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바이오폴리머를 이용한 화강잔류토 처리
-지반공학적 거동 특성 및 활용-

Biopolymer treated Korean Residual Soil
-Geotechnical behavior and Applications-

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Ilhan Chang

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-Geotechnical behavior and Applications

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위 논문은 한국과학기술원 박사학위논문으로 학위논문심사위원회에서 심사 통과하였음.

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DEDICATION

To my devoted parents
Mr. Han-Ryang Chang and Ms. Sang-Soo Shin

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Abstract

Soil is a natural material consisting variable minerals that differ from the parent materials in their morphological, physical, chemical, and mineralogical characteristics. Biological aspects and considerations of soil behavior is an important topic for geotechnical engineering problems. The strengthened and stabilized behavior of organic soil is induced by biological by-products such as biopolymers.

Korean residual soil (commonly known as Hwangtoh) is a common and environment-friendly material due to its high absorbency, self-purification, and far infrared ray radiation characteristics. However, its low strength and high drying shrinkage problems have restricted its broader usage and development. This dissertation centers on the treatment and strengthening behavior of Korean residual soil in relation to environment-friendly biopolymers.

Biopolymers are polymers produced by living organisms. Biopolymers are generally applied in medical, food, cosmetic, medicine fields and so on, according to their various beneficial properties. Recently, applications in the geotechnical field have been increasing; these applications are related to soil erosion control, aggregate stabilization, and drilling aspects. This study introduces typical biopolymers, such as Beta-1,3/1,6-glucan, Xanthan gum,

Chitosan, and Gellan gum, that can be used to treat Korean residual soil with the aim of improving engineering properties.

The inter-particle behavior and strengthening mechanism of β-1,3/1,6-glucan depends on the adsorption and tensile characteristics of β-1,3/1,6-glucan fibers. Under saturated conditions, free-floating polymers attach to Hwangtoh particles, increasing the shear modulus of the soil. The hydrophilic characteristic of β-1,3/1,6-glucan fibers alter the geotechnical behavior of Hwangtoh. During drying, polymer fibers tend to adsorb Hwangtoh particles, and vice versa. The adsorption process dominates until all Hwangtoh particles are primarily attached to β-1,3/1,6-glucan polymers. Then, regular strengthening is promoted by surplus polymers, which form additional inter-particle contacts and polymer bundles, increasing the internal strength of the soil.

Xanthan gum polymers (showing a Y-form) improve the inter-particle connection between soil particles forming a web matrix. The complex particle-polymer web matrix induced by Xanthan gum shows the highest strengthening behavior among other biopolymers used in this study.

Chitosan promotes a face-to-face connection between soil particles, induced by its strong hydrogen bonding ability. Chitosan shows the lowest strengthening result. Thus, I concluded that the strengthening behavior is maximized by fiber reinforced functioning biopolymers.

Gellan gum forms quick spherical gels in soil which accumulate soil particles. Gellan gum-treated Hwangtoh initially shows the highest improvement but the fastest degradation., Compared with existing engineered soil treatments (e.g. ordinary cement treatment), Xanthan gum and β-1,3/1,6-glucan show suitable strengthening performance and reliable durability. However, Chitosan and Gellan gum are insufficient for improving the engineering performance of soil because of their low strength and weak resistance against weathering.

With a commercial aim, the economic efficiency of biopolymer treatment was performed with additional consideration of the environmental impact. One of the most serious problems of the existing engineered soil materials is a high amount of carbon dioxide emission. Thus, the extent of environmental-impact is calculated in a form of total carbon dioxide emission related to material production and site application. The results show that even though the material prices of biopolymers are more expensive than existing materials (e.g. cement), they decrease the emission level of carbon dioxide significantly. Therefore, the effectiveness and feasibility of biopolymer treatment is expected to continue to increase with the increase of carbon emission taxes and trade costs.

Finally, practical application results reveal that biopolymer treatment shows sufficient mechanical and physical behavior compared to existing cement or gypsum treatment. In other words, biopolymers have a high potential with many opportunities to be used for engineered soil and in various fields such as building, interior, pavement, quick setting, CO_2 storage, and so on.

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CHAPTER I

INTRODUCTION

1.1 BACKGROUND

Soil is a natural material consisting of various minerals that differ from the parent materials in their morphological, physical, chemical, and mineralogical characteristics [Birkeland 1999]. Moreover, soil is a mixture of inorganic minerals and organic constituents that exist in solid, aqueous, and gaseous states [Paul and Paul 2007]. Soil itself is an independent ecosystem consisting of plants, insects, bacteria and fungi.

The last century saw major developments in modern geotechnical engineering. Important touchstones and discoveries led to and accelerated the tremendous development of knowledge on soil and earth materials. However, classical geotechnology focused mainly on the physical and mechanical behavior of soil, while chemical and biological effects were minor considerations or even neglected. However, unusual geotechnical phenomena (e.g. quick clay, waste and pollutant remediation, bio-fouling) raised the necessity and importance of chemical and biological considerations in geotechnical engineering [Mitchell and Santamarina 2005; Soga and Jefferis

2008].

The major paradigms in present civil engineering are ‘Mega structures’, e.g. long-span bridges, super high-rise buildings, large-scale underground facilities, and mega cities, and ‘Low-carbon green development’. As civil structures become larger and larger, the importance and absolute level of soil stability increases in the same manner. Thus, soil treatment, i.e. soil strength and stability improvement, has become a key issue for geotechnical engineers. For soil treatment (i.e. engineered soil), various materials – straw, bitumen, lime, salts, pozzolans, cement, petrochemicals – have been used over the course of human history. Among others, cement is the most common and widely used engineered soil material for strength improvement, seepage control, and waste barriers [Winograd 1981; Xanthakos et al. 1994].

However, cement is a high carbon dioxide emitting material. It is reported that 5% of global carbon dioxide emission is induced by chemical calcinations and fuel burning of cement [BP 2007]. Moreover, large-scale cement waste induces environmental problems such as pollutants and heavy metal leakage [Jang and Townsend 2001]. Thus, several attempts (e.g. ‘geopolymer’, ‘geocement’, ‘inorganic polymer concrete’, etc.) were introduced to replace cement or reduce its usage in the engineered soil field [Davidovits 2008; Krivenko and Kovalchuk 2007; Sofi et al. 2007]. However, those chemical approaches are insufficient to realize the aim of a “low environmental impact and green development" paradigm.

The biological aspects and considerations of soil behavior are an undiscovered "blue ocean" [Kim and Mauborgne 2005] for geotechnical engineers. Thus, several pioneering attempts have attempted to provide a basic understanding of the biological interaction and strengthening effect on soil behavior. The increase of soil aggregate stability induced by organic compounds in soil is reported to be a combined result of interparticle binding force and increased cohesion [Beekman 1987; Oades 1984; Piccolo and Mbagwu 1999], elasticity improvement [Nason 1987; O'Dogherty and Wheeler 1984], filament effect induced by biological fibers [Soane 1990], and electrical charge variation in pore fluids [Brown and Thomas 1987].

Generally, the aforementioned biological effects are induced by microscopic phenomena such as: (1) injection and attachment of microbials, (2) bacterial growth, multiplication, biomass accumulation; (3) expansion of micro colonies and biofilms on soil mineral surfaces; (4) by-product (e.g. biopolymer) excrement; and (5) particle – bio-product (biofilm, biopolymer) interaction affecting soil behavior [Baveye et al. 1992; Vandevivere and Baveye 1992a; Vandevivere and Baveye 1992b]. However, the growth, multiplication, accumulation, and biopolymer excrement processes of soil microbials require a long time and are sensitive to cultivation conditions (temperature, moisture, nutrients, light, gaseous concentrations, etc.) [Molz et al. 1986].

Therefore, a direct biological attempt using ready-made artificial biopolymers (i.e. β-1,3/1,6-glucan, Xanthan gum, Chitosan, and Gellan gum), which is reliable for consistent quality control (regardless of incubation time and condition), is introduced in this study. For engineered soil, biopolymers are used as soil stabilizers to control or reduce soil erosion [Orts et al. 2007], or even for soil drilling muds and temporary excavation support [Mitchell and Santamarina 2005]. However, theoretical and detailed understanding on the physical behavior of biopolymer-treated soil and their optimized conditions remain undiscovered.

The object material for application is Korean residual soil (i.e. Hwangtoh). Hwangtoh is a common and environment-friendly material due to its high absorbency, self-purification, and far infrared ray radiation characteristics. However, its low strength and high drying shrinkage problems have restricted its broader usage and development.

In this thesis, typical biopolymers – β-1,3/1,6-glucan, Xanthan gum, Chitosan, and Gellan gum – are introduced to improve the physical properties of Korean residual soil. Series of theoretical and experimental studies are performed to investigate the interparticle characteristics and strengthening phenomena of biopolymer-treated Korean residual soil, in both micro and macro attempts.

For each biopolymer-Korean residual soil treatment, optimal composition and cure conditions are derived. Then, economic analysis considering environmental impact (carbon dioxide emission) is performed to evaluate the possibility and economic feasibility of biopolymer treatment, compared to that of conventional engineered soil (e.g. cement mixing). Moreover, a prototype is suggested for commercializing the findings in this study.

1.2 SCOPE – ORGANIZATION

This research focuses on discovering the mechanical behavior and strengthening mechanism of biopolymer-treated Korean residual soil. Characteristics of Korean residual soil, commonly named Hwangtoh, are summarized preferentially. A fundamental understanding of biopolymers and the interparticle correlation between biopolymer chains (or gels) and soil particles is attained with emphasis on the mechanical behavior of biopolymer-treated soil. Four different typical biopolymers are introduced in this study to investigate their abilities and possibilities for soil stabilization. Then, practical applications are attempted in order to provide suggestions for commercialization. This information is organized into four chapters as follows:

Chapter 2 provides an overview of Korean residual soil, Hwangtoh. It also describes historical usage and current challenges to making it environment-friendly, with low carbon content, and health-giving properties.

The geotechnical properties of Hwangtoh are also defined.

Chapter 3 presents the interaction mechanism between β-1,3/1,6-glucan and Hwangtoh. Several laboratory attempts such as consistency testing, compaction testing, compressibility testing, compressive strength testing, and SEM analysis, are performed to discover and verify the geotechnical and mechanical behavior of biopolymer-affected Hwangtoh. Emphasis is placed on suitable strengthening performance and environment-friendly characteristics, compared to ordinary engineered soil materials (e.g. cement).

Chapter 4 exceeds the study performed in Ch. 3 to other typical biopolymers, which are Xanthan gum, Chitosan, and Gellan gum. Strengthening performance, durability, and economic efficiency of biopolymer treatment is discussed in detail. An environmental economic efficiency factor, C, is suggested to evaluate the feasibility of soil treatment using biopolymers.

Chapter 5 addresses practical applications of biopolymer-treated Hwangtoh. According to the synergized health-giving benefits, a prototype indoor finishing material is simply produced in the laboratory. Moreover, various possible applications are suggested based on an extensive literature review.

Finally, salient conclusions and recommendations for further study are summarized in Chapter 6.

CHAPTER II

KOREAN RESIDUAL SOIL: HWANGTOH

- DEFINITION AND ITS CURRENT STATE -

2.1 INTRODUCTION

A third or half of the world's population is estimated to live in buildings constructed of earth materials. Generally, earth buildings are perceived to be used only in poor or developing countries. However, there are earth buildings of almost every architectural type used around the world [Rael 2009]. Earth buildings were the most predominant construction type until the invention of ordinary Portland cement in 1824. However, earth buildings have problems such as poor durability, low strength, and low resistance to earthquakes. Thus, at the expansion of the Industrial Revolution, cement and steel replaced the role of earth materials.

Recently, the importance of low impact, environmentally friendly, low carbon, green, sustainable development has been increasing broadly across all industries and nations. Ordinary cement emits high levels of carbon dioxide [Worrell et al. 2001] and is environmentally harmful [Jang and Townsend

2001]. material. In the aim of environment-friendly construction, interests on earth materials are magnified once again, recently [Roy 1999].

In Korea, Korean residual soil, which is widely known as *Hwangtoh*, is a traditional earth material with various applications. However, even though Hwangtoh has a long history as the most common earth material, its characteristics, benefits, and opportunities are not fully defined and understood. For example, Hwangtoh is commonly mistaken for Chinese yellow soil [Jung et al. 1997].

Therefore, in this chapter, Korean residual soil (Hwangtoh) is defined from geological, geotechnical, medical, economic, and environmental perspectives. Reliable definition and classification is expected to promote the commercialization and global standardization of Hwangtoh as a salubrious, environmentally friendly earth material.

2.2 DEFINITAION OF KOREAN RESIDUAL SOIL: HWANGTOH

2.2.1.Residual Soil

Residual soil is soil that remains at the location where it is formed. Chemical and physical weathering processes of the parent rock formulate residual soil [Wesley 1990]. Thus, the characteristics of residual soil depend on the mineralogy of underlying rock (Fig. 2.1).

Meanwhile, most soils in nature are “transported / sedimented soil”, which consisting materials have been transported from other locations by wind, water, and gravity to form Alluvial, Colluvial, Aeolian, Glacial, Lacustrine, Loess, Marine, and Volcanic deposits [Boggs 1995].

Hwangtoh, which is a reddish brown colored, common surface soil type in Korea, was used to be known as Loess. Loess is an Aeolian sediment, which main component is silt, and contains lesser amounts of sand and clay [Jackson et al. 2005]. The most popular Loess deposit in Asia is located in north-west China, which is called “Yellow Soil (黃砂)”. However, present studies show that Hwangtoh is a residual soil, consisting high amount of kaoline group clay minerals, which X-ray diffraction result is similar to Granite [Hwang et al. 2000; Jung et al. 1997].

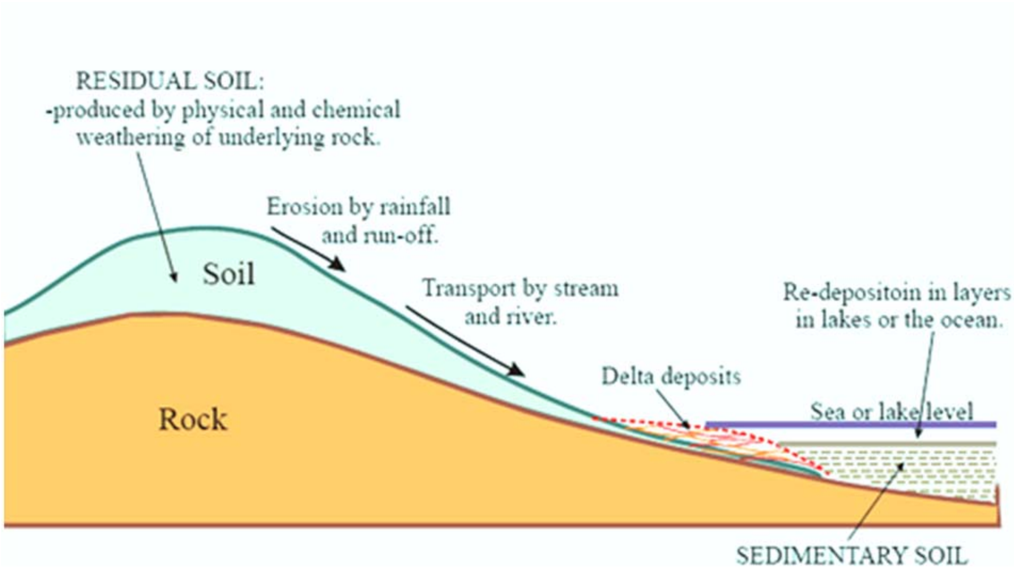


Figure 2.1 Diagrammatic representation of soil formation processes [Wesley 2009].

2.2.2.What is Hwangtoh: General Aspect

Hwangtoh is a primary residual soil in Korea, which is formulated by the weathering granite rocks. The main consisting minerals are Kaolinite ($Al_2Si_2O_5(OH)_4$) and Halloysite ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$), which is a 1:1 layer structure of Si-tetrahedral sheets and Al-octahedral sheets (Fig. 2.2) [Yang et al. 2007]. The micro structure of Hwangtoh shows “honey-comb structure” (Fig. 2.3) which exceeds its porosity up to 50% [Watanabe et al. 1992].

The high porosity of Hwangtoh induces several physiological characteristics, such as high absorbency, self-purification, deodorizing and sanitizing properties [Guth et al. 1996; Kim and Park 2009]. Moreover, Hwangtoh emits far infrared [Kim and Yun 2003; White 1971], which is more beneficial to human body [Hamada et al. 2003; Udagawa and Nagasawa 2000].

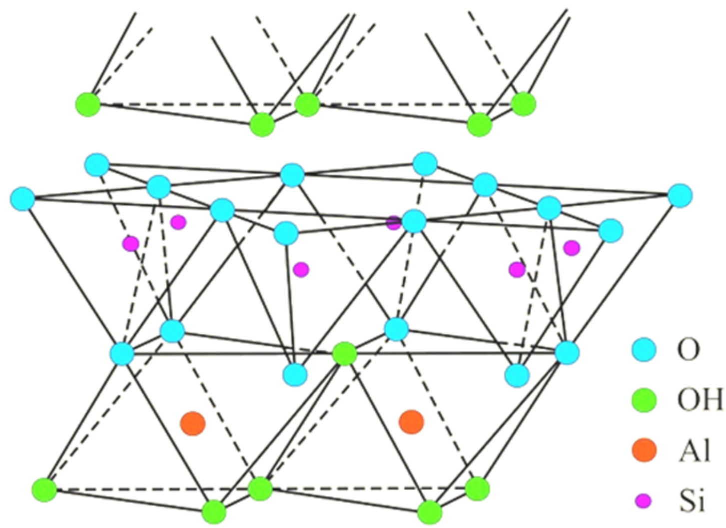


Figure 2.2 Structure of 1:1 layer of Si-tetrahedral and Al-octahedral sheets [Grim 1962].

Figure 2.3 Honey-comb structure of Hwangtoh [Hwang et al. 2008].

2.2.3. Geotechnical Properties of Hwangtoh

In a geotechnical aspect, Hwangtoh is defined as fine-grained silty and clayey soil (ASTM D2487-06). Basic geotechnical properties of Hwangtoh (sampled from Ha-dong, Korea) are summarized in Table 2.1.

Specific gravity (G_s; ASTM D854-06), Atterberg limits (*LL*, *PL*; ASTM D4318-05), and Particle size distribution (ASTM D422-63) were obtained by following the suggested standard laboratory procedures. The specific surface area (S_s) of soil was evaluated by following a methylene blue adsorption method suggested by [Santamarina et al. 2002].

Hwangtoh shows high liquid limit (LL=53.7%) with low plasticity (PI=16.3%), while the liquid limit ratio between oven-dried and non-dried soil ($LL_{oven\text{-}dried}/LL_{not\text{-}dried}$=0.94 > 0.75) concludes that Hwangtoh is inorganic. Thus, based on Unified Soil Classification System (USCS), Hwangtoh is classified to be "MH" type soil. The specific surface value of Hwangtoh (6.81 m^2/g) is lower than pure Halloysite (10~20 m^2/g; [Mitchell and Soga 2005]). Therefore, it can be concluded that natural Hwangtoh contains non-negligible amount of silty particles.

X-ray fluorescence spectrometer (XRF; Shimadzu MXF-1700) analysis result (Table 2.2) shows the 1:1 ratio between Si and Al, and high amount of iron(III) oxide (Fe_2O_3), which appears its color to be reddish.

Table 2.1 Geotechnical Properties of Hwangtoh (Ha-dong, Korea).

In-situ water content [%]	Specific gravity [G_s]	Atterberg limits [%]			Friction angle [º]	Particle size distribution [mm]		Specific surface [m^2/g]
		LL	*PL*	*PI*		D_{60}	D_{10}	
46.8	2.48	53.7	37.4	16.3	20~30	0.07	0.05	6.81

Table 2.2 XRF (X-Ray Fluorescence) result of Hwangtoh (Ha-dong, Korea).

Element	SiO_2	Al_2O_3	Na_2O	K_2O	Fe_2O_3	TiO_2	SO_3	H_2O
Content [%]	50.19	28.69	0.08	0.24	7.48	1.31	0.88	11.33

2.3 BENEFITS AND APPLICATIONS OF HWANGTOH

2.3.1.Historical Usages

The use of earth material (soil) as construction material has a rich history. The origin method for using soil was soil-mortar, which is a simple soil – water mixture. However, the use of soil construction increased rapidly according to the development of application technologies, such as natural bricks, baked bricks, compressed bricks, and reinforcement additives (straw, bitumen, volcanic ash, etc.) [Ngowi 1997]. Historic sites such as Jericho (B.C. 8000, West Bank, Palestine), Shunet ez Zebib (B.C. 2700, Egypt), Ziggurat (B.C. 2200, Iraq) are typical earth material build structures in the ancient era. The common point of these structures is the usage of soil existing nearby.

In the same manner, Hwangtoh, which is a local earth material in Korea, was used in Korean traditional constructions. Especially, Hwangtoh is a smart indoor environment controlling material according to its ability for absorbing surrounding moisture in high-humidity conditions, while discharges containing moistures in low-humidity conditions. Moreover, it has high insulation ability [Kim 2006]. Therefore, Hwangtoh was the most common building material in the Korean history.

The most common type of Hwangtoh application was building walls. Mostly, three wall types: (1) monolithic Hwangtoh wall without reinforcement,

(2) Rammed Hwangtoh wall using external form work, and (3) Hwangtoh bricks using straw or gypsum [Hwang 2008]. Even though, earth materials have poor tensile strength, Hwangtoh was used as roof material in Korea, as baked roof tiles (*Giwa*).

The most impressive application of Hwangtoh is *Ondol*, which is a floor heating systems originated in Korea. The main function of *Ondol* is to store the supplied heat consistently [Song 2005]. Hwangtoh has high thermal conductivity (k) as 3.15 [W/m·K], while typical range of soils is 0.25 to 2.5 [Mitchell and Soga 2005; Ochsner et al. 2001; Park and Hong 2002].

Meanwhile, volumetric heat capacity of Hwangtoh shows 8.06 $J/cm^3 \cdot K$ [Park and Hong 2002], which is higher than water (4.1796 $J/cm^3 \cdot K$) and soil (2.0~2.3 $J/cm^3 \cdot K$) [Noborio et al. 1996]. This fact indicates that Hwangtoh is a suitable floor material for the *Ondol* system, because it has an excellent performance on both quick heating and heat storage.

2.3.2.Advantages of Hwangtoh: Theoretical Aspects

According to the recent environment-friendly and LOHAS (Lifestyle of Health and Sustainability) concept, popular interests and demands are shedding new lights on the usage of Hwangtoh. In this section, the benefits and advantages of Hwangtoh are described.

Purification

The high porosity characteristic, followed by the honey-comb structure of Hwangtoh, induces several physiological characteristics, such as high absorbency, self-purification, deodorizing and sanitizing properties [Guth et al. 1996; Kim et al. 2010; Kim and Park 2009]. In practice, Kim et al. (2010) showed that Hwangtoh based indoor materials emits less VOC (Volatile Organic Compounds) than artificial chemical materials, such as plywood, gypsum, and synthetic textiles.

Far Infrared Ray Emission

Hwangtoh emits far infrared with high emissivity (0.914) in the range of 5 ~ 20 μm [Kim and Yun 2003; White 1971]. Generally, the human body can absorb far infrared ray (8 ~ 14 μm) according to its deep penetration ability [Hamada et al. 2003; Udagawa and Nagasawa 2000]. Far infrared ray energy vibrates water molecules which increases their hydration capacity. Combined with the heat expanded blood vessels, the circulation of contracted body fluids (blood, lymph, fat) is accelerated, which activates toxin removal [Lin et al. 2007]. In reality, far-infrared radiation caused significant acceleration of body growth in growing rats (7% heavier than non-exposed group) [Inoue and Honda 1986]. Thus, the restorative and healing properties are widely used in cosmetic and medical industries [Lee et al. 2008].

Environment-Friendly Material

Cement is one of a most common construction material worldwide. Most of cement (80%) is produced and consumed in emerging countries such as, China. However, cement industry is directly connected to pollution, in the form of carbon dioxide emissions [Rosenthal 2007]. Cement related industry plants account for 5 percent of global carbon dioxide emissions, which is the main cause of global warming [BP 2007]. Moreover, cement has no viable recycling potential, which means, each new road and building construction requires new cement.

Whereas, Hwangtoh is an environment-friendly material, which emits few amount of carbon dioxide and is recyclable after usage. The energetic index values (total amount of required energy for raw material production and commercial manufacture) of typical construction materials are listed in Table 2.3 [Kreijger 1979], show that the use of Hwangtoh (natural clay) embodies less energy compared with other construction materials, except water.

The environment-friendly merit becomes definite in the view of carbon dioxide emission. Table 2.4 shows that even 1% of Hwangtoh replacement instead of cement, reduces 20 times of carbon dioxide emission.

Table 2.3 Energetic index of construction materials [Alcorn and Wood 1998; Kreijger 1979].

Materials	Energetic index (kJ / kg)	Energetic index (kJ / L)
Natural clay	70	45
Natural sand	100	160
Lightweight aggregates	4,000	2,500
Wood	4,000	2,400
Lime	6,300	8,200
Portland cement	6,400	8,000
Gypsum	3,600	2,900
Water	4	4
Baked clay bricks	4,300	7,700
Sand lime bricks	840	1,500
Clay brick masonry	6,000	11,000
Glass	21,000	56,000
Steel	30,000	236,000
Reinforcement	23,000	180,000
Aluminum	120,000	325,000
Plastic	40,000	40,000

Table 2.4 Carbon dioxide emission of construction materials [Buchanan and Honey 1994].

Materials	Unit	Carbon dioxide emission [kg/Unit]
Natural clay	kg	0.6
Natural sand	kg	4.9
Lightweight aggregates	kg	31.4
Wood	m^3	102.8
Lime	kg	1.0
Portland cement	kg	1291.8
Gypsum	kg	0.7
Glass	kg	3
Steel	kg	5.1
Copper	kg	5.8
Aluminum	kg	23.7
Plastic	kg	19.4
Rubber	kg	17.0

Local Material

Embodied energy is a combination concept which represents the whole amount of energy that is taken through source, production, manufacture, storage and transportation. However, many environment-friendly materials highly depend on the globalised economy. This means that, even if a high value environmental construction material exists in a foreign region, its merit depreciates according to the additional amount of embodied energy caused by long distance transportation, as well as, rising oil prices [Morel et al. 2001]. Hwangtoh is one of a most common local material in Korea. Thus, increasing the usage of Hwangtoh (or other kind of rich local residual soil) is a roundabout way to increase the economic efficiency and decrease negative environmental impacts, which is not only applicable for Korea, but also for other different regions around the world.

2.3.3.Recent Applications of Hwangtoh

Building Material

Since the beginning of the 21st century, several attempts were applied to use Hwangtoh as environment-friendly building material. Additives such as gypsum, cotton, nylon, and cellulose were used to increase the strength of natural Hwangtoh, to produce indoor finishing Hwangtoh boards or tiles [Jang 2009; Kang 2009; Kim 2003].

The Geopolymer concept, which was compiled by Davidovits (2008), provided an idea to activate Hwangtoh to increase its pozzolanic tendency [Davidovits 2008]. Thus, thermal activated Hwangtoh (over 1,000ºC), which transforms to metakaoline, was mixed with cement mortars to activate the secondary pozzolanic reaction under the high pH condition induced by cement hydration [Choi et al. 2000; Go et al. 2009; Hwang et al. 2008; Lee and Go 2007]. However, these attempts have limitation on the dependency of ordinary cement.

Thus, recent studies are focused on the development of cementless Hwangtoh binder. Alkali material, such as $Ca(OH)_2$ accelerates the mineral dissolution of activated Hwangtoh, which shows better pozzolanic reaction performance [Yang et al. 2007]. Meanwhile, water soluble adhesives are mixed with Hwangtoh to decrease its amount of drying shrinkage [Kim et al. 2010].

Biological Activities

In the Korean traditional medical book <Dongui Bogam (동의보감; 東醫寶鑑)>, Hwangtoh is described as, "*Good Hwangtoh is nontoxic and has a sweet taste. It is effective to prevent diarrhea and dysentery*…". Thus, Hwangtoh was used as digestive medicine in Korean folk remedy.

Nowadays, Hwangtoh is used as feed additive in poultry and dairy farming. It is reported that kaoline group minerals (e.g. Hwangtoh), diminishes the adsorption of nasty bacteria on intestine epithelial cells, and increases the immunity level of livestock [Hanson et al. 1985; Murray 1999]. Moreover, including kaolin in feeds increases the spawning rate of hens [Spandorf 1973], and increases the growth rate and decreases ammonia and methane emission of beef cattle [Britton et al. 1978].

Adsorbents

Colloids of Hwangtoh have abilities to coagulate and adsorb suspensions [Lee et al. 2004]. Heavy metal adsorption ability of Hwangtoh increases as the surrounding pH increases, due to the stronger negative zeta potential formed on Hwangtoh particle surfaces [Gam et al. 2003].

For practical application, Hwangtoh is widely used to remove red tides. The remove of algal cells by clay minerals is governed by mutual flocculation and sedimentation. [Sengco et al. 2001]. Dispersed clay particles in seawater destabilizes immediately due to its high ionic charge. Thus, electrostatic repulsion decreases, while particle attractive forces (e.g. van der Waals force) dominate flocculation and coalescence of clay particles to form larger flocs which can be ascended. Then, falling flocs interact with algal cells, adsorb them, and forms larger flocs which sedimentation can be accelerated [Avnimelech et al. 1982; Yu et al. 1994; Yu et al. 1999].

2.3.4.Challenges and Limitations of Hwangtoh

Hwangtoh is a common earth material having a long history of civilized applications. The advantages and benefits of Hwangtoh are as: (1) common local material, (2) environment-friendly material, (3) Health giving material, (4) Well-being hygienic material. However, its low strength and weakness induced by drying shrinkage are major limitations of Hwangoth, compared to other modern construction materials.

In the aim to improve its mechanical performance, several attempts were performed by using additives, cement, and activated Hwangtoh. However, chemically improved Hwangtoh (cement mixing, chemical adhesives) has secondary problems rendering environmental impacts, while activated

Hwangtoh is expected to lose its inherent structure and characteristic according to the phase transform from halloysite / kaolinite into metakaoline.

Therefore, a new environment-friendly and high effective treatment method of Hwangtoh, to increase its mechanical performance and protect its inherent characteristic is required to be developed with high social demands.

2.4 SUMMARY AND CONCLUSIONS

In spite of Hwangtoh has a long history in Korea as a common and familiar earth material, its characteristics, benefits, and opportunities are not yet fully defined or understood.

According to the literature and a series of experimental studies, Hwangtoh is geologically defined as a kaolin group residual soil, the major minerals of which are halloysite and kaolinite. From a geotechnical perspective, Hwangtoh is defined as a fine-grained, silty, clayey soil with moderate plasticity (*MH*-type soil).

Recent medical rediscoveries have shed new light on the importance and use of Hwangtoh. The major salubrious properties of Hwangtoh are attributed to the following characteristics: a highly porous honeycomb structure, a high level of thermal conductivity and heat capacity, and a far-reaching infrared ray emission that stimulates physiological circulation in the human body. Thus, Hwangtoh applications have recently been expanded to housing, food, environmental treatment, and so on.

With regard to the use of Hwangtoh as a building material, researchers have made several attempts to increase its strength and control its drying shrinkage but they have not yet developed an adequate environmentally friendly method. Thus, a new environmentally friendly method is urgently needed so that Hwangtoh can be improved without losing its inherent characteristics.

