https://doi.org/10.1016/j.enggeo.2020.105631
This is the Pre-Published Version.

Effects of biopolymers on gas permeability of unsaturated clay

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Abstract

Using sustainable biopolymers, which absorb water to form viscous hydrated colloid, may further reduce the soil permeability for earthen structures like landfill cover. Previous studies mainly investigated the biopolymer effects on water permeability of saturated soils. However, performance of hydrated biopolymer in unsaturated soil is unclear, especially for gas permeability. This study examined effects of two biopolymers on gas permeability of recompacted clay for various degrees of compaction (DOC) and gravimetric water contents using flexible wall permeameter. Soil microstructure was then analyzed by mercury intrusion porosimetry (MIP) and scanning electronic microscopy (SEM). Results showed that the gas permeability of the clay with the biopolymers was always lower than that of the pure clay at all conditions. The permeability reduction by the biopolymers relied on reduction of soil macro pores and pore clogging effects with supports of MIP and SEM results. In the clay with and without the biopolymers, increasing gas permeability with increasing water content existed due to formation of larger soil pores at higher water content. Since high viscosity of the biopolymers helps to stick the soil particles and reduce the macro pores as evident by MIP and SEM analyses, adding biopolymers suppressed the increasing trend and reverse it at DOC of 95%. Moreover, the permeability reduction by the biopolymers was enhanced with increasing water content as more water is provided to hydrate the biopolymer and therefore facilitate the pore clogging, which was identified by the SEM images.

KEYWORDS: Gas permeability, unsaturated soil, recompacted clay, gellan gum, xanthan gum

Introduction

Consideration of soil permeability is important in most earthen structures for stability analysis and mitigation of environmental pollution. Especially for the soil barriers like landfill cover system, which is one of major methods to dispose waste in developed and developing countries (Ding et al., 2012; EEA, 2013), both soil water and gas permeability are crucial to control leachate production and harmful gas emission (Jones and Rowe, 2016; Zhang and Ke, 2017). Generally, soil with low permeability like clay is preferred in constructing the barriers to minimize the pollution. For some situations, conditioning the soil in a sustainable manner is necessary to further improve the performance of the barriers.

One improvement method is incorporating the soil with biopolymers which are long chains of natural polymers with high molecular mass, such as polysaccharides. It can be mainly produced by using non-food parts of plants (Khatami and O’Kelly, 2013) and relying on bacterial fermentation (Giavasis et al., 2000). Owing to the presence of numerous functional groups such as hydroxyl group, biopolymer is capable of absorbing water through hydrogen bonds to form viscous hydrated colloid. It is used in industries for food and pharmaceuticals and cosmetic products and potentially in waste water treatment (More et al., 2014). In geotechnical engineering, investigation of using these sustainable materials has focused on controlling soil or dust erosion (Orts et al., 2000; Chen et al., 2015), enhancing mechanical property (Khatami and O’Kelly, 2013; Chang et al., 2016) as well as hydrological property which is a prerequisite for the performance of the soil barrier.

Studies regarding hydrological property of soil incorporated with biopolymers are normally related to saturated water permeability and soil water retention behavior. For saturated water permeability, reducing the high permeability of sandy soil by adding different types and concentration of biopolymers to cause soil clogging is one of the main objectives among these studies. After addition of biopolymers (e.g. xanthan gum or gellan gum) at a concentration of 2% by weight, the saturated permeability of the sand at different grading were measured in flexible wall permeameter and reduced by nearly four orders of magnitude (Bouazza et al., 2009; Wiszniewski and Cabalar, 2014; Chang et al., 2016). Only coarse sand showed a maximum reduction of the permeability by around two orders of magnitude. Although all these studies generally prove that biopolymers can significantly reduce the saturated water permeability and potentially improve soil barriers, investigation about its performance in reducing the permeability of unsaturated soil is very limited, especially for gas permeability. For unsaturated soil, in contrast to the water permeability, decreasing water content of soil increases the gas permeability of the soil. Since the unique property of the biopolymers is to absorb water and form hydration, whether the performance of them to affect soil properties is significant at low water content is still unclear.

In this study, different biopolymers were added into soil to measure its gas permeability at different water contents by flexible wall permeameter. The soil was also prepared at various degrees of compaction to investigate biopolymer effects on different void ratio. Then, samples were extracted for quantitative and qualitative measurement of the microstructure of the biopolymer amended soil by using mercury intrusion porosimetry (MIP) and scanning electronic microscopy (SEM).

Testing materials and methods

Test program

Three series of tests were carried out to consider the effects of water content, void ratio and biopolymer types on the gas permeability of biopolymer amended clay. Each series is defined according to the types of the biopolymers mixed with the clay. These three test series, namely ‘Recompacted clay’, ‘With gellan’ and ‘With xanthan’, represent the clay without biopolymers, clay with gellan gum and clay with xanthan gum respectively. Firstly, investigating the soil at different water contents is to evaluate the hydration of the biopolymers at different water contents in affecting the gas permeability of the clay. Second, studying void ratio by considering various degrees of compaction (DOC) is to determine if the performance of the biopolymers is effective at any pore volume so that lower DOC can be adopted to optimize the soil barrier. Finally, different types of the biopolymers were used to investigate whether their different properties are significant to affect their performance and thus the gas permeability of unsaturated clay. Details of the test program are summarized in Table 1.

Soil and biopolymers

Kaolin clay in powder form was used in this study. Two types of biopolymers, xanthan gum and gellan gum, which are extensively used in previous studies, were selected to be mixed with the clay. Xanthan gum can be produced from waste (Yoo and Harcum, 1999) and provided at a relative low price (Chen et al., 2015). Its pore-clogging effects, such as reducing the saturated permeability of silty sand by four orders of magnitude at a concentration of 0.5% (Bouazza et al., 2009), further optimize the cost of improving soil barriers. For gellan gum, it has good thermal stability and is stable in a wide pH range from 2 to 10 (Moslemy et al., 2003) so it is expected that its performance is not affected in the soil contaminated with pollutants such as leachate. These two biopolymers are both anionic polysaccharides with molecular weight up to an order of 1000kDa (Hoefler, 2004). Since previous studies showed that increasing concentration of the biopolymers finally reaches constant reduction in the saturated water permeability (Bouazza et al., 2009; Chang et al., 2016), 3% biopolymer concentration (w/w) was considered to provide optimal effects in this study. Basic properties of the clay with and without biopolymers at concentration of 3% were measured summarized in Table 2. BS 1377-2 (1990) and BS 1377-4 (1990) were followed to measure the Atterberg limits and compaction curve respectively.

Specimen preparation

Kaolin clay powder was first oven dried at 100±5°C to remove any soil moisture. Powder form of biopolymers was then added to the dried soil and they were mixed thoroughly in a plastic bag. To minimize the clog formation and ensure the homogeneity of soil, water was sprayed over the soil mixture step by step to achieve the desired water contents (Zhan et al., 2014). In total, the soil was mixed with three gravimetric water contents at 25%, 30% and 35% which are on the dry side of optimum water content for compaction of the kaolin clay. The soil aggregates were also broken by hands during the soil mixing so that the soil particles were able to pass through 2-mm sieve. Finally, the soil mixture was sealed in a plastic bag for 48 hours to achieve moisture equalization.

