. However, for cohesive particles, there exist physicochemical forces between them besides inter-particle mechanical forces, the most important of which are double-layer repulsive force and Van der Waals' attractive force (Anandarajah 1994). Therefore, DEM simulations of cohesive soils are less common due to the complexity of the inter-particle forces. Some researches, however, have carried out DEM simulations to investigate the behavior of cohesive soil. For example, Anandarajah (1994, 2000) applied the DEM to simulate the behavior of cohesive soil by dividing each particle into a number of interconnected discrete elements and introducing suitable force-displacement laws to the contacts. The double-layer repulsive force and the bending of particles were reasonably modeled, but the attractive force between cohesive particles was not considered. MT that are usually

classified as loose sandy silts or silty sands contain an insignificant amount of clay, so it is assumed only pure mechanical forces exist between MT particles. However, the present biopolymer interacts with MT particles through ionic bond or hydrogen bond generating physicochemical forces in the system, which need to be considered in the numerical simulation.

Potyondy and Cundall (2004) proposed a bond-particle model, or called parallel bond model, to simulate the mechanical behavior of rock, in which the rock is represented by a dense assembly of circular (2D) or spherical (3D) particles bonded together at their contacts. This model has been extended to simulate the mechanical behavior of cemented sand and cohesive soil. Powrie et al. (2005) performed DEM simulations of biaxial tests on sands using parallel bond model in PFC3D. The results showed that the particular method was capable of reproducing the responds of sands in dense or loose state, as observed in laboratory tests, such as dilation behavior and shear bands. Zhang and Li (2006) performed a DEM simulation of the dynamic mechanical behavior of cohesive soils subjected to external forces using PFC2D. The water induced capillary and dynamic viscous forces between soil particles were simulated by using the parallel bond model. Wang and Leung (2008) carried out triaxial tests and DEM simulations to investigate the behavior of cemented sand. The triaxial test results revealed that increasing the amount of cementation led to higher peak strength and volumetric dilatancy. The authors used PFC2D to perform the simulation in which the sand and cement were represented as large and tiny particles which were bound together by parallel bonds. Numerical simulations showed that a more stable and stronger force-chain

network was found in the cemented sand which led to higher strength. The information from literature shows that the parallel bond model is capable of simulating the cemented behavior in a soil and accounting for the complex forces between soil particles and the cementing agents.

In order to investigate how the presence of biopolymer affects the mechanical behavior of MT, unconfined compression tests were performed on MT samples stabilized with and without biopolymer solutions of different concentrations. The parallel bond model in PFC3D was adopted to simulate the unconfined compression test to better understand the effect of biopolymer on the mechanical performance of MT from a micro-structural perspective.

6.2 EXPERIMENTAL DETAIL

6.2.1 Sample preparation for unconfined compression tests

MT was obtained from a local mining company. Xanthan gum was the biopolymer used in this study and was purchased from a gum company in Tucson, Arizona. MT were sun-dried and grinded to pass #20 sieve before used. Biopolymer solutions were obtained by dissolving xanthan gum powder in tap water at concentrations of 0.1, 0.3 and 0.5%. A hand mixer was used to facilitate the dissolution of xanthan gum and the mixing was kept until a homogeneous solution was obtained. Samples for UCS test were prepared by thoroughly mixing dried MT with water (used as control), 0.1, 0.3, and 0.5% biopolymer solutions. Then the pastes at different conditions were transferred into cylindrical molds with size of 50 mm × 25 mm and cured at 60^{o}C oven until

completely dried. To be comparable, all samples were prepared at the same water content, which meant they had the same density when dried.

6.2.2 Unconfined compression (UC) tests

The UC tests were performed on the dried samples with an ELE Tri Flex 2 loading machine at a constant loading rate of 0.1 mm/min following ASTM C39. The UC test is a simple and quick way to evaluate the strength of cohesive soils. Fig. 6.1 presents a sample before and after a UC test. For each condition, at least three samples were tested.

