Conditions to induce water repellency in soils with dimethyldichlorosilane

S. H. Y. NG* and S. D. N. LOURENÇO*

Dimethyldichlorosilane has been used as a hydrophobising agent for various applications, one of which is the treatment of soils. In geotechnical engineering, synthetic water-repellent soils can be used in barriers or ground improvement because of their wettability properties. This note examines the effect of dimethyldichlorosilane concentration on the soil type and time-dependent effects by means of contact angles measurements using the sessile drop method. The results reveal that the presence of organic matter, residual water and other non-mineral matter hinders the effectiveness of the treatment. Treated clean soil particle surfaces from crushed rocks achieve an immediate and high degree of water repellency.

KEYWORDS: geosynthetics; ground improvement; particle-scale behaviour; sands

INTRODUCTION

Water-repellent or hydrophobic soils, those with contact angles >90°, have been employed in water harvesting in dry regions (Fink *et al.*, 1980). In slopes, natural water-repellent soils reduce infiltration, increase surface runoff (Doerr *et al.*, 2000) and may inhibit vegetation growth (Osborn *et al.*, 1964). As water repellency can be induced in soils, opportunities arise for their use as synthetic water-repellent soils in impermeable or semi-permeable barriers in geotechnical applications. As opposed to clays, water-repellent sands have the unique advantage of remaining volumetrically stable when dried or wetted excessively.

Dimethyldichlorosilane (DMDCS), with composition $(CH_3)_2SiCl_2$, is a known hydrophobising agent used for various applications, from treating silica and glass surfaces (Gao & McCarthy, 2006) to ultra-water-repellent films (Shen *et al.*, 2012; Soeno *et al.*, 2004). In soil science, Bachmann *et al.* (2000) were among the first to use DMDCS to form a hydrophobic coating on soil samples. However, most studies only considered the hydrophobising capacity of DMDCS, with little consideration given to details such as the concentration required to attain a certain degree of water repellency, the effect of soil type and other soil characteristics.

The basic mechanism of the DMDCS treatment to induce water repellency in dry soils is based on the reaction of DMDCS with water menisci or water vapour to form polydimethylsiloxane (PDMS) and hydrochloric acid (HCl) (Ju *et al.*, 2008).

$$n[(CH_3)_2SiCl_2] + n[H_2O] \rightarrow [(CH_3)_2SiO]_n + 2nHCl \quad (1)$$
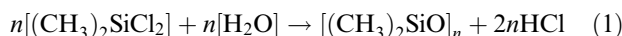
where n is the number of DMDCS repeating units. PDMS then interacts with the abundant polar groups on the soil particle surface, usually made up of a hydroxyl group (–OH) (Goebel *et al.*, 2007), leading to the formation of an outward-oriented hydrophobic methyl group (–CH$_3$) (Fig. 1). Other silane compounds, such as *n*-octyltriethoxysilane, have also been used to induce water repellency in soils (Byun *et al.*, 2011;

Lee *et al.*, 2015). For this study, DMDCS was preferred owing to the simplicity of sample preparation (the chemical is added directly to the soil). Organic acids such as stearic acid (Lourenço *et al.*, 2015a), oleic acid (Wijewardana *et al.*, 2015) and waxes (Bardet *et al.*, 2014) were considered, but there is uncertainty regarding their stability with time.

Bachmann *et al.* (2000) found that contact angles ~90° can be induced with 7·5 ml DMDCS per kg of sand and 50 ml DMDCS per kg of silt, with the difference assumed to be related to the higher surface area of the silt to the sand. However, other factors require consideration. Water repellency induced by DMDCS is assumed to be permanent, unlike natural soil water repellency that is time dependent and sensitive to the environment (relative humidity and ambient air temperature). The application of DMDCS has been mostly in clean sands; natural and infrastructure soils have organic matter, microorganisms and roots, which may alter the outcome.

To define the conditions that maximise the water-repellent effect of DMDCS in soils, the specific objectives are to (*a*) determine the relation between contact angles and DMDCS concentration, and (*b*) evaluate the contact angle stability after the treatment (i.e. the effect of time on contact angles) for different soils (particle size distribution and components).

MATERIALS AND METHODS

Natural and replicated soils

To ascertain the influence of the particle size distribution, four samples including three natural soils and one industrial soil were tested: a surface fine sand (SFS), a surface coarse sand (SCS), alluvium (ALL) and Leighton Buzzard sand (LBS). The natural soils SFS and SCS were collected from the Ap Lei Chau Formation (volcanic tuff) on Hong Kong Island. Samples were collected at 2 cm below the surface and sealed in plastic bags. ALL was collected at the same depth from the Fanling Formation in the New Territories, Hong Kong. Samples were sieved at 1·18 mm mesh size and air dried (soil water repellency is temperature dependent (Doerr *et al.*, 2000)).

