

Time-dependent hydrophobic characterisation of granular materials synthesised with commercial chemical agents

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Abstract. The impact of hydrophobicity on unsaturated granular materials is important because suction is a function of the degree of saturation as well as the surface tension and contact angle of the water menisci. In this study, coatings have been applied on the surfaces of a quartzitic sand at different concentrations following synthesis with eight commercial chemical agents and dimethyldichlorosilane (DMDCS) to induce hydrophobicity. Contact angle (CA) measurements and water drop penetration time (WDPT) tests have been carried out at different time intervals to investigate the hydrophobicity and its persistence. Scanning electron microscope (SEM)-energy dispersive X-ray spectroscopy (EDS) was performed to evaluate the resulting chemical composition of the sand. Results demonstrate that synthesis at high concentration (5%) caused fluctuations in CA and WDPT measurements within the first 24h. Except for one commercial chemical agent, the maximum CAs reached by the remaining agents after 24h were comparable to DMDCS (CA=119°). However, the critical concentration needed to achieve these CAs differed significantly: the lowest critical concentration amongst the commercial chemical agents was 0.2% whereas with DMDCS, the critical concentration was 0.0053%. The resulting surface properties of the synthesised granular materials with the commercial chemical agents showed increases in carbon content whereas with DMDCS, no change was recorded compared to the untreated sand. In addition to illustrating the efficacy of commercial chemical agents in inducing hydrophobicity in granular materials, this study has provided insights into the time-dependent hydrophobic behaviour of granular materials following synthesis.

1 Introduction

Granular materials such as soils can be chemically rendered hydrophobic by laminating their surfaces with coatings. The prevalence of hydrophobic soils in nature, mainly due to organic matter coatings inspires their use in ground engineering as barriers [1]. To this end, the hydrophobisation of granular materials via silanisation in liquid form has been generally favoured to other existing techniques because the synthesis is single-stepped, does not necessitate special equipment and is not energy-intensive. In addition, the silanisation of granular materials has shown to exhibit relatively high levels of hydrophobicity and persistence over time [2]. Chemical agents typically used to silanise granular materials include dimethyldichlorosilane (DMDCS) and trimethylchlorosilane [2-7]. However, a drawback of these chemical agents is that hydrogen chloride, a corrosive fume emanates as a by-product after addition to soils. Therefore, sufficient time should be allowed for the completion of the silanisation reaction. For instance, in the synthesis of a clean, medium-sized sand with DMDCS, Chan and Lourenço [5] allowed for 24h before further testing.

With the importance of hydrophobicity recognised in various technological fields, commercial agents in the

form of sprays, foams, waxes, and paints have been developed to ensure easy application of coatings. These agents are essentially aimed at hydrophobising glass surfaces such as windshields of cars. While their performances as regards to inducing hydrophobicity and their durability on such surfaces have been successfully commercialised, the influence of these agents on granular materials is still unknown. The premises behind the use of these commercial products on granular materials are the simple and innocuous nature of the synthesising procedure and their potential to reduce costs involved in field applications. The current work compares the hydrophobic effects of eight different commercial agents on granular materials to that of DMDCS. The specific objectives were to establish the relation between hydrophobicity as well as its persistence and the chemical concentration over time following synthesis.

2 Materials and methods

2.1 Granular material

Silica sand, quarried from Leighton Buzzard, Bedfordshire, UK and referred to as Leighton Buzzard

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sand (LBS) was used. LBS is a clean, well-documented and commercially available industrial sand that has been mined for more than a century. The median value of the particle size distribution (D_{50}) of LBS following a dry sieving analysis using 100g of the sand was 0.8 mm.

2.2 Chemical agents

Eight commercially available chemical agents in liquid form were purchased from Artekyta Ltd. Co. (Istanbul, Turkey). They were selected on the basis of ease of application and availability. The supplier broadly classifies the agents under two groups of four, namely bulk size and surface protection according to the application for which they are recommended. For instance, bulk size products are suited for the exterior of vehicles whereas surface protection products are intended for relatively smaller-scale objects such as goggles. In this study, to provide a clear presentation of the results and avoid cluttering, these agents were separated under the same two groups and referred to as category 1 (bulk size) and category 2 (surface protection). Category 1 consisted of chemical agents labelled as C, C1, SHB and SHC whereas category 2 comprised of chemical agents denoted as HS, GS, GSM and PS. The chemical compositions of these chemical agents were predominantly (>85%) ethanol, hydrocarbons, or acetone. The effects of adding these commercial agents to the granular materials were compared to the use of dimethyldichlorosilane (DMDCS), an organo silicon compound in liquid form obtained from Acros Organics (Morris Plains, NJ, USA). The densities of DMDCS and the commercial chemical agents were respectively 1.06 gcm^{-3} and 0.88 gcm^{-3} .