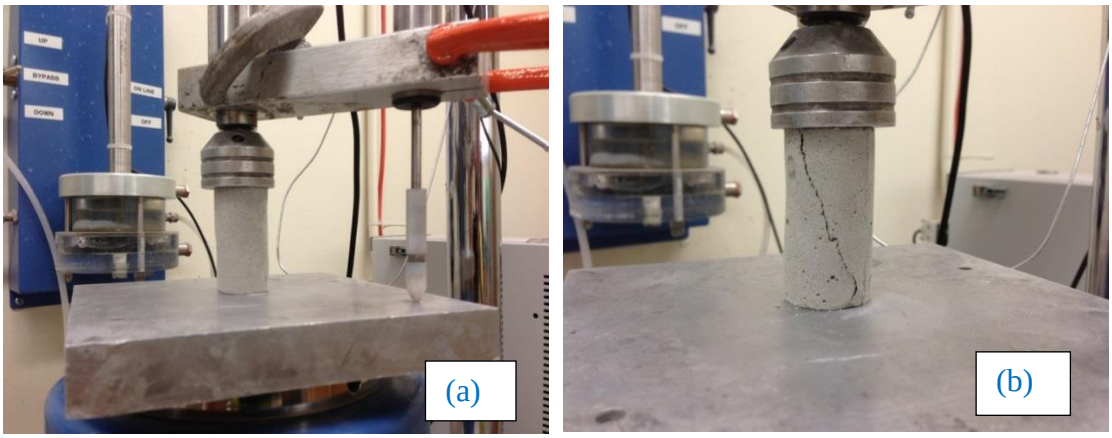


Figure 6.1. Sample before (a) and after (b) UCS test.

6.2.3 Test results and discussion

Fig. 6.2 presents the effect of xanthan gum concentration on the unconfined compressive strength (UCS) of MT. It is noticed that the UCS of MT increases with the xanthan gum concentration, 0.5% xanthan gum solution incorporation into MT leading to more than two times increase in UCS compared to the plain MT. This finding is well agreed with the results by Khatami and O'Kelly (2012). Previous study has shown that

the xanthan gum gel can bind the detached MT particles through its crosslinking network, providing tensile strength between them. Besides, the crosslinking biopolymer network can be considered as reinforcing fibers in the MT matrix leading to improved mechanical strength (Chang and Cho 2012).