To investigate the influence of the soil components (e.g. minerals, organic matter), the same four materials were replicated from freshly crushed granite in the same proportions in order to isolate the mineral particles and to
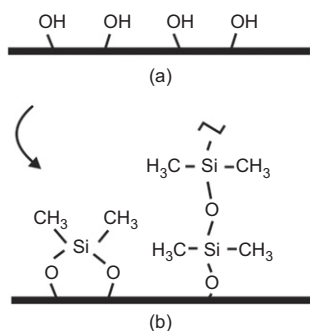
Fig. 1. Possible molecular configurations of the (a) natural soil particle surface and (b) treated soil particle surface

obtain the equivalent grain-size distributions (the fraction <63 μm was not measured). These are named repSFS, repSCS, repALL, repLBS ('rep' for replicated). All samples, natural and replicated were assumed to have similar mineralogy as they all originated from Hong Kong where the geology is mostly igneous. The particle size distribution is presented in Fig. 2. The field organic content (obtained by the loss on ignition test at a temperature of 550°C for 2 h), air-dried water content and D_{50} for all samples are available in Table 1.

Silanisation

The soil treatment with DMDCS involves the addition of a specific amount of DMDCS to soil samples (~100 g of air-dried soil) with a micropipette and stirring for ~30 s in a fume cupboard to avoid the hydrogen chloride (HCl) gas. All eight samples were treated with 0·5%, 1%, 1·5%, 2%, 2·5%
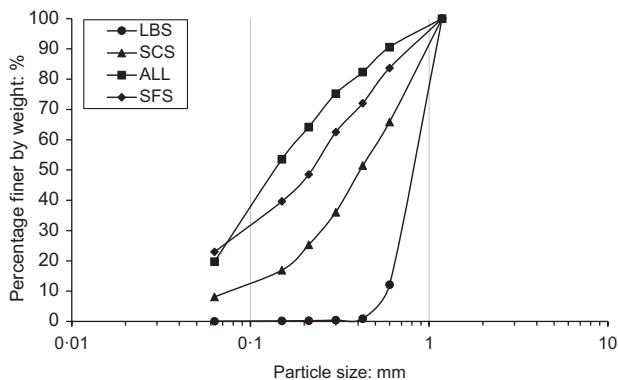

Fig. 2. Particle size distribution for all soils

and 3% by soil mass of DMDCS and the contact angles were measured 3 days after the preparation (to account for any short-term fluctuations). To further study the water-repellent behaviour at low DMDCS concentrations, LBS was treated with 0·005%, 0·008%, 0·01%, 0·02%, 0·05%, 0·1%, 0·15% and 0·25% by soil mass of DMDCS.

A second set of experiments was conducted to investigate the time stability of water repellency, that is, any time-related fluctuations. All eight samples were treated at different concentrations (1% and 2% by soil mass of DMDCS) and contact angle measurements were performed 1 h, 50 h, 150 h and 214 h after treatment.

Measurement of soil water repellency

Soil water repellency was determined by means of contact angle measurements with the sessile drop method (SDM), which is widely used in soil and materials science, and assessed by an index test, the water drop penetration time test (WDPT).

The WDPT assesses the persistency of water repellency of a soil surface (Doerr et al., 2000). Based on the time for a water drop to infiltrate, the samples are classified as wettable (<5 s), slightly water repellent (5–60 s), moderately water repellent (61–600 s), severely water repellent (601–3600 s) and extremely water repellent (3601–18 000 s) (Bisdom et al., 1993). The WDPT test was conducted 3 days after the soil treatment (the same for the SDM). The procedure consists of filling a Petri dish (60 mm × 15 mm) with treated soil, levelling the excess to the edge with a spatula, adding an 80 μl water drop onto the sample surface and recording the infiltration time; this is repeated three times to determine the median and the water-repellency rating.

The SDM measures the apparent contact angle (ACA) from the tangent of the three-phase point of a water drop on a layer of particles. 'Apparent' refers to the combined effect of the intrinsic material wettability and particle and layer roughness, that is, the heterogeneity of the layer surface (Lourenço et al., 2015b). ACAs were measured with a charge-coupled device equipped contact angle microscope (DSA 25, Krüss, Germany). The procedure consists of attaching a double-sided adhesive tape to a glass slide and adding the soil particles onto the tape evenly. Excess particles are removed by shaking the slide (Bachmann et al., 2000). A drop of deionised water of volume ~10 μl is placed on the glass slide while recording a video. The ACA is measured with the integrated software (version 1.92.1.1) from the initial video frames, typically within the first 30 ms, which is essential for wettable materials where water infiltrates immediately. To take into account the variability