2.3 Synthesising procedure

A single channel pipette (Pipetman P100, Gilson®, Villiers-le-Bel, France), with a minimum dispensing volume of $10 \mu\text{l}$ was used to add the chemical agents to a pre-determined mass of LBS in a glass beaker. This was followed by constant stirring by hand for a couple of minutes using a glass rod. The synthesising procedure was expressed in terms of concentration (%) according to equation (1) where M_g is the mass of LBS, V_c and ρ_c , are the volume and density of the chemical agents respectively. LBS synthesised with the DMDCS was carried out in a fume cupboard and synthesis with the other chemical agents were performed under laboratory conditions. To compare the effect of the chemical agents on the hydrophobicity of the LBS, the critical concentration, defined as the minimum concentration to achieve the maximum contact angle (CA) was used.

$$\text{Concentration (\%)} = \rho_c * V_c / M_g * 100 \quad (1)$$

2.4 Hydrophobicity assessment

Two techniques were adopted for the assessment and analysis of hydrophobicity of the LBS: the sessile drop

method (SDM) and the water drop penetration time (WDPT).

The SDM enables a direct measurement of the hydrophobicity using a goniometer (Drop Shape Analyser 25 from KRÜSS GmbH, Hamburg, Germany). The device allows CA measurements to be made on quasi-plain surfaces of the LBS obtained following the procedure described by Bachmann et al. [3]. A total of ten drops of water ($10 \mu\text{l}$ each) was dispensed at different positions by an automated syringe and their motions, as they reached the samples recorded by a charged-coupled device camera positioned laterally. To evaluate the CAs, a semi-automated technique proposed by Saulick et al. [7] was used; the mean value and the standard deviation were calculated and adopted as the measured values.

The WDPT, an index test that evaluates the persistency of hydrophobicity of a sample was carried out as follows: a 10-g mass of LBS was placed in a 5-cm diameter container and 4 drops of water ($50 \mu\text{l}$ each) were placed on the LBS. The mean penetration time of the drops was calculated and compared to the classification proposed by Doerr et al. [8]. The latter distinguishes 11 classes of hydrophobicity; for a very hydrophobic sample, the mean penetration time is large (up to several hours) and may correspond to either a class 9 or 10.

2.5 Scanning electron microscope-energy dispersive spectroscopy

A scanning electron microscope (SEM, Sigma HD FEG-ASEM from Carl Zeiss AG, Jena, Germany) was used for the qualitative inspections of the microscopic and nanoscopic features of LBS sand. The samples were first sputtered with a thin layer (thickness $\sim 5 \text{ nm}$) of a Gold-Palladium alloy in the ratio of 3:2 using a sputter coater. Images were acquired at working distances of 5–10 mm and at an acceleration voltage of 15 kV. The SEM, equipped with an energy dispersive spectrometer (EDS) was used to obtain semi-quantitative data on the elemental constituents (e.g. carbon content) of the LBS before and after synthesis.

3 Results and discussion

3.1 Wettability and concentration

The untreated LBS had a CA of $18 \pm 3^\circ$. Synthesis with all the chemical agents led to an increase in CA. The concentration curves of the category 1 chemical agents with the CAs measured immediately (within a couple of minutes) after synthesis are shown in Fig. 1(a). At 0.05% (the lowest concentration investigated), the CAs obtained with C, C1, SHB and SHC were respectively: $62 \pm 2^\circ$, $67 \pm 5^\circ$, $58 \pm 2^\circ$ and $61 \pm 3^\circ$. As concentration increased up to 3%, the hydrophobicity and its persistence increased, for instance, with C1, an increase in concentration from 0.1% to 0.5% led to an increase in CA from $75 \pm 2^\circ$ to $101 \pm 3^\circ$ and the WDPT rose steeply from class 0 (< 5s) to class 10 (> 18000s). With the category 2 chemical agents, an increase in concentration

up to 3% also resulted in an increase in CA (Fig. 1(b)). At the relatively lower concentrations (< 0.1%), CAs reached by PS were larger than the remaining category 2 chemical agents.