CHAPTER III

GEOTECHNICAL BEHAVIOR OF BETA-1,3/1,6-GLUCAN TREATED KOREAN RESIDUAL SOIL

3.1 INTRODUCTION

It is not an overstatement to define the construction history of modern civilization as the age of cement. Ever since the development of Portland cement (1824), cement has been widely used around the world as a basic ingredient of concrete, mortar, stucco and most non-specialty grouts. The global cement production increased rapidly at an average annual growth rate of 3.6% during the last quarter of the 20th century (594 M·ton in 1970 to 1453 M·ton in 1995) [Cembureau 1998]. Recently, developing countries such as China, India, and Brazil have been leading the growth of cement production. the chemical calcination and fuel burning stages of cement production emit carbon dioxide, which is a significant greenhouse gas. Five percent of global carbon dioxide emissions are reportedly induced by cement industries [BP 2007; Worrell et al. 2001]. Thus, there have been several attempts to reduce or replace the usage of cement: namely geopolymer [Davidovits 2008], alkali-activated cement [Alonso and Palomo 2001], geocement [Krivenko and Kovalchuk 2007], inorganic polymer concrete [Sofi et al. 2007]. However, the CO2 reduction efficiency of previous methods is insufficient because of their dependency on ordinary cement and bi-products of heavy industry.

Advanced countries are also experiencing environmental problems with the end of service of cement-based concrete. In the United States, annual building-related concrete demolition waste is estimated to be 65 million tons [Associates 1998]. Efforts are being made to reuse or recycle concrete waste as filling materials or aggregates [Guggemos and Horvath 2003] instead of discarding it as landfill waste. However, the disuse or recycling of concrete waste is hazardous to the environment because pollutants can leak into the soil and groundwater [Jang and Townsend 2001]. The so-called sick building syndrome, which refers to the health problems and displeasure induced by construction materials, has recently become a serious sanitation issue. The emission of ammonia (NH_3), formaldehyde (CH_2O), and hexavalent chromium (Cr^{6+}) from cement-based concrete is reportedly increasing the mobility rate of health problems such as atopy, asthma, rhinitis, and dermatitis [Kamijima et al. 2002; Tomoto et al. 2009]. Accordingly, there is now a high demand for the development of harmless, environmentally friendly construction material which can reduce dement dependency and be easily reused without any negative environmental impact.

Hwangtoh is a common residual soil type in Korea. With high absorbency, self-purification, and far-reaching infrared ray radiation, it is a traditional and typical environmentally friendly material [Yang et al. 2007]. However, the low strength and drying shrinkage problems have restricted its usage and development [Go et al. 2009]. Nevertheless, because of its salubrious, environmentally friendly benefits, several researchers have attempted to use Hwangtoh as a construction material [Go et al. 2009; Yang et al. 2007]. Existing methods, which are limited to concrete admixtures or to a modified type of activated meta-kaolin, emit huge amount of greenhouse gas [Davidovits 2008]. Therefore, a new application method without any property degeneration or environmental impact is needed to amplify the benefits and extend the use of Hwangtoh.

Biopolymers are polymers produced by living organisms. Most applications of biopolymers can be found in the medical engineering of drug delivery systems, wound healing, and surgical implantations [Van de Velde and Kiekens 2002]. Exopolysaccharides, such as welan gum and curdlan, have recently been used as a bio-admixture in concrete or as a dry-mix mortar with water-retention agents or superplasticizers on account of their pseudoplasticity property [Khayat and Yahia 1997; Sonebi 2006].

Biopolymers have also been used as soil-stabilizing additives to control or reduce soil erosion in a field [Orts et al. 2007]. The existence of biopolymers influences the surface and colloid chemistry of soil by means of adsorption reactions between the constituents of the soil solution and the solid phases in the soil [Sposito 1989]. Moreover, biopolymers are used for soil drilling muds and temporary excavation supports [Mitchell and Santamarina 2005]. However, from a geotechnical and geoenvironmental perspective, theoretical and experimental verification of the interaction between various types of biopolymers and soil media remains a high possibility and opportunity.

The production of biopolymers as a construction material is not as economically efficient as petrochemical polymer products (which are 2.5 to 7.5 times more expansive) [Kamm and Kamm 2004]. However, factors such as global environmental regulations, high oil prices, and the development of biopolymer technology are increasing the economic competitiveness of biopolymers. One typical example is the β-1,3/1,6-glucan biopolymer.

This study defines the β-1,3/1,6-glucan biopolymer in terms of its interparticle function and then applies it as an additive to Hwangtoh to increase the strength and stability of Hwangtoh. A series of laboratory tests were performed to investigate how the structural and engineering behavior of Hwangtoh is influenced by the interaction of β-1,3/1,6-glucan polymers and soil particles. The results are discussed in terms of efficiency and the possibility on Hwangtoh treatment with β-1,3/1,6-glucan.

3.2 MATERIALS AND EXPREIMENTAL METHODS

3.2.1 Beta-1,3/1,6-Glucan

Glucans is a polysaccharide of D-glucose ($C_6H_{12}O_6$) monomers. Type of glucan is distinguished from α- and β- glycosidic bonds. An α-glycosidic bond emerges below the plane of glucose, while β-glycosidic bond exists above the plane. Beta-1,3/1,6 glucans are biopolymers of D-glucose monomers linked by β-glycosidic bonds [Bacic et al. 2009]. Typical formulas are summarized in Table 3.1.

Beta-glucan has various formations in nature such as, cellulose in plants, bran of cereal grains, cell walls of yeast, fungi, mushrooms, and bacteria (Fig. 3.1). Especially, yeast and mushroom derived β-1,3/1,6-glucan has high biological activity which is used as immune system modulators in medical engineering [Ooi and Liu 2000].

Beta-glucans are biological response modifiers (BRM) due to their ability of immune systems activation [Miura et al. 1996]. Details of clinical applications are summarized in Table 3.2. In the aim of engineering applications, beta-glucan is used as additives such as, superplasticizer and water reducing agents in concrete [Khayat and Yahia 1997; Nagai et al. 1999].

Polycan^{TM} (Glucan Corp., Busan, Korea), which is a β-1,3/1,6-glucan compound produced by UV induced mutant of *Aureobasidium pullulans* SM-

2001 [Shin et al. 2007] is used in this study. Standard reagent was prepared by distilled water dilution under a concentration of 8.2 g of β-1,3/1,6-glucan per 1 L of dissolved solution. The liquid type standard reagent was defined as c_o=1.0 (amount of β-1,3/1,6-glucan: 8.2g/L; c_o=0 represents distilled water).

3.2.2 Beta-1,3/1,6-Glucan Solution Preparation

To verify the effect of the amounts of biopolymer on the strength behavior of Hwangtoh, beta-glucan solutions with different solubility were prepared. Details of beta-1,3/1,6-glucan solutions are listed in Table 3.3.

3.2.3 Hwangtoh: Korean Residual Soil

Hwangtoh material used in this study is from Ha-dong, Korea. The mineral constitution by mass is as: Quartz (8.4%), Kaolinite (45.8%), Halloysite (22.7%), Illite (14.8), Goethite (8.3%). Natural Hwangtoh is oven dried at 110 °C temperature to avoid organic contents (ASTM D 2216-05), and grinded (grain size < 75 μm) for mixing preparation.

Table 3.1 Typical beta-glucan materials.

Name	Glycoosidic bond	Molecular formula	CAS number
Cellulose	β-1,4	$(C_6H_{10}O_5)_n$	9004-34-6
Curdlan	β-1,3	$(C_6H_{10}O_5)_n$	54724-00-4
Laminarin	β-1,3 and β-1,6	$(C_6H_{10}O_5)_n$	9008-22-4
Chrysolaminarin	β-1,3	$(C_6H_{10}O_5)_n$	9013-94-9
Lentinan	β-1,6 and β-1,3	$(C_{42}H_{72}O_{36})$	37339-90-5
Lichenin	β-1,6 and β-1,4	$(C_6H_{10}O_5)_n$	1402-10-4
Sizofiran	β-1,3 and β-1,6	$(C_6H_{10}O_5)_n$	9050-67-3
Pleuran	β-1,3 and β-1,6	$(C_6H_{10}O_5)_n$	159940-37-1
Zymosan	β-1,3	$(C_6H_{10}O_5)_n$	9010-72-4

Table 3.2 Medical applications of beta-glucan.

Field	Major functions	Related studies
Cancer	Anti-tumor and anti-cancer activity.	[Morikawa et al. 1985]
	Improving service time of antibodies and cancer vaccines	[Vetvicka et al. 1996] [Ross and Vetvicka 1996]
Infection prevention	Reduces post-surgical nosocomial infections by promoting the phago-cytosis of pathogenic bacteria.	[Dellinger et al. 1999]
Radiation exposure	Hematopoiesis-stimulating activity.	[Patchen and Macvittie 1983]
Septic shock	Reduction of septic infection	[Onderdonk et al. 1992]
Surgery	Macrophage stimulation in healing wounds.	[Browder et al. 1990]
	Mortality reduction and stronger tensile strength of scar tissues.	[Portera et al. 1997]
Arthritis	Decline oxidative tissues damaging arthritis.	[Kogan et al. 2005]

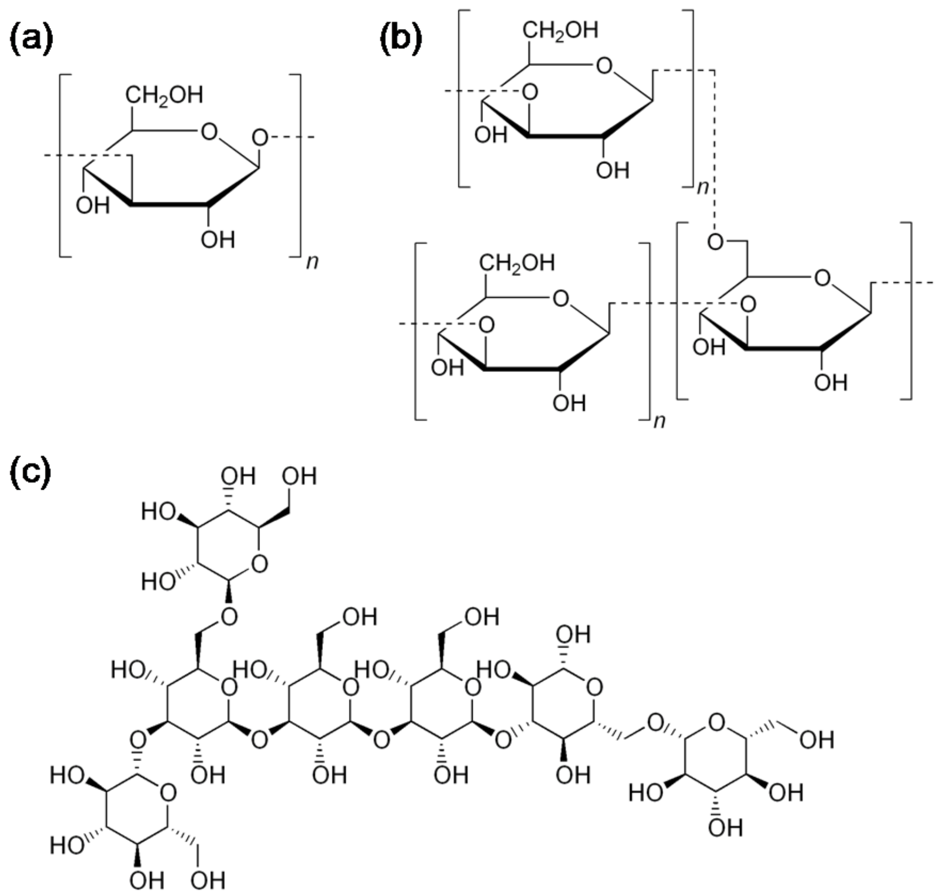


Figure 3.1 Molecular structures of typical beta-glucans. (a) Zymosan. (b) Sizofiran. (c) Lentinan.

Table 3.3 Solutions used for compaction test.

Solution notation [c_o]	1.0	0.5	0.1	0.05	0.01
Volumetric dilution ratio [pure liquid : solution]	1:1	1:2	1:10	1:20	1:100
Beta-glucan concentration [g/L: solid mass/solution volume]	8.2	4.1	0.82	0.41	0.08

3.2.4 Tensile Strength and Interparticle Behavior of Beta-1,3/1,6-Glucan

Dehydrated β-1,3/1,6-glucan solution forms thin film. The film was trimmed (10 mm width, 0.34 mm thickness) to be applicable for tensile testing. Tensile strength of β-1,3/1,6-glucan polymers were measured by UTM (Universal Testing Machine) device (INSTRON 5583).

However, specimen preparation and test performance of β-1,3/1,6-glucan polymer following the testing standard (ASTM D 882) was difficult according to its low strength compared with ordinary polymers. Therefore, an alternative method was introduced in this study. A simple β-1,3/1,6-glucan – filter paper (Whatman® No.4) composite was prepared, by coating liquid state β-1,3/1,6-glucan solution on both sides of the filter paper. After dehydration, the tensile strength of β-1,3/1,6-glucan – filter paper composite was measured, as well as pure filter paper for comparison. Finally, the tensile strength of β-1,3/1,6-glucan can be derived by comparing the strength of filter paper and β-1,3/1,6-glucan – filter paper composite.

Meanwhile, glass beads (uniform grain size; mean diameter = 1.5mm) were prepared to study how β-1,3/1,6-glucan polymer interacts with particulate materials. Pure β-1,3/1,6-glucan Polycan solution was mixed with glass beads within a solution/solid ratio as 60%. After dehydration, SEM (Philips XL30SFEG) images were taken to confirm the microscopic structure.

3.2.5 Mixing and Curing: Cubic Curing Test

Dried Hwangtoh and β-1,3/1,6-glucan solutions (Table 3.3) were mixed together using a laboratory automatic rotator. For mixing the initial moisture content (solution/solid ratio in mass) becomes an important criterion because it defines the initial density and workability of a soil mixture. Thus, the moisture content was set as 60% (*LL* of natural Hwangtoh = 53.7%). The mixing process should be performed long enough to provide uniform slurry. After mixing, the slurry was poured into cubic molds (4cm×4cm×4cm size for each cubic). Vibration compacter was used for leveling and to avoid air voids inside specimens. Finally, spatulas were used to smooth the top surface and the mold was removed for specimen curing. Molded specimens were cured at room (20°C), 60°C and 100°C temperature separately to identify the thermal effect and dehydration gradient on the behavior of β-1,3/1,6-glucan – Hwangtoh mixtures.

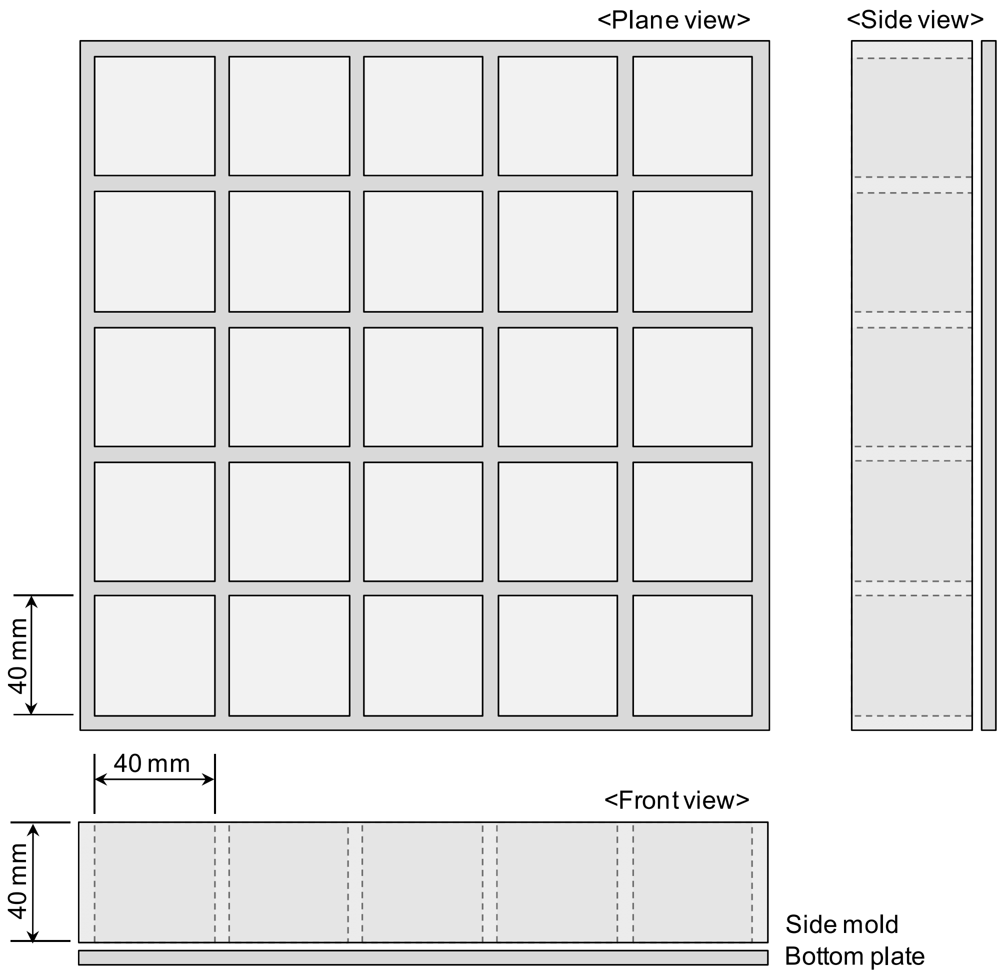


Figure 3.2 Schematic view of the cubic curing device.

(a) Laboratory rotator. (b) Vibration compactor.

Figure 3.3 Specimen mixing and compacting equipments.

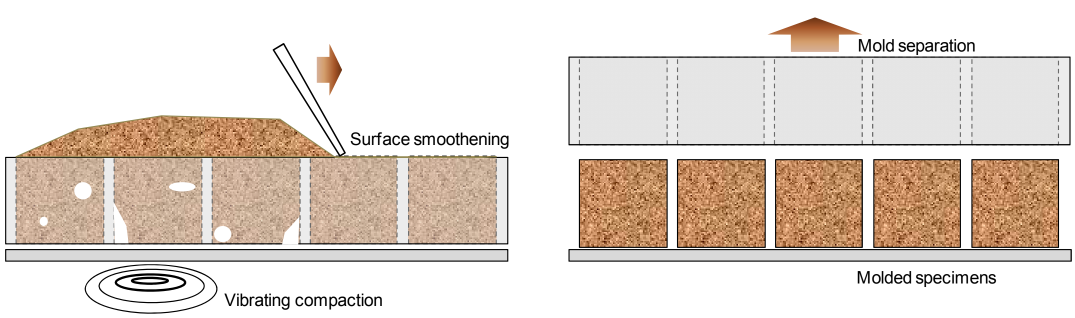


Figure 3.4 Specimen molding.

3.2.6 Initial Properties of Beta-1,3/1,6-Glucan – Hwangtoh Mixutres

Cone penetrometer test

The initial properties of β-1,3/1,6-glucan – Hwangtoh mixtures indicate interactions between β-1,3/1,6-glucan, solid Hwangtoh, and water. Fresh mixed β-1,3/1,6-glucan – Hwangtoh mixtures were sampled by ring-shape sampler to minimize soil disturbance. The liquid limit of fresh β-1,3/1,6-glucan – Hwangtoh samples were derived by the cone penetrometer (Fig. 3.5) method (BS 1377-2).

Compaction test

Compaction test (BS 1377-4) was performed to evaluate the maximum dry density and optimum water content of β-1,3/1,6-glucan – Hwangtoh mixed soil.

The density variation of Hwangtoh induced by biopolymers is evaluated by laboratory compaction testing. The main aims of this study are:

(1) The relation between dry density and moisture content for a given biopolymer concentration.

(2) The value of the maximum dry density for each biopolymer concentration condition.

(3) The optimum initial water content for maximum strength and minimum shrinkage.

Three different solutions (c_o=1.0; c_o=0.5; c_o=0, distilled water) were used. For each solution condition, five specimens with different moisture contents were prepared. 'Heavy compaction' (BS 1377-4) was performed consistently for each specimen.

<u>Compressibility Test</u>

In concrete engineering, biopolymers such as β-1,3/1,6-glucan are used for water reducing and inflating agents. Thus, the compressibility and consolidation behavior change due to biopolymer mixing should be classified.

Compressibility testing is performed for two purposes: (1) Characterize the stress-strain behavior and (2) Characterize the density-seismic wave velocity behavior of β-1,3/1,6-glucan mixed Hwangtoh. To evaluate both of those properties, a wave based oedometric method is introduced in this study.

Hwangtoh and β-1,3/1,6-glucan solution mixed soil is placed in an acryl oedometer cell having embedded piezoelectric transducers (PZT) on the bottom. A top cap is covered for load appliance, strain measurement and sensor housing. Two different types of PZT sensors are applied, plate type for compressive (P-) wave and bender element type for shear wave measurement

(Fig. 3.6). Detail methods for sensor soldering and housing can be find in [Chang and Cho 2010].

For signal measurement, bottom PZT sensors are connected to a waveform generator (Agilent 33120A) to generate single step signals with 5 to 10 volts amplitude at a 5 Hz frequency. The received signals pass the multi channel signal conditioner (Krohn-Hite 3944) to avoid unwanted noise (band pass filtering; 100 Hz high pass, 50 kHz low pass). Both input and output signals are displayed at the digital oscilloscope (Agilent DS 06104A) to detect the first arrivals of each signal. Details of signal interpretation correspond to [Lee and Santamarina 2005].

In this study, three different sample conditions were prepared to verify the β-1,3/1,6-glucan effect on the stress-strain and seismic character variation of Hwangtoh. Dried Hwangtoh was mixed with β-1,3/1,6-glucan solutions to prepare uniform remolded soil samples. The details of testing conditions are listed in Table 3.4. Each sample was placed in the cell and confined by bottom and cap devices. The whole setup was placed in the center of the oedometric device, and saturated with the same β-1,3/1,6-glucan solution to prevent chemical osmosis effects [Barbour and Fredlund 1989].

Step loading method was chosen for load application. Each amount of loading was decided upon by considering the logarithmic scale of effective stress increment. Subsequent loading was performed after the convergence of elastic wave increment and volumetric strain decrement, induced by the previous loading step.

After several loading steps, applied load was unloaded to induce swelling. Elastic wave velocity and volumetric strain were also measured simultaneously. Specimens were loaded again after unloading to recover swelling. Then, the specimens were reloaded to extend the virginal compression load.

3.2.7 Time Dependent Behavior of Beta-1,3/1,6-Glucan – Hwangtoh Mixtures

The compressive strength and stiffness of cured specimens under different temperatures were measured consistently at every 7 days. UTM (INSTRON 5583) was used to apply compression test (Fig. 3.7). For each single condition (amount of β-1,3/1,6-glucan and curing temperature), three specimens were applied, and the average value was selected to represent the mechanical behavior of certain condition. At the end of curing (28 days), SEM (Philips XL30SFEG) images were taken to confirm the interaction between β-1,3/1,6-glucan polymer chains and Hwangtoh particles.

(a) Automatic fall-cone tester.

(b) Cone (80 g, 30°),

(c) Specimen ring and penetration.

Figure 3.5 Cone penetrometer test device.

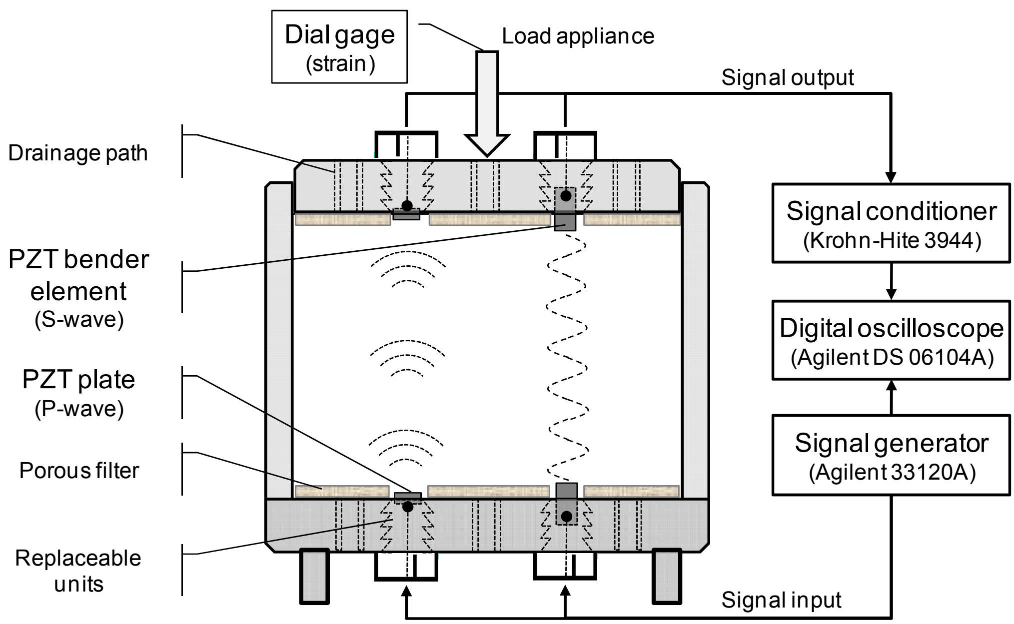
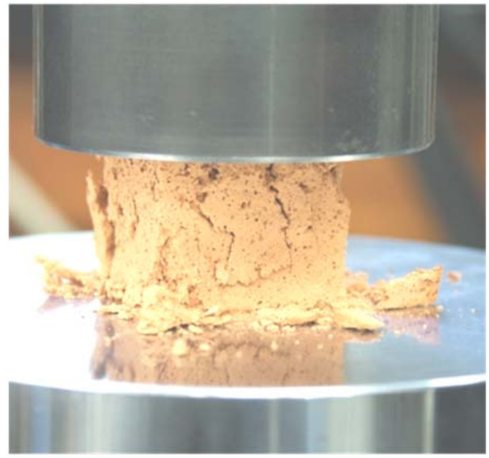


Fig. 3.6 Schematic diagram of wave based compressibility testing device.

Table 3.4 Testing setup of compressibility test of β-1,3/1,6-glucan – Hwangtoh mixtures.

Sample name	Initial water content [%]	β-1,3/1,6-glucan / solid ratio [*w/w*, %]	Initial volume [m^3]	Initial total weight [g]	Initial total density [ton/m^3]
$c_o = 0$	60	0	2.97×10^{-4}	468.7	1.58
$c_o = 0.1$	60	0.05	2.97×10^{-4}	476.9	1.61
$c_o = 0.5$	60	0.25	2.97×10^{-4}	406.1	1.37

(a) 7 days.



(b) 14 days.

(c) 21 days.

(d) 28 days.

Figure 3.7 Example of compressive strength testing on cubic cured samples (c_o=1.0; initial water content=60%; *w/w* = 0.5%; room cured).

3.3 RESULTS AND DISCUSSIONS

3.3.1. Tensile Strength and Micro Structure of Beta-1,3/1,6-Glucan

The adsorption of β-1,3/1,6-glucan polymers on particles during dehydration process, can be explained as a type of cementation. The behavior of cemented particulate materials is affected by cementation material content, confining stress, and strain level. In this study, the effect of confinement and stain is avoided. Thus, polymer coats formed on surfaces and enlarging contact area between spherical contacts govern the inter-particle behavior of β-1,3/1,6-glucan (Figure 3.8.a). The thickness t of cementation coat can be derived as [Fernandez and Santamarina 2001]:

$$t = R\left(\sqrt[3]{CC+1}-1\right) \tag{3.1}$$

where, R is radius of single particle and CC is weight ratio between cementation material (β-1,3/1,6-glucan in this study) and particles (CC=$W_{cement}/W_{particle}$). Weight ratio between glass beads and β-1,3/1,6-glucan solution was 60%. Polymer content of pure β-1,3/1,6-glucan solution was 0.0082 (Table 1). Thus, the CC value of β-1,3/1,6-glucan mixed glass beads becomes 0.00492. As R of glass bead is 1.5 mm, cementation coat thickness is approximately calculated to be t = 2.46 μm.

However, for non-spherical contact particles, β-1,3/1,6-glucan polymer extends as bridges between detached particles (Figure 3.8.b). In this case, adhesive strength and tensile strength governs the inter-particle behavior of β-1,3/1,6-glucan.

The tensile strength of β-1,3/1,6-glucan polymer show 48 MPa. Previous studies show the tensile strength of oat β-glucan having a typical range (20 – 80 MPa) which is affected by moisture content, attributed to their plasticizing phenomena [Park et al. 1993; Skendi et al. 2003].

The tensile strength of cemented soil can be simply defined as a function of cementation material ration, *CC* [Santamarina et al. 2001].

$$\sigma_t^{soil} = \frac{\pi}{4}\left[\sqrt[3]{\left(CC+1\right)^2} - 1\right]\sigma_t^{cement} \approx \frac{\pi}{6} CC \cdot \sigma_t^{cement} \tag{3.2}$$

As the tensile strength of β-1,3/1,6-glucan is 48 MPa, the tensile strength of β-1,3/1,6-glucan mixed particulate material approximately becomes as:

$$\sigma_t^{soil}\ [\mathrm{MPa}] = 8\pi \cdot CC \tag{3.3}$$

Therefore, when *CC* is 0.00492 (Figure 3.8.a and b), the tensile strength of β-1,3/1,6-glucan cemented soil is expected to be 0.123 MPa.

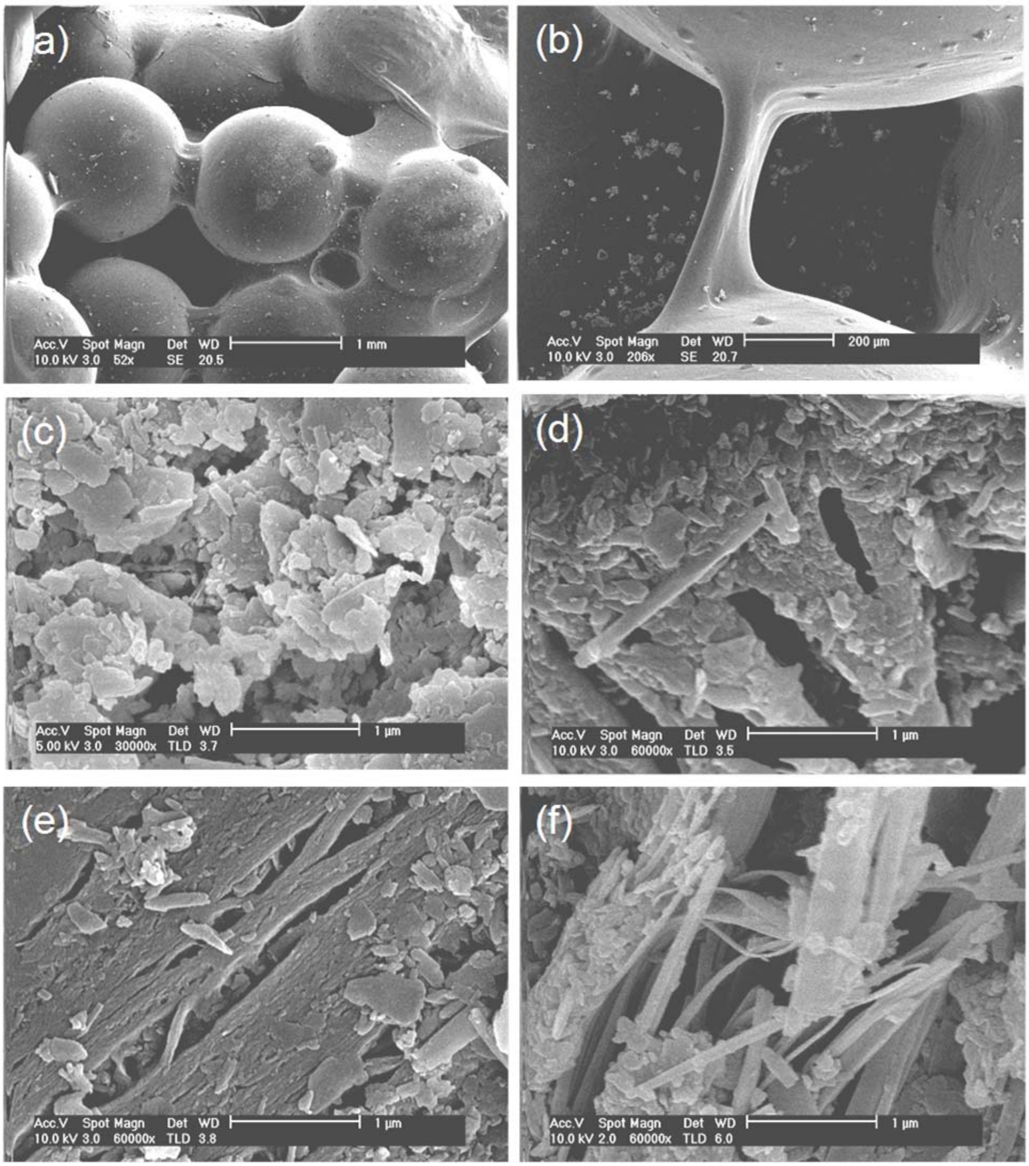


Figure 3.8 SEM imagaes. (a) and (b) Glass bead and β-1,3/1,6-glucan mixture. (c) Natural Hwangtoh (oven dried: 110°C). (d) β-1,3/1,6-glucan solution (8.2 g/L) treated Hwangtoh (20°C cured, after 28 days). (e) Polymer chains of 28 days cured by 20°C. (f) Polymer chains of 28 days cured by 100°C.