Subsequently, the soil mixture was compacted to a cylindrical specimen with diameter of 70mm and height of 70mm in seven layers. Thickness of each layer was 10mm while the interface between each two layers was scarified to ensure better layer contact. The specimen was then sealed in a plastic bag and allowed to reach moisture equalization for seven days (Bouazza et al., 2009) before gas permeability measurement. Three degrees of compaction (DOC) including 75%, 85% and 95% were considered. To ensure the repeatability of the experiment, three replicates were considered for DOC at 95%. It should be noted that all the desired degrees of compaction and gravimetric water contents are based on the clay without biopolymers. Fig. 1(a), (b) and (c) show the recompacted clay, clay with gellan and clay with xanthan respectively at DOC of 95% after the soil compaction. In comparison to the clay without the biopolymers, there were less large pores appearing on the surface of the clay with the biopolymers.

Gas permeability measurement by flexible wall permeameter

The gas permeability tests of the soil were carried out using flexible wall permeameter according to ASTM D6539 standard test method (ASTM, 2006). The photo of experimental set-up is shown in Fig. 2. A constant gradient of pressure was controlled by pressure regulators to generate air flow through the specimen while confining pressure of 20kPa was applied. Three pressure transducers were installed to monitor the confining pressure and pressure changes at both inflow and outflow. A mass flow meter was installed to measure the outflow rate. As the typical pressure of landfill gases is within 10kPa (McBean et al., 1995), differential pressures at 5kPa, 10kPa and 20kPa were supplied from the bottom to the top of each specimen for gas permeability measurement. The selected pressures also comply with ASTM requirement about the pressure control ranging from 5kPa to 35kPa. Gas permeability of each specimen was taken as the average of the measurement at these pressures. All tests were performed at 25±1°C. At the end of the tests, samples were taken to check gravimetric water contents of each specimen by oven drying. The final gravimetric water content of each specimen was ±1% of the target water content.

Data interpretation

Calculation of the gas permeability of the soil was based on Darcy's law, which is for steady-state incompressible flow through porous materials in one-dimensional isothermal condition (Vangpaisal and Bouazza, 2004; Moon et al., 2008). The volumetric flow rate (Q) [L^3T^{-1}] of flow through soil can be expressed as

$$Q_{outflow} = \frac{k}{\mu} A \frac{(P_{inflow}^2 - P_{outflow}^2)}{2P_{outflow}H}$$

where H is the height of the soil specimen [L]; A is the cross-sectional area of the specimen [L^2]; μ is dynamic viscosity of the fluid [$ML^{-1}T^{-1}$]; P_{inflow} and $P_{outflow}$ are the pressure of the fluid at inlet and outlet respectively [$ML^{-1}T^{-2}$]; k is intrinsic permeability [L^2]. The major assumption of Darcy's law considers only laminar advective flow, rather than gas diffusion. Unlike water flow, the velocity of gas flow along the pore surface may not be zero, which is called Klinkenberg effect or slip flow. This can be ignored when the differential pressure for gas flow is less than 20kPa (Brusseau, 1991).

Measurement of soil microstructure by MIP and SEM

When the gas permeability tests were finished, samples were extracted from the soil specimens at particular conditions and trimmed into small pieces (~1cm^3). To preserve the pore structure and minimize the shrinkage of samples, freeze-drying the samples using liquid nitrogen was adopted (Delage et al., 1982). The soil microstructure of the samples were then measured using mercury intrusion porosimetry (MIP, PoreMaster 33, Quantachrome Instruments) and scanning electronic microscopy (SEM, JSM-6390, JEOL).

Results and discussion

Reducing the gas permeability of the clay at different degrees of compaction (DOC) by the biopolymers

Fig. 3(a) and (b) shows the gas permeability of the clay with and without the biopolymers at different degrees of compaction for the water content of 25% and 35%, respectively. As the variation of the gas permeability of the soils with the degrees of compaction for the water content at 30% was similar to those at 25% and 35%, the data was not reported to avoid repetitiveness. Compared with the recompacted clay, the gas permeability of the clay with either gellan gum or xanthan gum was always lower at any degrees of compaction. For particular water content, increasing the degree of compaction further enhanced the difference between the gas permeability of the clay with and without the biopolymers. At water content of 25%, the gas permeability of the clay with the biopolymers was at least 25% and 60% lower than that of the recompacted clay at 75% and 95% of DOC, respectively. Only at DOC of 75%, the reduction of the gas permeability by xanthan gum was relatively higher than that by gellan gum and reached nearly 0.7 order of magnitude. When the water content became 35%, increasing DOC from 75% to 95% increased the permeability reduction due to the addition of both biopolymers from around 0.9 to 2 orders of magnitudes. The effects of using the biopolymers to reduce the gas permeability mainly rely on their hydrated biopolymer chains with high viscosity, which in turn affect the soil microstructure including the pore size distribution and the arrangement of the clay particles. Details of the mechanism for the biopolymer effects will be discussed in the next section about the gas permeability of the soils at different water contents. An increase in the degrees of compaction represents the increase in the soil dry density and the decrease in the pore volume. Since increasing DOC also increases the amount of the biopolymers, more biopolymer molecules are available to absorb water for hydration and cause the clogging in the decreased pore volume. As a result, the gas permeability of the clay with biopolymers was lower than that of recompacted clay at any degree of compaction. Addition of the biopolymer further reduced the gas permeability of the clay at the higher DOC.

Effects of water content on the gas permeability of the clay with and without biopolymers

i) Recompacted clay without the biopolymers

Fig. 4 shows the variation of the gas permeability of the recompacted clay with different water contents. Different lines represents the clay compacted at different DOC. At DOC of 75%, the gas permeability increased with increasing water contents. This trend was consistent with the gas permeability of the recompacted clay at 85% of DOC. Until the clay was compacted at 95% of degree of compaction, the gas permeability was nearly constant with increasing water contents. Once the clay was compacted at higher degree of compaction, the increasing trend in the gas permeability due to higher gravimetric water contents was reduced. Such increasing trend found in this study is in contrary to the theoretical expectation that increasing soil water content should decrease the gas permeability of soil since the pores for air flow in the soil are reduced and occupied by the water (Fredlund et al., 2012). Owing to the formation of different soil fabrics, especially in the fine-grained soils, the pore size distribution at the same void ratio is affected and thus the increasing trend in the gas permeability with the increase of the water content can be caused. Wickramarachchi et al. (2011) used a model following the power law to estimate the gas permeability of the silty sand with the change of soil-air content. After the soil-air content reached up to 0.2 $m^3 m^{-3}$, the gas permeability of the silty sand started to converge with the change in the soil-air content. This is consistent with Zhan et al. (2014), which indicated that the gas permeability of the compacted loess was constant below 30% of degree of saturation. It may be attributed to most of the gas flow occurring through the well-connected part of the macro pores. However, in this study, the increasing trend was present even at low DOC (75%) with degrees of saturation from around 23% to 33%, which are calculated from the gravimetric water contents with assumption of non-deformed soil specimens. Since the fine content in clay is higher than that in the loess, higher fine content has greater potential to alter soil structure under the change of the soil water contents (Moldrup et al. 2001). Therefore, increasing the water contents induces formation of more large pores in compacted clay and causes the increasing trend at low degree of saturation in the clay. Moreover, experimental results from Moon et al. (2008) found that at dry side of compaction using modified Proctor method, the gas permeability of the compacted soil decreased first and increased again with the increase in the water content even though the void ratio was reduced. As the focus of the study is to investigate the gas permeability of clayey soil prepared by different compaction methods at different water contents from dry to wet optimum, there is no intended interpretation given for this finding. The increasing trend in the gas permeability was also reported in Zhan et al. (2014) when the loess was added with water by different mixing methods to achieve the degree of saturation above 30%. Zhan et al. (2014) proposed that increasing water content makes the soil aggregates larger and more non-uniform. Such soil aggregates will then create large void of inter-aggregate in a heterogeneous compacted soil specimens and increase the gas permeability at higher water contents. Although the soil aggregates should play a role in changing the soil structure at the same void ratio to cause increasing gas permeability, direct measurements of the relevant soil structure by qualitative and quantitative analysis is very limited. In the later section of this study, soil microstructure of the particular soil specimens measured by MIP and SEM will be given and discussed to provide more insights about the increase of gas permeability of the compacted clay with increasing water content.