At 3%, the CAs of LBS synthesised with C, C1 and SHC were close to each other: their CAs were $112 \pm 4^\circ$, $116 \pm 4^\circ$ and $112 \pm 4^\circ$ respectively whereas synthesis with SHB gave a relatively lower CA of $92 \pm 4^\circ$. With the category 2 chemical agents, synthesis at 3% with HS, GS, GSM and PS respectively led to CAs of $114 \pm 3^\circ$, $117 \pm 5^\circ$, $124 \pm 6^\circ$ and $113 \pm 7^\circ$. However, the WDPT after synthesis at 3% were dependent on the chemical agents used (Fig. 2). Besides SHB and SHC which had a WDPT of class 10 (> 18000s), all the other chemical agents had a WDPT of class 0 (< 5s). The disparity in using CA and WDPT for assessing hydrophobicity with most of the chemical agents could be due to hydrophobicity not being stable. Carrillo et al. [9] mention that for a water drop to remain on the surface of a granular material as carried out with the WDPT test, the granular material should have a CA exceeding 90° as well as have stable hydrophobicity. Another possible reason justifying the low WDPT could be attributed to a change in CA from the measured value to a value less than 90° [10].

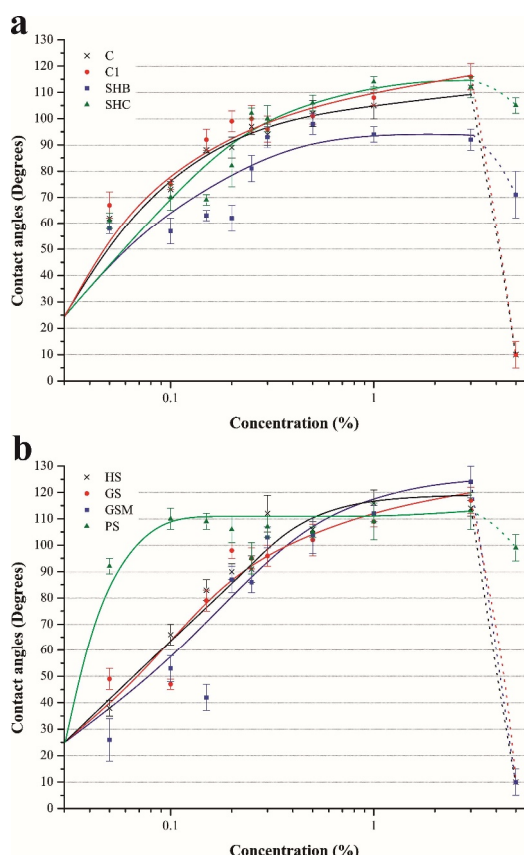


Fig. 1. Concentration curves of (a) category 1 and (b) category 2 chemical agents. Measurements have been carried out immediately after synthesis.

An increase in concentration to 5% resulted in a decrease in CAs with both category 1 and 2 chemical agents (dashed lines on Fig. 1(a) and (b)). A sudden drop

in CA to $10 \pm 5^\circ$ was observed with C, C1, HS, GS and GSM. With SHB, PS and SHC, decreases of 23%, 12% and 6% in CAs were noted when compared to the CAs measured at concentration of 3%. Visual inspection of the samples when synthesised at 5% revealed the presence of a colourless liquid likely to be the cause of the decrease in CAs. Besides SHC and SHB which had WDPT class 10 (> 18000s) and class 8 (901 – 3600s) respectively following synthesis at 5%, all remaining chemical agents exhibited WDPT class 0 (< 5s).