Table 1. Soil characteristics and selected results for the WDPT and SDM

Natural and replicated samples	Soil characteristics			Water repellency classification			Critical percentage of DMDCS to induce maximum water repellency	
	Organic content: %	Air-dried water content: %	D_{50}: μm	Untreated	0·5% DMDCS	3% DMDCS	WDPT: %	SDM: %
LBS	0·21	0·24	820	Wettable	Extreme	Extreme	<0·005	<0·005
repLBS	0·60	0·39	820	Wettable	Extreme	Extreme	<0·5	<0·5
SCS	4·59	1·77	425	Wettable	Extreme	Extreme	~2	~2·5
repSCS	0·58	0·53	425	Wettable	Extreme	Extreme	<0·5	<0·5
SFS	6·11	3·23	225	Slight	Extreme	Extreme	~1	~2
repSFS	0·71	0·41	225	Wettable	Extreme	Extreme	<0·5	<0·5
ALL	3·58	1·09	140	Wettable	Slight	Extreme	~1	~1·5
repALL	0·67	0·62	140	Wettable	Extreme	Extreme	<0·5	<0·5

associated with the ACA magnitude, a minimum of ten measurements were carried out on each slide, after which the mean and standard deviation were computed. The air temperature and relative humidity – were $23.6 \pm 0.5°C$ and $58.2 \pm 2.6\%$, respectively. No samples were reused.

RESULTS AND DISCUSSION

The results revealed that, for all replicated samples, the ACA reached the maximum value of 137°–143° at 0·5% DMDCS, remaining constant at higher DMDCS concentrations (Fig. 3). For the natural samples SCS and ALL, ACAs were substantially smaller than the equivalent repSCS and repALL, achieving 84° at 0·5% DMDCS, and increasing up to ~140° at 3% DMDCS. Sample SFS was the only one to show slight water repellency before treatment (ACA = 82°). Similarly to samples SCS and ALL, SFS also had a lower ACA than repSFS at high concentrations, 121° to 141°. For LBS, the ACA reached the maximum at 112° with no further increase.

The results suggest that the air-dried water content and organic matter may have altered the water repellency of the soil. Comparing samples SCS to repSCS, SFS to repSFS and ALL to repALL, the particle size distributions were identical, with the major difference being the higher water and organic content for the natural soil samples (Table 1). Natural samples reached the maximum water repellency in the range 2–3% DMDCS for a water content of 1·1–3·2% and organic content of 3·6–6·1%, while all replicated samples reached the maximum water repellency at <0·5% DMDCS for 0·4–0·6% water content and 0·6–0·7% organic content. This response is further substantiated by the behaviour of LBS, where the stability of the ACA matched the low water and organic content, 0·2% for both.

Table 1 shows that the majority of the treated samples were classified as extremely water repellent (Doerr, 1998), even at low percentages of DMDCS. With 0·5% and 3% DMDCS as a comparison, Table 1 shows that all natural samples were wettable before treatment, achieving extreme water repellency at 0·5% and 3% DMDCS, with the exception of SFS and ALL. All replicated samples and LBS displayed extreme water repellency at 0·5% and 3% DMDCS.

The critical percentage of DMDCS required to induce the maximum water repellency diverged slightly across the samples. According to the WDPT and SDM data (Table 1), the replicated samples and LBS showed maximum water repellency at the lowest concentration (<0·5%). In general, the critical percentage of DMDCS for the WDPT test was 0·5% to 1% lower than the SDM test for SCS, SFS and ALL.
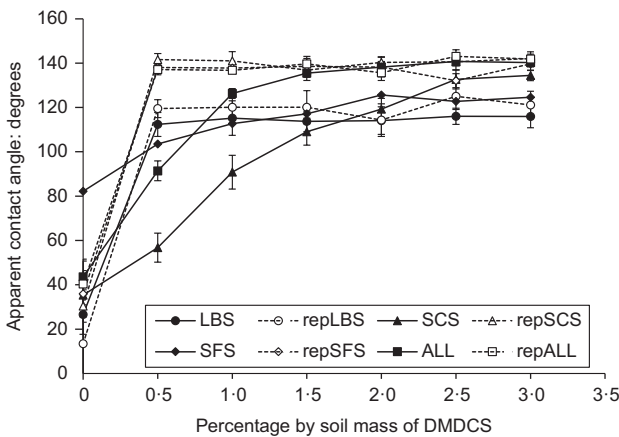
However, the critical percentage of DMDCS was not achieved in any of the replicated samples. Further tests were carried out at low concentrations for LBS, revealing that the water repellency was already at the maximum ACA at 0·005% DMDCS (Fig. 4).

