DISCUSSION

Critical state of polymer-coated sands

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Contribution by Zheng Zhou and Anthony K. Leung

Liu *et al.* (2019a) presented a set of high-quality triaxial data on the mechanical behaviour of synthetic water-repellent Fujian sand. It is exciting to see from Fig. 3 of the study that the treatment made by 3% dichlorodimethylsilane (DMDCS, by weight) caused a reduction of stress ratio under a confining pressure of 200 kPa. This was explained by the mechanism of particle surface smoothening by way of observation from the white-light interferometry measurements. This discussion explores whether the observed differences in soil mechanical properties could also possibly be attributed to any difference of void ratio, prior to shearing, between the natural and 3% coated sand. It was reported in Liu *et al.* (2019a) that the post-consolidation void ratio (i.e. the void ratio before shearing) was 0.711, yet it was not mentioned which soil specimen (i.e. natural, 0.05% or 3% coated sand) this void ratio referred to. Fundamentally, soil void ratio is estimated based on a known specific gravity (G_s ; ratio of soil particle density to water density). In Liu *et al.* (2019a), a single G_s of 2.66 was reported and the polymer coatings were deemed to introduce a negligible effect on the value. Interestingly, existing studies of synthetic water-repellent soil did not always report G_s , but when reported (see Table 1), only one value was given, and normally it was not stated whether the value referred to natural or synthetic water-repellent soil.

Measurements of specific gravity

The discussers have recent experience of measuring G_s of a synthetic water-repellent sand similar to the one tested in Liu *et al.* (2019a). The same chemical agent, DMDCS, was used, but the standard Toyoura sand was tested instead of Fujian sand. The values of G_s for both untreated (i.e. natural) and 3% DMDCS (by weight) treated sand were measured following the procedures outlined in the ASTM D854-14 (ASTM, 2014) (standard test methods for specific gravity of soil solids by water pycnometer). The standard recommends two wetting agents for sample preparation – deaired water and kerosene – depending on the origin and nature of the soil being tested. For example, for soils containing a significant fraction of organic matter, kerosene is considered to be a better wetting agent than water. As can be seen in Fig. 9(a), untreated sand can be wetted readily by water, and the particles were tightly packed. However, this was not the case for the treated sand, where aggregates were formed in the

water (Fig. 9(b)). The aggregation entrapped a significant amount of air (as indicated by the higher water level even though the volume of water added was identical in all cases), after applying for a constant vacuum for more than two hours, as suggested by ASTM D854-14 (ASTM, 2014). This kind of particle aggregation and air entrapment means that the measurements of G_s are not correct. When using kerosene instead, the treated sand formed a much more closely packed configuration (Fig. 9(c)) like the case of untreated sand mixed with water.

In the G_s measurements, five replicates were tested for both untreated and treated sands. Statistical analysis was performed to test the differences in G_s among the different treatments by one-way analysis of variance (Anova), followed by post hoc Fisher's least significant difference test. Results are considered statistically significant difference when the p -value ≤ 0.05 . For the case of treated sand mixed with kerosene, the measured values were the specific gravity with respect to kerosene. For fair comparison, the measured values were corrected by multiplying by the ratio of the density of kerosene (i.e. 0.845 g/cm³) to the density of water (i.e. 0.998 g/cm³) at 20°C.

The test data (Table 2) showed that G_s was statistically significantly different between untreated and treated sands, and the G_s of treated sand (by kerosene) was higher than that of the untreated case by 5%. This observation is different from what was observed in (a) Choi *et al.* (2016), where G_s of kaolin dropped by approximately 10% due to the addition of 10% n-octyltriethoxysilane (by weight); (b) Liu *et al.* (2019a) where G_s of Fujian sand was largely the same with and without treatment with DMDCS. Clearly, any hydrophobisation-induced change in G_s depends on the surface properties of the soil (e.g. surface charge) as well as the chemical reaction between the soil and the hydrophobic agent chosen. More research is needed to understand the effects of hydrophobisation on G_s .