ii) Recompacted clay with biopolymers

Fig. 5 shows the gas permeability of the clay with the biopolymers at different water contents. Each line represents the soil compacted at particular DOC. At any water content, the gas permeability of the clay with the biopolymers was always lower than that of the recompacted clay. In accordance with the recompacted clay in Fig. 4, an increasing trend with was also observed in the gas permeability of recompacted clay amended with both biopolymers for 75% and 85% of DOC when the soil water content increased. Until the degree of compaction was increased to 95%, the gas permeability of the clay with these biopolymers decreased with increasing water content. This is opposite to the change of gas permeability with the water content at DOC of 75% and 85%. More importantly, compared with the recompacted clay, adding the biopolymers suppressed the increasing trend at DOC of both 75% and 85% and finally reversed the trend at DOC of 95%. Besides, regardless of the degree of compactions, the permeability reduction by the biopolymers at high water content was always more significant than that at low water content. Addition of either xanthan gum or gellan gum to the clay showed negligible difference in reducing the gas permeability, except the one at DOC of 75% and the water content of 25%. This implies that the mechanism for these two hydrated biopolymers to affect the gas permeability of the clay at different water contents was similar.

In this study, the biopolymer effects to reduce the gas permeability predominately depend on reducing the large soil pores by high viscosity of the hydrated biopolymer chains. Also, the hydration of the biopolymer chains causes the clogging in the soil pores. It should be noted that the term 'gelation' is not defined as the hydration of the biopolymer chains in the following discussion. Generally, hydrated biopolymers can be classified into two types, thickening agents and gelling agents. Thickening agents refer to the hydrated biopolymer chains that are randomly associated with each other to form non-specific entanglement while gelling agents are defined as the orderly association between the biopolymer chains through the linkage by the junction zone (Saha and Bhattacharya, 2010). The junction zone is formed by the attraction between the biopolymer molecules through the chemical bonding such as ionic bond and hydrogen bond. This links the biopolymer chains to construct a three-dimensional network, confine the solvents like water in the network and finally become the gelation. In terms of the effects caused by the hydrated biopolymers after the water absorption, the thickening agent increases the viscosity of the solution without suspending the particulates owing to weak interaction between the hydrated biopolymer chains (Hoefler, 2004). In addition to increasing the viscosity, the gelling agent is able to permanently trap the particulates in the three dimensional network of the gelation. Gellan gum and xanthan gum used in this study are the gelling and thickening agent respectively. The desired water contents in the clay only allowed only the biopolymer chains to hydrate while the formation of gelation by the gellan gum was not effective. The SEM analysis showing the hydration of the biopolymer chains in the soil will be discussed in the later section to support the above explanation. Such phenomenon implies that gellan and xanthan gum contributed similar effects to reduce the gas permeability of the clay by the hydration of the biopolymer chains. The hydrated biopolymer chains in both types helped to stick the clay particles together owing to their highly viscous nature so the soil particles were packed closely with the others and the amount of large pores for the gas flow were reduced. Referring to Fig. 1 which is a photograph showing the surface of recompacted clay with and without the biopolymers after compaction, there were lots of pores on the surface of the recompacted clay while no obvious pores were found on the smooth surface of the clay with the biopolymers. The results of MIP presented in next section also supported that adding the biopolymers does reduce the macro pores in the clay. It is expected that presence of the biopolymers can ensure the homogeneity of the soil specimens by decreasing the size of macro pores and decrease the preferential paths for the gas flow.

On the other hand, the hydration of biopolymers after absorbing the water helped to fill and clog the pores between the clay particles and thereby reducing the available paths for the gas flow in the clay. When the water contents in the soil increased at particular DOC, more water was provided to hydrate the biopolymer chains and enhance their clogging effects in the soil pores. This is why the permeability reduction by the biopolymers increased with increasing water content, as indicated in Fig. 5. Furthermore, since the clogging effects caused by the gelation was relatively less significant, addition of gellan and xanthan gum in the clay resulted into similar trends in the gas permeability of the soil with the change in the water content, except the one at DOC of 75% and the water content of 25%. At this particular condition, the void ratio was higher and the amount of large pores were most abundant while the least amount of water was provided for the biopolymers to hydrate and clog the soil pores. The reduction of gas permeability by reducing the large pores due to the high viscosity of the biopolymers dominated that by the pore clogging at this condition. The intrinsic viscosity of the biopolymer solution is proportional to their molecular mass (Saha and Bhattacharya, 2010). Higher molecular mass represents higher viscosity of biopolymer solution at a constant concentration. Since the molecular mass of xanthan gum is higher than that of gellan gum (Hoefler, 2004), the reduction of large pores by xanthan gum was more effective than that by gellan gum. Consequently, xanthan gum gave a better reduction in the gas permeability than the gellan gum at DOC of 75% and water content of 25%. The better performance by the xanthan gum is also consistent with the previous results showing that xanthan gum at concentration of 1% reduced the saturated water permeability of the soil more than that by gellan gum (Bouazza et al., 2009; Chang et al., 2016). With the promising improvement in the water and gas permeability of the soil, using biopolymers provides a sustainable alternative to enhance landfill covers for minimizing the water infiltration and odour.

Pore size distribution of the clay with and without gellan gum at DOC of 95% by using MIP

As high compaction is usually constructed for the landfill covers while the effects of both gellan and xanthan gum on gas permeability of the clay were similar, the pore size distribution of the clay with and without gellan gum at DOC of 95% was measured and shown in Fig. 6. Both the differential intruded pore volume with respect to log of entrance pore size and cumulative percentage of the pore volume are reported. Bimodal pore size distribution, which has clear peaks of the micro and macro pores were observed in most the conditions. This is commonly found in the soil compacted on the dry of optimum due to the formation of aggregates during the compaction (Romero et al., 2011). Only for the recompacted clay at the water content of 25%, the peak of the macro pores did not exist while the large pore having similar differential pore volume appeared over a range of the pore diameter until the peak of micro pore was reached. In recompacted clay, increasing the water content of the soil from 25% to 30% did not change the intensity of the peak of the micro pores. A sharp increase in the intensity of the peak for micro pores by around 40% occurred when the water content increased to 35%. Negligible changes in the pore diameter were found for the peak of micro pores in the clay at any water content. At the same time, when the clay at the water content of 30% is compared with that at the water content of 25%, there was reduction in the amount of the macro pores over a range of pore diameter from 2μm to 7μm. Together with increased intensity of the micro pores, the gas permeability of the clay at 30% water content was lower than that at 25% water content, as indicated in Fig. 5. However, once the water content of the clay was increased to 35%, there were larger macro pores with the diameter ranging from 10μm to around 80μm. These larger macro pores were dominant and increased the flow rate of gas through the clay. Although increasing the water content in the clay tends to reduce the pores filled with air, larger macro pores induced at the high water content lower its portion filled with water and increase the connectivity of air-filled pores. Such larger pores also increased the heterogeneity of the soil and provided more preferential flow paths for gas. Accordingly, the gas permeability of the clay shown in Fig. 4 decreased slightly at the water content of 30% and then increased again at the water content of 35% due to the presence of larger macro pores. Based on the above results, it is believed that the formation of larger macro pores increased with increasing water content. Such larger macro pores dominated the effects by the reduction of pores filled with air at higher water content. This leads to increasing gas permeability with the increase of the water content in the clay for DOC of 75% and 85% as shown in Fig. 4.