3.3.2. Tensile Strength of Beta-1,3/1,6-Glucan – Filter Paper Composites

Under an assumption that the β-1,3/1,6-glucan – filter paper interfacial bond is sufficient, such that β-1,3/1,6-glucan and filter paper are under isostrain situation, the total load is equal to the sum of the loads carried by the filter paper phase F_p and β-1,3/1,6-glucan phase F_b.

$$F_t = F_p + F_b \tag{3.4}$$

From the definition of stress, $F = \sigma A$, the cross-sectional areas (A_t, A_p, A_b) are substituted into Equation 3.4.

$$\sigma_t A_t = \sigma_p A_p + \sigma_b A_b \tag{3.5}$$

Thus, the tensile strength of β-1,3/1,6-glucan approximately becomes as:

$$\sigma_b = \frac{\sigma_t A_t - \sigma_p A_p}{A_b} = \frac{\sigma_t A_t - \sigma_p A_p}{A_t - A_p} \tag{3.6}$$

The properties and results of tensile strength are summarized in Table 3.5 As substituting data from Table 3.5 into Equation 3.6, the average tensile strength of β-1,3/1,6-glucan polymer is calculated as 36.27 MPa, which is lower than 48 MPa.

Table 3.5 Tensile strength properties and results of β-1,3/1,6-glucan – filter paper composites.

Material	Width [mm]	Thickness [mm]	Max. Load [kPa]	Tensile strength [MPa]	E_{50} [MPa]
Filter paper	10.0	0.20	0.015	7.5	493.7
β-1,3/1,6-glucan – filter paper composite	10.0	0.23	0.026	36.7	682.4
	10.0	0.22	0.022	35.0	642.5
	10.0	0.24	0.028	37.1	757.7

While σ = Eε, and according to the isostrain assumption ($\varepsilon_c = \varepsilon_p = \varepsilon_b$), Equation 3.5 can be reproduced (Equation 3.7) to deliver the average tensile stiffness, E_{50} = 2.11 GPa.

$$E_b = \frac{E_t A_t - E_p A_p}{A_b} = \frac{E_t A_t - E_p A_p}{A_t - A_p} \tag{3.7}$$

3.3.3. Consistency of Hwangtoh and Beta-1,3/1,6-Glucan Mixture

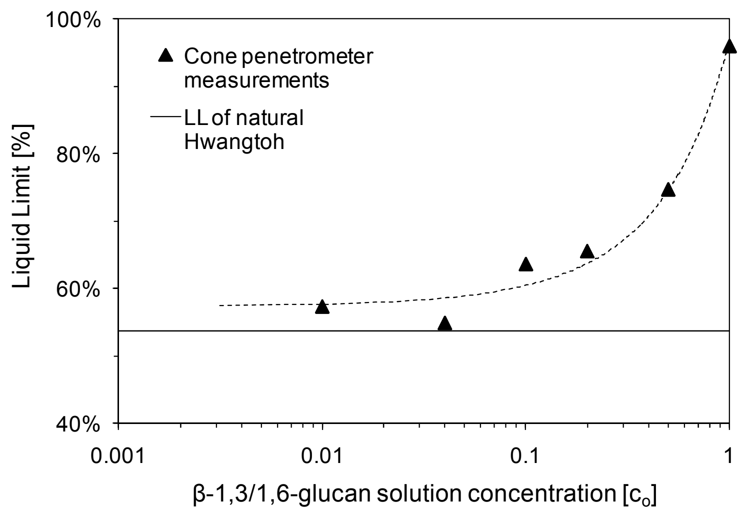
Fresh β-1,3/1,6-glucan – Hwangtoh mixture is a two-phase material (solid and liquid), which behavior strongly depends on the hydraulic characteristic. The liquid limit (*LL*) of soil strongly depends on the specific surface of soil particles [Farrar and Coleman 1967]. The hydrogen bonds, ion exchange, and van der Waals forces between organic materials and soil particles affect the double-layer characteristic of soil [Mitchell and Soga 2005]. Thus, the presence of β-1,3/1,6-glucan is available to increase the liquid limit of Hwangtoh.

The liquid limit of β-1,3/1,6-glucan – Hwangtoh mixture in regard to β-1,3/1,6-glucan concentration, is derived using the cone penetrometer method [British Standards 1990]. The liquid limit of natural Hwangtoh used in this study is 53.7%. Addition of β-1,3/1,6-glucan rises its value near to 100%. The result (Fig. 3.9) show that the liquid limit approximately increases as Equation

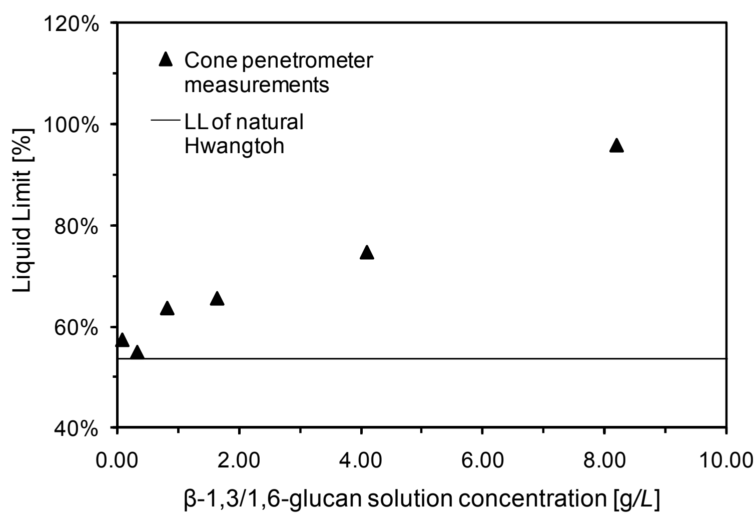
3.8. As the β-1,3/1,6-glucan content in mass of c_o=1.0 solution is 8.2 g/L, the direct correlation between the amount of β-1,3/1,6-glucan (m, in mass [g]) and liquid limit can be derived as Equation 3.9. The results are in line with previous studies [Coutinho and Lacerda 1987; Odell et al. 1960], which show both liquid limit and plasticity index increment with organic content increment.

$$LL\ [\%] = 57.37e^{0.52c_o} \tag{3.8}$$

$$LL\ [\%] = 57.37e^{4.28m} \tag{3.9}$$



(a) In the view of β-1,3/1,6-glucan solution concentration.



(b) In the view of absolute quantity of β-1,3/1,6-glucan.

Figure 3.9 Liquid limit behavior of β-1,3/1,6-glucan treated Hwangtoh.

3.3.4. Compressibility behavior of Hwangtoh treated by Beta-1,3/1,6-Glucan

Elastic Wave behavior

The elastic wave velocity variation results of each sample with time and load increment are shown in Figures 3.10, 11, and 12. The results show that both compressive wave and shear wave increases continuously with time, and converge to a stable value, which indicates the dissociation of the excess pore water pressure induced by loading. The lack of P-wave measurements after the 3rd load step of the c_o=0.1 specimen, was due to the operation failure of P-wave PZT sensor, during the testing.

Generally, the P-wave (V_p) velocity is higher than the S-wave (V_s) velocity under same physical conditions (specimen, amount of load). Thus, the P and S wave relationship derives the poisson's ratio (ν) for each specimen in average as: 0.34 (c_o=0), 0.31 (c_o=0.1), and 0.31 (c_o=0.5), following the equation [Santamarina et al. 2001]:

$$\nu = \frac{\frac{1}{2}\left(\frac{V_p}{V_s}\right)^2 - 1}{\left(\frac{V_p}{V_s}\right)^2 - 1} \tag{3.10}$$

The initial elastic wave velocities of β-13/1,6-glucan treated Hwangtoh mixtures are low, according to its loose particle packing. In the case of one-dimensional consolidation, when the load is applied to the specimen, the applied total stress is resisted by excess pore water pressure. The hydraulic pressure head difference causes the pore fluid to flow upward and downward through the drainage path, and thus the pore water pressure decrement transfers to the vertical effective stress increment.

The rate of pore water pressure dissipation depends on the permeability of soil, drainage path, viscosity of pore fluid, etc. In this study, specimens were remolded under uniform initial water content (60%). However, the contain of β-1,3/1,6-glucan increases the static viscosity of fluids due to its high molecular weight and long molecular chain [Burkus and Temelli 2005]. However, according to the data shown in Figs. 3.10, 11, and 12, do not show significant time delay results on elastic wave velocity convergence. Thus, it can be considered that the fluid viscosity difference amount different β-1,3/1,6-glucan concentrations, is not a major parameter affecting the effective stress-strain relationship of Hwangtoh.

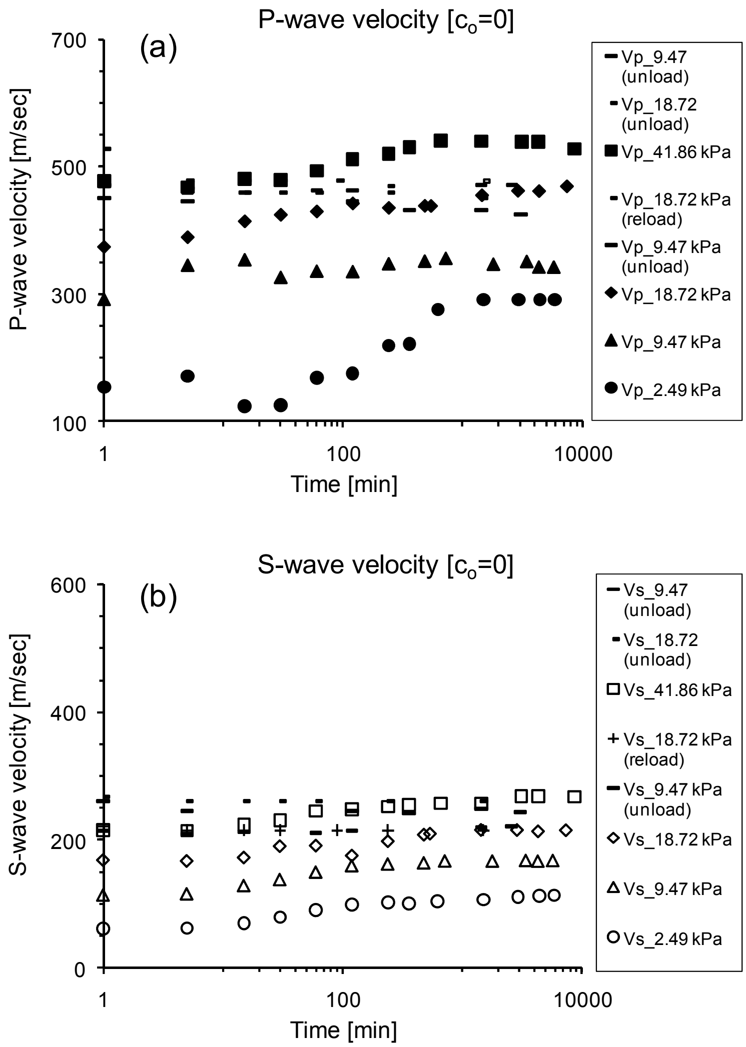


Figure 3.10 Elastic wave velocities with time and load step increment: (a) P-wave. (b) S-wave. (c_o=0, natural Hwangtoh).

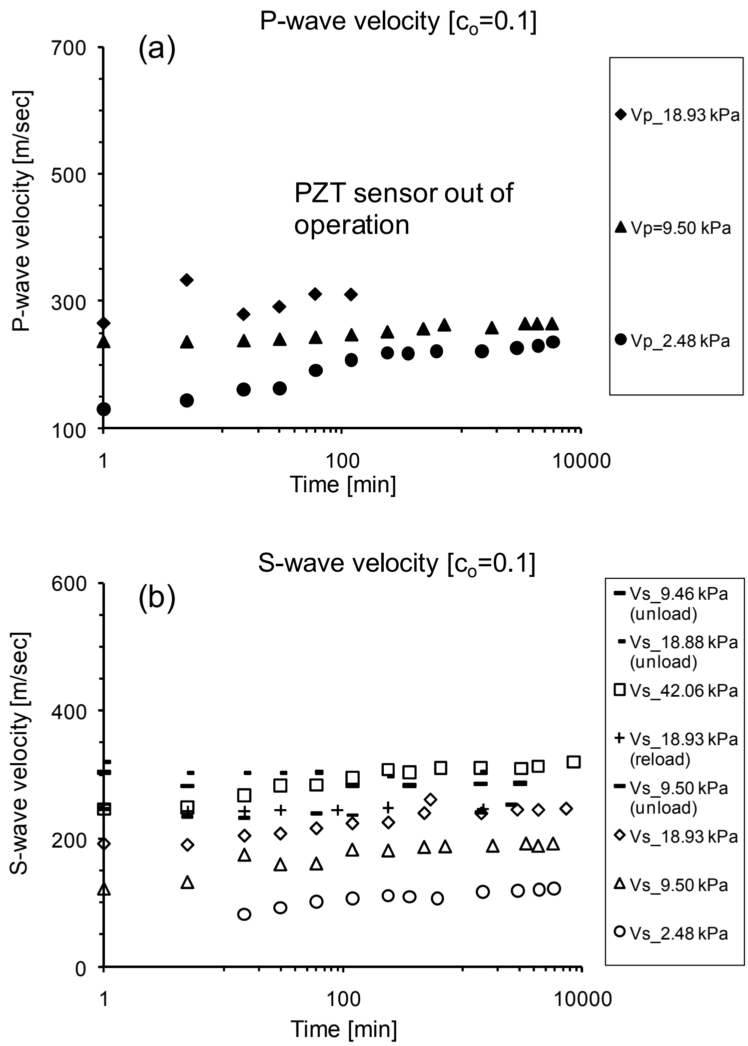


Figure 3.11 Elastic wave velocities with time and load step increment: (a) P-wave. (b) S-wave. (c_o=0.1).

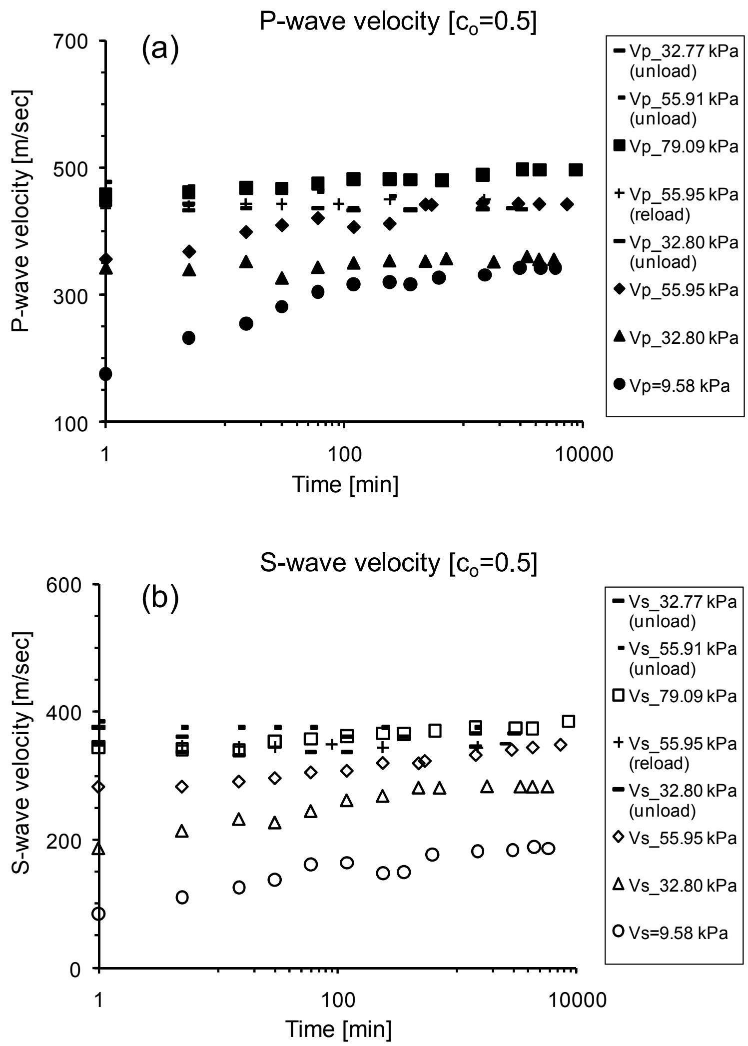


Figure 3.12 Elastic wave velocities with time and load step increment: (a) P-wave. (b) S-wave. (c_o=0.5).

The converged final elastic wave velocity and void ratio values (final measurements at each step) for each specimen and loading step are summarized in Table 3.6.

The shear wave velocity-vertical effective stress relationship can be expressed as [Santamarina et al. 2001]:

$$V_{s-v}\ [\text{m/sec}] = \alpha \left(\frac{\sigma'_v}{1\text{kPa}} \right)^{\beta} \tag{3.11}$$

Thus, the final S-wave velocity values of each specimen are displayed with the applied load, which can be assumed to be the final exact vertical effective stress acting on the soil matrix, without excess pore-water pressure [Chang and Cho 2010], in Figure 3.13. Curve fitting approximation using the least-square-solution is applicable to derive the vertical effective stress (σ'_v) - vertical shear wave velocity ($V_{s\text{-}v}$) relationship for each specimen.

$$V_{s-v}\ [\text{m/sec}] = 86.498 \left(\frac{\sigma'_v}{1\text{kPa}} \right)^{0.32} \qquad \text{for } c_o=0 \tag{3.12}$$

$$V_{s-v}\ [\text{m/sec}] = 93.61 \left(\frac{\sigma'_v}{1\text{kPa}} \right)^{0.34} \qquad \text{for } c_o=0.1 \tag{3.13}$$

$$V_{s-v}\ [\text{m/sec}] = 103.07 \left(\frac{\sigma'_v}{1\text{kPa}} \right)^{0.35} \qquad \text{for } c_o=-0.5 \tag{3.14}$$

Table 3.6 Experimental results of the compressibility and elastic wave variation of β-1,3/1,6-glucan treated Hwangtoh.

c_o	Experimental properties		Step of loading/unloading						
			1st	2nd	3rd	4th	5th	6th	7th
0	Final load [kPa]		0.50	2.49	9.47	18.72	9.47	18.72	41.86
	Elastic wave velocity [m/s]	V_p	123.2	287.0	337.3	463.1	464.3	470.5	519.8
		V_s	59.4	112.9	168.2	215.0	221.2	214.9	267.4
	Void ratio		1.46	1.32	1.15	1.06	1.07	1.06	0.94
0.1	Final load [kPa]		0.49	2.48	9.50	18.93	9.50	18.93	42.06
	Elastic wave velocity [m/s]	V_p	120.0	232.3	260.4	-	-	-	-
		V_s	62.6	120.5	192.0	242.3	249.1	255.0	330
	Void ratio		1.47	1.34	1.18	1.08	1.09	1.08	0.95
0.5	Final load [kPa]		1.00	9.58	32.80	55.95	32.80	55.95	79.09
	Elastic wave velocity [m/s]	V_p	195.4	399.8	420.3	525.4	518.1	534.4	629.0
		V_s	97.7	217.4	334.5	414.8	415.8	409.5	460.0
	Void ratio		1.41	1.16	1.01	0.92	0.93	0.92	0.87

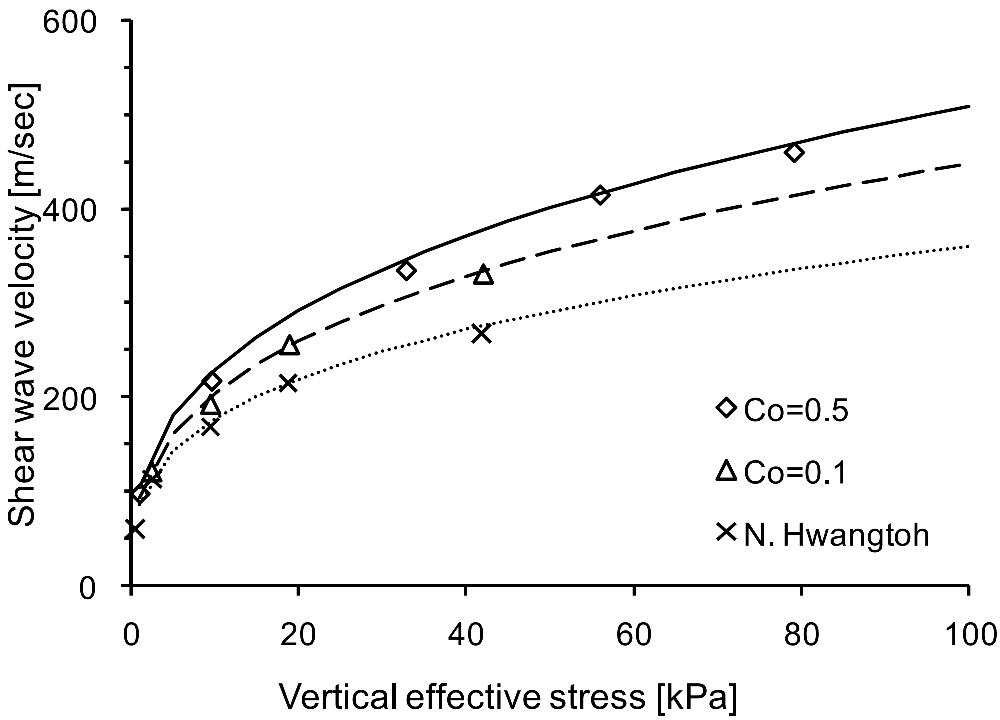


Figure 3.13 Vertical shear wave velocity variations, with the increase of applied vertical effective stress. The results show that the α factor increases as the concentration of β-1,3/1,6-glucan increases.

Figure 3.13 and Eqs. 3.12, 13, and 14 show α factor increase, with β-1,3/1,6-glucan concentration increase. Generally, α factor depends on soil porosity, coordination number, contact behavior, and fabric [Santamarina et al. 2001]. In this study, as all specimens were remolded, different porosity effect is offset by the vertical effective stress term. Thus, it can be concluded that the increase of β-1,3/1,6-glucan in Hwangtoh, increases the fabric and contact behavior, as well as the shear modulus. This finding is in line with previous studies which reported that the increase of organic matter in soil increases the internal particle friction and cohesion, which causes higher shear resistance [Hartge and Stewart 1995; Zhang 1994].

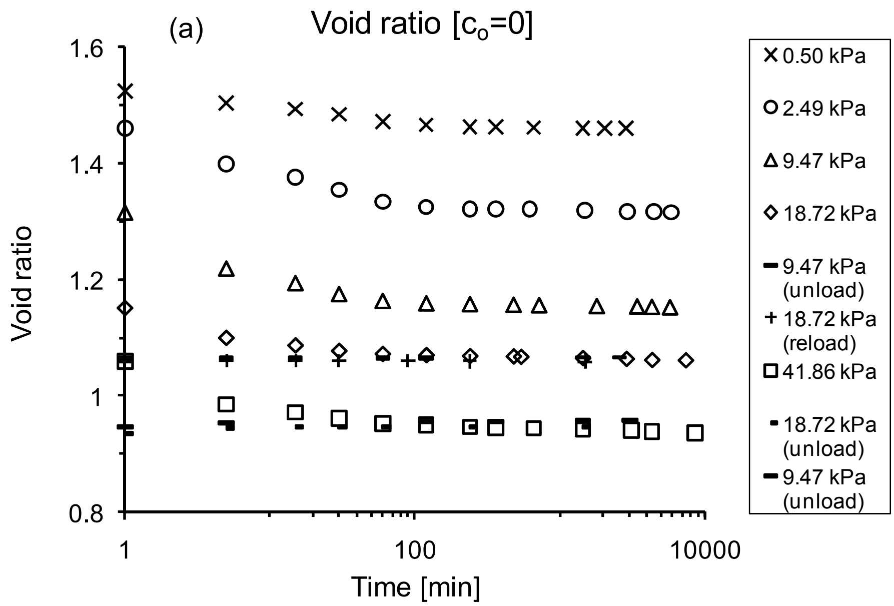
The result of elastic wave velocity increase with the amount of biopolymer increase verifies the improved stability of biopolymer treated residual soil, under the existence of water. Therefore, it can be concluded that biopolymer treatment in-field is suitable for quick soil stabilization demands, such as landslides, deep excavations, and slurry walls.

Compressibility

The void ratio variation results of each sample with time and load increment are shown in Figure 3.14. All specimens show similar initial void ratio value (1.46 ~ 1.52). For each single load, the void ratio decreases significantly during the initial 100 ~ 200 minutes, and converges to a certain value, while elastic wave velocity values increase continuously, even more than 1000 minutes. This indicates the existence of excess pore water pressure even though the apparent strain deformation appears to be completed.

The final void ratios and applied vertical effective stress values of load step and specimen is summarized in Figure 3.15. The organic matter effect on soil compressibility is not certainly defined in literatures. Several studies show that the compression index (C) decreases with the increase of organic matter in soil [Angers 1990; Etana 1995], while there exists an opposite view that the organic matter does not have significant effect on the compressibility [O'Sullivan 1992; Smith et al. 1997; Zhang 1994].

From the results of this study, the compressibility of Hwangtoh seems to have low correlation with organic matters, especially organic carbon, coexisting inside, showing a unique compressibility index (C_c = 0.27), regardless of the amount of β-1,3/1,6-glucan.



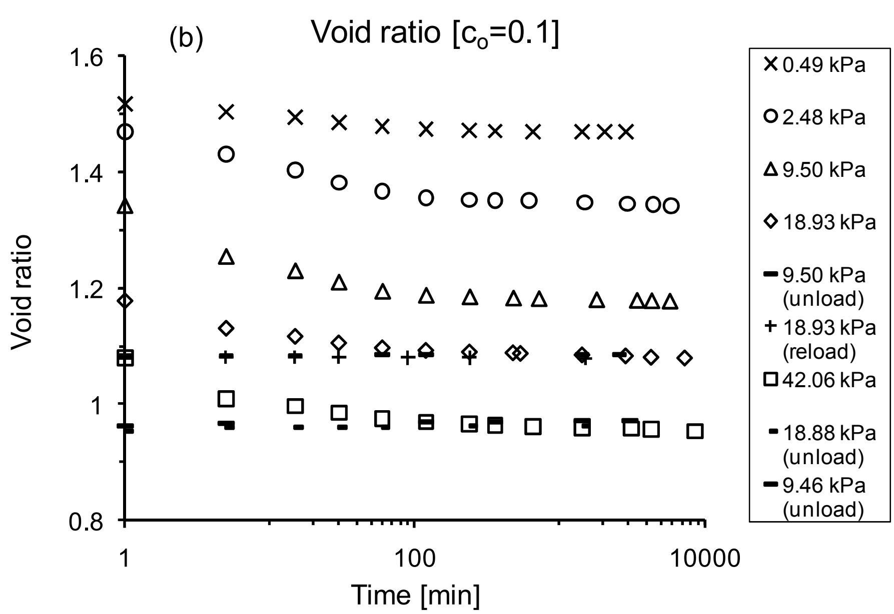


Figure 3.14 Void ratio variations with time and load step increment. (a) Natural Hwangtoh. (b) c_o=0.1. (c) c_o=0.5.

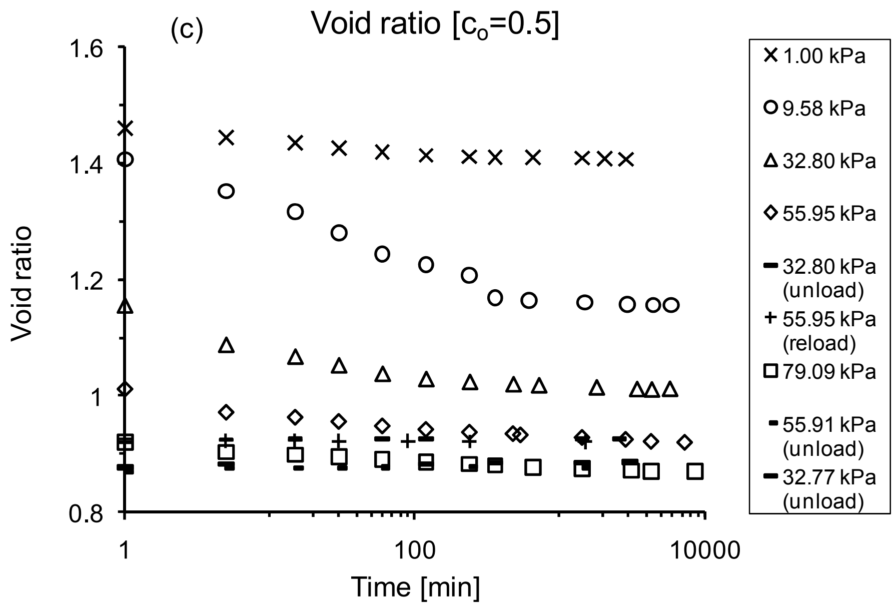


Figure 3.14 *Continued*.

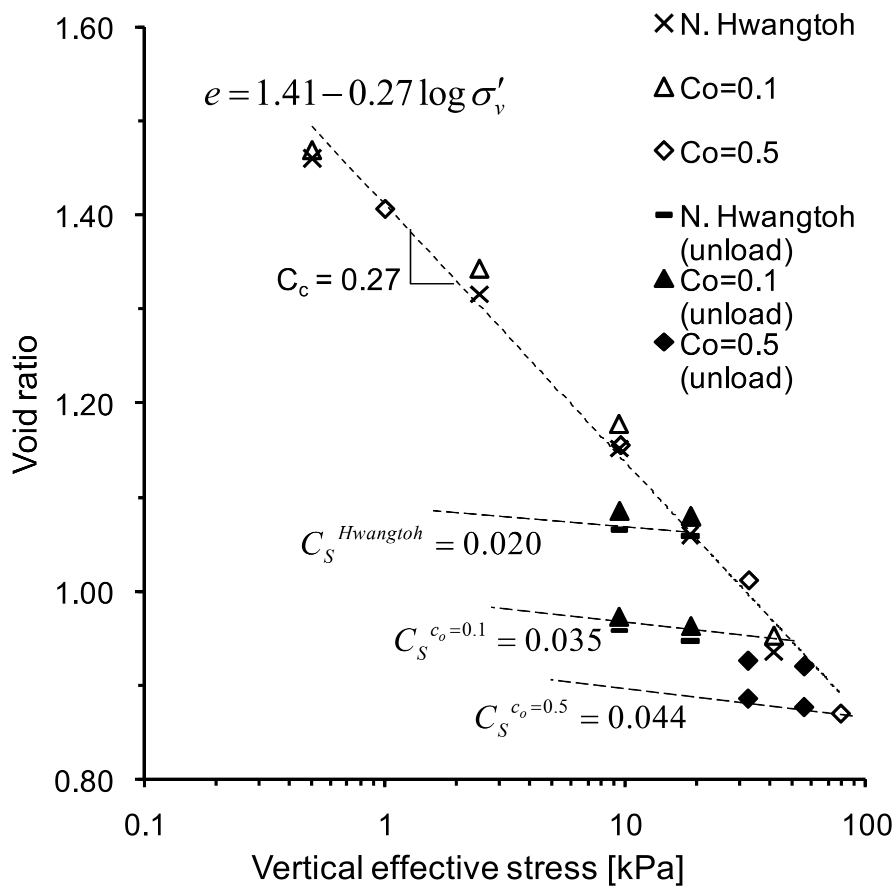


Figure 3.15 e – log σ relationship of β-1,3/1,6-glucan affected Hwangtoh. The results indicate the independency between compressibility and presence of β-1,3/1,6-glucan.