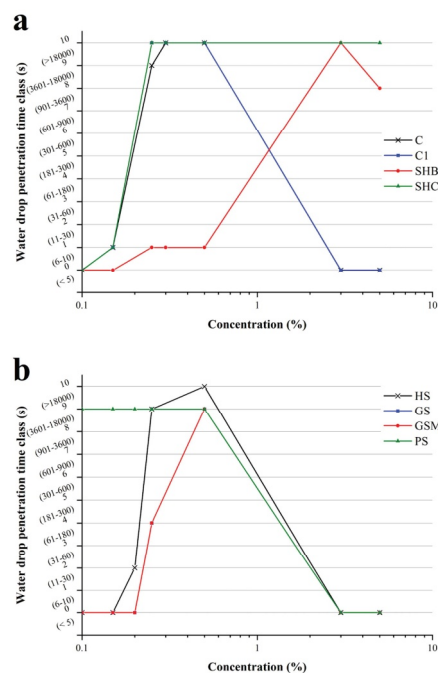


Fig. 2. Water drop penetration time of (a) category 1 and (b) category 2 chemical agents against concentration. Measurements have been carried out immediately after synthesis.

3.2 Wettability and time effects

To investigate the time effects on the hydrophobicity of the LBS, CAs of the synthesised LBS were measured at regular intervals. Two time periods were distinguished to probe the changes in hydrophobicity: they were short-term (up to 180 min) and long-term (from 24h to 576h). LBS synthesised at 5% with both category 1 and 2 chemical agents were first investigated. This was followed by synthesis at two relatively lower concentrations with the category 1 (0.1% and 0.3%) and 2 (0.1% and 0.2%) chemical agents and the changes in hydrophobicity monitored over long-term. These concentrations were selected based on the CA recorded immediately following synthesis: LBS synthesised with the category 1 chemical agents at 0.3% gave a CA above the 90° threshold while synthesis carried out at 0.1% gave values below 90° . The WDPT for all concentrations was measured immediately, 1h, 24h, 168h and 576h after synthesis.

3.2.1 Synthesis at 5%

Fig. 3(a) illustrates the short-term time effects of the CAs when synthesis was carried out with the category 1 chemical agents. While considerable fluctuations were noted with C during the first 20 min following synthesis, measurements after 30 min showed a general increase with a CA of $108 \pm 3^\circ$ recorded after 180 min. The changes observed with C1, SHB and SHC were relatively less fluttered and gradual increases noted over the short-term investigation. With the category 2 chemical agents, gradual increases were observed during the short-term time effects (Fig. 3(b)). Compared to HS and PS where increases were recorded during the first 10 min, synthesis with GS and GSM showed no change in CAs (stayed constant at $10 \pm 5^\circ$).

The long-term effects on the CAs of the category 1 and 2 chemical agents are shown in Fig. 4. Compared to the short-term effects, there were relatively less fluctuations in the CAs. Except for a slight drop in CA with C (from $113 \pm 1^\circ$ at 48h to $108 \pm 2^\circ$ at 72h) and with SHC (from $110 \pm 4^\circ$ at 24h to $104 \pm 4^\circ$ at 192h), CAs were generally constant 24h after synthesis.

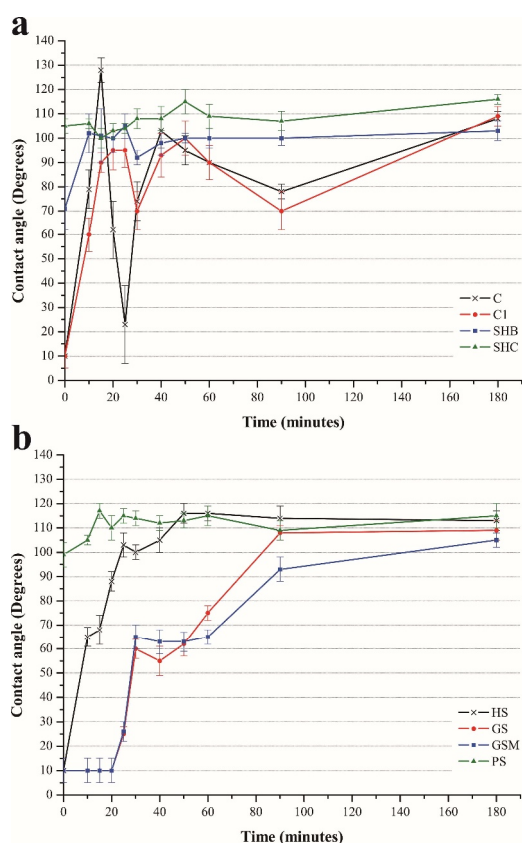


Fig. 3. Short-term variation of contact angle of LBS synthesised at 5% with the (a) category 1 and (b) category 2 chemical agents.