In the clay added with gellan gum, increasing water content from 25% to 35% increased the intensity of the peak for micro pores by around 45%. The pore diameter of the peak for micro pores was slighted increased by 0.1μm. The trend in changing the micro pores with increasing water content in the clay with gellan gum was similar to that in the recompacted clay but the intensity of the micro pores was reduced by the biopolymers. For the peak of macro pores in the clay with gellan gum, the pore diameter was increased from 1μm to 5μm when the water content increased up to 35%. However, the intensity for the peak of macro pores at the water content of 25% was two times higher than that at the water content of 35%. It is believed that the amount of macro pores predominates over the effects of the diameter of the macro pores so the gas permeability was higher at the water content of 25%. Also, higher water content in the soil provides more water for hydrating the biopolymer chains. The hydrated biopolymer chains can effectively clog more pores in the specimen with higher water content. As a result, the gas permeability of the clay with gellan gum at the water content of 35% was much lower than that at the water content of 25%, as reported in Fig. 5. When the clay with gellan gum is compared with the clay at particular water content, the diameter for the macro pores was always reduced by the biopolymers to increase the homogeneity of the soil pores and reduce the preferential path for gas flow. Eventually, the gas permeability of the clay with gellan gum was always lower than that of the clay while the increasing trend of the gas permeability with the water content was reversed by the gellan gum. Equivalently, for other DOC of 75% and 85% by comparing Fig. 4 with Fig. 5, presence of the biopolymers helps to reduce the formation of larger pores at the particular water content and clog more pores at higher water content. Hence, using the biopolymers suppressed the increasing trend in the gas permeability of the clay with increasing water content.

Microstructure of the clay with and without the biopolymers by using SEM

Fig. 7 indicates measurement of the microstructure of the clay without biopolymer (a), with gellan gum (b) and xanthan gum (c) by the SEM analysis when the specimen was compacted at DOC of 95% and the water content of 35%. The microstructure of the clay without the biopolymers was composed of both flocculated and dispersed structure of the soil particles while that of the clay with gellan and xanthan gum mainly consisted of dispersed structure. Normally, the flocculated structure can be observed in the clay compacted at the dry side of optimum (Das, 2008). The flocculated structure in the clay causes the formation of larger soil pores, which are in accordance with the pore size distribution shown in Fig. 6. As long as the biopolymers were added, the soil particles were packed together to mainly form the dispersed structure and give smaller soil pores. The negative charges of both gellan and xanthan gum increase the repulsion between the biopolymer molecules and the soil particles and finally cause a lower degree of flocculation. This situation can be analogous to clay particles under the effects of increasing pH, which provides more hydroxide ions (OH^-) to make more clay particles negatively charged. Therefore, the clay particles increase their repulsion force and decrease the final volume of the soil during the sediment test (Wang and Siu, 2006). Such analogy implies that in the clay with biopolymers, the most clay particles were closely packed to reduce larger pores. Besides, in Fig. 7(c), some dispersed clay particles were shown to stick on the hydrated biopolymer chains. Owing to the highly viscous biopolymer chains, when some clay particles form the flocculated structure like a card house, the particles rotate to stick on the biopolymer during the soil compaction and the structure changes from flocculated structure to the dispersed structure with the particles closely packed. These are why the diameter for the peak of macro pores in clay with gellan gum is lower than that in the only clay in Fig. 6.

In addition to the structure changes by the biopolymers, the biopolymer chains also help to clog the soil pores by their hydration, which is identified by the arrows in Fig. 7(c). Presence of the hydrated biopolymers occupied the soil pores and reduce the available pores for the gas flow so the gas permeability of the clay with the biopolymer was then reduced. This direct evidence supports that pore clogging by the biopolymers is one of the reasons to cause lower gas permeability in the clay with biopolymers in Fig. 5. Moreover, the hydration of both gellan and xanthan gum had similar effects on the gas permeability of the clay, irrespective of their different properties. Fig. 8(a) and (b) show the hydrated biopolymer chains at lower magnification in the clay with gellan and xanthan gum respectively. The appearance of both hydrated biopolymers were thread-like structure. Although the gellan gum has ability to form gelation as discussed previously, similar hydration of both biopolymers in these SEM images proved that the effects of gelation by the gellan gum was negligible. Either gellan gum or xanthan gum reduced the gas permeability of the clay by their high viscosity and clogging of the hydrated biopolymer chains. Even compared with the SEM images taken at equal magnification for the sand added with gellan gum (Chang et al., 2016), the hydration of the gellan gum in this study was thinner and relatively less bulky. It may be due to the limited water content provided in the unsaturated soil, unlike the soil subjected to saturation in the previous study. As a result, the gas permeability in the clay with these biopolymers had similar trends in Fig. 5 even though the properties of the gellan and xanthan gum are different.

Conclusions

When the biopolymers were applied, the gas permeability of the clay with the biopolymers were always lower, regardless of the degree of compaction and the water content. The mechanisms for both gellan and xanthan gum to reduce the gas permeability are based on the reduction of larger soil pores as well as the pore clogging. Since the hydrated biopolymer chains is highly viscous, they can help to hold the soil particles together and thus reduce the formation of larger soil pores. Also, after absorbing the water, the biopolymer can hydrate and cause the clogging in the soil pores. These two mechanisms supported by the MIP and SEM results enable the biopolymers to reduce the gas permeability of the clay.

For the effects of the water content, the gas permeability of the clay compacted at DOC of 75% and 85% increased with increasing water content while it became nearly constant with the water content at DOC of 95%. Similar trend was also found in the gas permeability of clay with the biopolymers at DOC of 75% and 85%, except 95%. Such increasing trend was attributed to the formation of the larger pores in the soil at higher water content. These larger pores leaded to the heterogeneity of the soil and provided more preferentially flow paths for gas. The MIP results confirmed that the pore diameter for the peak of macro pores was finally increased in the clay with and without the biopolymer at the water content of 35% and DOC of 95%.

However, presence of the biopolymers suppressed the increasing trend and finally reversed the increasing trend at DOC of 95%. The pore diameter for the peak of the macro pores in the clay with the biopolymer was smaller than that in the recompacted clay at particular water content. In addition, SEM analysis supported that the clay particles combined to mainly form dispersed structure due to the biopolymers, unlike the recompacted clay consisting of both flocculated and dispersed structure. Some dispersed particles was also stuck on the hydrated biopolymer chains. As a result, this implies that less large pores were formed by adding the biopolymers, which cause lower gas permeability in the clay with the biopolymers.

Furthermore, at particular DOC, the permeability reduction by the biopolymers was always higher at higher water content. Increasing water content can provide more water and enhance the hydration of the biopolymer chains so more soil pores were clogged at the higher water content. Although gellan gum and xanthan gum are different in properties, the effects of gelation, which is an additional property of gellan gum, was insignificant in this study. This is evident by the SEM images showing that the hydration of the biopolymers existed in the soil pores while similar size of the hydrated biopolymer chains was observed in the clay added with gellan and xanthan gum.

When the performance of the biopolymer at different DOC was considered, the permeability reduction by the biopolymers was enhanced with increasing DOC. As increasing DOC decreases the void ratio of the specimens and increases the amount of the biopolymer and the water, more hydrated biopolymer molecules are available at higher DOC to cause clogging in more soil pores. Overall, the use of the biopolymers, which can be produced by non-food parts of plants and bacterial fermentation, can substantially further reduce the gas permeability of the clay in unsaturated soil barriers such as landfill cover to minimize odour emission.