The ACA measurements with time revealed distinctive responses for the natural and replicated samples (Figs 5(a) and 5(b)). The results matched the previous findings on the effect of water content and organic matter, with samples SFS, SCS and ALL showing that the degree of water repellency increases after treatment. For instance, the increase in ACA immediately after treatment, after 50 h and 215 h was,
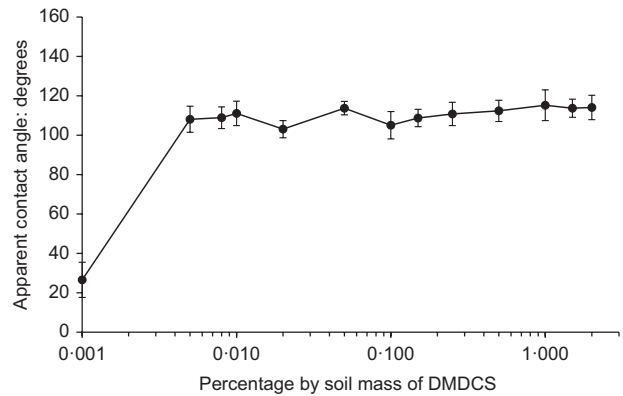

Fig. 4. Apparent contact angles for LBS at low percentages by soil mass of DMDCS
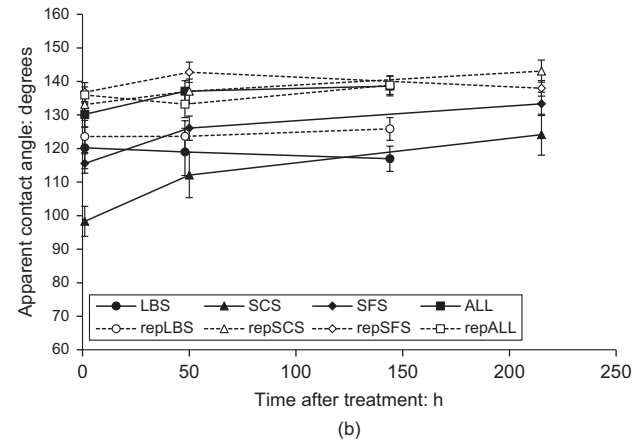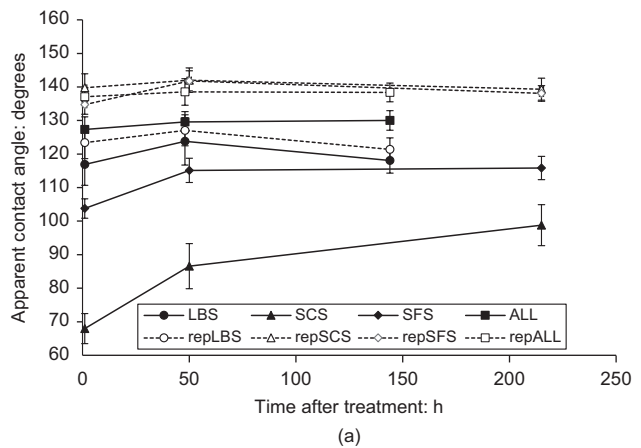

(a)

(b)

Fig. 5. Apparent contact angles with time after the soil treatment for the natural and replicated samples: (a) for 1% by soil mass of DMDCS; (b) for 2% by soil mass of DMDCS

Fig. 3. Apparent contact angles for natural and replicated samples at increasing percentages by soil mass of DMDCS

respectively, 68°, 87°, 98° for 1% DMDCS in SCS and 140°, 142°, 139° for 1% DMDCS in repSCS. For the replicated samples and LBS, the ACA remained relatively constant with time, and for the natural and replicated SFS, SCS and ALL they were found to be at ~140°, whereas the LBS and repLBS were at ~125°.

This study suggests that organic matter and residual water content dominate the efficiency of the DMDCS treatment. A possible reason for the higher DMDCS consumption for the natural soils (Fig. 3) is that the soil particles are not fully covered with the water-repellent layer at low DMDCS concentrations, probably owing to the DMDCS reacting with the residual water to form long chains of PDMS and thus reducing the number of molecules available to bond with the –OH groups in the soil. At high concentrations, the DMDCS molecules outnumber the number of sites available, even if long chains of PDMS are formed.

CONCLUSION

This study has shown that the treatment of a soil with DMDCS to induce water repellency is very sensitive to the soil components. The presence of residual water, organic matter and other non-mineral matter strongly constrains and delays the development of water repellency. In particular, the results revealed that less than 0·005% DMDCS was sufficient for clean soil particle surfaces to reach the maximum water repellency with no further changes with time. As a new technology, it would be preferable to induce water repellency in crushed rocks due to the lower consumption of DMDCS and their post-treatment stability.

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