Introduction

Due to their low permeability, clays are the main material used as a liner in solid waste disposal landfills. They become exposed there to various chemical, biological and physical events and the clay is affected by the resulting leachate (Yılmaz et al., 2008). Researchers are thus interested in surfactants and polymers for modifying clays’ engineering properties. Surfactants are surface-active agents which alter fluid interface properties. Surfactant modified clay (SMC) or surfactant–clay complexes have been considered appropriate landfill liners (Lo, 2001; Ashmawy et al., 2002; Gates et al., 2004; Matott et al., 2006) and also potential sorbents for wastewater and contaminated soils (Zhu and Zhang, 1997; Mulligan et al., 1999a, b; Mulligan et al., 2001; Al-Asheh et al., 2003; Li et al., 2003; Wibulswas, 2004; Ghiaici et al., 2004; Yang et al., 2005).

Consistency limits (Atterberg limits) have been repeatedly shown to be useful indicators of clay behaviour (Jefferson and Rogers, 1998; Dolinar et al., 2007). Reconstituted clay sample liquid and plastic limits can be correlated with various engineering properties, such as specific surface area, cation exchange capacity, permeability, shrinking and swelling behaviour, shear strength and soil compressibility (Sharma and Lewis, 1994; Abdullah et al., 1999; Yukselen and Kaya, 2006; Dolinar et al., 2007). Consequently, soil consistency limits are determined, then some other geotechnical properties whose determination may take a long time can be easily estimated with acceptable accuracy. Evaluating consistency limits in soils affected by surfactants is of great interest.
Table 1. The chemical composition of clay.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ %</td>
<td>53.28</td>
</tr>
<tr>
<td>Al₂O₃ %</td>
<td>20.67</td>
</tr>
<tr>
<td>Fe₂O₃ %</td>
<td>6.13</td>
</tr>
<tr>
<td>CaO %</td>
<td>1.71</td>
</tr>
<tr>
<td>MgO %</td>
<td>2.82</td>
</tr>
<tr>
<td>K₂O %</td>
<td>0.82</td>
</tr>
<tr>
<td>Na₂O %</td>
<td>0.02</td>
</tr>
<tr>
<td>TiO %</td>
<td>0.63</td>
</tr>
<tr>
<td>LOI %</td>
<td>13.9</td>
</tr>
</tbody>
</table>

Table 2. Clay's index properties

<table>
<thead>
<tr>
<th>Index properties</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay content &lt;0.002 mm (%)</td>
<td>74</td>
</tr>
<tr>
<td>Finer content &lt;0.075 mm (%)</td>
<td>99</td>
</tr>
<tr>
<td>Specific gravity Gₛ</td>
<td>2.72</td>
</tr>
<tr>
<td>Liquid limit Wₗ (%)</td>
<td>88.4</td>
</tr>
<tr>
<td>Plastic limit Wₚ (%)</td>
<td>38.0</td>
</tr>
<tr>
<td>Plasticity index Iₚ (%)</td>
<td>50.4</td>
</tr>
<tr>
<td>Cation exchange capacity (meq./100 g dry soil)</td>
<td>38.59</td>
</tr>
<tr>
<td>Contact angle o</td>
<td>35</td>
</tr>
</tbody>
</table>