Acknowledgements

This study was funded by the National Natural Science Foundation of China (Grant no. 51778166), the Ministry of Science and Technology of the People's Republic of China through its 973-Program (Grant no. 2012CB719805) and the Research Grants Council of the Hong Kong SAR through its Collaborative Research Fund (Grant no. HKUST6/CRF/12R).

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Table 1. Test program

Test ID	Gravimetric water content	Degree of compaction	Biopolymer type
Recompacted clay	25%, 30%, 35%	75%	None
		85%	
		95%	
With gellan		75%	Gellan gum
		85%	
		95%	
With xanthan		75%	Xanthan gum
		85%	
		95%	

Note: Three replicates were considered for the condition at degree of compaction of 95%

Table 2. Physical properties of kaolin clay with and without biopolymers

Property	Value		
Condition	Clay	With gellan	With xanthan
Specific gravity, G_s	2.52		
Atterberg limits			
Liquid limit, LL	80	70	69
Plastic limit, PL	35	40	36
Plasticity index, PI	45	37	33
Standard compaction curve			
Maximum dry density, ρ_d (kg/m^3)	1264	1287	1259
Optimum moisture content (%)	36.2	34.5	34.3

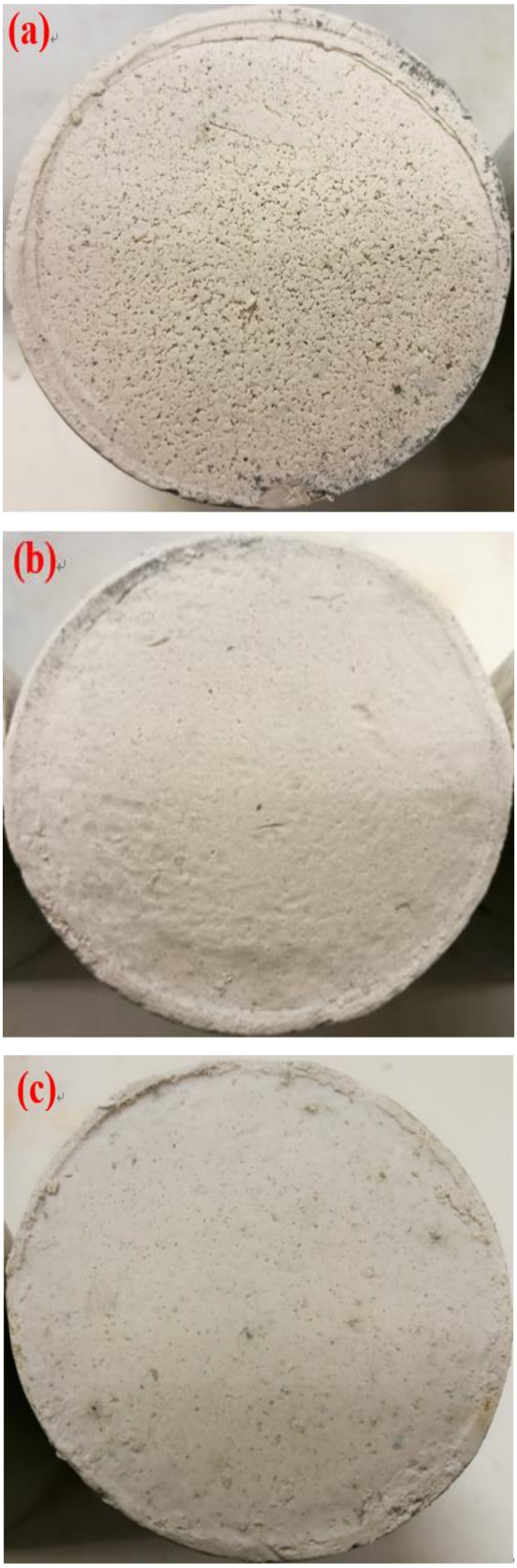


Fig. 1. Photographs taken on the surface of the recompacted clay (a), clay with gellan gum (b) and xanthan gum (c) at DOC of 95% and water content of 35% after compaction