All chemical agents except for SHC (which displayed class 10 (> 18000s) immediately after synthesis) increased WDPT from class 0 (< 5s) to class 10 (> 18000s) after 24h. Measurements performed at 168h and 672h showed that all chemical agents had a constant WDPT of class 10 (> 18000s). For example, C,

C1, HS, GS, and GSM all showed class 0 (< 5s) when measured immediately and 1h after synthesis. However, after 24h, WDPT rose to class 10 (> 18000s) and stabilised.

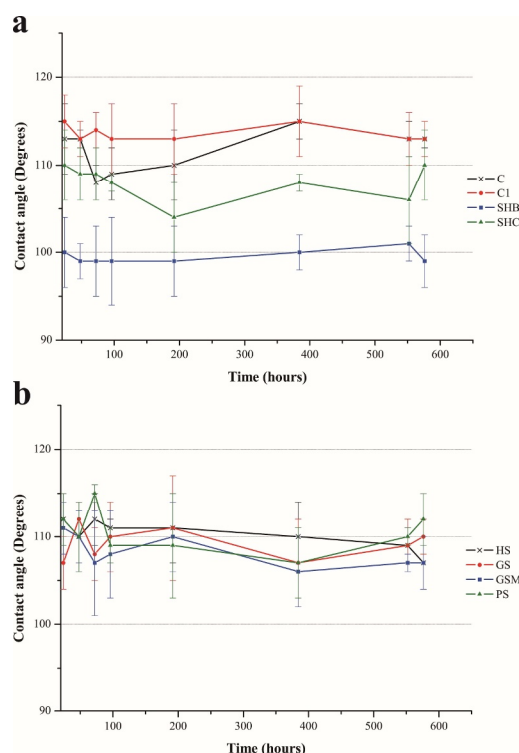


Fig. 4. Long-term variation of contact angle of LBS synthesised at 5% with the (a) category 1 and (b) category 2 chemical agents.

3.2.2 Synthesis at low concentrations

Comparison between concentrations of 0.1% and 0.3% for the category 1 chemical agents showed that synthesis at 0.3% was always larger than at 0.1% regardless of the time at which measurement was made. A sharp rise in CA was observed 96h after synthesis at 0.3% whereas at 0.1%, the change in CA was either gradual or minimal). Similarly, for the category 2 chemical agents, synthesis at 0.2% increased CA over time e.g., with GS, CA measured immediately after synthesis was $98 \pm 3^\circ$ and 48h later, rose to $116 \pm 5^\circ$. In contrast, synthesis at 0.1% yielded changes in CAs that were relatively marginal. These results indicate that there exists a threshold concentration for each of these chemical agents beyond which time will lead to increase in CA up to a maximum value. For the category 1 chemical agents, this concentration is expected to lie between 0.1% and 0.3%.

Except for SHB, the WDPT of the category 1 chemical agents when used to synthesise LBS at 0.3% was constant at class 10 (> 18000s) irrespective of time. However, synthesis at 0.1% with the same chemicals caused WDPT to fluctuate between class 0 (< 5s) and class 6 (601–900s) when investigated for a time period of up to 672h. With the category 2 chemical agents, the WDPT of the LBS synthesised at 0.2% varied from class 2 (11–30s) to class 10 (> 18000s) while at 0.1%, except

for PS, the LBS had WDPT between class 0 ($< 5s$) and class 1 (6–10s) for a time period of up to 672h.

3.3 Comparisons with DMDCS

Fig. 5(a) illustrates the concentration curve of LBS synthesised with DMDCS after a time period of 24h. The CAs recorded at the two lowest concentrations investigated, 0.00424% and 0.0053% were respectively $108 \pm 5^\circ$ and $115 \pm 4^\circ$. Beyond 0.0053%, an increase in concentration did not markedly influence CAs. Therefore, the critical concentration of DMDCS was taken as 0.0053%. The CA measured after a time period of 168h ($116 \pm 2^\circ$) and 576h ($115 \pm 5^\circ$) did not change and the WDPT measured at 24h, 168h and 672h were all class 10 ($> 18000s$) at the critical concentration. Similar observations have been reported by Ng and Lourenço [4] who measured the WDPT of LBS, 96h following synthesis with DMDCS.