Generally, soil organic matters are reported to decrease the wettability (or swelling) of soil induced by the hydrophobic properties of soil organic matters [Chenu et al. 2000; Sullivan 1990]. However, the Figure 3.15 show higher swelling index (C_s) with higher β-1,3/1,6-glucan content. This seems to be an effect of the hydrophilic property of β-1,3/1,6-glucan [Lee et al. 2003].

In Figure 3.16, the shear wave velocity and void ratio values are plotted together. The unique consolidation tendency (e-log σ) relationship shown in Fig. 3.15, expects a single void ratio-shear wave velocity relationship, because shear wave velocity is a function of effective stress (Eq. 3.11). However, the results in Figure 3.16 show that shear wave velocity increases as β-1,3/1,6-glucan content increases, and this phenomenon maximizes at high density conditions.

For a certain void ratio value (e.g. 1.00), the effective stress value acting on β-1,3/1,6-glucan treated (c_o=0.1 and 0.5) and non-treated (natural Hwangtoh) soils is expected to become 33 kPa (unique e – log σ relationship). However, the shear wave velocity values are shown as: 255 (natural Hwangtoh), 307 (c_o=0.1), and 347 m/sec (c_o=0.5). This result is in line, with Eqs. 3.12, 13, and 14 (α factor increases as β-1,3/1,6-glucan content increases).

Thus, it is concluded that the existence of β-1,3/1,6-glucan improves the shear modulus (G, related to V_s; $G=\rho V_s^2$) of Hwangtoh.

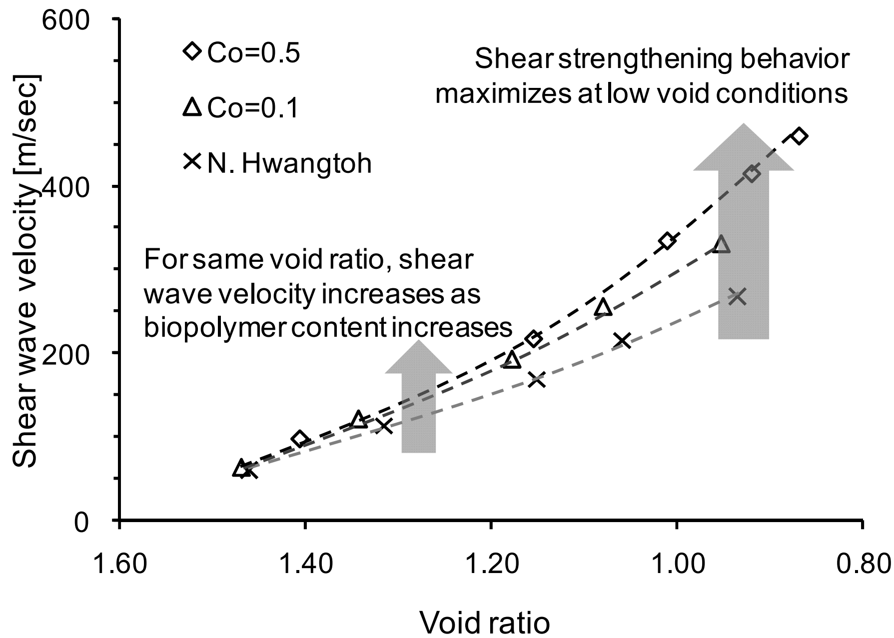


Figure 3.16 Void ratio and shear wave velocity relationship of β-1,3/1,6-glucan treated Hwangtoh.

For further verification, the compressive wave velocity data are presented with void ratios in Figure 3.17. The result does not show any significant relationship between the compressive wave velocity and β-1,3/1,6-glucan content.

In overall, the compressive and shear wave results show the increase of β-1,3/1,6-glucan fibers affects the shear resistance increment (G, related to shear wave velocity increase), while it has minor or even no effect on the axial deformation constraint (M, related to compressive wave velocity; $M=\rho V_p^2$).

The low compressive strength (10 kPa in average), and stiffness (20 kPa in average) of β-glucan polymer [Lazaridou et al. 2003] are extremely smaller than its tensile strength properties (48 MPa in average strength and 2.11 GPa in average stiffness) measured in this study (section 3.3.1). Thus, it can be concluded that β-1,3/1,6-glucan polymer plays a significant role in strengthening soil as a tension member, increasing the shear resistance between particles.

Figure 3.18 shows a schematic image of the axial and shear strain behavior of β-1,3/1,6-glucan treated Hwangtoh. Under axial deformation, the particle-void fluid characteristic governs the response of soil, while β-1,3/1,6-glucan fibers have no important role.

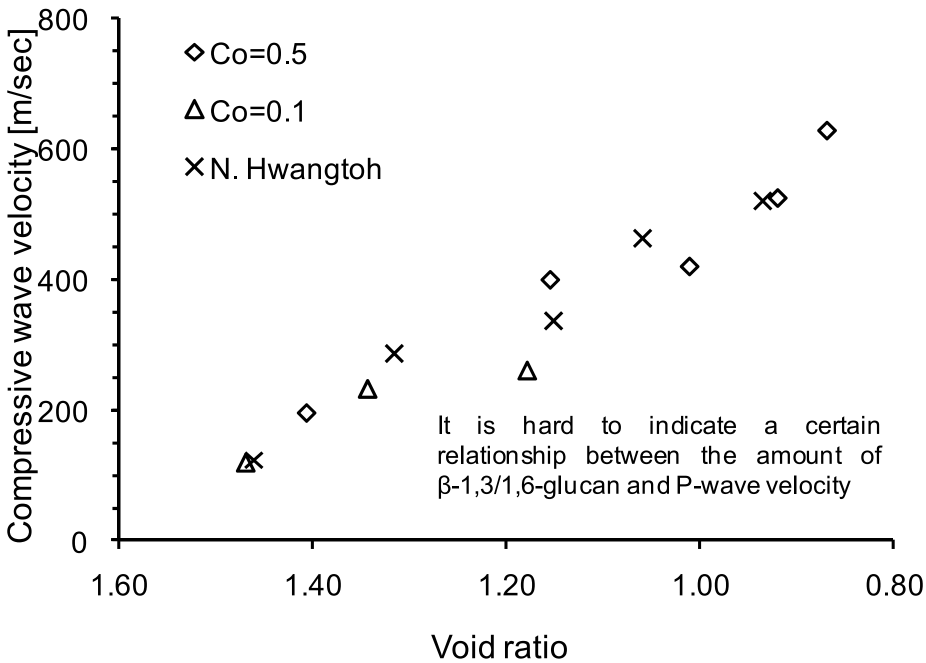


Figure 3.17 Void ratio and compressive wave velocity relationship of β-1,3/1,6-glucan treated Hwangtoh.

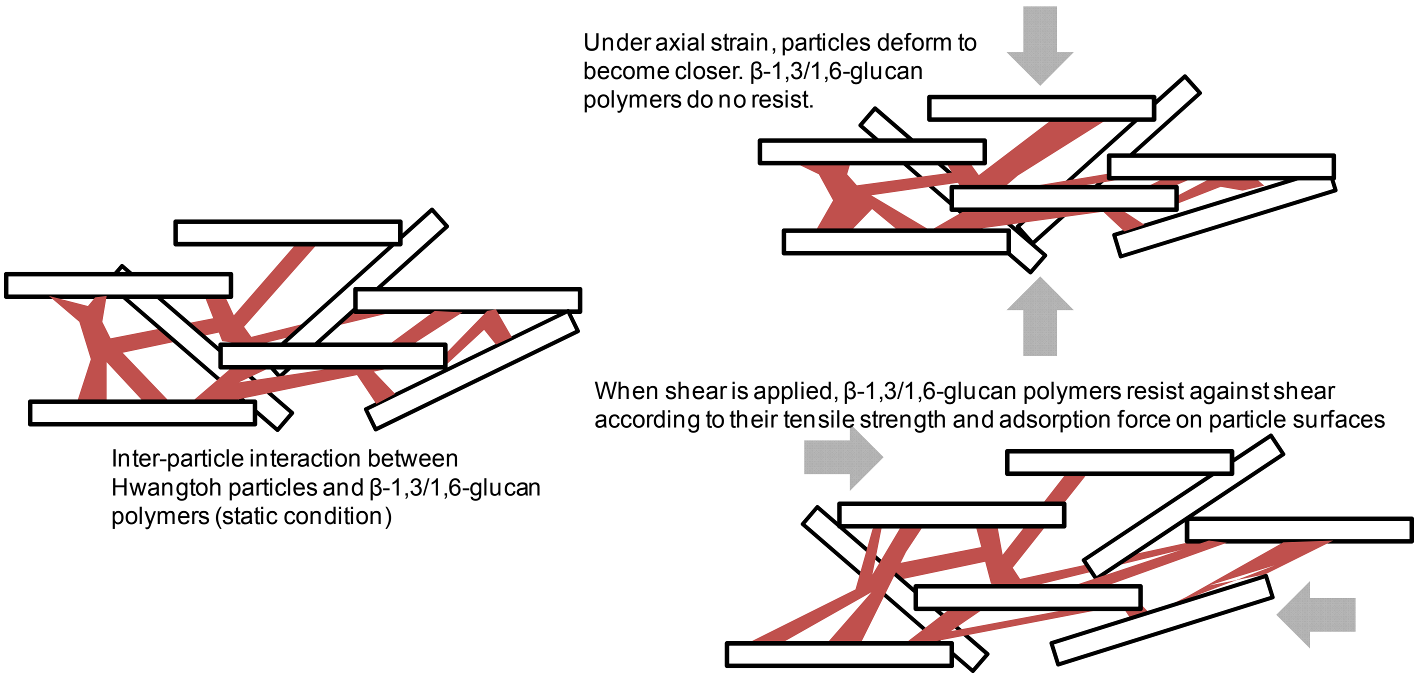


Figure 3.18 Schematic diagram of the inter-particle behavior between β-1,3/1,6-glucan and Hwangtoh particles, under axial and shear strain.

Meanwhile, in the case of shear strain, particle surface adsorbed and binding β-1,3/1,6-polymer fibers resist against the shear according to their high tensile strength and stiffness. Therefore, the major strengthening function of β-1,3/1,6-glucan polymer is explored to be result of: (1) high adsorptivity, (2) high tensile strength and stiffness.

3.3.5. Strength behavior of Hwangtoh treated by Beta-1,3/1,6-Glucan

Strength behavior of Hwangtoh treated by Beta-1,3/1,6-Glucan. The strength increment effected by β-1,3/1,6-glucan described in Equation 3.3 is derived from ideal (spherical particle) condition. Actually, Hwangtoh particles are plate-type because the main consisting minerals are halloysite and kaolinite. Adsorption of polymers on clay particle surfaces, which is an entropy driven process, increases as the size and molecular weight of polymers increase [Parfitt and Greenland 1970]. The surface conformation of polymer can be classified in three modes: directly attached "trains", three-dimensional "loops", and two free-suspended "tails" [Theng 1982]. The fraction of train segments (p; 0.3~05 for uncharged polymers) governs the interaction between polymers and soil particles. β-1,3/1,6-glucan is positively charged polymers which adsorption leads more contacts with particle surface ($p > 0.7$) [Hesselink 1977]. Thus, the electrical interaction between polymer – particle surfaces governs the inter-particle behavior of β-1,3/1,6-glucan with Hwangtoh.

Figure 3.8(c) shows the SEM image of natural Hwangtoh and β-1,3/1,6-glucan solution (8.2 g/L) treated Hwangtoh (20°C cured, 28 days; Figure 3.8.d). In Figure 3.8(d), platy Hwangtoh particles are attached on β-1,3/1,6-glucan polymer bundles, not vice versa. The molecular weight (M_w) of β-glucan is reported to be 20 ~ 3000 × 10^3 [Cui 2001]. As the length of single glucose molecule (M_w = 180) is approximately 1 nm, the length of β-glucan polymers are derived as 0.1 ~ 16.7 μm. Then, the size of a single β-glucan polymer becomes similar or even larger than a single Hwangtoh particle (d < 1 μm). Thus, the adsorption phenomeneon of β-1,3/1,6-glucan on Hwangtoh alters with the inter-particle behavior of β-1,3/1,6-glucan with granular soil (Figure 3.8.a and b).

The accurate strengthening and cementing behavior of Hwangtoh influenced by β-1,3/1,6-glucan treatment was investigated by experimental approaches. The curing time and temperature dependent compressive strength responses of β-1,3/1,6-glucan – Hwangtoh mixture are summarized in Figure 3.19. Each trend in Figure 3.19 represents the compressive strength and stiffness variation under different curing temperature condition (20°C, 60°C and 100°C) during 28 days. Generally, the compressive strength of β-1,3/1,6-glucan treated Hwangtoh increases continuously with curing time and increment of the amount of β-1,3/1,6-glucan.

The organic matter effect on soil strength and stiffness strongly depends on whether the organic matter is decomposed or consists of fibers. In the former, soil properties such as strength, stiffness or modulus are expected to be reduced due to the high water content and consistency induced by the organic matter. In the latter, the fibers act as reinforcements, which increases the strength of soil [Mitchell and Soga 2005]. The results of this study show that the main function of β-1,3/1,6-glucan polymers are reinforcement fibers in soil.

The compressive strength of 20°C and 60°C cured samples increases conspicuously after the 1.0 g/L point of β-1,3/1,6-glucan solution concentration. 60°C cured samples show better improvement results. However, 100°C cured samples show lower strengthening, moreover, strength degradation with time. Thus, it can be concluded that 100°C temperature decreases and disturbs the strengthening function of β-1,3/1,6-glucan polymers, while 60°C temperature optimizes strength revelation.

Meanwhile, Young's modulus increment, which represents the reinforcement of soil elasticity induced by β-1,3/1,6-glucan polymers, continuously increases with time under 20°C curing. However, the stiffness of 60°C and 100°C specimens increases initially, while show diminutions after 14 days. In this case, 100°C specimens show higher degradability compared to 60°C cured specimens.

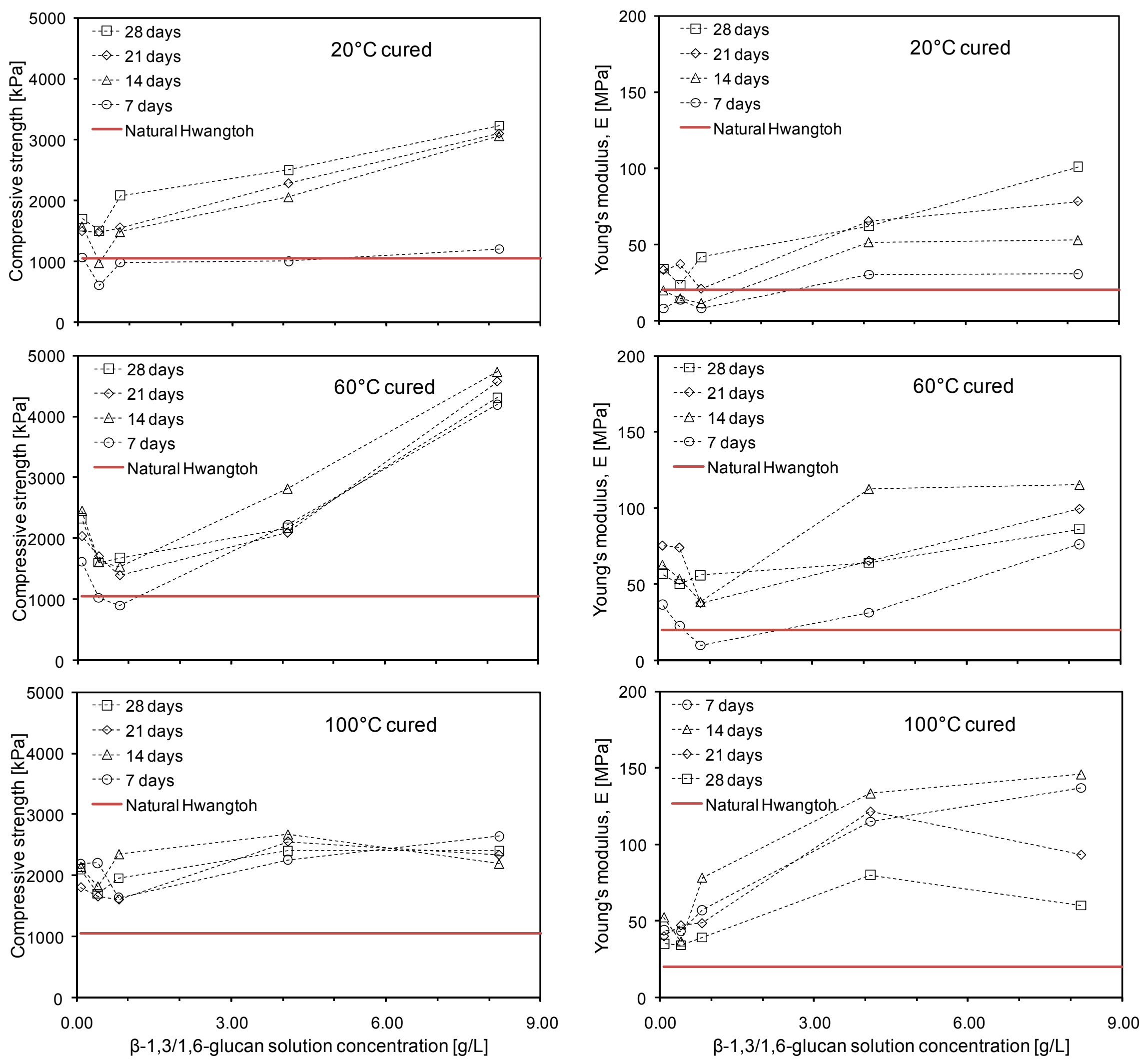


Figure 3.19 Compressive strength and stiffness (Young's modulus, *E*) variation of β-1,3/1,6-glucan – Hwangtoh mixtures according to curing temperature and time.

The behavior is clearly observed in the SEM images of 20°C (Figure 3.8.e) and 100°C cured samples (Figure 3.8.f). In Figure 3.8(e), β-1,3/1,6-glucan polymer chains remain consistently, while Figure 3.8(f) show bended, collapsed and even melted fibrils. Curdlan (β-1,3-glucan) forms gel by endothermic reaction at 60°C which occurs swelling [Konno and Harada 1991]. Meanwhile, β-1,3-glucan fibers heated by 120°C show loose structure and separated fibrils [Harada et al. 1994]. Therefore, the better performance of 60°C cured samples is expected to be an effect of thermosetting induced by the heat adsorption during β-1,3/1,6-glucan gel formation at is optimum temperature. Moreover, it can be concluded that the thermal degradation of β-1,3/1,6-glucan is promoted above 100˚C temperature. Thermal degradation (pyrolysis) is reported to produce levoglucosan in a sequence: polysaccharides → oligosaccharides → disaccharides → monosaccharide [Patwardhan et al. 2009].

Soil strength is strongly influenced by water content and bulk density, which are soil structure indicators [Byrd and Cassel 1980]. Dry density of soil (ρ_d) is a soil parameter which represents both water content (w) and total density (ρ_t) of soil, because it is defined as, $\rho_d = \rho_t$ / (1+w). Figure 3.20 shows the dry density – compressive strength relationship of β-1,3/1,6-glucan, compared with cement treated engineered silty-clay (cement/soil ratio in mass = 10%) [Walker 1995]. The results show: (1) β-1,3/1,6-glucan treated

Hwangtoh shows higher dry density, rather than natural Hwangtoh; (2) For a certain dry density condition, compressive strength varies with different β-1,3/1,6-glucan concentration. Generally, c_o=1.0 specimens show highest value, otherwise c_o= 0.05 or 0.1 show the lowest end; (3) Improvement efficiency of β-1,3/1,6-glucan treated Hwangtoh is more effective than cement mixing [Walker 1995] in low dry density range (1.0 ~ 1.5 Mg/m^3), and the overall reliability increases as temperature increases.

In details, Figure 3.21 represents the strengthening efficiency of β-1,3/1,6-glucan treated and cement mixed (10%) in practical condition (room curing). The compressive strength, as well as dry density of non-treated natural Hwangtoh increase as a result of drying shrinkage. The lower broken line in Figure 3.21 represents the dry density–compressive strength relationship of cement mixed (10%) soil, strengthened by CSH or CAH gels formed inside soil, referred to Walker (1995) and results of this study. The dry density and compressive strength data should appear between the two boundaries.. In a dry density range 1.25 ~ 1.35 Mg/m^3, β-1,3/1,6-glucan treated c_o = 0.1, 0.05, and 0.01 specimens show similar or lower performance compared to cement. However, shaded zone which points c_o = 1.0 and 0.5 measurements, guarantees better strengthening behavior of Hwangtoh containing 0.25 to 0.49% (ratio to the soil mass) of β-1,3/1,6-glucan.

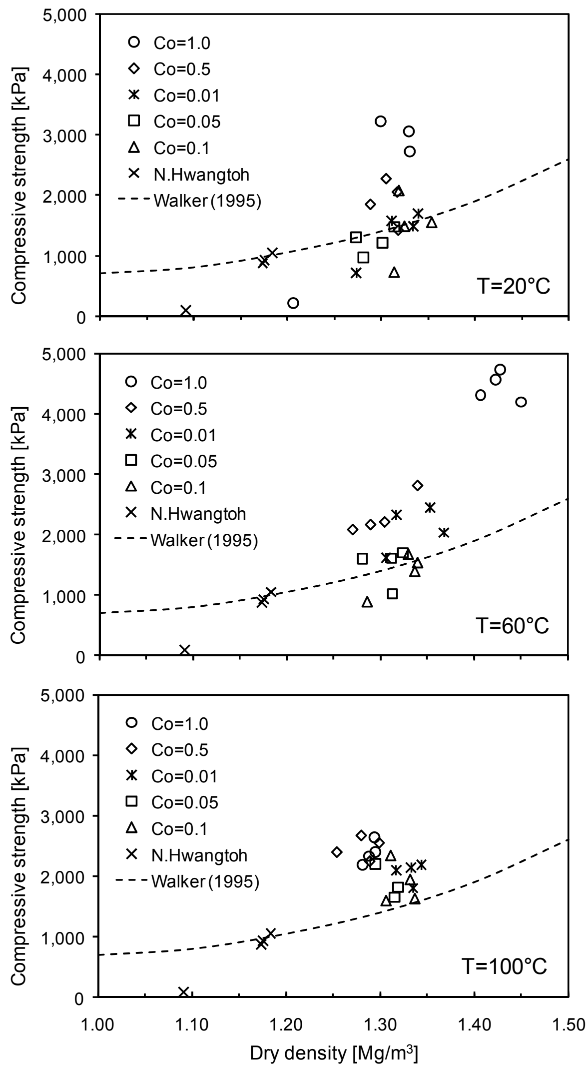


Figure 3.20 Compressive strength against dry density.

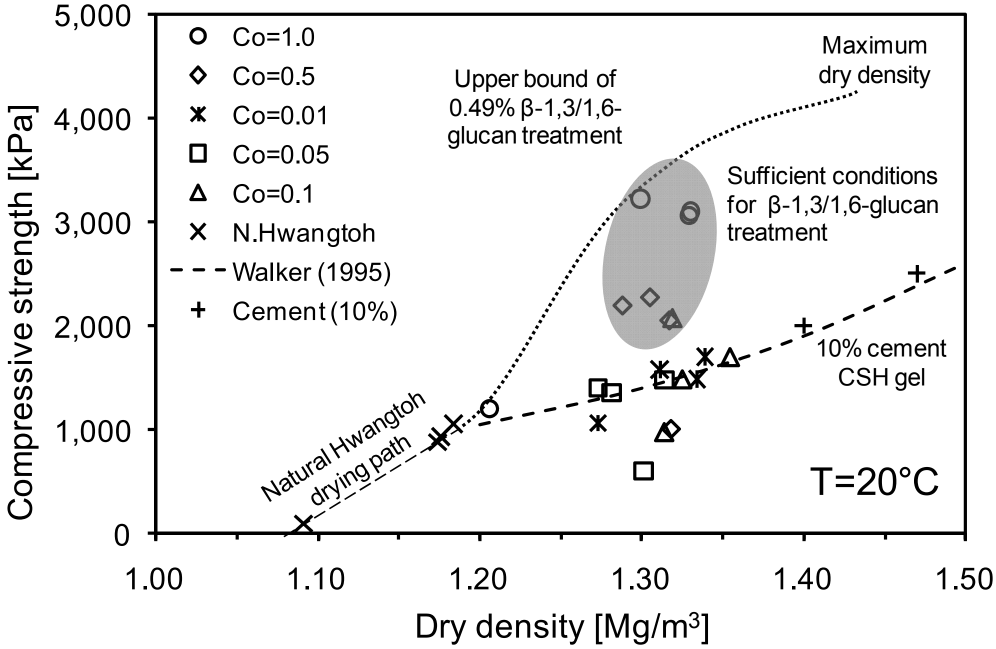


Figure 3.21 Strengthening results using β-1,3/1,6-glucan, compared to 10% cement mixed Hwangtoh.

3.3.6. Beta-1,3/1,6-Glucan Effect on Soil Density.

The initial density is an important parameter controlling the strength of soil. Especially, the dry density (density of solid particles), which represents particle arrangement, strengthens soil as its value increases. The compaction test results are summarized in Figure 3.22. The optimum water content increases slightly from 25% (natural Hwangtoh) to 28.5% (compacted by 8.2g/L β-1,3/1,6-glucan solution). The increment of optimum water content is expected to be a result of the hydrophilic property of strongly absorbed β-1,3/1,6-glucan polymers on particle surfaces [Lee et al. 2003]. Meanwhile, the compacted maximum dry density also increases with increased β-1,3/1,6-glucan content. While, previous studies [Coutinho and Lacerda 1987; Franklin et al. 1973] show significant decrease of the compacted density with organic content increase.

The considered range of organic content in previous studies were 10 ~ 80 % (organic content/soil solid ratio in mass), whereas, the maximum β-1,3/1,6-glucan content in this study is 0.49 %. In detail, the trend of maximum dry density in Figure 3.22 show a turning point at 0.82 g/L (tendency changes into decreasing trend), while the optimal water content shows at 27.5 g/L. Thus, in a wide range of β-1,3/1,6-glucan content, it can be concluded that the maximum dry density initially increases with β-1,3/1,6-glucan content (< 0.82 g/L), and decreases with macro amount of β-1,3/1,6-glucan (> 0.82 g/L).

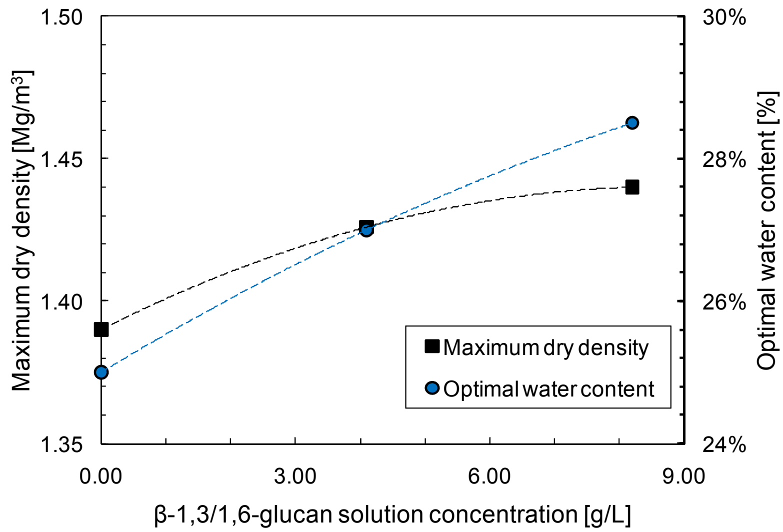


Figure 3.22 Compaction test results of β-1,3/1,6-glucan treated Hwangtoh.

3.3.7. Strength function of Beta-1,3/1,6-Glucan: Microscale Explanation

From the aforementioned studies and results, specific explorations on the geotechnical and engineering behavior variation of β-1,3/1,6-glucan treated Hwangtoh can be summarized as:

With the increase of β-1,3/1,6-glucan content, Hwangtoh shows,

- Continuous (geometric) increase of the liquid limit (*LL*).
- Shear wave velocity (shear modulus) increment.
- Initially poor strengthening behavior.
- Strengthening effect increment after a certain break point (0.06% [g] to soil mass).
- Compactibility (maximum dry density and optimal water content) increase.
- Final dry density (after curing) decrease.

Each finding demonstrates the interaction characteristic between β-1,3/1,6-glucan polymers and Hwangtoh particles as:

- Strong water adsorptibility of hydrophilic β-1,3/1,6-glucan polymers [Lee et al. 2003].
- Soil cohesion improvement induced by particle surface attached β-1,3/1,6-glucan polymers.
- Initial particle adsorption stage and strengthening dominated stage after the break point (0.06% [g] to soil mass).

- Adsorbed water expends the double layer thickness of Hwangtoh particles, increasing its compactibility.

Thus, the strengthening mechanism induced by β-1,3/1,6-glucan polymers can be defined as follow:

(1) Adsorption: Hydrogen bonding ability of β-1,3/1,6-glucan polymers attach on Hwangtoh particles or vice versa (Fig. 3.23.a), increasing the zeta-potential (double layer) of particle surfaces [Gam et al. 2003].

(2) Full attachment: The adsorption process is dominated until all Hwangtoh particles are considered to be primarily attached with β-1,3/1,6-glucan polymers.

(3) Strengthening: Regular strengthening is promoted by surplus polymers after full attachment. They increase contacts between soil particles and form bundles (Fig. 3.23.b) increasing the tensile strength between particles.

The adsorption and strengthening process is described minutely by a schematic diagram in Figure 3.24.