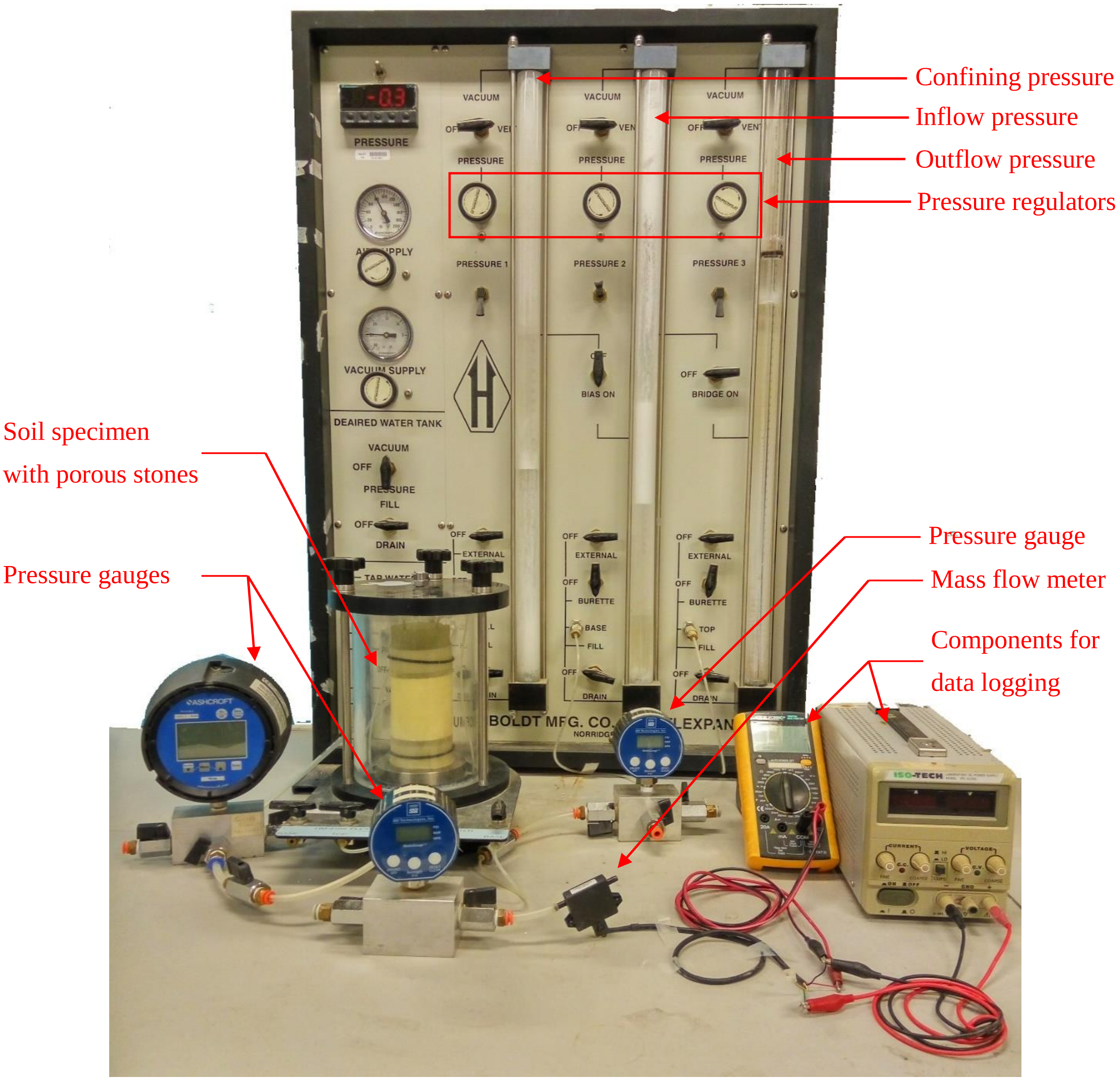
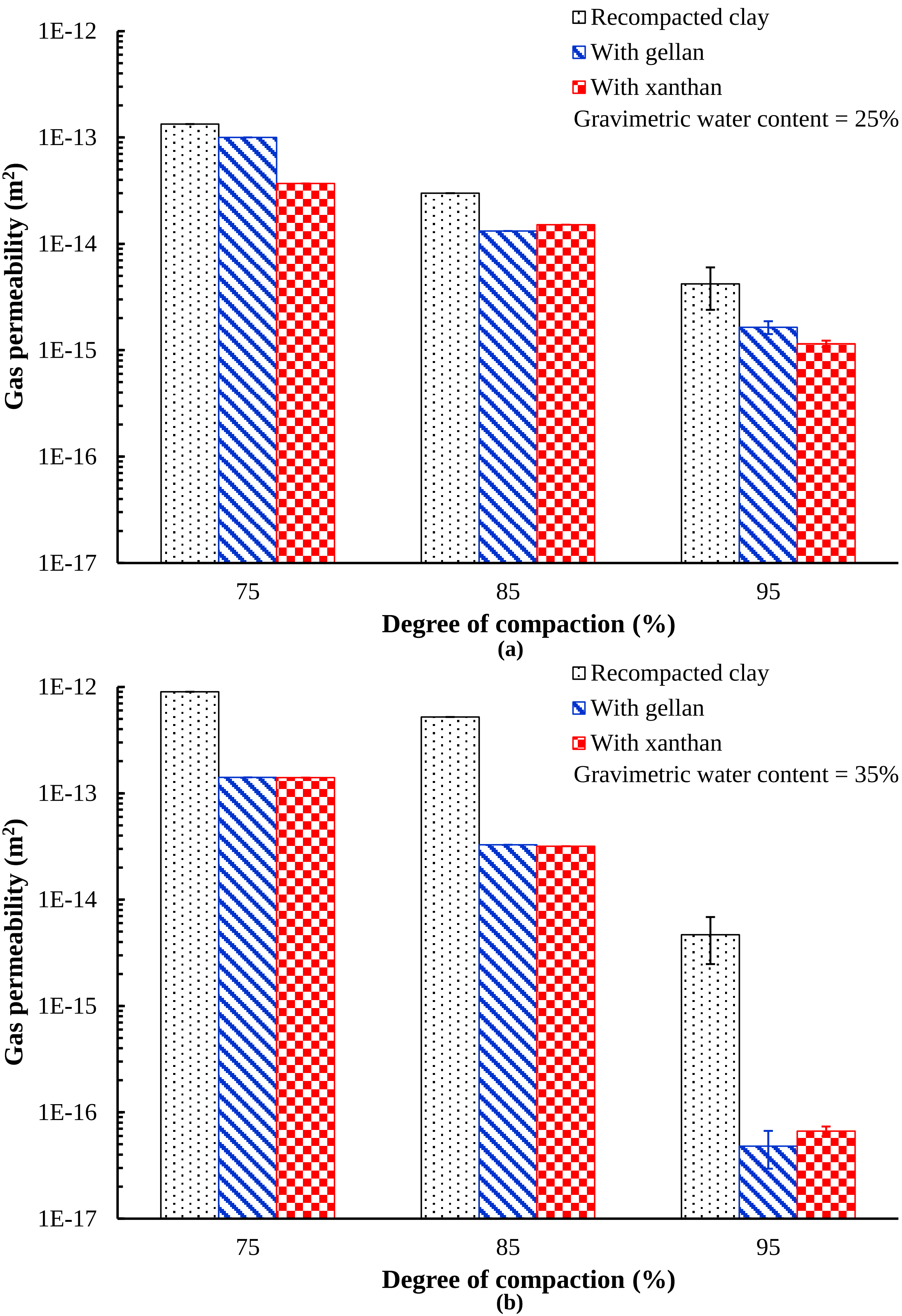


Fig. 2. A photo of flexible wall permeameter for measuring gas permeability of soil



(a)

(b)

Fig. 3. Gas permeability of the soil at various degrees of compaction for the water content of (a) 25% and (b) 35%

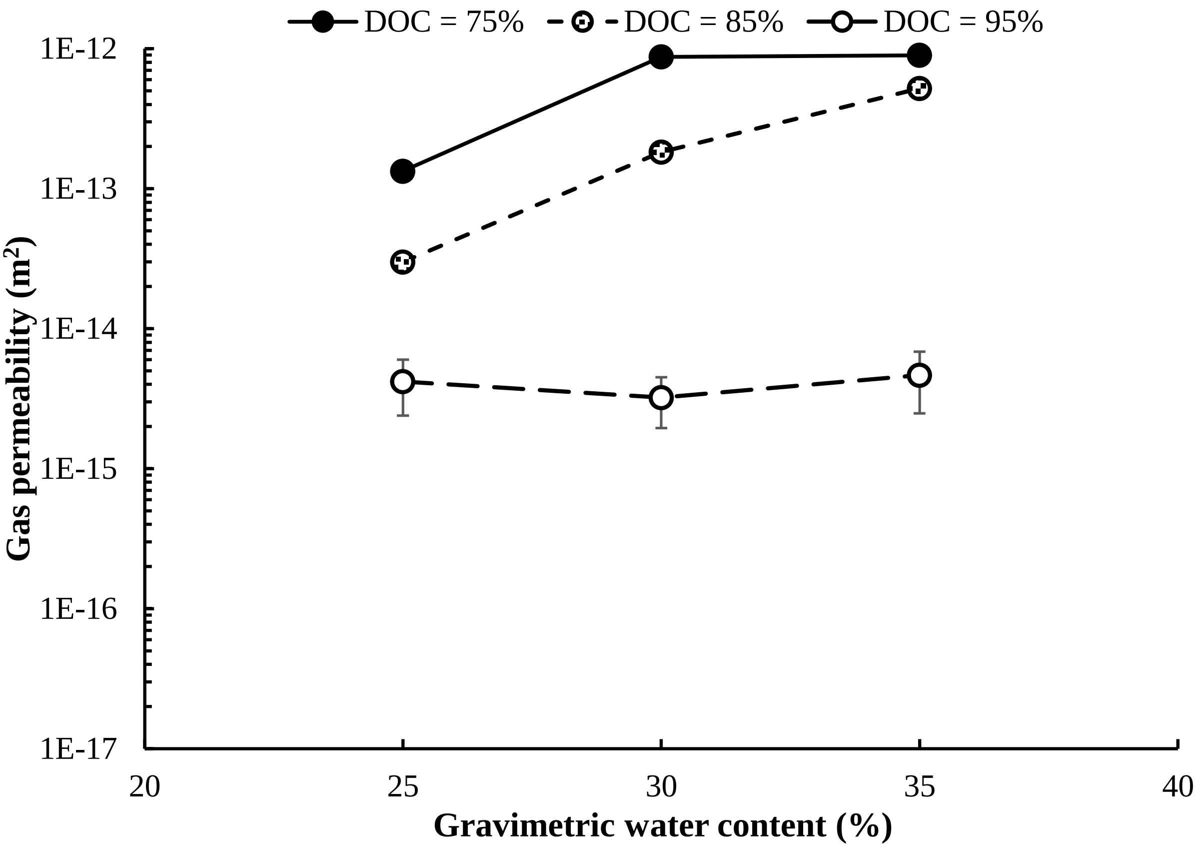


Fig. 4. Variation of gas permeability of recompacted clay with different water contents at various degrees of compaction