Table 3. Some properties of the surfactants used in the tests

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Abbreviation</th>
<th>Formula</th>
<th>Surfactant type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylglycine</td>
<td>TMG</td>
<td>(CH₃)₃N⁺CH₂CO₂⁻</td>
<td>Zwitterion</td>
</tr>
<tr>
<td>Hydroxyethylcellulose</td>
<td>HEC</td>
<td>(C₆H₁₀O₅)n</td>
<td>Nonionic</td>
</tr>
<tr>
<td>Octyl phenol ethoxylate</td>
<td>TRITON X-100</td>
<td>C₆H₁₃O(C₂H₄O)n</td>
<td>Nonionic</td>
</tr>
<tr>
<td>Linear alkylbenzene sulfonate</td>
<td>LABSA</td>
<td>CH₃(CH₂)₇C₆H₄SO₃H</td>
<td>Anionic</td>
</tr>
<tr>
<td>Sodium lauryl ether sulfate</td>
<td>SLES</td>
<td>CH₃(CH₂)₁₇CH₃(OCH₂CH₂)₁₆OSO₄Na</td>
<td>Anionic</td>
</tr>
<tr>
<td>Cetyl trimethyl ammonium chloride</td>
<td>CTAC</td>
<td>(C₁₅H₃₁)₃N(CH₃)₃Cl</td>
<td>Cationic</td>
</tr>
<tr>
<td>Quaternised ethoxylated fatty amine</td>
<td>QEFA</td>
<td>(fatty amine) R - (OCH₂CH₂)₉ - NH</td>
<td>Cationic</td>
</tr>
</tbody>
</table>
Surfactants and modified clay preparation

Seven surfactants were used in this research; Table 3 gives the surfactants’ abbreviation, formula and type. SMCs were prepared following the procedure described by Xi et al., (2007) and Liu et al., (2008). Briefly, 40 g of clay was first dispersed in 8 l of deionised water, then stirred with a magnetic stirrer at about 1,000 rpm for about 2 h. Previously-prepared surfactant solution was slowly added to the clay suspension at 30°C. All modified products were dried at room temperature. The surfactants were used at 5% (250 ppm), 10% (500 ppm), and 15% (750 ppm) of clay by weight.

Consistency limits

Consistency limit tests (i.e. liquid limit and plastic limit) were carried out following the procedure outlined in BS 1377, Part 2, 1990. The cone penetrometer (fall cone) method was used to determine liquid limit. Specimens were prepared for the liquid limit tests by mixing an air-dried SMC mass (passing through a 425-μm sieve). Plastic limit tests were performed on material prepared for the liquid limit test; both liquid and plastic limit tests were conducted at room temperature.

Contact angle measurements

A contact angle is defined as being the angle made by the liquid/solid interface intersection with the liquid/air interface; alternately, it can be described as being the angle between a solid sample’s surface and the tangent of a droplet’s ovate shape at the edge of the droplet. A high contact angle indicates low solid surface energy or chemical affinity; this is also referred to as a low degree of wetting. A low contact angle indicates high solid surface energy or chemical affinity and a high, or sometimes complete, degree of wetting (Anonymous, 2009). Figure 2 illustrates a drop of the reference liquid (water for Fig. 2a and air for Fig. 2b) resting on a solid surface in the presence of another fluid (air for Fig. 2a and water for 2b). The interface between the two fluids meets the solid surface at contact angle $\theta$ (Mitchell and Soga, 2005).

The simplest way of measuring a contact angle is with a goniometer which allows the user to measure the contact angle visually. The droplet is deposited by a syringe pointing down vertically onto the sample surface and a high-resolution camera captures the image which can then be analysed either by eye (with a protractor) or using image analysis software. The contact angles were measured with a goniometer (CAM 101, KSV Instruments, Finland) in this study, using clay and modified clay pellets.
Results and Discussion

Consistency limits

Figures 3, 4, 5, 6, 7, 8 and 9 give the variation of modified clays’ consistency limits by TMG, HEC, TRITON X-100, LABSA, SLES, CTAC, and QEFA, respectively. For clays modified with zwitterion, nonionic and anionic surfactants (TMG, HEC, TRITON X-100, LABSA and SLES), it was seen that the liquid limit and plasticity index increased when surfactant percentage was increased. The plastic limit also decreased when increasing the percentage of surfactant. On the other hand, the liquid limit and plasticity index for clays modified with CTAC and QEFA decreased drastically when surfactant percentage was increased. However, plastic limit values’ variation was insignificant for CTAC and QEFA (Figures 8-9).