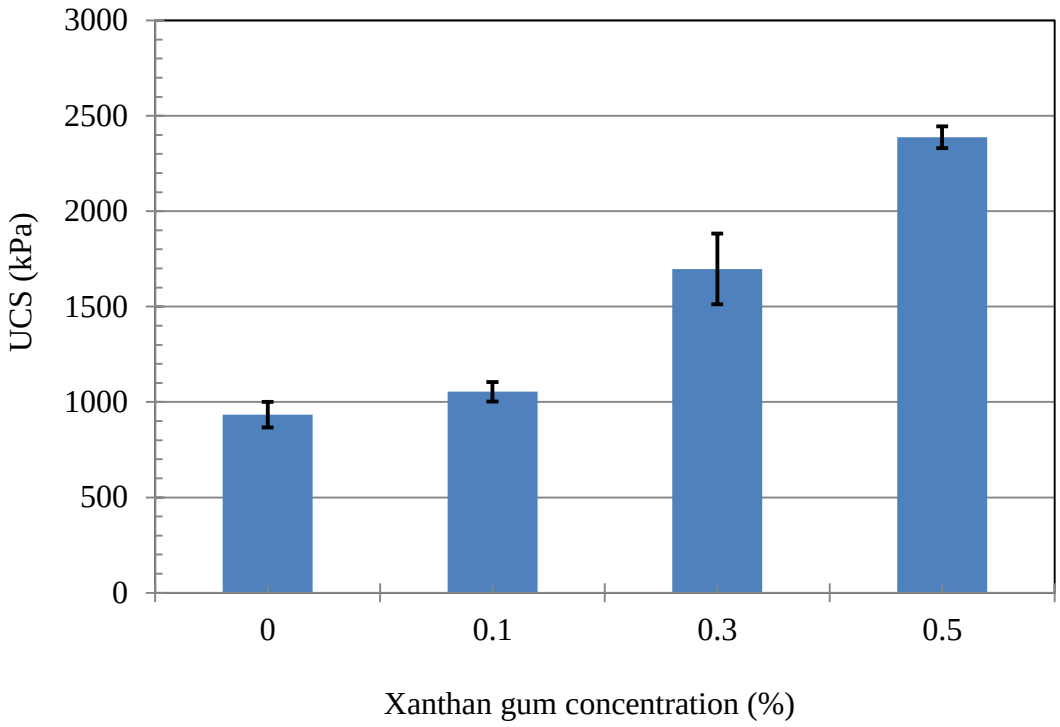


Figure 6.2. Effect of xanthan gum concentration on the UCS of MT.

6.3 DEM SIMULATION

6.3.1 Detail of DEM simulation

The specimen modelled in the UC test simulation had dimensions of (length × diameter) 50 mm × 25 mm, which was the same size used in the UC laboratory tests. Fig. 6.3 shows a sample used in the UC test simulation, in which the MT particles is simulated using an assembly of spherical balls with ball radii range from 0.38 mm to 0.76 mm.

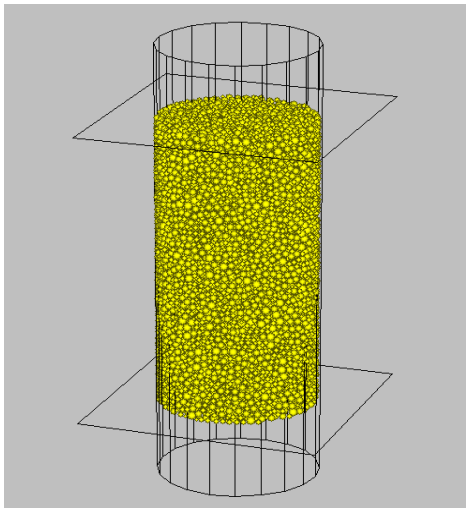
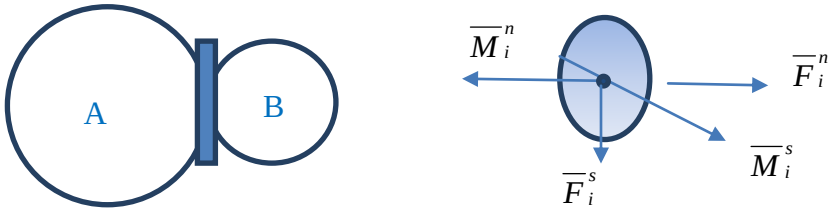


Figure 6.3. Numerical specimen used in DEM simulation.

The balls were randomly generated in the cylindrical vessel to a specific density, and then a small target isotropic stress was applied to create a compacted assembly. The sample shown in Fig. 6.3 contains 21727 balls. Note that it is impractical to use real particle size in the simulation due to limitation of computational capacity. In fact, all modellings reported in the literature used larger particle size than in reality. Hence, it is important to calibrate the micro-parameters used in the numerical model in order to truly reflect the response of the simulated material. The parallel bond in the PFC3D software was adopted to simulate the physicochemical forces between MT particles. The advantage of parallel bond over the contact bond is that it not only can transmit compressive and tensile forces but also moment. The parallel bond model, which is shown in Fig. 6.4, can simulate a finite piece of cement between two spherical particles which can transmit both force and moment. The parallel bond breaks when the exerted stress exceeds the predetermined values. The model density was set the same as the dry

density of MT (1650 kg/m^3), which was kept the same in all simulations. The micro-parameters used in the simulation are summarized in Table 6.1.



(a) (b)

Figure 6.4. Parallel bond model in PFC3D: (a) cylindrical bond between two balls; (b) forces carried by the parallel bond (Itasca 2008).

Table 6.1. Summary of micro-parameters used in numerical simulations.