Implications

Since the G_s of Toyoura sand presented in this discussion did show a statistically significant increase by hydrophobisation, it would be worth investigating how the associated change in G_s would affect the sand's mechanical behaviour. According to the basic volume–mass relation of a soil, one can use the following equation to relate void ratio (e) to the soil dry density (ρ_d) by way of G_s

$$e = \frac{G_s \rho_w}{\rho_d} - 1 \quad (1)$$

where ρ_w is the density of water (i.e. 0.998 g/cm³ at 20°C). Hence, for a given dry density (the variable typically controlled in an experiment), the choice of G_s would make an impact on the estimation of void ratio. For instance, at a targeted dry density of 1.60 g/cm³, using G_s of untreated sand and treated sand (by kerosene) would give a value of e of 0.642 and 0.730, respectively. This 14% difference is deemed non-negligible. The chemical treatment thus has apparent

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Table 1. A summary of measured specific gravity reported in existing studies of synthetic water-repellent soil

Author(s)	Soil type	Chemical agent	G_s	Standard quoted
Kim <i>et al.</i> (2011)	Jumunjin sand	n-Octyltriethoxysilane	2.59	Not mentioned
Kim <i>et al.</i> (2013)	Jumunjin sand	n-Octyltriethoxysilane	2.59	Not mentioned
Kim <i>et al.</i> (2014)	Jumunjin sand	n-Octyltriethoxysilane	2.59	Not mentioned
Choi <i>et al.</i> (2016)	Kaolin clay	n-Octyltriethoxysilane	2.35–2.65*	Not mentioned
Liu <i>et al.</i> (2019a, 2019b)	Fujian sand	Dichlorodimethylsilane (DMDCS)	2.66	Not mentioned

*Values depend on the concentration of n-octyltriethoxysilane added (0.5–10% by weight).

Fig. 9. Images of particle arrangement for (a) untreated sand mixed with water; (b) treated sand mixed with water; and (c) treated sand mixed with kerosene**Table 2.** Summary of the measured specific gravity in this discussion

Treatment	Wetting agent	No. of replicates	G_s^*	p -value
Untreated sand	Water	5	2.627 ± 0.001 a	<0.05
Treated sand	Water	5	2.561 ± 0.011 b	
Treated sand	Kerosene	5	2.768 ± 0.003 c	

*Values are reported in mean $\pm$ standard error of mean; the symbol a, b or c after each number is a statistical letter indicating significant differences among groups, after statistical testing.

loosening effects on the Toyoura sand due to hydrophobisation. To put this into the context of geotechnical engineering, the following equation can be used to describe the relation between void ratio and the shear modulus of Toyoura sand (Lo Presti *et al.*, 1997)

$$G_0 = CF_{(e)} P_a^{1-n} (P')^n \quad (2)$$

where C and n are material constants, $F_{(e)} = e^{-x}$ is the void ratio function, where x is also a material constant; P_a is the atmospheric pressure; and P' is the isotropic effective confinement pressure. For a given P' , say, 200 kPa, the use of different void ratio (0.642 and 0.730) would lead to a 15% difference in G_0 (176 and 149 MPa, respectively), which can be significant for the estimation of, for instance, soil volume change. This discussion highlights the importance of not overlooking the effects of soil hydrophobic treatment on G_s since the potential changes of soil void ratio would affect the subsequent interpretation of the soil mechanical behaviour.

Authors' reply

The authors wish to thank the discussers for their interest in the topic of synthetic hydrophobic granular materials and appreciate their recent experimental research work in this area. The discussers (a) queried the potential of G_s in influencing the void ratio of the coated sands; (b) quoted different G_s values for hydrophobic sands reported in the literature; and (c) highlighted the importance of the G_s measurement method on the accuracy of G_s . All the issues raised have been addressed in the following five sections in systematic order.