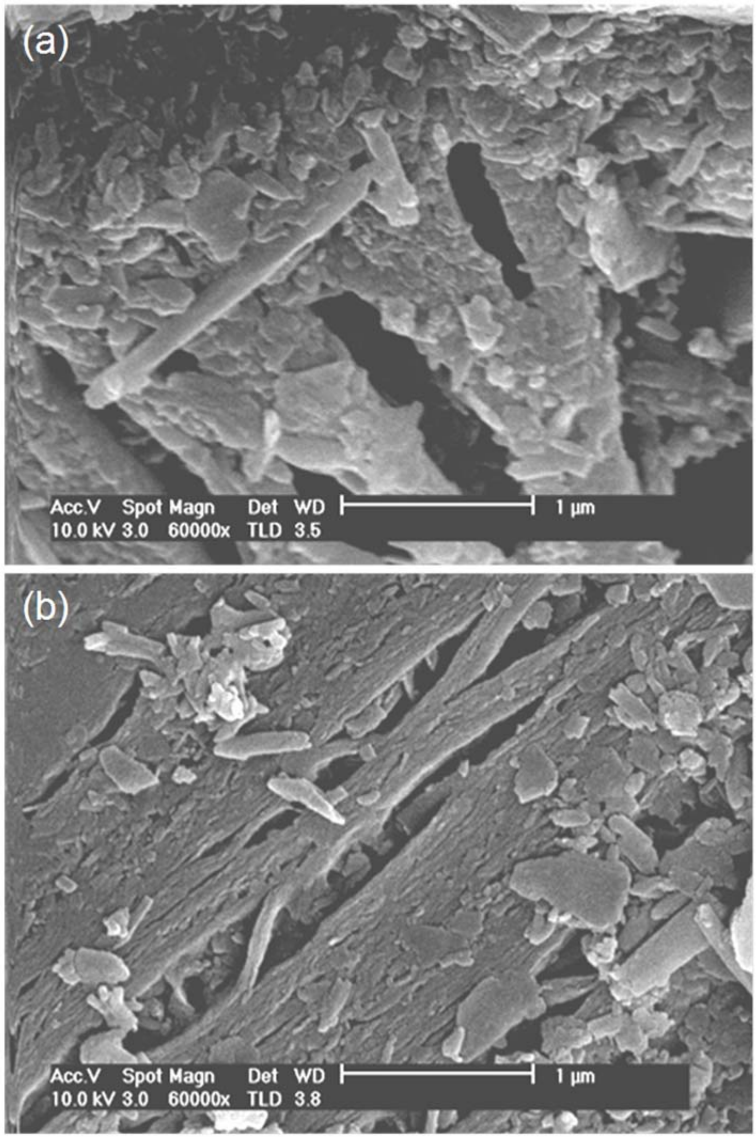


Figure 3.23 SEM images of the strengthening mechanism of β-1,3/1,6-glucan. (a) Adsorption state (0.005% [g] to soil mass). (b) Strengthening state (0.5% [g] to soil mass).

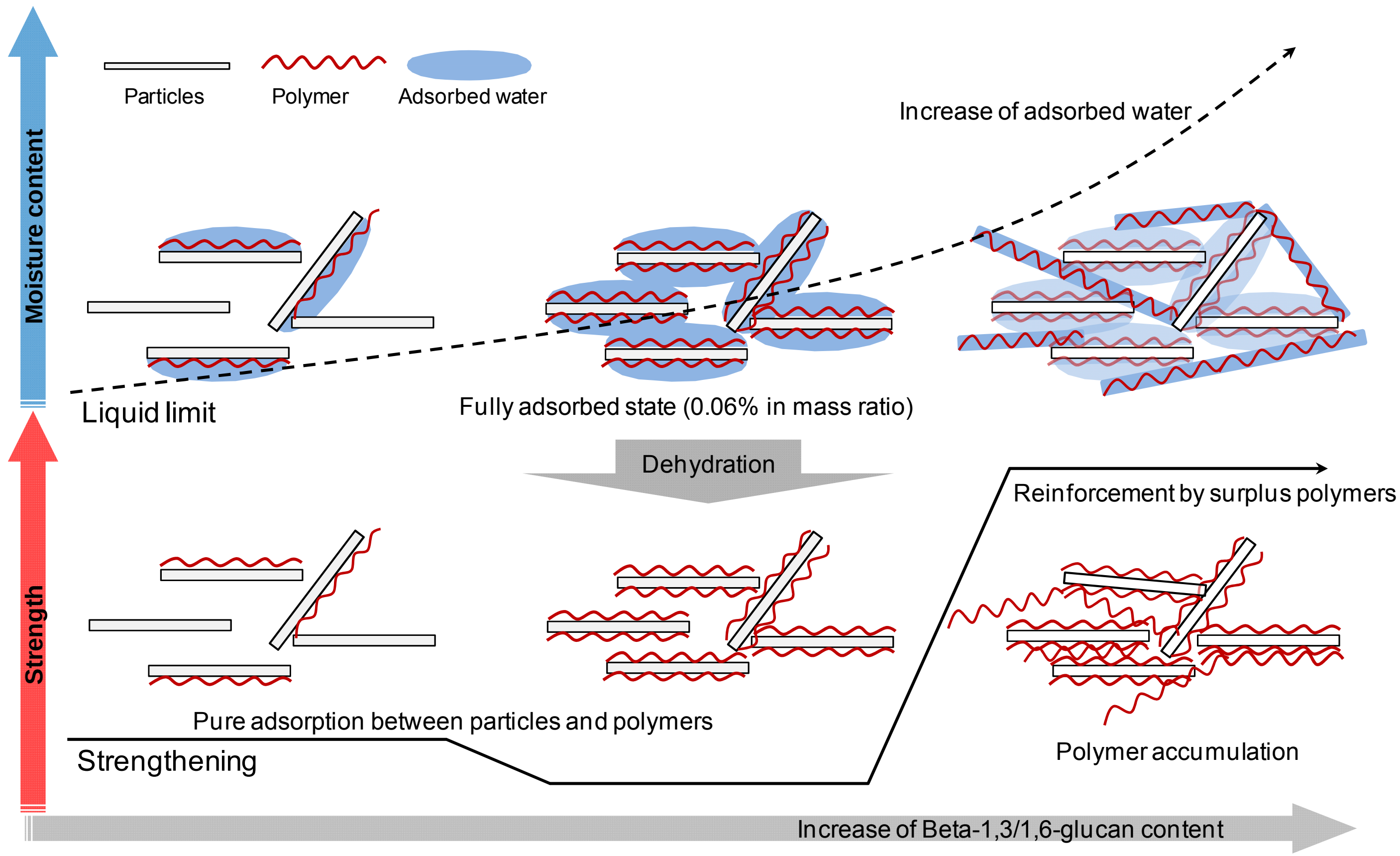


Figure 3.24 Adsorption and strengthening phenomena induced by β-1,3/1,6-glucan polymers.

3.3.8. Economic Efficiency of Engineered Hwangtoh using Beta-1,3/1,6-Glucan

Compared to cement, the compressive strength results of β-1,3/1,6-glucan treated Hwangtoh show higher performance in low dry density range (Figure 3.21). In a view of engineered soil, the economic efficiency analysis between 10% cement mixed Hwangtoh and 0.49% β-1,3/1,6-glucan treated Hwangtoh is presented in Table 3.7.

Generally, biopolymers are quite expansive than cement. For a same quantity (unit weight), β-1,3/1,6-glucan (320 $/kg; Sigma-Aldrich) is 533 times more expensive than ordinary Portland cement (60 $/ton; Lafarge Halla Cement). For a same amount of soil treatment (1 ton), 0.1 ton of cement is required, while 4.92 kg of β-1,3/1,6-glucan should be applied. Thus, the material price difference decreases to half (533 times to 262 times), however, biopolymer treatment is still insufficient to replace the role of ordinary cement.

Meanwhile, expanding the considerations on environment-friendly and carbon emission trade derives interesting results. According to literatures, 1 kg of cement production emits 1,291.8 kg of CO_2 related to fuel burning and chemical calcinations[Alcorn and Wood 1998; Kreijger 1979], while 1 kg of β-1,3/1,6-glucan only emits 13.56 kg of CO_2 [Conti and Sweetnam 2008; Seo et al. 2002]. Thus, total indirect environmental impact (CO_2 emission in kg) induced by 1 ton soil treatment becomes 129,180 (cement) and 66.72 (β-1,3/1,6-glucan).

To fulfill the United Nations Framework Convention on Climate Change (UNFCCC) and Kyoto Protocol (1997), EU nations impose carbon tax on high carbon emitting industries. The recent CO_2 emission trade is 22 \$/ton CO_2 (in 2008) [Grubb and Neuhoff 2006; Vetris 2010]. Then, the total economical price (direct material cost + indirect CO_2 emission expense) for 1 ton of soil improvement become as 2,848 \$ for 10% cement mixing and 1,576 \$ for 0.49% β-1,3/1,6-glucan treatment. Therefore, in an overall view, biopolymer treatment has advantages in engineering performance, environmental impact, and finance.

Table 3.7 Economic and environmental analysis of OPC and β-1,3/1,6-glucan treated Hwangtoh.

Material	Ordinary Portland Cement	Beta-1,3/1,6-glucan	Note
Market price	60 USD/ton	320 USD/kg	
Required amount for 1 ton soil treatment[1]	0.1 ton (c/s = 10%)	4.92 kg (w/w= 0.49%)	
Material price for 1 ton soil treatment	6 USD	1574 USD	β-1,3/1,6-glucan 262 times expensive
CO_2 emission per 1 kg material production[2,3]	1291.8 kg CO_2/kg	13.56 kg CO_2/kg	Chemical reaction, electricity, fuel burn.
Total CO_2 emission for 1 ton soil treatment[4]	129,180 kg CO_2	66.72 kg CO_2	OPC emits CO_2 194 times more
Total CO_2 emission cost	2,842 USD	1.5 USD	β-1,3/1,6-glucan 1,900 times inexpensive

※ Refer to. 1: [Walker 1995], 2: [Alcorn and Wood 1998; Kreijger 1979], 3: [Conti and Sweetnam 2008; Seo et al. 2002], 4: [Grubb and Neuhoff 2006]

3.4 SUMMARY AND CONCLUSIONS

3.4.1. Summary

The full research flow of this study is summarized in Figure 3.22. The main purpose of this study is to verify whether β-1,3/1,6-glucan-treated Hwangtoh has the potential to become a new environmentally friendly engineered soil.

In a geotechnical verification, the liquid limit, maximum dry density, optimal water content, compression and swelling indexes, and SEM images were evaluated for the purpose of determining the influence of β-1,3/1,6-glucan interaction.

The strengthening efficiency of the β-1,3/1,6-glucan polymer was examined through an investigation of the engineering properties, particularly the tensile strength, the compressive strength (which is affected by dehydration and the curing temperature), and durability (which is discussed in detail in Chapter 4).

Finally, economic factors and the environmental consideration of carbon dioxide emission were converged in an economic efficiency analysis to validate the feasibility and applicability of β-1,3/1,6-glucan treatment..

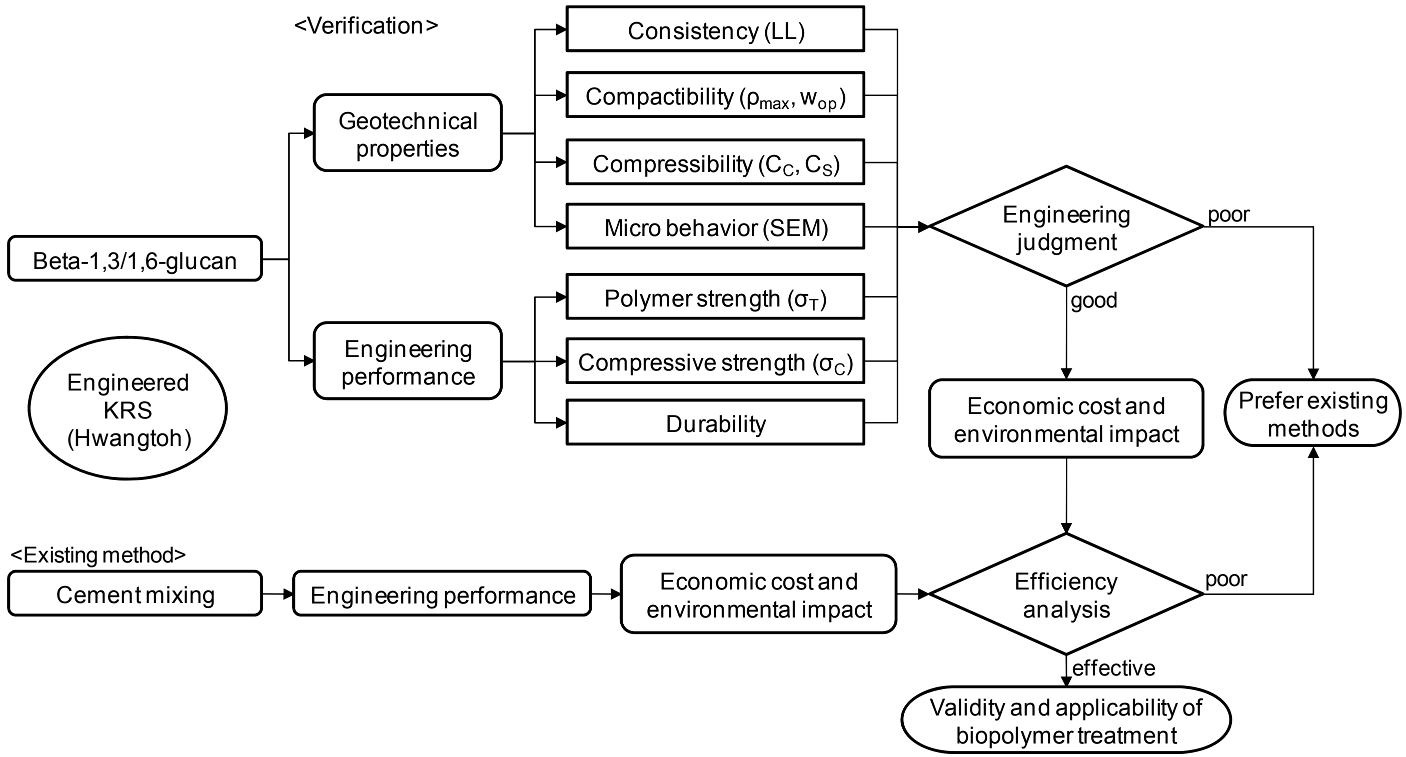


Figure 3.25 Summary. Flow chart of the studies performed in this chapter.

3.4.2. Conclusions

Comprehensive theoretical and experimental approaches were adopted to explore the effect of β 1,3/1,6-glucan on the geotechnical and engineering behavior of Korean residual soil. The most important findings are as follows:

- A series of direct and indirect (filter paper – β-1,3/1,6-glucan composite) approaches showed that the β-1,3/1,6-glucan polymer has an average tensile strength of 36.27 MPa to 48 MPa and a tensile stiffness of 2.11 GPa.
- The adsorption of β-1,3/1,6-glucan polymers on particles during the dehydration process can be explained as a type of cementation. Thus, the polymer coats that form on surfaces and the enlarged particle contact areas govern the interparticle behavior of β-1,3/1,6-glucan. For dispersed particles, the β-1,3/1,6-glucan polymer extends as a bridge between detached particles. In this case, the adhesive strength and tensile strength govern the interparticle behavior of β-1,3/1,6-glucan.
- The liquid limit of a β-1,3/1,6-glucan-hwangtoh mixture increases exponentially in relation to the concentration (c_o values) of β-1,3/1,6-glucan.
- An increase in the β-1,3/1,6-glucan content in hwangtoh improves the fabric and contact behavior, inducing an increment in the shear wave velocity and shear modulus. The α factor in the equation of effective stress

and shear wave velocity increases as the amount of β-1,3/1,6-glucan increases.

- The compressibility of hwangtoh (which seems to have a low correlation with organic matters that coexist inside, especially organic carbon) has a unique a unique value in the compressibility index (C_c = 0.27), regardless of the amount of β-1,3/1,6-glucan.
- The presence of β-1,3/1,6-glucan fibers increases the shear modulus of soil (G), which is related to an increase in the shear wave velocity, but has only a minor or even no effect on the soil axial deformation characteristics (namely the constraint modulus, M, which is related to the compressive wave velocity).
- The compressive strength of samples cured at 20°C and 60°C increases conspicuously after the 1.0 g/L point of the β-1,3/1,6-glucan solution concentration. The samples cured at 60°C show the best improvement in performance. However, the samples cured at 100°C show lower strengthening and strength degradation over time. Thus, a temperature of 100°C decreases and disturbs the strengthening function of β-1,3/1,6-glucan polymers, whereas a temperature of 60°C optimizes the strengthening.
- In a dry density range of 1.25 to 1.35 Mg/m^3, the specimens of β-1,3/1,6-glucan treated at c_o = 0.1, 0.05, and 0.01 have a similar or lower

performance than cement mixed with hwangtoh (10%). However, the strengthening behavior of the c_o = 1.0 and 0.5 conditions (0.25 and 0.49% of β-1,3/1,6-glucan) is higher than that of the 10% cement treatment.

- The optimum water content of 8.2 g/L of hwangtoh compacted with a β-1,3/1,6-glucan solution increases slightly from 25% (natural hwangtoh) to 28.5%. The increment of optimum water content is attributed to the hydrophilic property of strongly absorbed β-1,3/1,6-glucan polymers on particle surfaces. The compacted maximum dry density also increases as the β-1,3/1,6-glucan content is increased (from 1.39 to 1.44 Mg/m^3).
- In terms of cost-effectiveness and environmental impact, the total cost (of direct material costs plus indirect CO_2 emission expenses) for 1 ton of soil improvement is \$2848 for a 10% cement mixture and \$1576 for a 0.49% *β*-1,3/1,6-glucan treatment. Therefore, β-1,3/1,6-glucan biopolymer treatment has advantages in terms of engineering performance, environmental impact, and cost-effectiveness.

CHAPTER IV

IMPROVEMENT OF KOREAN RESIDUAL SOIL USING BIOPOLYMER MATERIALS: ADDITIONAL STUDY

4.1 INTRODUCTION

In Chapter 3, the interparticle, strengthening, and geotechnical behaviors of β 1,3/1,6-glucan was explored through various theoretical and experimental attempts. However, other biopolymers such as Xanthan gum, Chitosan, and Gellan gum are widely applied in various fields—food, cosmetics, agriculture, medicine, the oil industry, and so on.

The aim of soil treatment is to increase the soil's aggregate stability, cultivation performance, and water erosion resistance. To this end, researchers have used Xanthan gum [Chaney and Swift 1986], Chitosan [Ren et al. 2001], and Gellan gum [Ferruzzi et al. 2000]. However, the interparticle relation and strengthening behavior of biopolymer-soil matrices are not well reported in the literature.

The purpose of this chapter is to verify and exemplify the engineering performances and efficiency of biopolymer-treated soil. This study reports on several laboratory attempts to discover the strengthening characteristics of Hwangtoh that has been treated with Xanthan gum, Chitosan, or Gellan gum. Compressive strength measurement and SEM analysis are performed to investigate the macrointeractions and microinteractions of Hwangtoh-biopolymer mixtures. Durability is evaluated to verify the usability and sustainability of biopolymer-treated Hwangtoh. A brief economic and environmental analysis is introduced to evaluate how the efficiency of biopolymer treatment compares with ordinary cement. The chapter starts with an overview of the current status of the biopolymers introduced in this study.

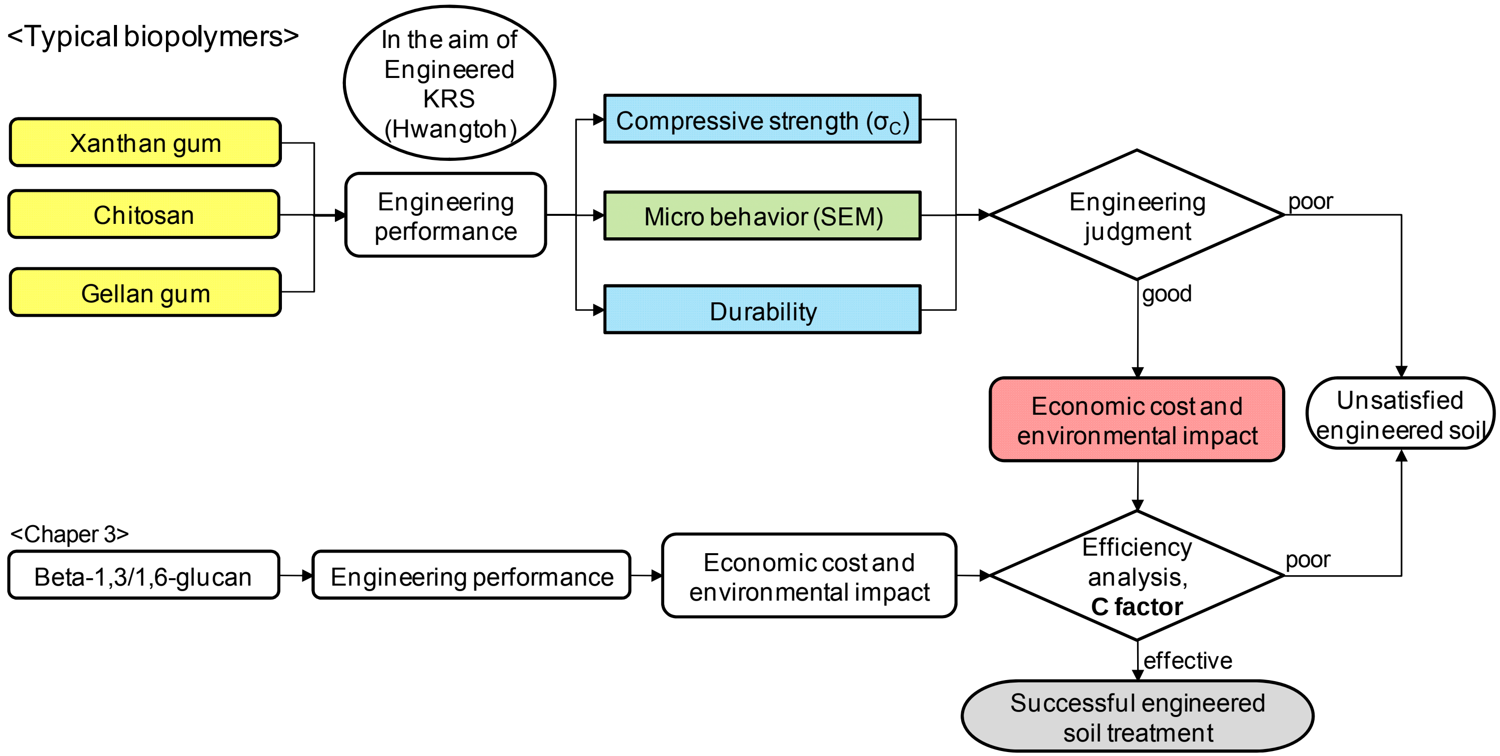


Figure 4.1 Research procedure of Chapter 4.

4.2 BIOPOLYMER MATERIALS

4.2.1.Xanthan Gum

Xanthan gum is a polysaccharide commonly used as food additives and rheology modifiers, produced by fermentation of glucose or sucrose by the *Xanthomonas campestris* bacterium [Becker et al. 1998; Davidson 1980].

Xanthan gum is an anionic polysaccharide composed of D-glucuronic acid, D-mannose, pyruvylated mannose, 6-O-acetyl D-mannose, and a 1,4-linked glucan [Cadmus et al. 1982]. The best well known characteristic of Xanthan gum is pseudo plasticity (viscosity degradation depending on increase of shear rate). In static conditions, small amount of Xanthan gum adding (in most foods, 0.5%) induces large increase in the viscosity of a liquid. Moreover, unlike other gums, Xanthan gum shows high stability under a wide range of temperatures and pH [Davidson 1980].

Its properties make it useful matrix component for drug delivery systems [Mundargi et al. 2007]. It forms stable drug suspensions in aqueous media and soft gels with locust bean gum or guar gum [Sandolo et al. 2007]. Its interaction with polysaccharides such as, glucose, mannose ($C_6H_{12}O_6$), potassium gluconate ($C_6H_{11}KO_7$), acetate ($CH_3CO_2^-$), and pyruvate ($CH_3COCOOH$), forms hydrophilic colloids [Laneuville et al. 2006].

Xanthan gum is used in dairy products and salad dressings as a thickening agent and stabilizer. Xanthan gum prevents ice crystals formation in ice creams, and provides 'fat feel' in low or no-fat dairy products [Sandford et al. 1984]. Another application of Xanthan gum is stabilizer and binder in cosmetic products. Xanthan gum is a long durability material. In cosmetics, Xanthan gum prevents ingredient separation.

In field, Xanthan gum is used in oil industry as drilling mud thickener, because Xanthan gum provides consistent rheology through the drilling hole [Becker et al. 1998]. It is also applied as additives in concrete for viscosity increase and washout prevention [Plank 2004].

4.2.2.Chitosan

Chitosan is a linear polysaccharide, randomly composed of β-1,4-D-glucosamine ($C_6H_{13}NO_5$) and N-acetlyglucosamine ($C_8H_{15}NO_6$). The amino group (N-) in chitosan charges it to be positive and soluble in acidic to neutral solution depending on pH [Goosen 1997]. Chitosan is a high biodegradability material [Hirano et al. 1991], widely used as ecologically friendly fertilizers and biopesticides in agriculture and horticulture [Linden et al. 2000].

Flocculation is another major property of Chitosan. Chitosan binds fine particles in suspension, and also removes phosphorus, heavy metals, and oils from water. Thus, Chitosan importantly used for water filtration [Juang and

Shiau 2000]. Especially, Chitosan is suitable for adsorption of metal, such as Cd^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, etc., due to the chelating property of Chitosan [Liu et al. 2002].

Furthermore, according to its biocompatible, antibacterial and polyelectrolytic characteristics [Kobayashi et al. 1996], chitosan is used in various applications including water treatment, chromatography, additives for cosmetics, textile treatment for antimicrobial activity [Shin et al. 1999], novel fiber for textiles, photographic papers, biodegradable films, biomedical devices, and microcapsule implants for controlled release in drug delivery [Bartkowiak and Hunkeler 1999; Sezer and Akbuga 1999; Suzuki et al. 1999]

4.2.3.Gellan Gum

Gellan gum is a water-soluble polysaccharide, widely used primarily as a gelling agent, alternative to agar. It is a polymer consisting, glucose, glucuronic acid ($C_5H_9O_5$-COOH), and rhamnose ($C_6H_{12}O_5$). It forms high qualified gel even under low concentrations (0.05~0.25%). Gellan gum is a thermal sensitive material, which can disintegrate without melting in 150°C. The conditions for gel formation are as:

(1) Heating (60~80°C ; [Norton and Lacroix 1990].

(2) Coagulation with the presence of cation (Na^+, K^+, Mg^{2+}, Ca^{2+}).

(3) Cooling process forms gel.

Gel formed by Na^+ and K^+ can renew after heating (reversible), while gel formed by Mg^{2+} and Ca^{2+} cannot (irreversible gel). As food additive, gellan gum is used as thickener, emulsifier, and stabilizer [Jansson et al. 1983]. According to its high stability at high temperature and low pH, especially acid gel has comparatively long shelf life [Giavasis et al. 2000], it can be a well performing biopolymer for soil improvement and stabilization [Ferruzzi et al. 2000].

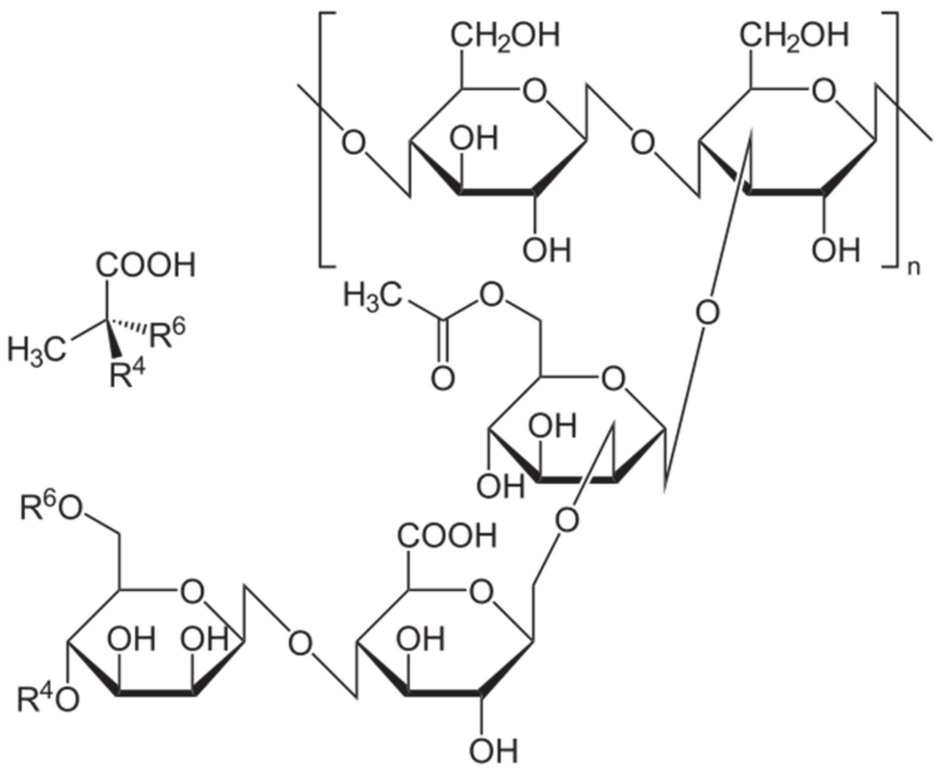


Figure 4.2 Structure of Xanthan gum.

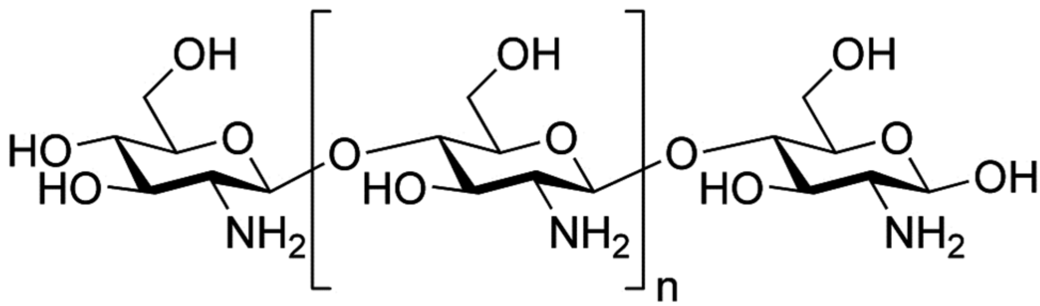


Figure 4.3 Molecular structure of Chitosan.

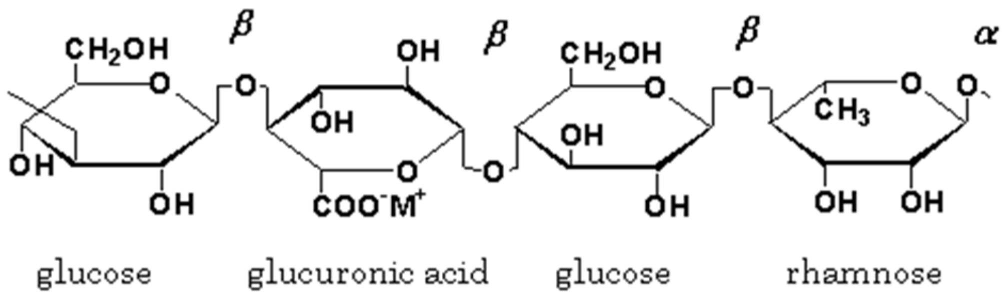


Figure 4.4 Structure of Gellan gum.

4.3 EXPERIMENTAL METHODS

4.3.1.Biopolymer – Hwangtoh Mixing

Biopolymers described in previous sections (*4.2.1*, *2*, and *3*) are usually used at concentrations at/or below 1% in weight (*w/w*: weight of biopolymer/weight of total solid) [Ross-Murphy 1995]. The maximum *w/w* (%) value applied in Ch. 3 was 0.492% (β-1,3/1,6-glucan c_o=1.0). However, for generalization, biopolymers are mixed with Hwangtoh at *w/w* = 1.0% in this chapter. Thus, the initial water content becomes an independent parameter to control the initial mixing, according to the different viscosity behavior of different biopolymers.

Experientially, for each cubic curing mold (Figure 3.2), 1,600 g of dried Hwangtoh is enough for specimen preparation. Thus, for each biopolymer, 16g of solid powder type reagents were prepared. Amount of water and kind of additives varies according to the solubility of each biopolymer. Details of initial mixing conditions are summarized in Table 4.1.

Xanthan Gum

Gum Xanthan (Sigma-Aldrich, CAS No.: 11138-66-2; 87,000 KRW / 100g) used in this study is a biological source from *Zanthomonas campestris*. 16 g of Gum Xanthan was dissolved in 1,000 mL of distilled water. To increase the solubility, the solution was heated to 60°C.