Micro-parameters	Description	Value
Grain		
d_{min} *(mm)*	Minimum ball diameter	0.38
d_{max}/d_{min}	Ratio of maximum to minimum ball diameter	2
E_c *(GPa)*	Modulus of ball	0.07~0.1
k_n/k_s	Ratio of ball normal to shear stiffness	1
μ	Ball friction	0.6
Parallel bond		
$\overline{k}_n / \overline{k}_s$	Ratio of normal to shear stiffness of parallel bond	1
λ	Radius multiplier	1.0
$\overline{E}_C$ *(GPa)*	Modulus of parallel bond	0.07~0.1
$\overline{\sigma}_c$ *(MPa)*	Tensile strength of the parallel bond	0.94~3.8
$\overline{\tau}_c$ *(MPa)*	Shear strength of the parallel bond	1.8

The parallel bond tensile and shear strength $\bar{\sigma}_c$ and $\bar{\tau}_c$ are of great importance in governing the mechanical response of the simulated material. To date, there is no consensus on the inclusion of biopolymer into soil matrix leading to increase of internal friction angle. Cabalar and Canakci (2011) carried out direct shear tests on sand treated with xanthan gum and found that sand samples treated with 1% xanthan gum showed a decrease in the internal friction angle of 33 to 50%. However, sand samples treaded with 3 and 5% xanthan gum showed increases in internal friction angle of 23 to 46% and 73 to 90% respectively. Khatami and O'Kelly (2012) reported that sand treated with 1-4% biopolymer solution showed a reduction in internal friction angle. It was postulated that the biopolymer coating on the sand grains smoothened the grain surface causing reduction in the roughness, hence decreasing the internal friction angle. In this study, it is presumed that the inclusion of biopolymer into MT only increases the tensile strength (cohesion) between MT particles without contribution to increase of internal friction (shear strength). Therefore, the tensile strength of the parallel bond was varied with the biopolymer concentration while kept the shear strength of the parallel bond constant in the simulations.

6.3.2 DEM simulation results and comparison with experiments

Fig. 6.5 shows the experimental and numerical stress-stain curves of UCS test results of MT samples treated with biopolymer solutions of different concentrations. It can be seen that the numerical simulation is well captured the real mechanical response of biopolymer treated MT samples. Higher biopolymer concentration causes greater UCS.