Concentration to synthesise hydrophobic coatings

Prior to addressing the points raised by the discussers, it is worth mentioning that the criteria used for selecting the concentrations (of chemical agents) to synthesise hydrophobic coatings are critical features to the development of synthetic hydrophobic granular materials. Soils can be hydrophobic (both in persistency and with a similar

magnitude) for a range of concentrations. Because hydrophobicity is controlled by surface chemistry, once the particles become coated, any subsequent increase in concentration will not generate any benefit in terms of hydrophobicity. For instance, according to Fig. 9, the coated sand achieves its highest hydrophobicity for concentrations greater than 0.05% (CA = 114°). The rationale for choosing the concentrations (up to 3%) in the literature and reported in Table 1 are not given. In the authors' paper, a predetermined objective was to ascertain that the coatings' thickness (rendered thicker by an increase in concentration) influenced soil behaviour (including G_s). Therefore, the high concentrations reported in the literature and tested by the discussers (around 3%) may be excessive and therefore may be of limited interest to the development and application of synthetic hydrophobic granular materials.

G_s method

To measure the G_s of natural sand, 0.05% and 3% coated sand, the authors followed BS 1377-2 (BSI, 1990), whereby the small pycnometer method with water as the wetting agent was used. The results showed G_s to be $2.661, 2.661 \pm 0.004$ and 2.657 ± 0.012 , respectively, out of six measurements per sample on a balance readable to 0.0001 g. Based on these values, the authors assumed differences in G_s among the three materials to be negligible.

Decrease in G_s (from 2.627 to 2.561)

A reduction in G_s , as reported in Table 2 with water as a wetting agent, is possible for coatings with a thickness in excess of approximately 10 μm as reported in the authors' paper. Thicker coatings could be produced if, for instance, the samples are not allowed to cure after silanisation and the concentration is increased. A period of time is required to complete silanisation and for hydrophobicity to establish. Other factors likely to play a role are the material properties (e.g. particle diameter and particle shape) and silanisation procedure (e.g. Howarter & Youngblood, 2006). Therefore, it is difficult to identify and isolate the root cause(s) for the non-negligible reduction in G_s because no information has been provided by the discussers on the thickness of the coatings, the time allowed for curing, the hydrophobicity level (contact angle and its persistency) and method used to quantify hydrophobicity, including material properties and synthesising procedure.

Increase in G_s (from 2.627 to 2.768)

The increase in G_s reported in Table 2 is debatable. The coatings resulting from the silanisation process are made of polydimethylsiloxane (PDMS) with a specific gravity of $1.04\text{--}1.51\text{ g/cm}^3$ (Owen, 2001), which is significantly smaller compared to that of sands. Therefore, a thickening of the coatings should a priori reduce the overall G_s . The authors concur that air entrapment due to aggregation is a challenge that may underestimate G_s and that the use of kerosene as a wetting agent may improve this, but not in the form of an increase of G_s as reported in Table 2. The origin of the sand (Toyoura as opposed to Fujian) is not relevant, because both are quartz sands – that is, they share a similar chemical composition. PDMS is a widely studied material with its properties already reported elsewhere (e.g. Owen, 2001) and the silanisation process requires the presence of hydroxyl groups to which methyl groups bond to form the PDMS.

Void ratio

Controlling the void ratio for the coated sands at the different testing stages was a challenge. Therefore, the void ratio was determined after consolidation based on the method proposed by Yang & Wei (2012), and was calculated with the measured G_s values reported above. A factor likely to play a role in the control of the void ratio is the adhesion between PDMS coatings, reported in the materials literature (Yu *et al.*, 2012) and by the authors (Liu *et al.*, 2019b), which creates an aggregation effect similar to the one reported in Fig. 9(b) and strongly influences the micromechanical behaviour of coated sand (Liu *et al.*, 2019b).

NOTATION

C, n, x	material constant
e	void ratio
G_s	specific gravity
P'	isotropic effective confinement pressure
P_a	atmospheric pressure
ρ_d	soil dry density
ρ_w	density of water

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