The consistency limit test results were marked on the Casagrande plasticity chart to determine the new soil classification according to the USCS. Figure 10 shows the changes after modification with anionic surfactants and Figure 11 shows the changes after modification with cationic surfactants. It can be clearly seen that the points representing soil classification approached the A-line when anionic surfactant percentage was increased. However, cationic surfactants changed the clay class when the
percentage was increased, resulting in cationic SMCs becoming MH (high plasticity silt) (Figure 11). Consistency limit test results would suggest that clay water affinity became significantly increased by LAbSA and HEC; however, TMG and SLES did not significantly change water affinity. CTAC and QEFA also decreased water affinity.

It should be pointed out that there has been no general consensus regarding the effect of surfactants and chemicals on clays’ consistency limits. Most researchers have reported that chemicals have decreased the liquid limit of clays (Gleason et al., 1997; Shackelford et al., 2000; Schmitz et al., 2004; Lee et al., 2005; Jo et al., 2005). However, little research has indicated that chemicals have increased CL or kaolinite clay liquid limit (Rao and Mathew, 1995; Sivapullaiah and Manju, 2005; Park et al., 2006; Arasan and Yetimoglu, 2008). Different patterns have most likely arisen from a difference in clay mineralogy and surfactant/chemical type (i.e. zwitter-ion, anionic, nonionic and/or cationic). In line with previous studies, this research has shown that anionic SMCs were the most hydrophilic and cationic SMCs were the most hydrophobic (Figures 12, 13). Nevertheless, it could be said that the net electrical forces between clay mineral layers were affected by surfactant percentage and type; anionic and cationic surfactants would result in an increase and a decrease in net repulsive forces, respectively (increased and decreased repulsive forces cause dispersion and flocculation of clay particles, respectively).

Figure 10. Zwitterion, nonionic, and anionic surfactants modified clay results on the plasticity chart.

Figure 11. The cationic surfactants modified clays results on the plasticity chart.

Figure 12. Zwitterion, nonionic and anionic surfactants modified clays’ contact angle results.

Figure 13. Cationic surfactants modified clays’ contact angle results.

Figure 14. The contact angles for some modified clays. a) Contact angle image of natural clay (35°); b) Contact angle image of TMG (10%) modified clay (14°); c) Contact angle image of QEFA (15%) modified clay (54°)
Contact angle measurements

Figure 12 gives the effect of zwitterion, nonionic and anionic surfactants on modified clays’ contact angles and Figure 13 shows the cationic surfactants effect. Figure 14 presents some images of the smallest contact angle obtained from natural and SMCs.

Figure 12 shows that zwitterion, nonionic and anionic surfactants significantly decreased modified clays’ contact angles; however, cationic surfactants increased the contact angles (Figure 13). TMG and QEFA were the most effective surfactants when contact angle results were taken into consideration; similar to consistency limit results, contact angle measurements indicated that clay water affinity was increased by zwitterion, nonionic and anionic surfactants and also became decreased by cationic surfactants. Cipriano et al., (2005) indicated that cationic surfactants increased modified clays’ contact angles and produced a hydrophobic surface.

Conclusions

The following conclusions were thus drawn:

• Consistency limits were significantly changed compared to those for natural clay. The points representing soil class came further towards the A-line when zwitterion, nonionic and anionic surfactant percentage increased. Cationic surfactants changed the clay classification from CH to high plasticity silt (MH) when the percentage of surfactant added to the clay was increased;

• Clays modified with zwitterion, nonionic and anionic surfactants gave the lowest contact angles compared to those for natural clay; however, the clays modified with cationic surfactants gave the highest contact angles; and

• It could also be said that clay water affinity was increased by zwitterion (TMG), nonionic (HEC, TRITON X-100) and anionic surfactants (LABSA, SLES), also that cationic surfactants (CTAC and QEFA) decreased the water affinity used in this research. Hence, zwitterion, nonionic and anionic SMCs may be used as hydrophilic materials in waste water remediation and the cationic SMCs may also be used as hydrophobic materials (liner) in waste disposal landfills and dams.

It should be pointed out that further studies on SMCs’ engineering properties (e.g. XRD, XRF, DTA and TG for mineralogy and cation exchange capacity, zeta potential for electro-kinetic properties) are needed to make more reasonable judgments. Such studies should aim at explaining SMC behaviour more reasonably.

Acknowledgements

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References