Then, Gum Xanthan solution was mixed with 1,600 g of dried Hwangtoh using a laboratory rotator (Fig. 3.3.a). During mixing, 200 mL of distilled water was added to control the workability to perform uniform mixture. Finally, a Xanthan gum – Hwangtoh mixture (*w/w* = 1.0%, initial water content: 75%) is prepared and molded into cubic size samples (Figure 3.4).

<u>Chitosan</u>

Chitosan (Sigma-Aldrich, CAS No. 9012-76-4; 74,000 KRW / 50g) is used in this study. According to the amino group (N-) of Chitosan, it is recommended to dissolve chitosan in sub-acids (range of pH 4.0 ~ 5.0). Hydrochloric acid (HCl) was used to control the initial pH of the 1,000 mL solvent. During the dissolution process of chitosan, small amount of HCl was frequently added to maintain the optimized pH condition for dissolution.

Initially, 1,000 mL of Chitosan solution was mixed with 1,600 g of dried Hwangtoh. However, the mixing performance was very poor (shows initially high viscosity), compared to other biopolymers. Thus, additional amount of water (600 mL) was added to satisfy homogeneous mixing. Finally, a Chitosan – Hwangtoh mixture (*w/w* = 1.0%, initial water content: 100%) is molded as same as Xanthan gum.

Gellan Gum

In this study Gelzan™ (CP Kelco, CAS No.: 71010-52-1; 140,000 KRW / 250g) was used to represent Gellan gum. Thermal activated Gellan gum forms high performance gel when cooled, in the presence of alkali (Na^{+}, K^{+}) or alkaline-earth metals (Mg^{2+}, Ca^{2+}). For higher stability, alkaline-earth metals are recommended to be used to for irreversible gels. In food science, Gellan gum and alkaline-earth metal chlorides are dissolved in heated water, mixed with other ingredients, and finally cooled [Jansson et al. 1983].

However, in soil mixtures, there exists a possibility of Gellan gum solution to be cooled down during mixing, and forming insufficient gels. Thus, in this study, Gelzan™ and calcium chloride ($CaCl_2$, Junsei, CAS No.: 10043-52-4) solids were uniformly mixed with dried Hwangtoh first. Then, distilled water was added to perform uniform Gellan gum – Hwangtoh paste. Molded cubic type specimens were putted in an oven for thermal activation (100°C; 1 hour). Finally, specimens were taken out and cooled down in room temperature.

Table 4.1 Mixing conditions of Biopolymer – Hwangtoh mixtures.

Specimen	Mixing condition [g]				Initial mass ratio [%]	
	Dried Hwangtoh	Biopolymer	Additive	Water	Biopolymer/ soil [*w/w*]	Water content
Xanthan gum	1,600	16	-	1,200	1.0	75.0
Chitosan	1,600	16	0.01 (HCl)	1,600	1.0	100.0
Gellan gum	1,600	16	1.6 ($CaCl_2$)	1,000	1.0	62.5

4.3.2. Cubic Curing and Compressive Test

Each molded biopolymer – Hwangtoh cubic size specimens (4cm×4cm×4cm size for each cubic) were cured at room temperature (20ºC) to make comparison with same condition cured β-1,3/1,6-glucan treated Hwangtoh, described in Chapter 3.

The compressive strength and stiffness values of biopolymer treated Hwangtoh were measured consistently during 28 days. Xanthan gum, Chitosan samples were measured at 7, 14, 21, and 28 days, while Gellan gum sample has an additional measurement at the beginning (1 day) of curing. Details are in line with the compressive test described in section 3.2.7.

4.3.3. Durability Testing (ASTM D 559-03)

Testing Procedure

For engineered soil, the degree of durability is defined by moisture adsorption resistance, strength reduction, according to wetting and drying cycles. ASTM standard D 559-03 offers a test method to evaluate the durability of compacted cemented soil. However, the cubic specimens used in this study are comparably small in size (ASTM D 559-03 covers compacted cement-soil mixture in 1 L volume). Thus, the experimental procedures are modified to suit cubic size samples. Details are as below:

(1) At the end or curing, submerge at least two specimens (Specimen 1: water content and volume change indicator; Specimen 2: soil-biopolymer loss indicator) of each biopolymer treatment in potable (tap) water at room temperature for a period of 10 minutes and remove. Measure the mass and volume of Specimen 1.

(2) Place both specimens (Specimen 1 and 2) in an oven at 71°C for 23 hours and remove. Record the mass and volume of Specimen 1.

(3) Perform two firm strokes on each side of Specimen 2, using the wire scratch brush. Then, measure the mass and volume of Specimen 2.

(4) The procedures described in (1) – constitute single cycle (24 hours) of wetting and drying. Submerge the specimens again in water (for 10 minutes) and continue the procedure for 6 cycles.

(5) After the whole cycle of testing, dry the specimens at 110°C and determine the final mass of the specimens

<u>Calculation</u>

Soil volume and water content variations and soil-biopolymer losses can be calculated as follows:

(1) Calculate the volumetric strain of subsequent volumes (at each cycle) of Specimen 1 as a percentage of the initial volume.

(2) Calculate the water content change of Specimen 1, subsequently.

(3) Derive the final oven-dried (110ºC) mass of Specimen 2.

(4) Evaluate the soil-biopolymer loss of Specimen 2 as below:

$$\text{Soil-biopolymer loss [\%]} = \frac{\Delta \text{dry mass (initial-final) [g]}}{\text{initial dry mass [g]}} \times 100[\%] \qquad (4.1)$$

4.4 RESULTS AND DISCUSSIONS

4.4.1. Compressive Strength of Hwangtoh – Biopolymer Mixtures

The strength and stiffness behavior of biopolymer – Hwangtoh mixtures are shown in Figure 4.5. Each trend in Figure 4.5 represents the compressive strength and stiffness variation effected by different biopolymers, with time. The results are compared with room temperature (20ºC) cured natural Hwangtoh and β-1,3/1,6-glucan treated Hwangtoh (*w/w* = 0.49%).

Xanthan Gum

Compressive strength of Xanthan gum treated Hwangtoh increases rapidly during the first 14 days. The tendency slows down, and points a peak value 6.31 MPa at the 21st day. After 21 days, the stress tends to diminish. This result is in agreement with the stiffness variation. The stiffness behavior shown in Figure 4.5(b) also records a peak at the 21st day, and decreases thereafter.

Xanthan gum shows satisfactory strength improvement result. Compared to natural Hwangtoh (maximum strength 1.05 MPa), Xanthan gum treatment improves Hwangtoh 6 times higher in strength. Moreover, Xanthan gum shows better performance compared to β-1,3/1,6-glucan (2 times stronger).

Generally, the biodegradability (carbon dioxide generation) of Xanthan gum increases continuously showing a considerably high value (1.182 mg CO_2/day at 80 days) [Kim et al. 2006].

Chitosan

Compressive strength of Chitosan treated Hwangtoh increases slightly during the beginning 14 days. According to the maximum compressive strength value (1.38 MPa), the improvement efficiency of Chitosan is only 31.4% compared to the maximum strength of natural Hwangtoh (1.05 MPa). While, the main purpose of this study is to improve the mechanical behavior of natural residual soil using biopolymers with high efficiency (more than 100%), Chitosan shows insufficient possibility. The similar residual strength behavior after 14 days, could be an evidence that Chitosan treatment and degradation have minimal effects on the strength and stiffness behavior of Hwangtoh.

From the test results, the poor mechanical strength of Chitosan is confirmed. It is, therefore, necessary to modify Chitosan to improve its mechanical strength [Lin and Lin 2005]. To improve its strength behavior, polymers such as PVAL (Poly-Vinyl alcohol) can be added to Chitosan [Liu et al. 2002].

Gellan Gum

The compressive strength of Gellan gum treated Hwangtoh, increases fast, due to its gelation below setting temperatures 45~60ºC, similar to Agar [Kang et al. 1982]. Initially, Gellan gum shows highest stiffness among other biopolymers, which indicates the well performed inter-particle binding. However, both strength and stiffness decreases continuously after 7 days.

The maximum compressive strength was measured to be 2.55 MPa. The tensile strength of Gellan gels are reported as 9 to 350 kPa [Ferruzzi et al. 2000]. Compared to β-1,3/1,6-glucan (tensile strength 36.27~48 MPa, from Chapter 3) treated Hwangtoh (highest compressive strength: 3.23 MPa), gelation shows an effective strengthening performance, because gellan gels are expected to coagulate particles [Omoto et al. 1999]. Meanwhile, the relatively quick degradation in strength and stiffness becomes an awaiting challenge.

Gelation of Gellan gum strongly depends on both ionic strength and the identity of the cations. For monovalent cations, gel strength increases in the order [Grasdalen and Smidsrod 1987]:

$$Li^+ < Na^+ < K^+ < Cs^+ < H^+$$

For divalent cations, the order is as:

$$Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} < Zn^{2+} < Cu^{2+} < Pb^{2+}$$

Therefore, various attempts are possible to increase the strengthening performance of Gellan gum.

4.4.2. Shrinkage and Dry density of Hwangtoh – Biopolymer Mixtures

The shrinkage characteristic of biopolymer treated Hwangtoh is shown Fig. 4.6(a). According to the different initial water content (depending on the workability and mixing performance), the amount of volumetric strain is expected to be proportional to the initial water content increase. As Gellan gum mixture has the lowest initial water content (62.5%), its final volumetric strain also shows the lowest amount (27%). However, for Xanthan gum and Chitosan, even though Xanthan gum has lower initial water content (75%; Chitosan: 100%), its volumetric strain (43%), is higher than Chitosan (35%).

The high drying shrinkage of Xanthan gum mixed Hwangtoh can be explained by the initially rapid swelling behavior of Xanthan gum, when it is dissolved in water [Miller and Hoseney 1993]. On the other hand, Chitosan is known to inhibit gel shrinkage according to the highly polar polymer backbone which is capable of forming hydrogen-bonded bridges between silica particles [Ayers and Hunt 2001]. Thus, even though Chitosan has higher initial water content, it can be regarded that its shrinkage behavior is inhibited by the Chitosan polymer – Hwangtoh particle interaction.

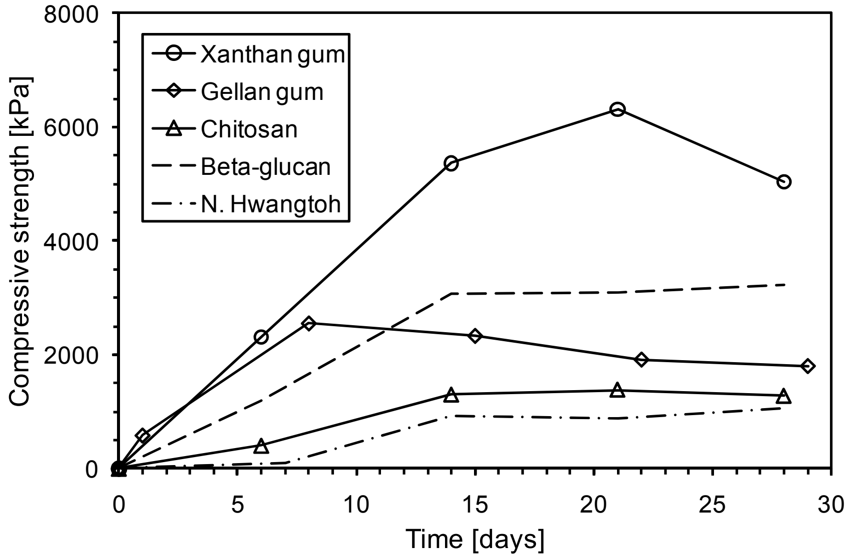
The water-biopolymer interaction also affects the strength and quality of biopolymers. Biopolymers (i.e. Carbohydrate polymers) stabilize a large amount of water [Mao et al. 2001]. However, according to the its intrinsic instability, hydrogels loses water as a result of syneresis (passive diffusion) [Glicksman 1979; Sanderson and Clark 1983] . The loss of water induces gel shrinkage, texture change, and quality reduction [Mao et al. 2001]. Generally, brittle biopolymeric gels (e.g. Agar gels) are more sensitive to syneresis than elastic gels (e.g. κ-carrageenan gels) [Glicksman 1979].

Generally, the volume change behavior of a single clay soil shows a unique relationship with water content [Crescimanno and Provenzano 1999]. Thus, the normalized volume change parameter (volumetric strain [%] / initial water content [%]) should also show a single trend [Tripathy et al. 2002].

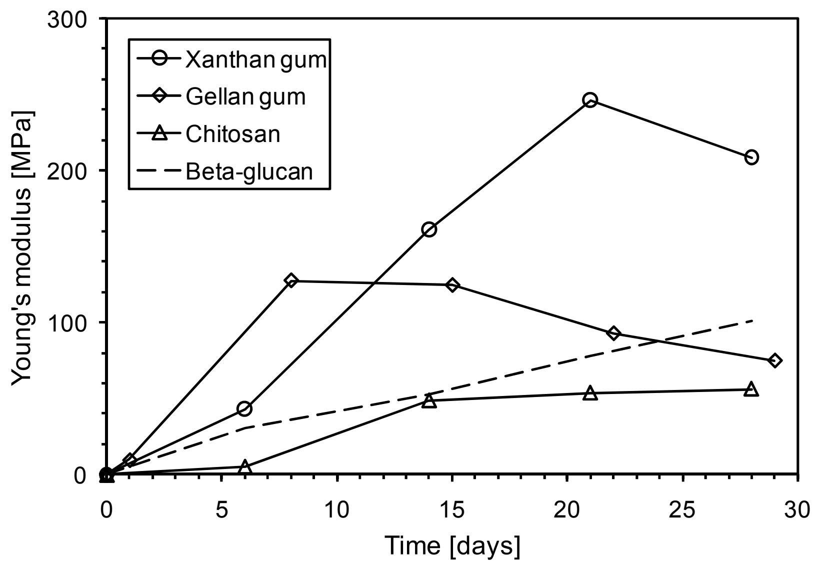
Figure 4.7 shows the normalized volume change results of different type of biopolymer treated Hwangtoh. As natural Hwangtoh, converges to 0.4, Chitosan shows that its inhibition characteristic for soil shrinkage. However, other biopolymers (β-1,3/1,6-glucan, Xanthan gum, and Gellan gum) show higher contractibility. The increase of shrinkage tendency is caused by the swelling behavior of those biopolymers in aqueous condition [Kulicke and Nottelmann 1989]. From the result, the shrinkage resistance of biopolymers increases in order as: Xanthan gum → β-1,3/1,6-glucan → Gellan gum → Chitosan.

Compared with β-1,3/1,6-glucan, the dry density values of biopolymer treated Hwangtoh converges to a similar range (1.30 ~ 1.39 Mg/m^3), except Chitosan (Fig. 4.8). Although, β-1,3/1,6-glucan, Xanthan gum and Gellan gum treated samples show similar (or almost equal) dry density values (after dehydration), the maximum compressive strength varies depending on the biopolymer type. For a simultaneous dry density condition, the strengthening effect is maximized in order of: Xanthan gum → β-1,3/1,6-glucan → Gellan gum.

Finally, it is concluded that the long period, soil-water interaction governs the strength increment, while the syneresis of biopolymers decreases both strength and stiffness of biopolymer treated soil. Thus, the structural behavior of biopolymer treated Hwangtoh, becomes a multi-variable function, which requires deep concerns.

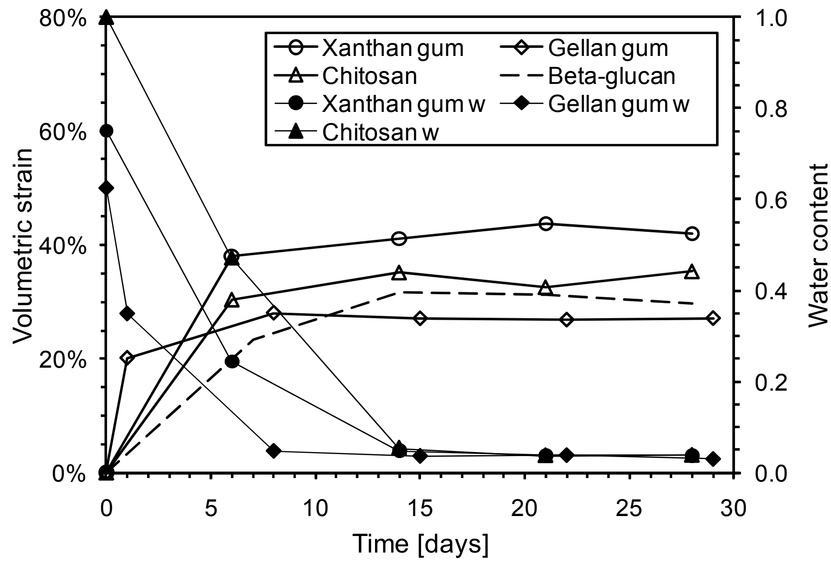


(a) Compressive strength variation.

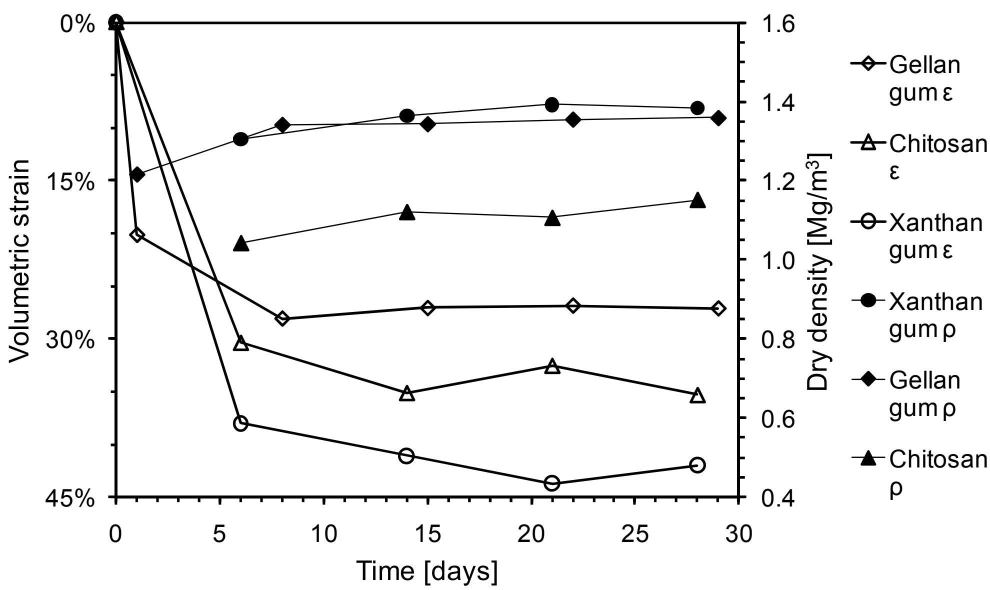


(b) Young's modulus variation.

Figure 4.5 Strength and stiffness behavior of biopolymer treated Hwangtoh.



(a) Volumetric strain (hallow points) and water content (bold points) variation.



(b) Volumetric strain (hallow points) and dry density (bold points) variation.

Figure 4.6 Drying shrinkage behavior of biopolymer treated Hwngtoh.

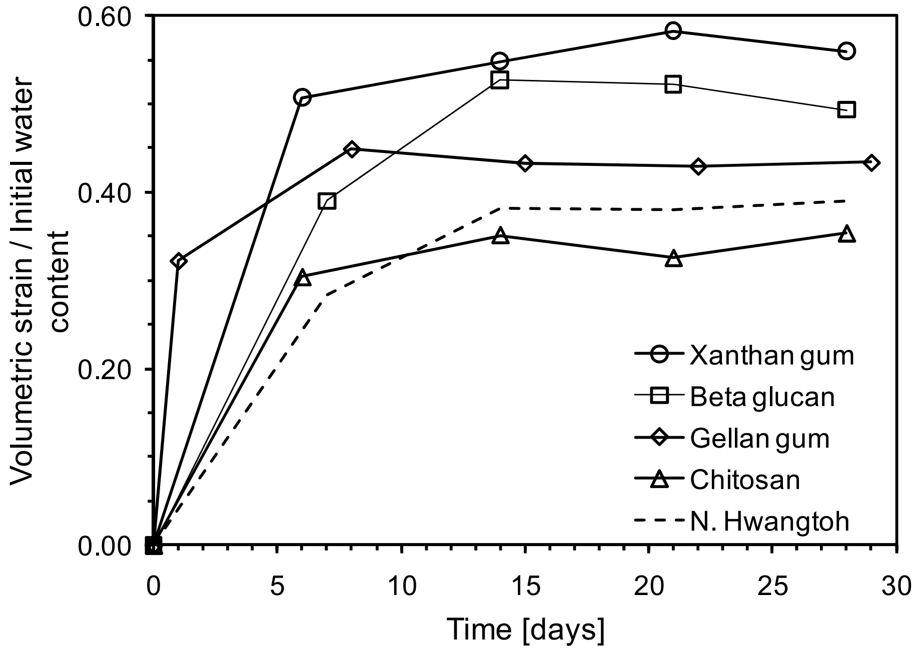


Figure 4.7 Normalized volumetric strains with initial water content, which indicates the shrinkage tendency of soil affected by different type of biopolymers.

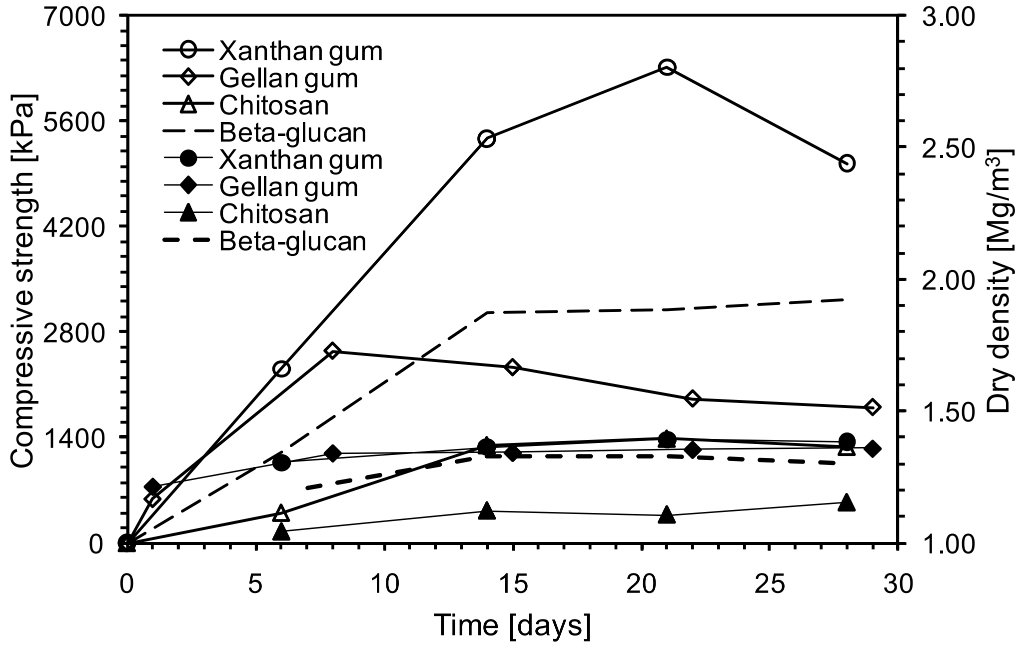


Figure 4.8 Compressive strength (hallow points) and dry density (bold points) variation of biopolymers (Xanthan gum, Gellan gum, Chitosan, and Beta-glucan) treated Hwangtoh.

4.4.3. SEM Image of Hwangtoh – Biopolymer Mixtures

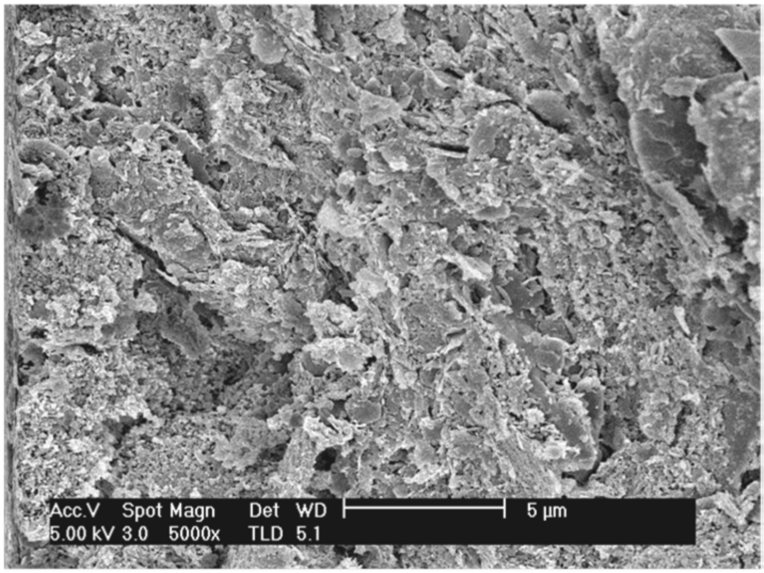
To verify the inter-particle behavior of the treated biopolymers in this study, scanning electron microscope (SEM; Philips XL30SFEG) images were taken for each sample after 28 days of curing.

Xanthan Gum

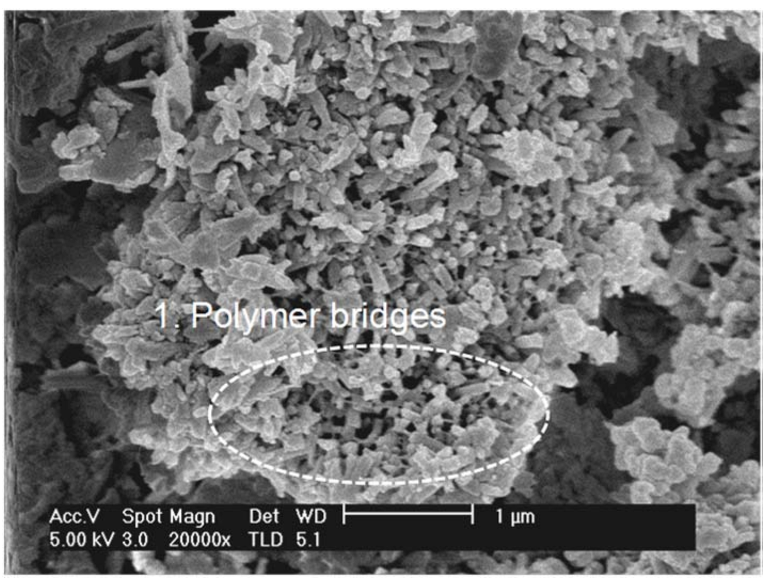
The SEM images of Xanthan gum treated Hwangtoh are shown in Figure 4.9. Figure 4.9(b) shows a clear example of Xanthan gum polymers forming bridges between Hwangtoh particles. In a closer view (Fig. 4.9.c & d), Xanthan gum polymers show a "Y-type" form. Each edge of Xanthan gum connects to nearby particles forming a "Xanthan gum – Hwangtoh particle web matrix". This phenomenon explains the highest compressive strength behavior of Xanthan gum among other biopolymers used in this study (Fig 4.5).

Chitosan

SEM images of Chitosan treated Hwangtoh are appeared in Figure 4.10. Compared with other biopolymers, Chitosan treated Hwangtoh shows a distinctive appearance. As Chitosan forms strong hydrogen bonding with adjacent particles [Ayers and Hunt 2001], it can be considered that Chitosan initially densifies soil particles to form a face-to-face contact.

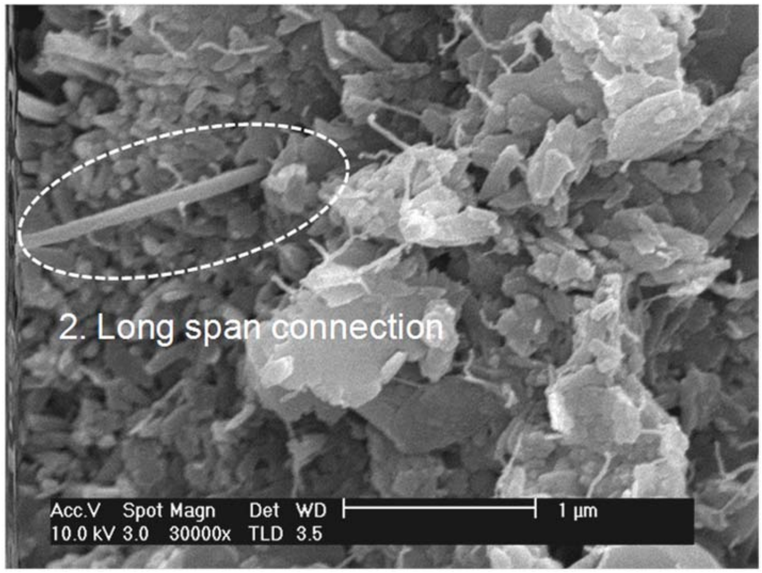


(a) Overall view (5,000 times magnified).

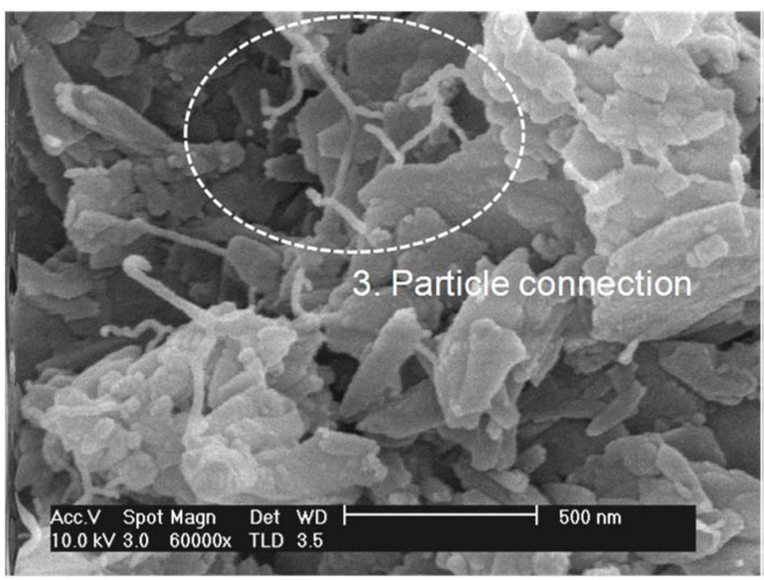


(b) Xanthan gum polymer bridges between particles (× 20,000 view) .

Figure 4.9 SEM image of Xanthan gum – Hwangtoh mixed sample.

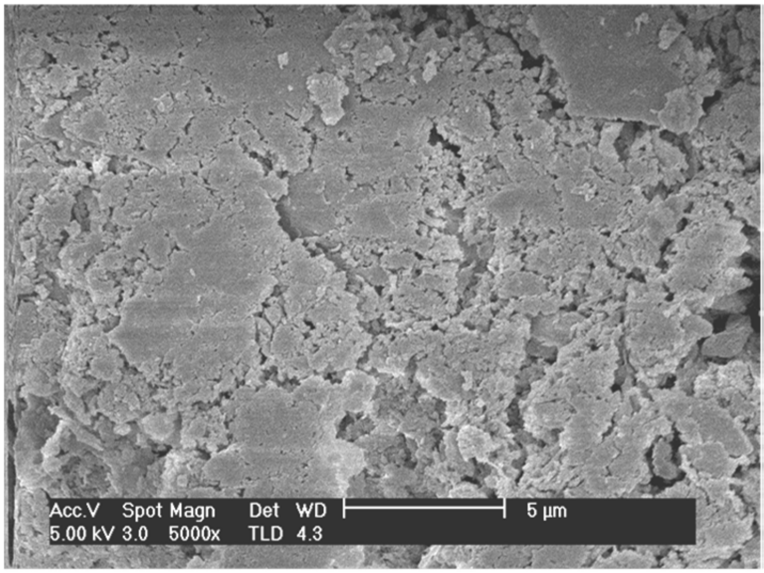


(c) Long length polymer chain (× 30,000 view).