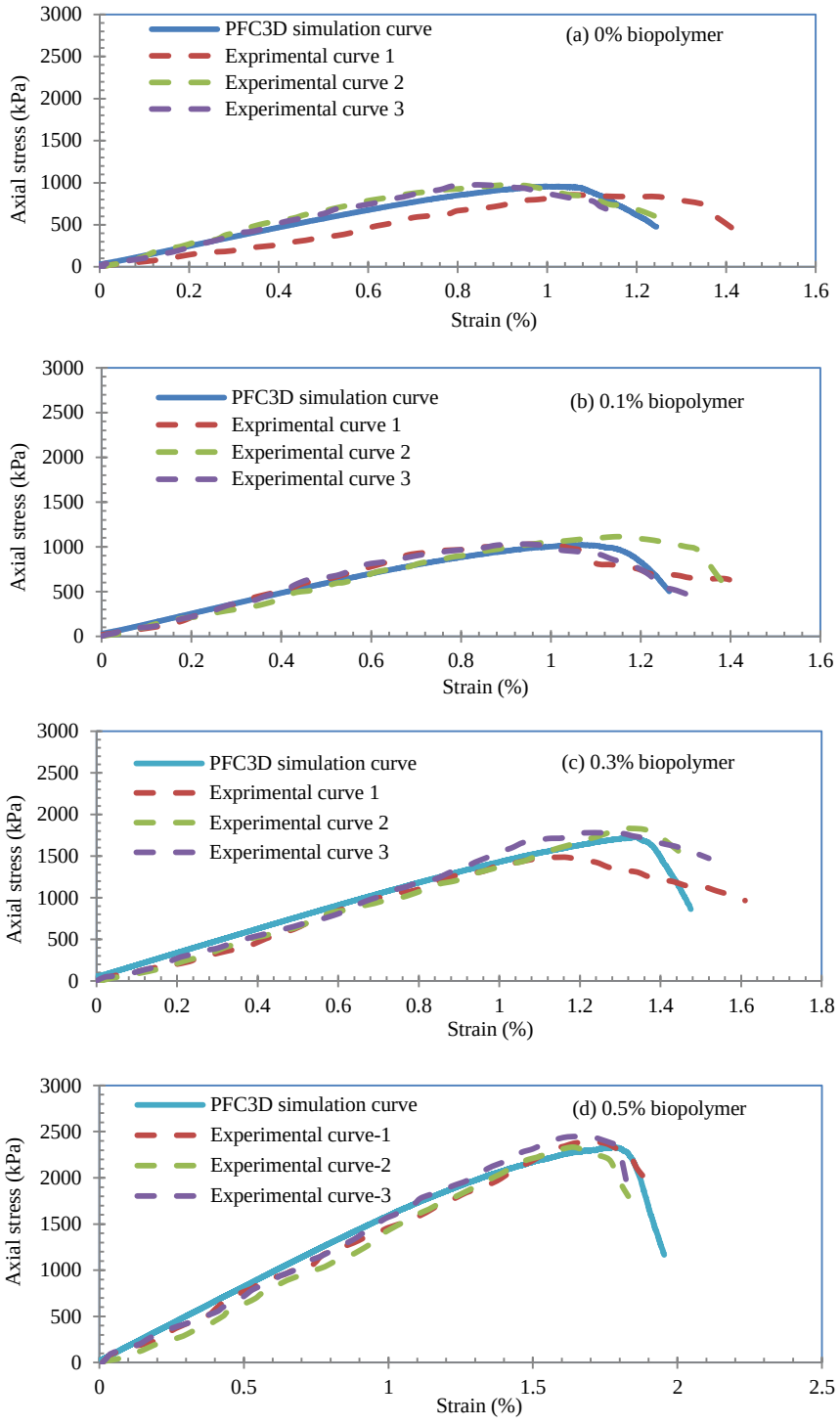


Figure 6.5. Experimental and numerical stress-stain curves of UCS tests on MT samples treated with biopolymer solutions of different concentrations.

Fig. 6.6 presents the relationship between the xanthan gum concentration and the tensile strength of the parallel bond. It shows that the tensile strength of the parallel bond between MT particles increases with xanthan gum concentration, higher xanthan gum concentration inducing greater tensile strength, which proves the inclusion of biopolymer enhances the cohesion between MT particles, from a microstructural point of view.

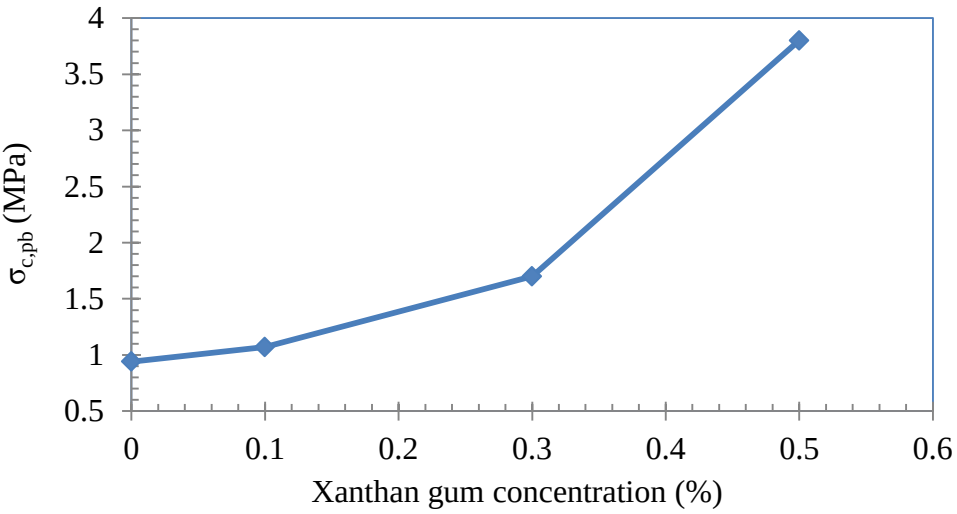


Figure 6.6. Tensile strength of the parallel bond versus xanthan gum concentration.