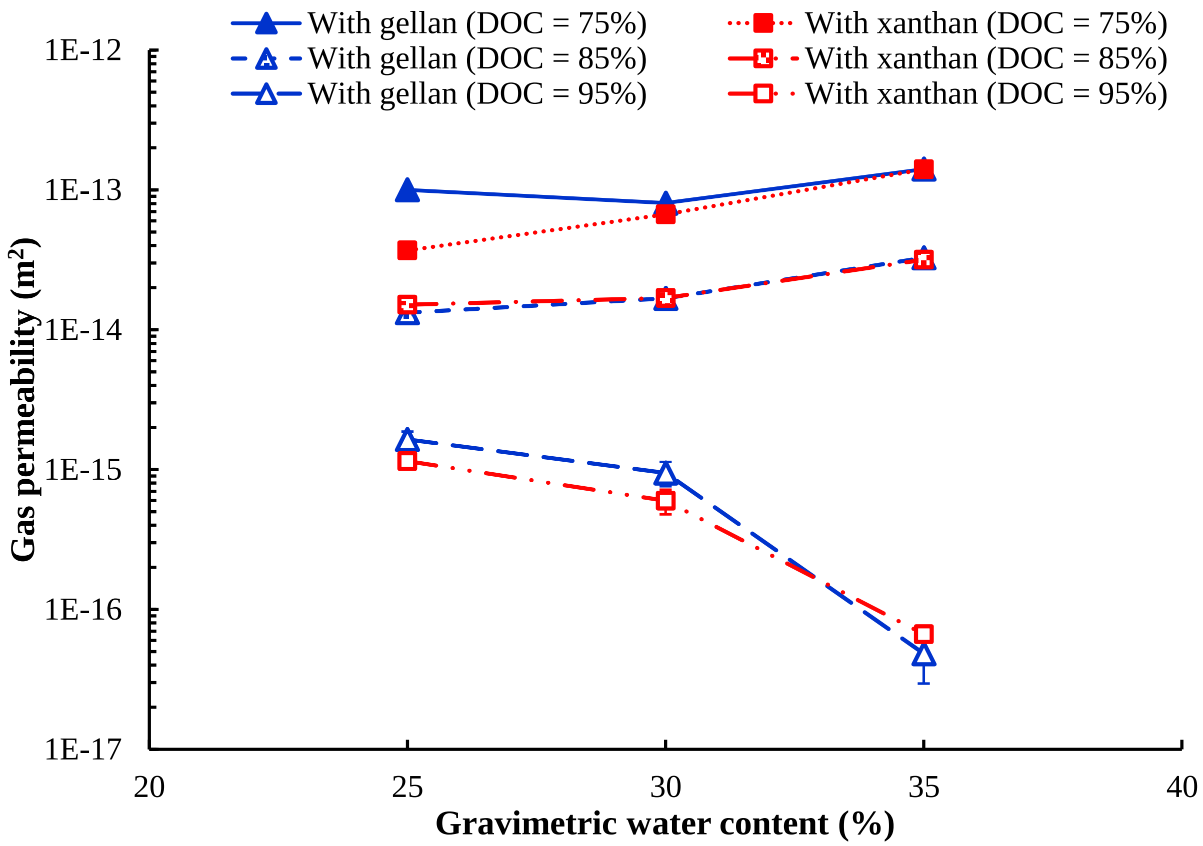
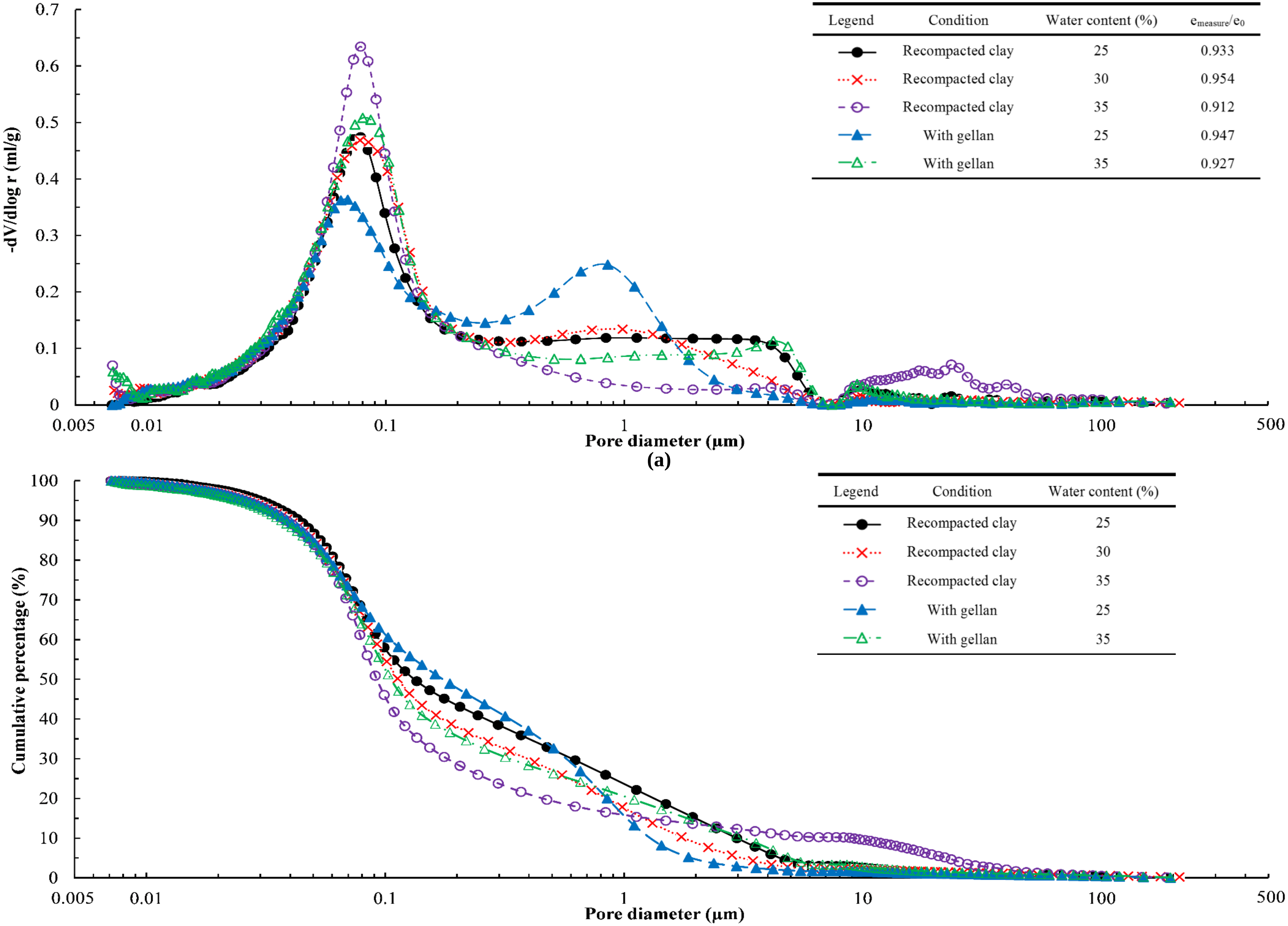


Fig. 5. Variation of gas permeability of clay with the biopolymers with different water contents at different degrees of compaction



(a)