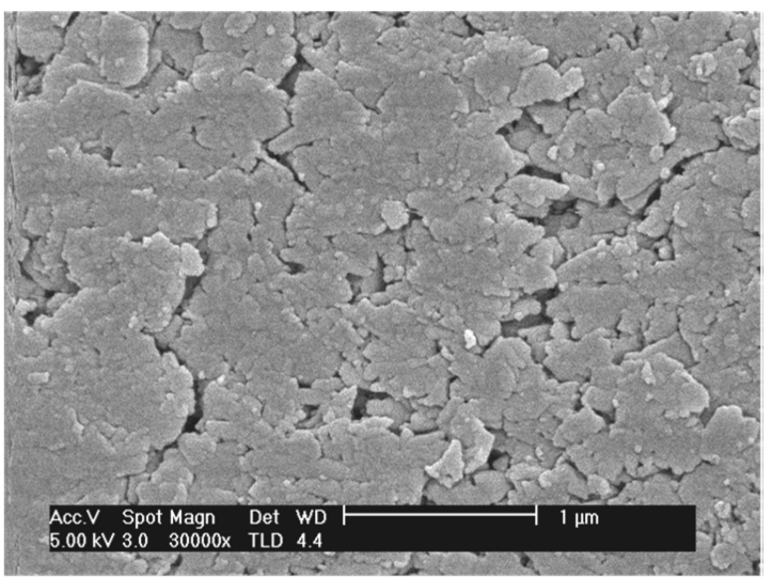


(d) “Y type” inter-particle connection (× 60,000 view).

Figure 4.9 *Continued*.



(a) Overall view (5,000 times magnified).



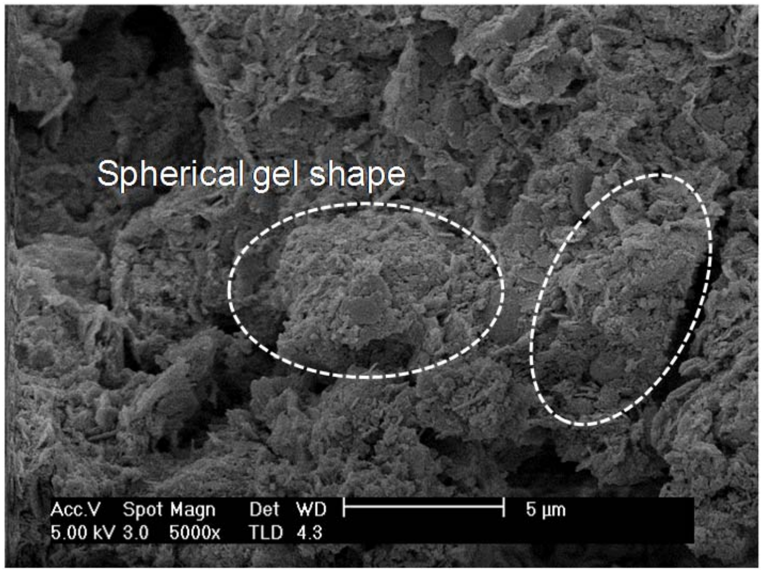
(b) Smooth and flatten Hwangtoh matrix (× 30,000 view).

Figure 4.10 SEM image of Chitosan – Hwangtoh mixture.

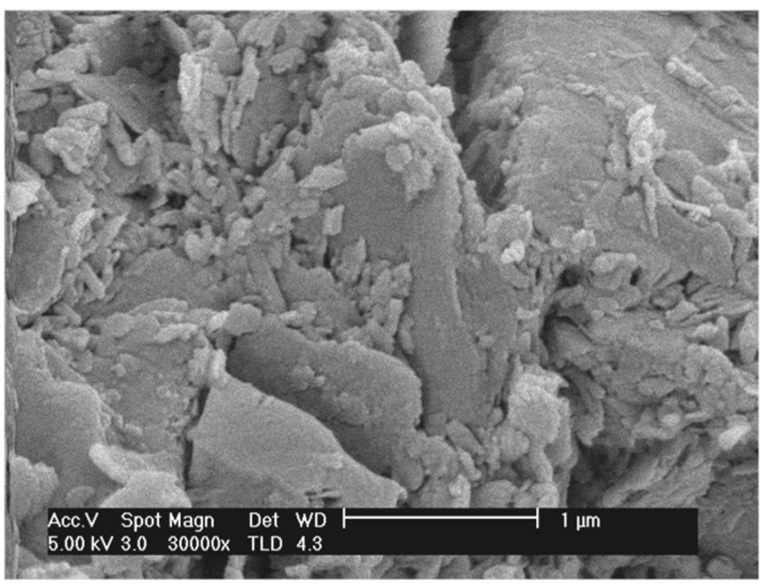
The face-to-face behavior of Chitosan tablets is verified in a previous study [Picker-Freyer and Brink 2006]. The low volumetric strain tendency of Chitosan (Fig. 4.7) can be explained the same reason. Generally, for clay particles, they accumulate to face-to-edge connections under low stress and high water content conditions, while they collapse to form face-to-face structures when stress increases and pore fluid drains [Mitchell and Soga 2005]. However, Chitosan treated Hwangtoh seems to form face-to-face contacts, promoted by Chitosan polymers, as shown in Figure 4.10(b). Meanwhile, the low dry density result of Chitosan (Fig. 4.6.b) indicates that the face-to-face contact is far from a direct contact, whereas, it can be considered to be an indirect bonding bridge formed by Chitosan.

<u>Gellan Gum</u>

The gel of Gellan gum is an assemblage of fine gel particles, generally, having spherical shapes [Fuchigami and Teramoto 2003; Omoto et al. 1999]. Thus, the inter-particle behavior of Gellan gum differs with other biopolymers, because they form global gels, while others (e.g. β-1,3/1,6-glucan, Xanthan gum) interact directly with soil particles. Thus, it is considered that Gellan gum gels flocculate Hwangtoh particles into a spherical shape during the gelation process. In reality, Hwangtoh particles affected by Gellan gel, are highly adhered to each other, forming spherical lumps (Fig. 4.11).



(a) Overall view showing spherical lumps (5,000 times magnified).



(b) Highly adhered Hwangtoh matrix (× 20,000 view).

Figure 4.11 SEM image of Gellan gum – Hwangtoh mixture.

4.4.4. Durability of Hwangtoh – Biopolymer Mixtures

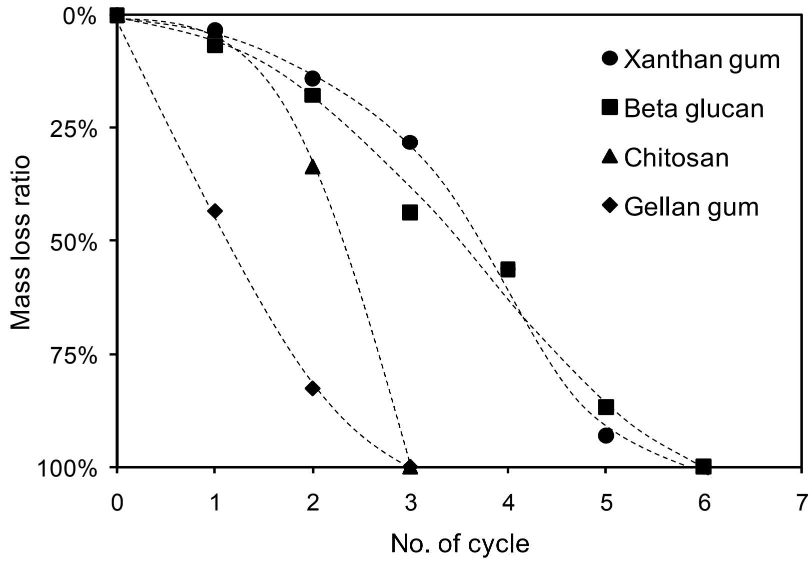
For every single submerging and drying cycle, the volume, mass, and water content of samples were measured during durability test. The durability test results are shown in Figure 4.12.

Biopolymer gels lose their capacity when they are subjected to temperature fluctuation [Mao et al. 2001]. Figure 4.12(a) shows the dry mass loss ratio with number of cycles. The increase of mass loss ratio means that the internal strength of biopolymer-Hwangtoh decreases according to the cementation material (biopolymer in this case) loss induced by the repetition of wetting and drying process. Gellan gum treated Hwangtoh shows rapid degradation initially, which shows that it has poor durability. Meanwhile, Xanthan gum and β-1,3/1,6-glucan treated Hwangtoh show high resistance against physical weathering. In average, the half-weight period of Xanthan gum and β-1,3/1,6-glucan was 4 cycles, while Gellan gum is reached at the first cycle.

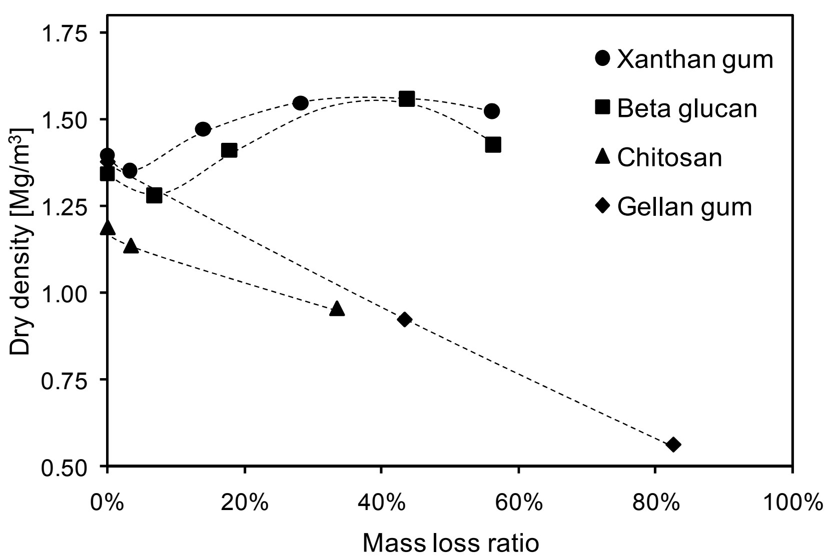
Figure 4.12(b) represents the dry density variation with mass loss along test cycles. If there is no volumetric expansion or attraction, but only surface erosion during the durability test procedures, the dry density should remain constant. However, the results in Figure 4.12(b) show that not only structural erosion, but also volumetric strain variation exist during the cyclic wetting and drying process.

The soil aggregate stability affected by wetting and drying is not clearly theorized. However, three major functional possibilities are suggested as: (1) Additional intermolecular interaction between organic matters and soil mineral surfaces [Kemper and Rosenau 1984], (2) Soil structure disruption induced by drying [Denef et al. 2001], and (3) Incipient failure zones and cracks induced by non-uniform drying strains [Haynes and Swift 1990]. In field, without solid lost, the structure of soil is repaired and improved with greater cycles of wetting and drying [Pillai and McGarry 1999]. Generally, the strength and bulk density increase of drying and wetting on soil is enlarged with the presence of organic matters [Denef et al. 2001].

The dry density of Xanthan gum and β-1,3/1,6-glucan treated Hwangtoh increases, while Chitosan and gellan gum decreases straightly with the increase of wetting and drying cycles. Thus, it seems that biopolymer chains or gels of Xanthan gum and β-1,3/1,6-glucan remains inside the soil, increasing the aggregate during drying process, and impeding the erosion affected by wetting. On the other hand, Chitosan and Gellan gum do not show meaningful behavior sustaining the soil stability. Therefore, it can be concluded that Xanthan gum and β-1,3/1,6-glucan treated Hwangtoh shows high durability, while Chitosan and Gellan are in the opposite.

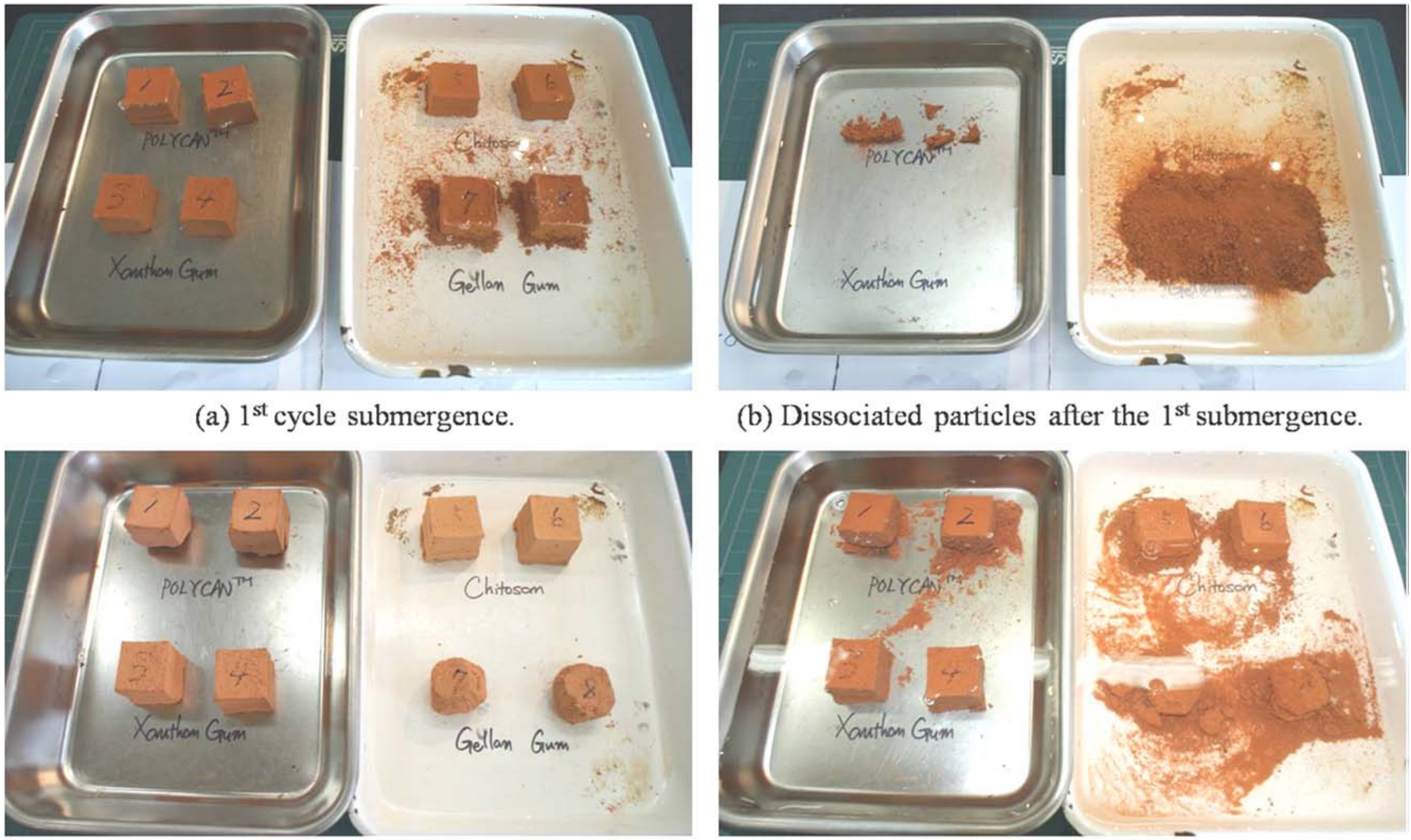


(a) Mass loss ratio of biopolymer – Hwangtoh mixtures.



(b) Dry density variation with the mass loss ratio.

Figure 4.12 Durability of biopolymer treated Hwangtoh.



(a) 1st cycle submergence.

(b) Dissociated particles after the 1st submergence.

(c) Dried samples after the 1st test cycle.

(b) 2nd cycle submergence.

Figure 4.13 Example of the durability test (1st and 2nd cycle of wetting and drying).

4.4.5. Environmental and Economic Efficiencies of Biopolymers

A similar economic and environmental impact analysis of the used biopolymers in this Chapter is performed, following the method provided in wasection 3.3.6 (Table 4.2). According to the lack of detail information about the CO_2 emission related to the production of biopolymers (i.e. Xanthan gum, Chitosan, and Gellan gum), the amount of CO_2 emission per 1 kg of biopolymer production was assumed to be 13.56 kg CO_2/kg biopolymer [Conti and Sweetnam 2008; Seo et al. 2002] because the production process of most biopolymers are similar: using bioreactors (sealed vessels) to perform exact environmental conditions (temperature, pH, aeration, agitation, etc.) [Mangina and Giavasis 2003].

The results shown in Table 4.2 indicate that the material prices of biopolymers are extremely expansive compared to ordinary cement. Among the four different biopolymers, β-1,3/1,6-glucan shows the best economic efficiency, while Chitosan shows both low engineering performance and cost efficiency. Moreover, the price fluctuation among different biopolymers is high enough to interrupt the growth of using biopolymers as engineered soil materials.

In the aim of environment-friendly and low carbon concept, the economic efficiency gap between biopolymers and ordinary cement decreases significantly, according to a consideration of carbon emission price [IATA

2008]. Recently, carbon emission trade is 22 USD/ton CO_2 (EU ETS; Vertis Finance 2009). However, the economic efficiency of biopolymers (except β-1,3/1,6-glucan) is still insufficient due to their high raw material price.

It is true that biopolymers are still cost more than conventional polymers, and also have lower performance in terms of lower heat and moisture resistance. [Kamm and Kamm 2004]. However, current increasing technology convergence which is defined as "biorefinery" – overall concept of a processing plant where biomass feed stocks are converted and extracted into a spectrum of valuable products, based on the petrochemical refinery (U.S. Department of Energy 1997) – is expected to decrease the material price of biopolymers [Kamm and Kamm 2004]. Moreover, careful expectation considering the future carbon emission market [IATA 2008], shows that the growth of carbon emission trade increases the financial merit choosing biopolymers as engineered soil materials (Fig. 4.14). At 2020, the global carbon emission trade is expected to rise up to 58.53 USD/ton CO_2 [IATA 2008]. In that case, well-performing Xanthan gum also becomes suitable to replace the use of ordinary cement.

Table 4.2 Economic and environmental analysis of OPC and β-1,3/1,6-glucan treated Hwangtoh.

Material	Xanthan gum	Chitosan	Gellan gum	Polycan^{TM}	Cement
Market price [USD/kg]*	725	1,235	470	320	60
Required amount for 1 ton soil treatment [kg]	10 (*w/w*= 1%)	10 (*w/w*= 1%)	10 (*w/w*= 1%)	4.92 (*w/w*= 0.5%)	100 (*w/w*= 10%)
Material price for 1 ton soil treatment [USD]	7,250	12,350	4,700	1,574	6
Total CO_2 emission for 1 ton soil treatment [kg]**	135.6	135.6	135.6	66.72	129,180
Total CO_2 emission cost [USD]***	3.0	3.0	3.0	1.5	2,842
Total cost induced by 1 ton soil treatement [USD]	7,253	12,353	4,703	1,576	2,848

* : Material prize referred to Sigma Aldrich (www.sigmaaldrich.com/).

**: 13.57kg CO_2 / 1kg biopolymer [Conti and Sweetnam 2008; Seo et al. 2002].

***: 22 $ /ton [Grubb and Neuhoff 2006]; Vetris – Carbon newsletter 2010).

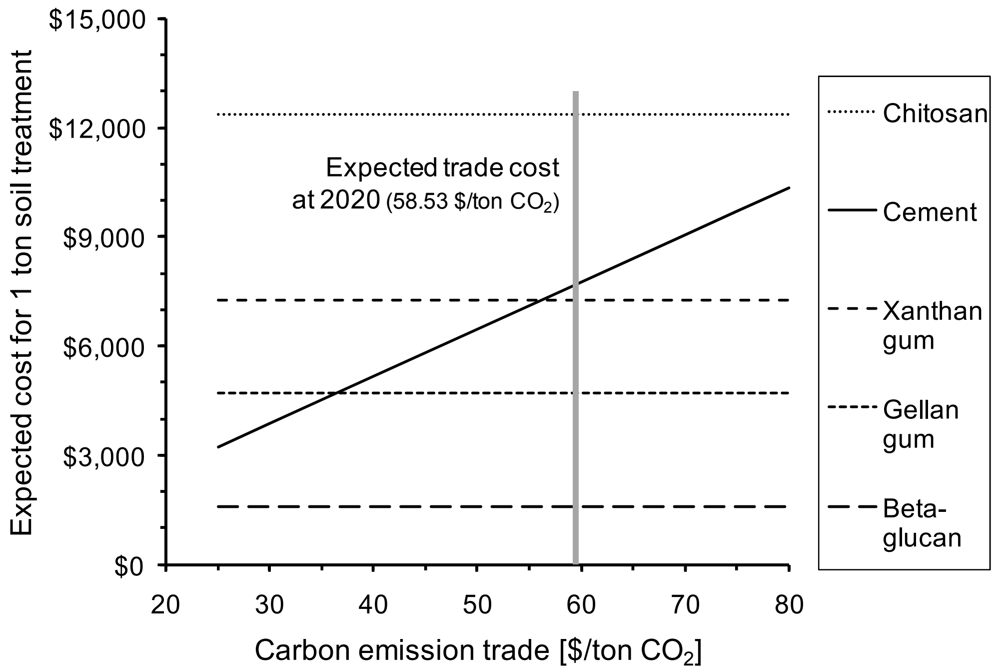


Figure 4.14 Expected economic efficiency of biopolymers related to the growth of global carbon emission trade.

4.5 SUMMARY AND CONCLUSIONS

4.5.1. Summary of Hwangtoh – Biopolymer Mixtures

The properties of the biopolymer-treated hwangtoh are summarized in Table 4.3.

Xanthan gum shows the best performance in terms of soil strengthening and durability. However, it is more expensive than β-1,3/1,6-glucan or Gellan gum. The results show that Chitosan is an unsuitable biopolymer for engineered soil on account of its high cost and poor mechanical performance. The following efficiency factor (E^4) is recommended for a reliable evaluation:

$$E^4 = \frac{\text{Max. compressive strengh [kPa]} \times \text{Durability coefficient}}{\text{Material cost[\$/kg]} \times \text{Biopolymer / soil [\%]} \times (\varepsilon_v / w_i) \times \text{CO}_2 \text{ emission [\$/ton soil]}}$$

Tables 4.2 and 3 show the maximum compressive strength, the material cost, the biopolymer-soil ratio, the dimensionless volume change tendency, and the CO_2 emission cost for 1 ton of soil treatment. The following values are recommended for the durability coefficient: 5 (very good), 4 (good), 3 (moderate), 2 (poor), 1 (very poor). The E^4 factors are derived in the bottom row of Table 4.3.

Table 4.3 Characteristics summary of biopolymer treated Hwangtoh.

Biopolymer	Xanthan gum	Chitosan	Gellan gum	β-1,3/1,6-glucan
Biopolymer / soil mixing ratio (*w*/*w* [%])	1	1	1	0.49
Initial water content [w_i, %]	75	100	62.5	60
Maximum compressive strength [MPa]	6.31	1.38	2.55	3.23
Dimensionless volume change tendency [ε_v/w_i]	0.55	0.33	0.44	0.48
Durability	Good	Poor	Very poor	Good
Material cost [$/kg]	725	1,235	470	320
Expected cost for soil treatment [$/ton soil]	7,253	12,353	4,703	1,579
Efficiency (E^4 factor)	0.47	0.05	0.01	0.52

The E^4 factor of ordinary cement is given as 0.42 in the data of Walker (1995). In this study, Xanthan gum and β-1,3/1,6-glucan have a higher E^4 value than cement, which means that Xanthan gum and β-1,3/1,6-glucan can be used for soil improvement instead of ordinary cement without any economic loss. However, Chitosan and Gellan gum require more development before their cost can be lowered and their mechanical performances improved.

4.5.2. Conclusions

This chapter explores the performance of hwangtoh treated with the typical and popular biopolymers of Xanthan gum, Chitosan, and Gellan gum. A series of laboratory analyses (namely volumetric strain monitoring, compressive strength measurement, SEM image analysis, and durability testing) was performed to verify the mechanical behavior of biopolymer-treated Hwangtoh. Moreover, a brief analysis of the economic and environmental effect was performed to verify the feasibility of using those biopolymers as treatment materials for engineered soil.

- Xanthan gum shows the highest compressive strength behavior and good durability. However, it is relatively expensive and its volumetric strain level is higher than the other polymers. It also has a higher E^4 value than ordinary cement.

- Chitosan is unsuitable for engineered soil in terms of strength, durability, and cost. The material is too expensive for commercialization.
- Gellan gum initially shows high strengthening behavior but also the fastest strength degradation. It also has the poorest durability behavior and, consequently, the lowest E^4 value. However, the material is competitively priced. Alternative strengthening technology needs to be developed to increase its applicability for engineered soil.

Biopolymers such as Xanthan gum and β-1,3/1,6-glucan have a better mechanical performance than cement treatment. However, most biopolymer treatments are less cost-effective than cement mixing because of their high material cost. Thus, decreasing the material cost is the most important challenge for biopolymer treatment. Recent attempts such as the biorefinery approach and finding new hypha are expected to improve the cost-effectiveness of biopolymer treatment in the near future.

CHAPTER V

PRACTICAL APPLICATIONS

5.1 INTRODUCTION

In previous chapters (Chapters 3 and 4), the interparticle behavior and strengthening phenomenon of biopolymer-treated hwangtoh was investigated through a series of theoretical and experimental studies. The final goal of this study is to suggest biopolymers as an effective, economic, and environmentally friendly material for engineered soil. The results show that β-1,3/1,6-glcuan, Xanthan gum, and Gellan gum are suitable for improving compressive strength and that Chitosan has strong resistance to drying shrinkage.

A practical application is discussed in this chapter. The materials used in this study (hwangtoh and various biopolymers) are salubrious, environmentally friendly materials. The study attempts to develop an earth material product that can be used as an indoor interior material and also foster well-being and harmony with the environment.

Optimized mixing, molding and curing conditions are defined to produce a prototype of an eco-friendly interior material that can be used with

PolycanTM. The engineering performance is verified with a qualification test suggested by the Korean Agency for Technology and Standards and compared with existing products.

A number of potential uses and challenges of biopolymer technology are suggested. Some examples of biopolymer usage that could be realized in the near future include hydraulic isolation and water waste control, quick environmentally friendly pavement, and CO_2 storage.

Besides the cost-effectiveness of biopolymers (which can be boosted by the development of production technology such as biorefineries), the engineering and marketing of biopolymer treatments are expected to undergo tremendous improvements.

5.2 PROTOTYPE: ECO-FRIENDLY INTERIOR MATERIAL

5.2.1.Materials

Natural Hwangtoh powder (described in 3.2.3) and liquid type β-1,3/1,6-glucan solution (Polycan^{TM}; described in 3.2.1) was used for production. Because β-1,3/1,6-glucan treated Hwangtoh shows the highest durability (section 4.4.4) among other biopolymers (Xanthan gum, Chitosan, and Gellan gum).

5.2.2.Manufacture

According to the Korean Agency for Technology and Standards (KATS), interior boards for housing (KS F3504 2007) must satisfy performances listed in Table 5.1.

From Chapter 3, the optimum condition for Hwangtoh improvement using β-1,3/1,6-glucan (Polycan^{TM}) can be concluded as:

(1) Solution concentration: c_o=1.0 (8.2g of β-1,3/1,6-glucan / L).

(2) Initial water content: w_o=28.5% (optimum water content for compaction).

(3) Curing temperature: 60ºC.

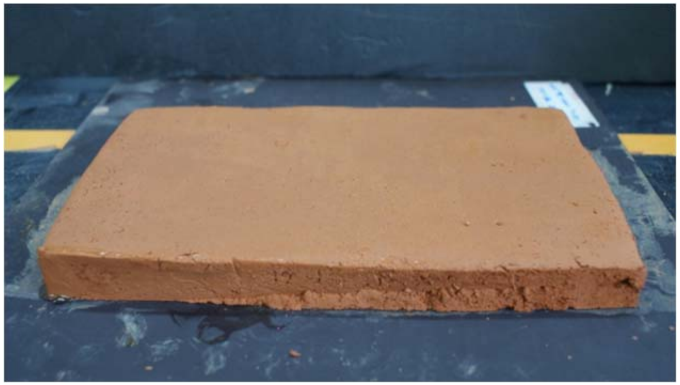
Thus, the initial mixing condition of materials was selected to be 40% (mass ratio of Polycan^{TM} / Hwangtoh).

Following sequences were performed to produce the prototype product of eco-friendly Hwangtoh interior board.

1. Mix the prepared Hwangtoh and Polycan^{TM} solution consistently using an automatic rotator (Fig. 3.3.a).
2. Place the mixed paste in a compaction mold, and compact the Hwangtoh - β-1,3/1,6-glucan mixture, to minimize air voids inside.
3. Place the compacted mixture on a flat plate. Roll the mixture thin to the target thickness (9.5, 12.5, or 15,0 mm).
4. Trim the sides and sharpen the edges using a knife, to form a rectangular shape (Fig. 5.1.a & b).
5. Measure the size (length × width × thickness) and mass of the initial extrude product.
6. Put the prepared boards in an oven (60ºC) for dehydration and biopolymer bonding activation.

Table 5.1 Standard criteria of interior boards (KS F3504 2007).

Thickness [mm]		9.5	12.5	15.0
Moisture content [%]			Under 3.0	
Breaking strength	Flexural [kPa]	94.7	100	108.3
	Moment [kPa·m]	9.5	10	10.8
Combustibility			Incombustible	
Thermal resistance [$m^2 \cdot K/W$]		0.043	0.060	0.069



(a) Sample 1 (before curing).

(b) Sample 2 (before curing).

(c) Sample 1 (after curing).

(d) Sample 2 (after curing).

Figure 5.1 Photographs of prototype samples before and after curing.

5.2.3. Curing Performance

The curing results are summarized in Table 5.2. From the same mixture (section 6.2.2), three samples were prepared. After curing, the volumetric strain induced by drying shows a range 6.5 ~ 10.7 %. Thus, the dry density increases from 0.84 ~ 0.88 to 1.33 ~ 1.35 Mg/m^3.

In general, planar components (length and width) shrink, while expands vertically. That has caused drying shrinkage crack across the board in parallel, with the width direction (Fig. 6.1.c & d). Therefore, the volume shrinkage still remains as a challenge for β-1,3/1,6-glucan polymer treatment on Hwangtoh.

Soil cracking of compacted soil occurs when pore water evaporates, inducing negative pore water pressure inside the soil. As the negative pore pressure increases effective stress in all directions, soil volume reduces consequently, remaining cracks [Kleppe and Olson 1985]. Thus, additives which can resist shrinkage (e.g. fiber reinforcement) [Miller and Rifai 2004] or initial shape control (perhaps, circular shape) can be suggested to increase the curing performance.

Table 5.2 Sample properties before and after curing.

Condition	Sample	Size [mm]			Water content [%]	Volumetric strain [%]	Dry density [Mg/m^3]
		length	width	thickness			
Before curing	1	134	233	18.6	42.2	-	0.88
	2	131	233	18.5	42.8	-	0.84
	3	128	194	12.1	42.6	-	0.88
After curing	1	127	218	19.5	1.5	7.0	1.35
	2	118	219	19.5	1.5	10.7	1.33
	3	115	181	13.5	1.5	6.5	1.33

5.2.4. Quality Testing (Flexural Test: ASTM D1635-00)

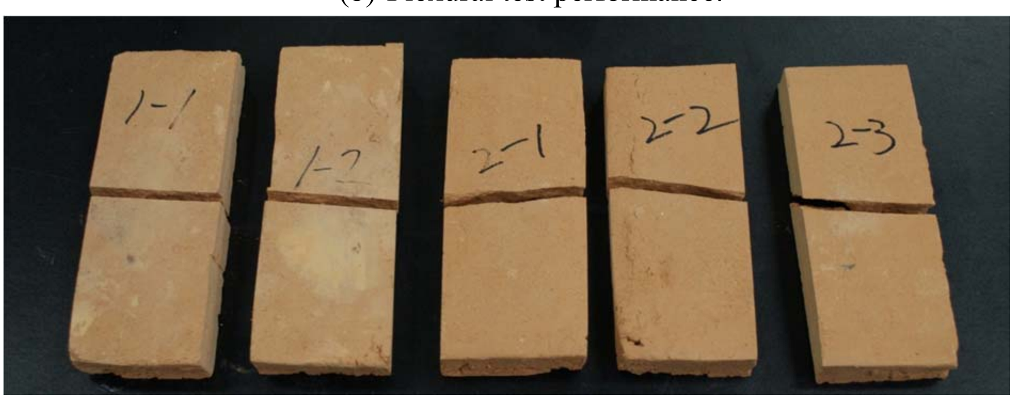
Three-point loading flexural test was performed to verify the mechanical behavior of the β-1,3/1,6-glcuan treated Hwangtoh board, using the UTM device (INSTRON 5583).