To provide a systematic comparison between the CAs reached by DMDCS and the category 1 and 2 chemical agents, the critical concentrations after a time period of 24h were compared. The concentration curves of the category 1 and 2 chemical agents with CAs measured after 24h are shown in Fig. 5(b) and 5(c) respectively. The critical concentrations of these chemical agents were larger than DMDCS. Except for C1, all category 1 chemical agents had a critical concentration of 0.5%. With C1, a gradual increase in CAs from $102 \pm 1^\circ$ to $115 \pm 3^\circ$ was observed as the concentration switched from 0.25% to 5%. For the category 2 chemical agents, the critical concentration was 0.2% for PS and 0.5% for HS, GS and GSM. Besides synthesis with SHB where a maximum CA of 104° was recorded, synthesis with the other chemical agents had maximum CAs varying between 112° and 117° and were close to the maximum CA recorded with DMDCS (119°).

3.4 SEM-EDS analysis

A total of three areas on each sample of LBS were investigated and their elemental constituents determined. The analysis of the treated LBS was carried out 6 weeks after synthesis at 3%. Fig. 6(a) and (b) illustrate the SEM microphotographs of the untreated LBS particle and LBS synthesised with SHB. Clearly, on the LBS particle synthesised with SHB, films and polymers are adhered to the particles, which not only altered the surface morphology of the particles but also their chemistry as evidenced by their respective EDS spectra (Fig. 6(c)-(h)). While both untreated and synthesised LBS had carbon, oxygen and silicon as their predominant constituents, their relative compositions differed: following synthesis with SHB, the carbon content of the particle increased from $\sim 17\%$ to a maximum of $\sim 67\%$. Similar increases have also been observed by Choi et al. [11] following the synthesis of clay particles using Zycosoil, a commercially available chemical agent and by Wang et al. [12] after hydrophobising flat metallic substrates. In this study, the increase in carbon content is primarily attributed to the

presence of the films and polymers. Fig. 6(b) also shows the non-uniform nature of the coatings on the particle, with regions where the polymers adhered to (areas 4 and 5) having a significantly larger carbon content. Similar increases in carbon content were also observed with the remaining category 1 and 2 chemical agents. However, synthesis with DMDCS showed no change in composition from the untreated particle possibly because of the relatively thin silane coating on the particle compared to the coatings induced by the commercial chemical agents. This leads to the X-rays analysed emanating from within the particle (similar to an untreated particle) and not from its surface.

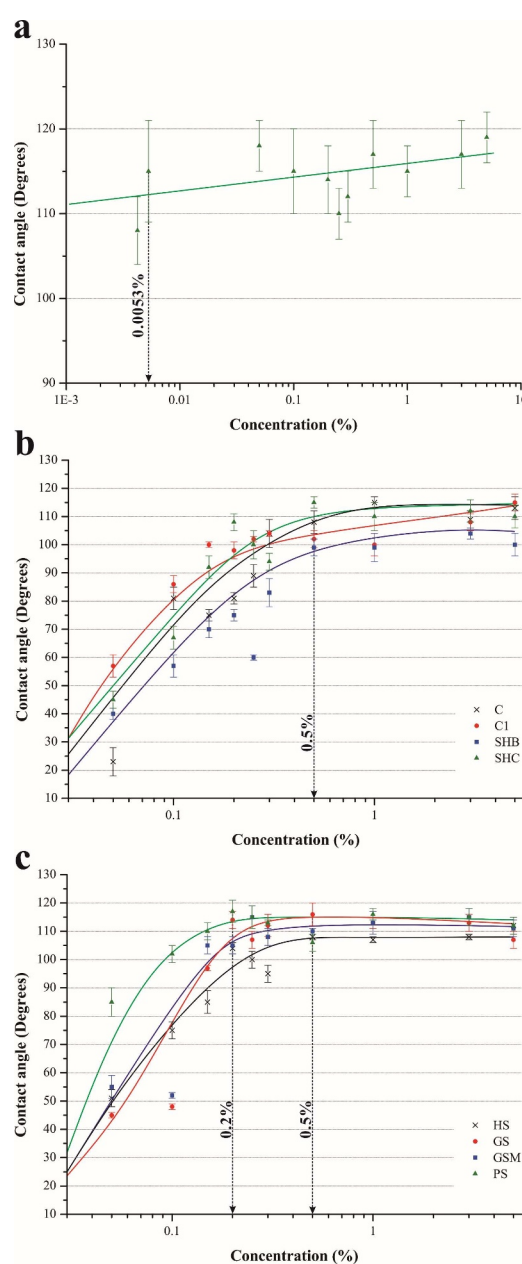


Fig. 5. Concentration curves of (a) dimethyldichlorosilane, (b) category 1 and (c) category 2 chemical agents. Measurements have been carried out 24h after synthesis.