6.4 CONCLUSIONS

The results presented in this study provide experimental and numerical evidences to support that the inclusion of xanthan gum into MT is beneficial for the increase of cohesion between MT particles leading to increase of the UCS of MT. The experimental results show that higher xanthan gum concentration leads to greater increase in UCS of MT, which may attribute to the increased cohesion between MT particles and the fiber reinforcing effect provided by the xanthan gum crosslinking gel. The numerical

simulations were performed by keeping the shear strength of the parallel bond constant while varying its tensile strength with the xanthan gum concentration. The results show that the parallel bond model can well capture the mechanical behavior of xanthan gum treated MT. Higher xanthan gum concentration causes greater increase of tensile strength of the parallel bond, which confirms the experimental findings that the presence of biopolymer benefits the increase of cohesion between MT particles.

CHAPTER 7
SUMMARY AND FUTURE WORK

7.1 SUMMARY

7.1.1 Natural fiber enhancement of geopolymer

The literature review presented in **Chapter 2** shows that:

1. Natural fibers have been excellent replacements to manmade fibers as reinforcements to enhance cementitious materials and promising resutls have been obtained.
2. Geopolymer emerging as an ideal cementitious material for sustainable development has comparable performance to OPC with additional advantages, but shows the same sensitivity to crakcing as OPC. Although studies have been carried out to enhance geopolymer with fibers of different nature, the utilization of natural fibers to reinforce geopolymer is rarely explored.
3. Different methods have been attempted to treat natural fibers in order to improve the durability of reinforced composites. Alkaline treatment seems to be a good method to pretreat natural fibers for enhancement of geopolymer because of its compatibility with the alkaline environment in geopolymer.

Chapter 3 presents the study of using alkali pretreated sweet sorghum fiber to improve the mechanical properties of fly ash-based geopolymer. Based on the results, the following conclusions can be drawn:

1. The unit weight of geopolymer paste decreases with higher sweet sorghum fiber content.
2. The inclusion of sweet sorghum fibers in geopolymer paste slightly decreases the UCS.
3. The tensile and flexural strengths both increase with the content of sweet sorghum fibers up to 2% and then decrease to be lower than that of the plain geopolymer paste.
4. The post-peak toughness increases significantly with the content of sweet sorghum fibers up to 2% and then slightly decreases but is still much higher than that of the plain geopolymer paste.
5. There is a clear transition from the brittle failure of the plain geopolymer paste specimen to the “ductile” failure of the geopolymer paste specimen containing sweet sorghum fiber.
6. The UCS and tensile strength of 2% sweet sorghum fibers reinforced geopolymer composite progressively decrease with increasing the number of wet/dry cycles. The degradation of natural fiber reinforced geopolymer composite may attribute to (1) fiber-geopolymer debonding and formation of microcracks caused by swelling/shrinking of the sweet sorghum fiber; (2) hydration of geopolymer matrix; and (3) sweet sorghum fiber degradation due to fiber mineralization.

7.1.2 Biopolymer stabilization of mine tailings for dust control

Chapter 4 presents a study of using two natural biopolymers, xanthan gum and guar gum, to strengthen MT. The following conclusions can be drawn based on the experimental results:

1. Inclusion of either xanthan gum or guar gum increases the liquid limit and undrained shear strength of MT, higher biopolymer concentration leading to greater increase. The increase is mainly due to the higher viscosity of the biopolymer pore fluid and the bonding between the biopolymer and the MT particles.
2. Guar gum is more effective than xanthan gum in increasing the liquid limit and undrained shear strength of MT because the guar gum solution is more viscous than the xanthan gum solution at the same concentration, the guar gum-MT particle bonding is stronger than the xanthan gum-MT particle bonding, and guar gum causes less degree of aggregation of MT particles than xanthan gum.
3. For MT mixed with biopolymer solutions, the variation of undrained shear strength with water content follows the general trend of empirical equations for soils, although the magnitudes can be quite different. For better prediction of the undrained shear strength of MT, the two newly proposed equations can be used.