Prototype boards were trimmed into a unique planar dimension: 50 mm in width, 120 mm in length. 5 samples were prepared (Fig. 5.2.a). Flexural test was performed on each specimen, with a strain rate 0.2 mm/sec and lateral span fixed at 80 mm (Fig. 5.2.b). The maximum failure (Fig. 5.2.c) load of each specimen was calculated automatically by the data acquisition program (INSTRON Series IX). Test results are summarized in Table 5.3.

In a mechanical aspect, the flexural strength quality of β-1,3/1,6-glucan mixed Hwangtoh board satisfies the Korean Industrial Standard. The flexural strength qualification for indoor-housing board materials is 100 kPa (in average; KS F3504). The average flexural strength values of β-1,3/1,6-glucan treated Hwangtoh samples was derived to be 100.9 kPa (Fig. 5.3). Therefore, it can be concluded that biopolymers, such as β-1,3/1,6-glucan have high potentials on the development of environment-friendly housing materials.

(a) Initial view of flexural test specimens.

(b) Flexural test performance.



(c) Failure mode of flexural test specimens.

Figure 5.2 Flexural test results.

Table 5.3 Flexural test results.

Sample	Size [mm]			Weight	Maximum	Flexural
	length	width	thickness	[g]	load [N]	strength [kPa]
1-1	125.05	49.06	19.86	169.63	154	103.55
1-2	127.16	49.44	19.17	164.50	164	103.22
2-1	120.34	51.30	19.27	160.69	140	91.29
2-2	119.71	50.18	18.59	149.51	160	107.58
2-3	119.23	50.10	18.98	153.34	150	98.79
Average flexural strength [kPa]						100.89

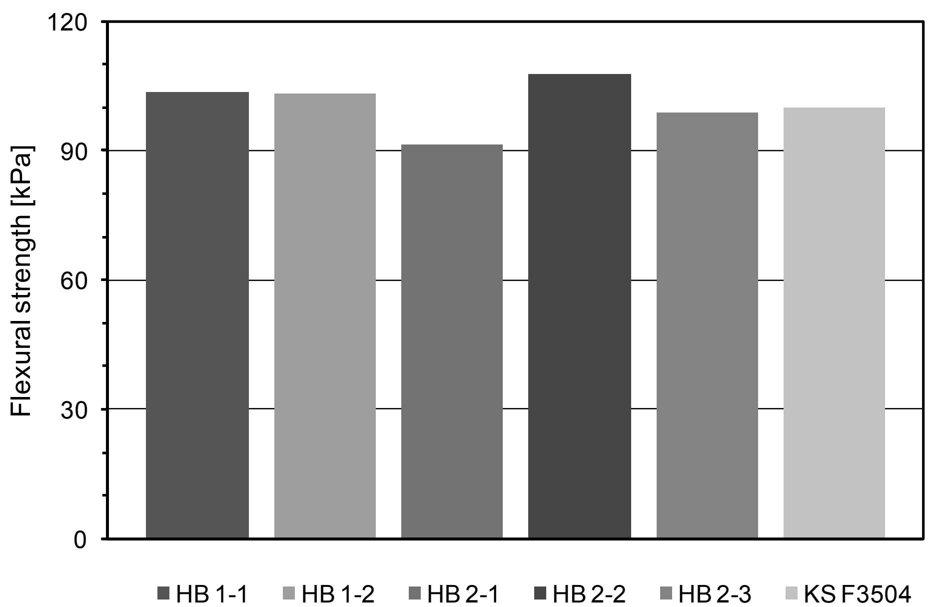


Figure 5.3 Flexural strength distribution and Korean industrial standard.

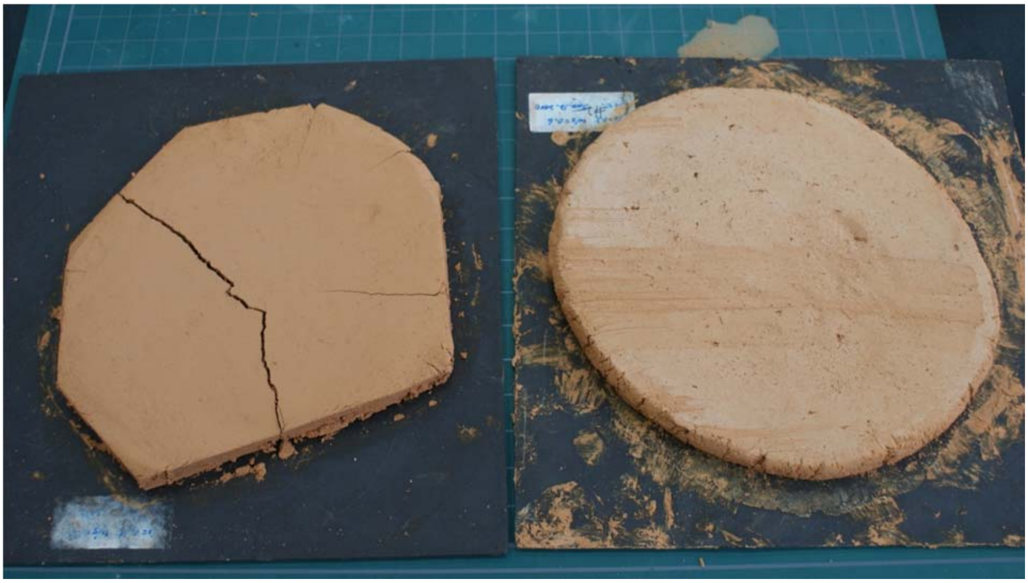
5.2.5. Verification

For detail verification, natural Hwangtoh and gypsum mixed Hwangtoh boards were prepared in laboratory (Fig. 5.4). Natural Hwangtoh (initial water content = 40%), and gypsum-Hwangtoh (gypsum / Hwangtoh ratio in mass = 10%, water / solid (Hwangtoh+gypsum) ratio in mass = 45.5%, referred to [Jang 2009]) boards were made into prototypes, following the descriptions in section 5.2.2. During curing, shrinkage cracks were generated on natural Hwangtoh board, while gypsum mixed Hwangtoh shows no cracks (Fig. 5.4.a). Thus, it seems that gypsum has resistance again crack generation.

Flexural test (section 5.2.4) was performed to evaluate the average flexural strength of each mixture board. Natural Hwangtoh board showed an average flexural strength value 50.2 kPa, while gypsum-Hwangtoh board was measured to be 103.4 kPa.

Figure 5.5 compares the flexural strength of each condition: KS qualification standard, natural Hwangtoh, β-1,3/1,6-glucan treated Hwangtoh, gypsum mixed Hwangtoh. The results show that both β-1,3/1,6-glucan and gypsum improve the flexural strength up to 2 times higher than natural Hwangtoh, satisfying the KS qualification (KS F3504), simultaneously.

Therefore, in the aim of physical performance, β-1,3/1,6-glucan treated Hwangtoh is suitable to become an indoor finishing or interior material.



(a) Natural Hwangtoh board (left), Gypsum-Hwangtoh board (right) after oven drying.

(b) View of flexural test specimens.

Figure 5.4 Natural and gypsum mixed Hwangtoh boards.

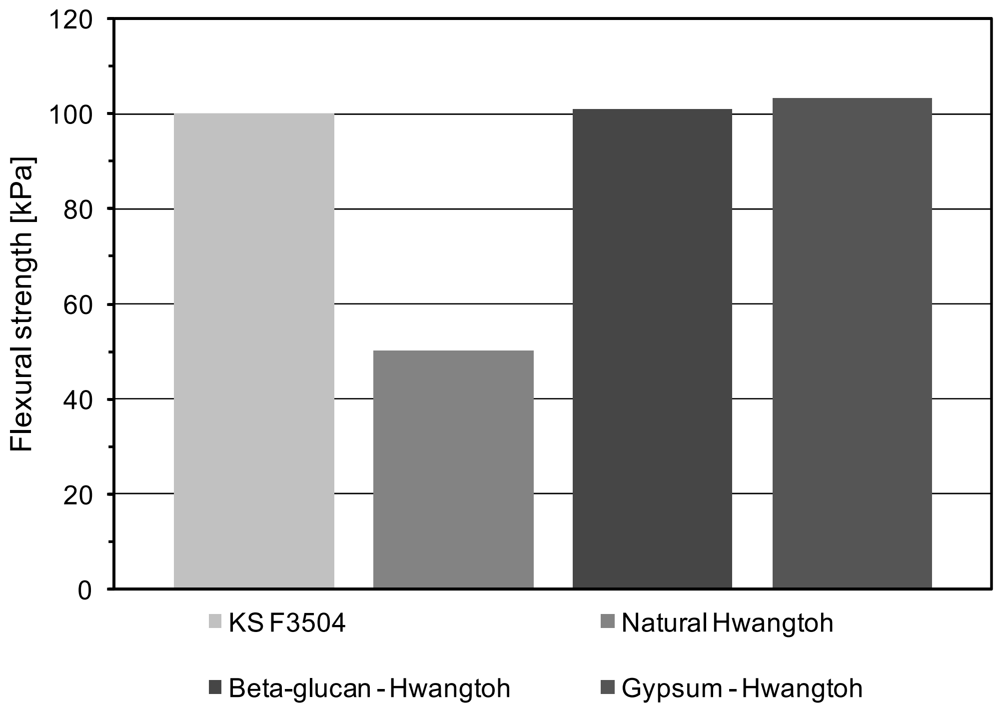


Figure 5.5 Flexural strength values of KS F3504 standard, natural Hwangtoh, β-1,3/1,6-glucan – Hwangtoh, and gypsum – Hwangtoh boards.

5.2.6.Economic Analysis

The international gypsum price in 2008 was 9 \$/ton [Roskill 2009]. The recent market price of Polycan™ (liquid type β-1,3/1,6-glucan solution used in this study) is 3 \$/L (www.glucan.co.kr/). For an environmental view, carbon dioxide emission related the gypsum is 0.7 kg CO_2/kg [Buchanan and Honey 1994], while 1L of Polycan™ production emits 0.006 kg CO_2 [Seo et al. 2002].

If *W* ton of Hwangtoh is assumed to be manufactured to produce indoor materials, 0.4*W* ton of Polycan™ is required, on the other hand, 0.1*W* ton of gypsum is required. When the manufacture (mixing, packing, rolling, and curing) cost (*M*) is assumed to be equal, the total production cost, considering economic and environmental factors is derived as:

$$C_{gypsum}\ [\$/\mathrm{t}] = \{9\ [\$/\mathrm{t}] \times 0.1W\} + \{22\ [\$/\mathrm{t\ CO_2}] \times 700\ [\mathrm{t\ CO_2/t}] \times 0.1W\} + M \quad (5.1)$$

$$C_{Polycan}\ [\$/\mathrm{t}] = \{3,000\ [\$/\mathrm{t}] \times 0.4W\} + \{22\ [\$/\mathrm{t\ CO_2}] \times 6\ [\mathrm{t\ CO_2/t}] \times 0.4W\} + M \quad (5.2)$$

Equation 5.1 represents the case of 10% gypsum treatment, while Eq. 5.2 indicates the situation of 40% Polycan™ treatment. Both equations can be simplified as:

$$C_{gypsum}\ [\$/\mathrm{ton}] = 1540.9W + M \quad (5.3)$$

$$C_{Polycan}\ [\$/\mathrm{ton}] = 1252.8W + M \quad (5.4)$$

Eqs. 5.3 and 4 show that, even the material cost using Polycan™ is extremely expansive ($0.9W << 1{,}200W$), consideration on the environmental impact evaluates Polycan™ treatment to become an economic and environment-friendly production, regardless of the production scale.

5.3 POSSIBLE APPLICATIONS

5.3.1. Bioclogging

Bioclogging is a biological activity inducing hydraulic conductivity degradation in soil [Mitchell and Santamarina 2005]. Generally, bioclogging is the result of micro-scale phenomena such as: (1) Bacterial transportation and attachment on mineral surfaces, (2) Growth, multiplication, mass accumulation of bacteria, and development of micro by-products on mineral surfaces, reducing the void size, (3) excrement of by-product polymers, and (4) trap and occlusion of void throats induced by extracellular polymers [Mitchell and Santamarina 2005]. However, the period required for biomass accumulation (step 2) for sufficient bioclogging is long and also unpredictable [Seki et al. 2006].

Thus, investigating appropriate biopolymers and examining their clog and isolation performance is an important topic for further studies. Main considerations should be:

- Clogging effect appearance and maintenance period.
- Duration of the clogging effect related with biodegradation.
- Heavy metal adsorptivity and critical point for leakage.
- Selective filtering phenomena and efficiency.

5.3.2. Carbon Dioxide Storage

Biopolymers such as proteins can indeed stabilize carbon dioxide water emulsions effectively [Murray et al. 2006]. Generally, both liquid and supercritical CO_2 are not miscible with water [McHugh and Krukonis 1994; Mesiano et al. 1999]. However, the existence of proteins improves the potential of emulsification of CO_2 in water.

In details, a beta-1,3-polyglucan (KUSP1) is reported to form gels with CO2 molecules in carbon dioxide miscible [Raje et al. 1999]. Meanwhile, Chitin and Chitosan, which are biologically renewable, biodegradable, biocompatible, not-toxic, and biofunctional biopolymers, are efficient and reversible fixing agents for carbon dioxide [Xie et al. 2006].

Therefore, further studies are required to investigate and explore new biopolymers which can adsorb and stabilize CO_2. CO_2 storage is a recently spotlighting technology to reduce the amount of greenhouse gas inducing global warming. Storage rate improvement and CO_2 well stabilization are key issues in the field. Thus, biopolymer technology is expected to promote the development of CO_2 sequestration and storage.

5.3.3. Pavement: Earthzyme

Earthzyme is a non-toxic soil stabilizing technology used on clay-based soils that reduces road maintenance costs due to the increased and lasting compaction and strength conditions reliably [Mgangira 2009]. Meanwhile, organic matters are reported to stabilize tropical residual soils with good performance [Huat 2006].

Earthzyme technology uses alkaline solutions and salts. Even though, they are inorganic harmless materials, they can induce indirect effects on the ground water quality and soil erosion. From previous chapters of this thesis, the strengthening behavior of biopolymers is sufficiently verified. Thus, pavement technology related to biopolymer treatment becomes a possible suggestion for future applications.

5.4 CONCLUSIONS

This chapter suggests practical applications for biopolymer-treated soil. A β-1,3/1,6-glucan-treated Hwangtoh indoor finishing board was produced as a salubrious, environmentally friendly building material. The related findings are as follows:

- Prototype Hwangtoh-Polycan™ board was produced with the following manufacturing sequence: mixing, compaction (for densification), rolling (for additional densification and unique thickness), and thermal curing (at 60ºC).
- The average flexural strength of Hwangtoh-Polycan™ boards is 100.89 kPa, which satisfies the KS F3504 qualification criteria for indoor interior boards.
- Natural hwangtoh-gypsum mixed hwangtoh boards were produced and tested for verification. The flexural test results show that the β-1,3/1,6-glucan-treated hwangtoh board compares favorably with existing hwangtoh products in terms of engineering performance and cost-effectiveness.
- Further applications such as bioclogging, carbon dioxide storage, and environmentally friendly pavement are expected to expand the practical usage of biopolymer technology.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

This dissertation centered on the inter-particle characteristic, geotechnical behaviors, strengthening performance, and economic efficiency of Korean residual soil in relation to biopolymer treatment. Environment friendly biopolymers – β-1,3/1,6-glcuan, Xanthan gum, Chitosan, and Gellan gum – improve the strength properties of Korean residual soil. The main findings and conclusions from this study follow.

Korean Residual Soil (Hwangtoh)

Hwangtoh is geologically defined as kaolin group residual soil, which major minerals are halloysite and kaolinite. In a geotechnical aspect, Hwangtoh is defined as fine-grained silty and clayey soil, having moderate plasticity (*MH* type soil).

Recently, medical rediscoveries shed new light on the importance and use of Hwangtoh. Major health-giving properties of Hwangtoh can be defined as:

(1) high porosity according to its honeycomb structure, (2) high thermal conductivity and heat capacity, and (3) far infrared ray emission stimulating physiological circulation in human body. Thus, applications of Hwangtoh have been expanded to housing, food, environmental treatment, and so on, recently.

Beta-1,3/1,6-glucan effect on the behavior of Korean Residual Soil

- The average tensile strength of β-1,3/1,6-glucan polymer is examined as 36.27 ~ 48 MPa, while the tensile stiffness becomes 2.11 GPa.
- The adsorption of β-1,3/1,6-glucan polymers form coats on particle surfaces and enlarge particle contact areas. Meanwhile, β-1,3/1,6-glucan polymer extends as bridges between detached particles.
- The liquid limit of β-1,3/1,6-glucan – Hwangtoh mixture increases exponentially, in regard to the concentration (c_o values) of β-1,3/1,6-glucan.
- The presence of β-1,3/1,6-glucan fibers increases the shear modulus of soil (*G*, related to shear wave velocity increase), while it has minor or even no effect on the soil axial deformation characteristics (constraint modulus, *M* related to the compressive wave velocity).
- The strengthening mechanism induced by β-1,3/1,6-glucan polymers are defined as:

(4) Adsorption: Hydrogen bonding ability of β-1,3/1,6-glucan polymers attach on Hwangtoh particles or vice versa, increasing the zeta-potential (double layer) of particle surfaces.

(5) Full attachment: The adsorption process is dominated until all Hwangtoh particles are primarily attached with β-1,3/1,6-glucan polymers.

(6) Strengthening: Regular strengthening is promoted by surplus polymers after full attachment.

- The compressive strength of 60°C cured samples show best improvement performances. However, 100°C temperature decreases and disturbs the strengthening function of β-1,3/1,6-glucan polymers.
- The strengthening behavior of 0.25% and 0.49% of β-1,3/1,6-glucan contents (ratio to soil mass) are stronger than 10% cement treatment.
- Through considerations of the economic price and environment impact, β-1,3/1,6-glucan biopolymer treatment shows advantages in engineering performance, environmental impact, and finance.

<u>Xanthan gum effect on the behavior of Korean Residual Soil</u>

Xanthan gum shows the highest compressive strength behavior and good durability. However, its price is relatively high, and volumetric strain level is highest among others.

Chitosan effect on the behavior of Korean Residual Soil

Chitosan is not suitable for engineered soil in the view of strength, durability, and cost. Especially, its material price is too expensive for commercialization. However, it shows high resistance against drying shrinkage.

Gellan gum effect on the behavior of Korean Residual Soil

Gellan gum shows initially high strengthening behavior, but shows the fastest strength degradation. Gellan gum has low durability. However, the material price of Gellan gum is competitive, so alternative strengthening technology development is required to increase its applicability for engineered soil.

Prototype Eco-friendly Interior Material

Prototype Hwangtoh – β-1,3/1,6-glucan board show similar flexural strength compared to existing interior boards, also satisfying the industrial qualification criteria. Thus, biopolymer treatment on soil is suitable and has strong opportunities to be developed in the future.

6.2 RECOMMENDATIONS AND FUTURE RESEARCH

From scientific and engineering points of view, it is recommended to extend this study to explore new biopolymers and related applications to control and improve the geotechnical and engineering behavior of soil. It requires numerous approaches as follows:

Scientific study

- Electro-static behavior of biopolymer fibers and their adsorption phenomenon (progress and adhesive strength).
- Critical conditions for the degradation behavior of biopolymers and the induced carbon emission characteristic.
- Multi-convergence of biopolymers (mixing several biopolymers together) for improved complementary functions.

Engineering and Geotechnical study

- Biopolymer treatment on other soils: rock, coarse soil, sand, weak clay, etc.
- Extend geotechnical verifications to other typical biopolymers.
- Bioclogging and hydraulic conductivity variation induced by biopolymer treatment.
- Optimal strengthening condition evaluation.

Numerical study

- Develop an enhanced algorithm to consider the adsorption and strengthening effect of biopolymers.
- Prediction algorithm of the degradation of biopolymers.

Practical applications

- CO_2 adsorption and storage efficiency improvement using biopolymers.
- Development of an environment-friendly pavement method using biopolymers and verification through test-bed application.

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요 약 문

지반, 즉 흙은 원재료(모암)의 형태학적, 물리적, 화학적, 그리고 광물 특성에 따라 다양한 구성 성분으로 이루어진 천연재료이다. 흙의 생물학적 구성 및 거동 특성은 지반공학적으로 매우 중요한 고려사항 중 하나이다. 하지만, 아직까지 유기물 함량토의 거동 특성 및 발현 메커니즘에 대한 포괄적이고 체계적인 접근이 부족한 실정이다. 따라서 본 연구에서는 흙 속의 유기질 함량이 흙의 거동에 미치는 영향을 파악하기 위해 다양한 이론적, 실험적 접근 방법을 통해 미시적, 거시적 관점에서 유기질 함량토의 거동 특성을 규명하였다. 이를 위해, 미생물 및 박테리아의 생명활동 부산물인 바이오폴리머(biopolymer)를 주 재료로 삼아 다양한 조건에 따른 흙의 강도 발현 및 안정화 특성을 파악하였다.

본 연구의 대상토로 흔히 황토로 잘 알려진 화강잔류토를 사용하였다. 황토는 지반공학적으로 무기질의 실트질 점토로 분류되며, 주요 구성광물은 할로이사이트(halloysite)와 카올리나이트(kaolinite)이다. 황토는 높은 흡착능, 자정능력, 그리고 원적외선 방사 특성을 지닌 친환경 재료이다. 하지만, 낮은 강도와 내구성은 다양한 환경적, 의학적, 그리고 건강상의 장점을 지녔음에도 불구하고 건설 재료로써 황토의 공학적 적용 및 저변 확대를 저해하는 장애요소로 작용하고 있다. 따라서 본 연구에서는 친환경 바이오폴리머 기술을 이용하여 황토의 공학적 거동을 증진시키고자 하였다.

바이오폴리머는 살아있는 미생물 또는 박테리아들이 생산하는 중합체로써 의가소성(pseudoplasticity), 높은 흡착력 및 인장강도, 안정화 및

팽창성을 지닌 재료로, 이미 의학, 의약, 식품, 미용 분야에서 폭넓게 사용되고 있다. 최근에는 지반공학 분야에서도 토양 안정제 및 이수(mud) 팽창제로 이용되는 사례가 보고되고 있으나, 전반적으로 그 적용 및 거동 특성에 대한 이해가 부족한 실정이다.

따라서 본 연구에서는 대표적인 바이오폴리머인 베타글루칸(beta-1,3/1,6-glucan), 잔탄검(Xanthan gum), 키토산(Chitosan), 그리고 젤란검(Gellan gum)을 사용하여, 각 바이오폴리머들이 황토와 반응하여 어떠한 거동 특성을 보이는지 파악하였다. 이를 위해, 다양한 실험 연구를 통해 바이오폴리머를 처리한 황토의 액성한계, 다짐특성, 응력-변형률 관계, 탄성파 속도, 불구속일축압축강도, 건조수축률, 풍화저항성, 굽힘강도, SEM(주사전자현미경) 영상 등을 평가 및 분석하였고. 나아가 처리 기술에 대한 경제성 및 환경비용 분석을 실시하였다.

베타글루칸을 처리한 황토의 거동 특성은 베타글루칸 폴리머와 황토 입자간 흡착 및 인장강도에 지배되는 결과를 보였다. 포화 및 불포화 조건에서는 베타글루칸 폴리머들이 황토 입자간의 전단 강성을 증진시키고, 동시에 높은 친수성으로 인해 흙 전체의 습윤 함유량을 높이는 결과를 보였다.

반면, 건조 상태에서는 베타글루칸 폴리머들이 우선적으로 황토 입자와 흡착 관계를 형성하고자 하는 거동을 보였다. 하지만 베타글루칸 함유량이 증가하게 되면, 흡착되고 남은 잉여 폴리머들이 입자와 입자, 폴리머와 폴리머 간 결합 상태 특성을 증진시키는 작용을 하여 전체적인 흙의 강도가 증가됨을 확인할 수 있었다.

잔탄검은 황토 입자와 입자 사이를 거미줄처럼 연결하여 전체적으로

매우 견고한 황토–잔탄검 매트릭스를 형성하였다. 이로 인해 잔탄검은 본 연구에서 다룬 네 가지 바이오폴리머 중 가장 높은 강도 및 내구성을 보였다.

키토산은 아미노기(NH_3)를 함유하고 있어 수소결합력이 매우 강한 바이오폴리머이다. 실제로 키토산을 처리한 황토는 입자와 입자들이 면–면(face-to-face)의 판상구조를 보였다. 이로 인해 폴리머 자체의 인장 특성은 저하되어 매우 낮은 압축 강도 특성을 보였다. 하지만, 건조수축 저항성은 다른 바이오폴리머 보다 높은 경향을 보여, 변형률 제어에 효과가 있는 것으로 판단되었다.

젤란검은 온도에 민감한 바이오폴리머로 가열한 후 냉각시키면서 흙 속에서 젤(gel)을 형성하여 초기 강도는 가장 높은 결과를 나타냈다. 하지만, 생분해(biodegradation) 속도가 빨라 장기 거동에서는 강도가 점점 낮아지는 결과를 보였다.

기존의 공학적 지반 개량 공법(시멘트 주입)과 비교해보면, 강도, 내구성 그리고 경제성 측면에서 베타글루칸과 잔탄검이 시멘트를 대체할 수 있는 경쟁력 있는 친환경 지반개량 재료로 판명되는 반면, 키토산과 젤란검은 낮은 강도 및 내구성으로 인해 경제성 및 효율성이 저하되는 것으로 판단되었다. 바이오폴리머의 가장 큰 장점은 시멘트 등과 비교했을 때 이산화탄소의 배출량이 현저히 낮다는 점이다. 따라서 향후 지속적으로 강화될 탄소배출규제 및 탄소세 정책을 고려하면, 바이오폴리머를 이용한 건설 기술의 개발은 매우 경쟁력 있는 분야로 성장할 것으로 전망된다.

실용화 모색 방안으로 베타글루칸을 이용한 친환경 건축 내장재의 시제품을 직접 제작하여, 기존의 황토 관련 내장 제품들과 비교하였다.

연구 결과, 베타글루칸을 이용한 친환경 건축 내장재료의 성능이 한국산업규격을 만족시킴과 동시에 기존의 제품들(천연황토 또는 석고처리 황토보드)과 비교해도 강도 및 내구성 그리고 가격 면에서 경쟁력이 있음을 검증 하였다.

본 연구에서는 바이오폴리머 응용 기술이 흙에 대한 기존의 시멘트 및 화학처리 기술들을 대체할 수 있다는 점을 공학적, 경제적, 그리고 환경적 측면에서 검증하였다. 따라서 향후 바이오폴리머와 관련된 다양한 실용화 및 상업화 기술들의 개발이 예상된다. 특히, 지반공학적 측면에서 친환경 건축 및 내장 재료, 도로포장, 급속시공 및 안정화, 이산화탄소 저장 분야 등에 폭넓게 적용할 수 있을 것으로 기대된다.

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항상 지근거리에서 부족함 많은 제자에게 가르침과 조언을 아끼지 않으신 이승래 교수님과 김동수 교수님께 감사 드립니다. 또한 학위논문 심사위원으로서 제 연구에 큰 관심을 갖고 환경 측면에서의 고려사항을 보강해주신 한종인 교수님과 늘 실험적 열정과 탄성파에 대한 고민을 함께 나눠주신 고려대학교 이종섭 교수님께도 감사드릴 일이 너무 많습니다. 아울러, 지난 10년 동안 다양한 지식과 경험을 쌓게 해주신 헌신적인 KAIST 건설 및 환경공학과의 모든 교수님들께도 감사의 인사를 드립니다.

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감사를 표합니다.

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나의 평생 지기인 충북과학고 10기 동무들 – 곽철빈, 이민수, 김창현, 이윤희 군, 이동준 박사, 표상연, 정주리, 이정아 양 – 모두 고맙다. 너희가 있기에 10년 넘게 정진해 올 수 있었다. 그리고 늘 형을 믿고 따라준 김병주, 남윤성, 신영재, 염철민 군을 비롯한 모든 후배님들에게 고마움을 표합니다. 아울러, 대학원 생활의 재충전 공간이었던 스윙피버와 볼링클럽 마핀에서의 소중한 인연들을 잊지 않겠습니다.

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2010년 5월, 싱그러운 KAIST 교정에서
장일한 배상

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3. Chang, I.H., and Cho, G.C., 2006, "Monitoring of the Consolidation Behavior of Reclaimed Clay using Piezoelectric Bender Elements", *Proceedings of the 3rd International Workshop on Smart Materials and Structures Technology 2006*, May 29-30, 2006, Lake Tahoe, USA, DEStech Publications, Inc., pp. 53.
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6. Chang, I., Cho, G.C., and Lee, S.W., 2007, "Characterization of Reclaimed Clay using Shear Waves", *Proceeding of the Sri Lankan Geotechnical Society's First International Conference on Soil and Rock Engineering*, Edited by Pinnaduwa H.S.W Kulatilake, August 5-11, 2007, Galadari Hotel, Colombo, Sri Lanka, CD paper 1450.
7. Chang, I., Kwon, T., Cho, G.C., and Kim, J.H., 2007. "Estimation of In-situ Undrained Shear Strength of Soft Clays from Shear Wave Velocity", *Proceedings of the 2nd International Conference on Advanced Nondestructive Evaluation*, October 17-19, 2007, BEXCO, Busan, Korea, paper #2007-185, p. A86.
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1. 장일한, 송기일, 조계춘, 이주공, 2005, "전단파속도를 이용한 연약지반 압밀상태 평가" Current Geotechnical Issues of Thick Clay Deposits, Joint Symposium of ISSMGE ATC 7 and KGSTC, September 21-22, 2005, Busan, Korea, pp. 57-64.
2. 장일한, 고영희, 이정학, 조계춘, 2005, “전단파를 이용한 준설매립 점토 지반의 압밀 상태 평가”, 대한토목학회 2005년도 정기학술대회 논문집, 대한토목학회, pp. 3421-3424.
3. 장일한, 조계춘, 고영희, 2006, “전단파를 이용한 매립 점토지반 압밀상태 평가”, 준설매립기술위원회 학술발표회, 한국지반공학회, February 3, 2006, Seoul, pp. 91-100.
4. 오태민, 장일한, 조계춘, 방은석, 김정호, 2008, “전단파속도를 이용한 해안점토의 비배수 전단강소 산정”, 대한토목학회 2008년도 정기학술대회 발표논문 초록집, Vol. 3: 지반공학, 터널공학, 대한토목학회, 대전, p. 2115-2118.

HONORS AND AWARDS

2000.03	Excellent Freshmen Scholarship (U.C Berkeley summer session visiting, June-August, 2001), KAIST, Korea.
2004.09	Kim, Bo-Jung Fundamental Science Scholarship (Research Fund 20,000,000 Won), KAIST, Korea.
2005.12	KKCNN Adachi Award for Outstanding Young Researcher, 18^{th} KKCNN Symposium on Civil Engineering, Taiwan.
2007.11	Included in "Who's Who in the World", Marquis (November 2007) 25th Edition.
2009.03.19	Exemplary Trainee Award, the 28^{th} training regiment, Korea Army Training Center, Korea.