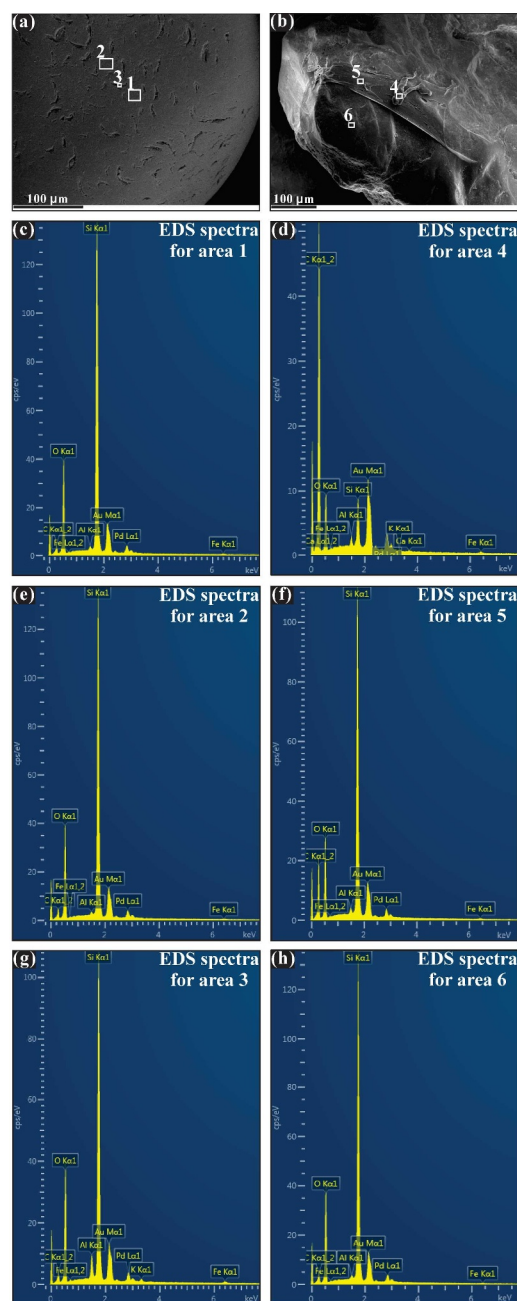


Fig. 6. Scanning electron microscope microphotographs of (a) untreated LBS and (b) LBS synthesised with SHB. (c) – (h) EDS spectra of the areas identified on the untreated and synthesised LBS

4 Conclusions

The hydrophobicity of LBS after synthesis with eight commercial chemical agents were investigated at different time intervals and comparisons were made to DMDCS. The findings are as follows:

1. The assessment of hydrophobicity immediately following synthesis with the commercial chemical agents showed increases in CAs as concentration rose up to 3%. However, at this concentration, the persistence of hydrophobicity, measured using the WDPT were dependent on the agents used.

2. An increase in concentration to 5% led to a decrease in CAs with all the commercial chemical agents and except for SHC, the WDPT also dropped. Short-term and long-term time investigations of LBS synthesised at 5% showed increases in both CAs and WDPT with all agents; after 24h, the CAs were generally constant and the WDPT reached class 10.

3. The long-term time investigation of the commercial chemical agents at relatively lower concentrations (0.1% to 0.3%) indicated a threshold concentration, beyond which an increase in CA occurs over time.

4. Except for SHB, the maximum CAs reached by the commercial chemical agents after 24h were comparable to DMDCS (119°). However, the critical concentrations differed significantly: the lowest critical concentration amongst these agents was 0.2% whereas with DMDCS, the critical concentration was 0.0053%.

5. SEM-EDS analysis of the synthesised LBS with the commercial chemical agents showed increases in carbon content while no change could be observed on the LBS synthesised with DMDCS due to the relatively thinner coating.

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