Chapter 5 presents an extensive experimental study on utilization of two biopolymers, xanthan gum and guar gum, for MT dust control. The following conclusions can be drawn from the experimental results:

1. MT treated with biopolymer solution show higher moisture retention capacity than MT treated with just water, higher biopolymer concentration leading to greater increase of moisture retention capacity. The biopolymer stabilization is still effective for water retention capacity enhancement after five wet-dry cycles.
2. MT treated with biopolymer solution show greater dust resistance than MT treated with just water, higher biopolymer concentration leading to greater increase of dust resistance. The biopolymer stabilization is still effective for dust resistance improvement after five wet-dry cycles.
3. MT treated with biopolymer solution show increased surface strength (maximum penetration force), higher biopolymer concentration leading to greater increase of the surface strength.
4. Biopolymer forms coating on the MT particle surface, generates cross-linking network between MT particles and leads to a denser structure of MT, thus increasing the surface strength, enhancing the moisture retention capacity and improving the dust resistance.
5. There is a strong relationship between the dust resistance and the surface strength (maximum penetration force), indicating that penetrometer test method is a promising technique for characterizing the dust resistance of MT.
6. MT treated with biopolymer solutions of low biopolymer concentrations (0.1, 0.3, and 0.5%) do not show improved water retention capacity but show improved dust resistance compared to MT treated with water. MT treated with biopolymer solutions of low concentrations progressively lose the dust resistance with

increasing the number of wet/dry cycles. The biopolymer treatment of 0.5% concentration is still effective for dust control after 10 wet/dry cycles. The loss of dust resistance for biopolymer treatments may attribute to the degradation of biopolymer including: mechanical degradation induced by wind dragging and saltating particles' impact; photodegradation caused by sunlight; and most importantly the chemical degradation caused by water and oxygen.

Chapter 6 presents the experimental and numerical studies of the UCS of MT stabilized with biopolymer solutions of different concentrations. The following conclusions can be drawn based on the results:

1. The results presented in this study provide experimental and numerical evidences to support that the inclusion of xanthan gum into MT is beneficial for the increase of cohesion between MT particles leading to increase of the UCS of MT. The experimental results show that higher xanthan gum concentration leads to greater increase in UCS of MT, which may attribute to the increased cohesion between MT particles and the fiber reinforcing effect provided by the crosslinking xanthan gum gel.
2. The numerical simulations were performed by keeping the shear strength of the parallel bond constant while varying its tensile strength with the xanthan gum concentration. The results show that the parallel bond model can well capture the mechanical behavior of xanthan gum treated MT. Higher xanthan gum concentration causes greater increase of tensile strength of the parallel bond,

which confirms the experimental findings that the presence of biopolymer benefits the increase of cohesion between MT particles.

7.2 FUTURE WORK

It is not possible to investigate every aspect of the problems addressed in this thesis due to time limit. Future research is definitely needed to advance the current understanding.

For natural fiber enhancement of geopolymer, future research should include:

1. The bonding between the geopolymer matrix and the reinforcing natural fiber should be investigated because it is of great importance to produce a good composite. Pull-out tests can be conducted in the future.
2. The durability of natural fiber reinforced geopolymer composites significantly affects its application. Therefore, the degradation mechanisms of natural fiber reinforced geopolymer composites should be studied in more detail.

For biopolymer stabilization of MT, future research should include:

1. In situ application of biopolymer stabilization to demonstrate its performance in mitigating MT dust.
2. The effect of inclusion of biopolymer on the internal friction angle of MT should be studied since it affects the stability of the MT impoundments. This can be done both experimentally and numerically.

3. Studies should be carried out to understand the degradation of biopolymer coating in the field so that relevant measures could be taken to improve the durability of biopolymer stabilization.
4. More detailed experimental and numerical studies should be performed to understand how the presence of biopolymer enhances the mechanical properties of MT from a microstructural perspective.

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