(b)

Fig. 6. Pore size distribution of the clay with and without the gellan gum, expressed in terms of differential pore volume (upper) and cumulative percentage of particular pore size (bottom)

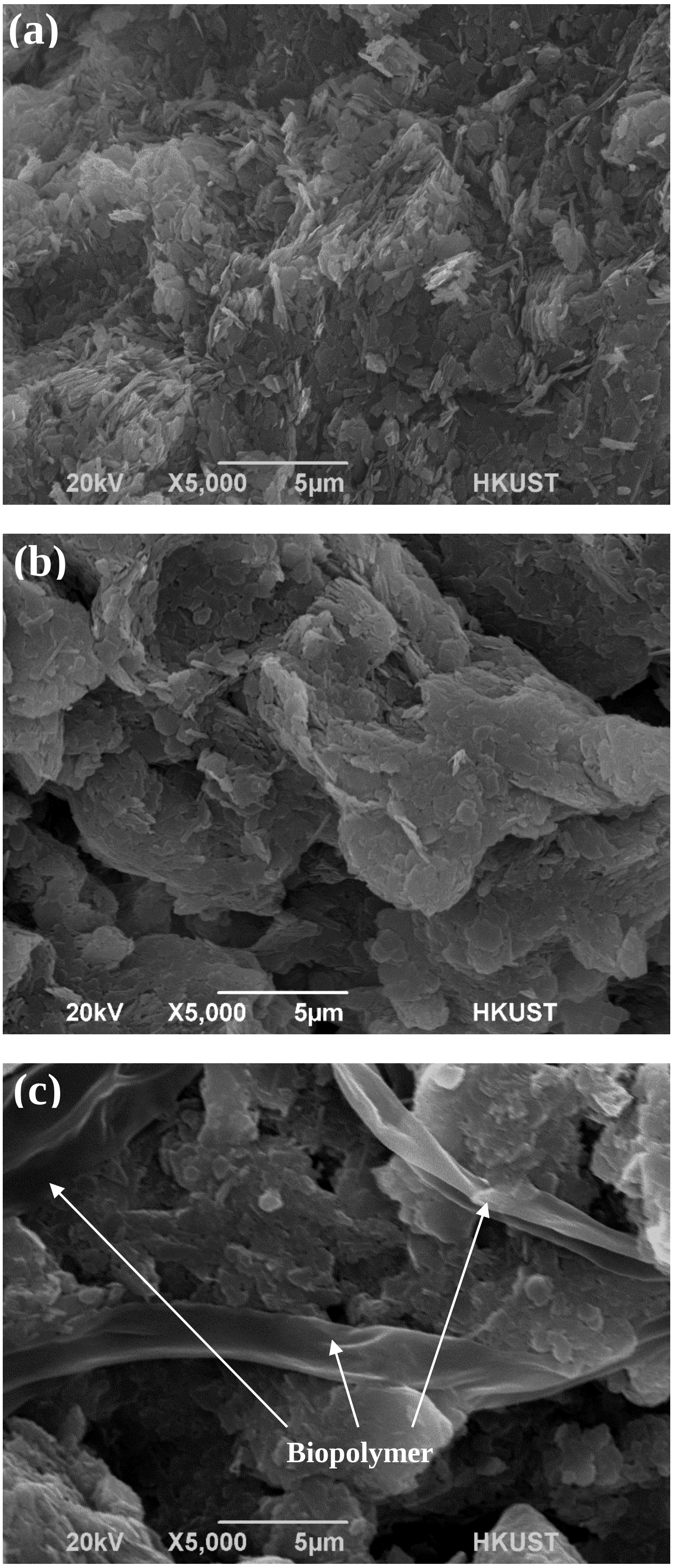


Fig. 7. SEM analysis (x5000) for the microstructure of the soil samples in recompacted clay (a), with gellan gum (b), with xanthan gum (c) at DOC of 95% and water content of 35%

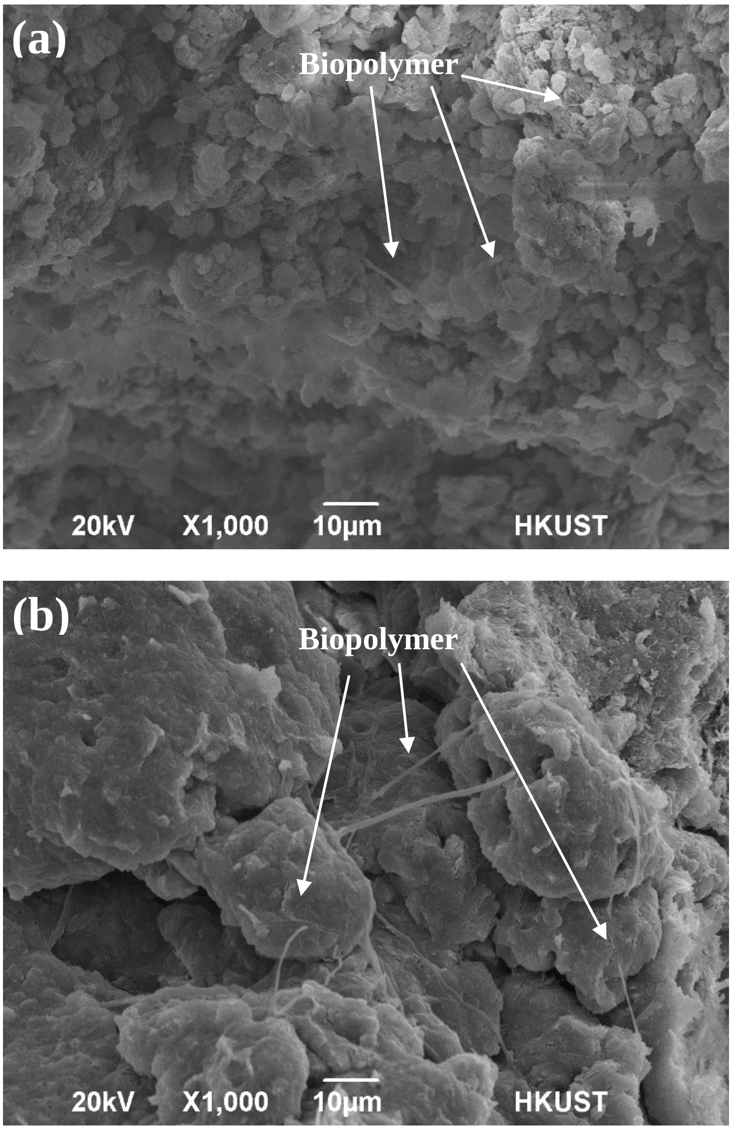


Fig. 8. SEM images (x1000) of the hydrated biopolymers in sample with gellan gum (a), xanthan gum (b) at DOC of 85%

List of Table Captions

Table 1. Test program

Table 2. Physical properties of kaolin clay with and without biopolymers

List of Figure Captions

Fig. 1. Photographs taken on the surface of the recompacted clay (a), clay with gellan gum (b) and xanthan gum (c) at DOC of 95% and water content of 35% after compaction

Fig. 2. A photo of flexible wall permeameter for measuring gas permeability of soil

Fig. 3. Gas permeability of the soil at various degrees of compaction for the water content of (a) 25% and (b) 35%

Fig. 4. Variation of gas permeability of recompacted clay with different water contents at various degrees of compaction

Fig. 5. Variation of gas permeability of clay with the biopolymers with different water contents at different degrees of compaction

Fig. 6. Pore size distribution of the clay with and without the gellan gum, expressed in terms of differential pore volume (upper) and cumulative percentage of particular pore size (bottom)

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