

Reuse of spent bleaching earth by polymerisation of residual organics

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ABSTRACT

Spent bleaching earth (SBE) is a waste generated by the edible oil industry that currently has limited options for beneficial reuse. In excess of ~2 million tonnes per year of SBE is generated world-wide with major quantities available in the middle-east where significant volumes of edible oils are produced. Low pressure compaction followed by heat treatment at 150 °C causes polymerisation of the residual organic components in SBE and this produces monolithic samples with high unconfined compressive strengths (54 MPa). SBE can therefore be used to manufacture novel clay blocks for use in construction that are bonded by polymerised vegetable oil. This represents a new, innovative and resource efficient application for SBE. In this research, commercial SBE has been characterised and the effects of key processing variables (temperature and compaction pressure) on the compressive strength, porosity and density of the SBE clay blocks are reported and the mechanisms responsible for strength development are discussed.

Keywords: spent bleaching earth; polymerisation reactions; clay products; stabilisation; resource efficiency.

1. Introduction

Vegetable oils for human consumption are subjected to a bleaching process during refining to remove non-glyceride components and impurities such as carotenoids, chlorophylls, trace metals, free fatty acids and hydro-peroxides. This ensures that the oil meets the necessary requirements for colour. Bleaching also improves product shelf-life and is

achieved by mixing the oil with bleaching earth, typically bentonite clay, under a vacuum for 15 to 30 minutes. Montmorillonite is the dominant clay mineral of bentonite and this has a typical crystalline structure consisting of an octahedral sheet of aluminium cations sandwiched between two tetrahedral sheets of silicon cations (Bergaya, 2006; Zschau, 2001). At the end of the process, the oil/bleaching earth mix is filtered to separate the treated oil from the waste clay, which then forms spent bleaching earth (SBE).

SBE typically contains 20 to 40% (w/w) of residual vegetable oil and pigments, oxidation products, free fatty acids (FFA), phosphatides and trace metals (Pollard et al., 1991a). When SBE leaves the refining process at temperatures between 80 and 120 °C, exposure to atmospheric oxygen initiates oxidation of the residual oil. This is catalysed by the high surface area of the bleaching earth. The oxidation reactions cause SBE to self-heat and it can spontaneously combust causing a potential fire hazard. SBE is therefore classified as a hazardous waste in many countries, and is banned from landfill by the EU Landfill Directive due to flammability and the high organic content which exceeds the 6% waste acceptance criteria limit on total organic content. SBE is therefore a problematic waste with worldwide generation estimated to be in excess of ~2 million tonnes per year, based on world consumption of vegetable oils of 128 million tonnes (USDA, 2009) and assuming 1 wt.% of SBE is produced relative to the amount of vegetable oil produced (Pollard, 1990).

Oxidation reactions of triglycerides involve the formation of hydro-peroxides which decompose into free radicals following a chain reaction mechanism. At later stages of oxidation, the triglyceride molecules cross-link at free radical sites to form polymeric products and the residual oil transforms to produce a solid film (Bentley and Turner, 1998; Formo, 1979a). The oxidation of residual vegetable oil in SBE therefore has potential to form a cross-linked polymer-clay composite material. Processing would not require any additional materials and the self-heating of SBE could be used to oxidise and polymerise the residual oil, resulting in minimal requirements for additional heat energy. The objective of this research was to investigate this effect and optimise the physical properties of blocks formed by compacting and polymerising SBE.

2. Material and methods

2.1. Materials

Commercial SBE from bleaching sunflower oil was obtained from a vegetable oil refiner in South East England (ADM Pura refinery, Unilever, UK). This was a dark brown, non-flowing powder. Raw acid activated bleaching earth (BE) was also collected in order to prepare fresh SBE surrogate samples. This was a flowable, light coloured homogeneous material. Refined sunflower oil (Unilever brand *Flora*) was also used as a surrogate for the residual oil present in SBE. This contained 63% (w/w) linoleic acid, 24% (w/w) oleic acid and 12% saturated acids.

2.2. Characterisation of SBE

The particle size distribution of SBE was determined by laser diffraction (Beckman Coulter LS-100) on approximately 0.2 g representative samples. Loss on ignition tests were completed on 5g of SBE heated to 550 °C following BS EN 12879:2000, with tests performed in triplicate. The moisture content was determined on separate samples following BS EN 14346:2006. SBE samples was also analysed by thermogravimetric analysis/differential thermogravimetric analysis (TG/DTG, Polymer Laboratories, PL-STA thermal analyser) using a heating rate of 10°C/min.

2.3. Characterization of residual oil

The residual oil present in SBE was extracted using acetone and analysed for the free fatty acid (FFA) content (BS EN ISO 660:2000) with the peroxide value determined using the method in BS 684-2.14:2001. Samples of recovered oil were analysed by Fourier Transform Infrared Spectroscopy (FTIR) using 7 to 8 mg samples placed between two NaCl discs.

2.4. Preparation of SBE monolithic samples

Monolithic samples were prepared by uni-axially compacting SBE in a 2 cm diameter steel pressing die. The sample height was controlled to 4.00 ± 0.05 cm and the pressed sample weight was recorded. Compacted samples were transferred to an oven for heat treatment. After heat treatment, samples were stored in a desiccator prior to weighing and testing.

SBE monolithic samples were compacted using two different uniaxial pressing pressures, 1 and 5 MPa. Compacted samples were heat treated to induce polymerisation of

the residual oil at two temperatures, 60 °C and 150 °C, and samples were held at these temperatures for times ranging between 0.5 and 48 hours. In total, 32 different SBE compaction and thermal treatments were used with 6 samples prepared for each set of conditions.

Additional samples were prepared using 100% bleaching earth (BE) to confirm that strength development in compacted SBE was due to the presence of the residual oil. A second set of surrogate samples were prepared by mixing 37% (w/w) refined sunflower oil with 63% (w/w) BE. The moisture content was adjusted to 2.6 % to be equivalent to that of SBE. These were used to assess the effect of hydro-peroxides, pigments, free fatty acids and other components removed from the unbleached oil but present in the residual oil in SBE, on the efficiency of polymerisation.

2.5. Properties

Bulk density was determined for all monolithic samples before and after curing. The apparent porosity of monolithic samples, which represents the volume of pores connected to the external surface, was determined according to BS EN 10545-3:1997.

The unconfined compressive strength (UCS) of heat treated/polymerised SBE monolithic samples was determined using a loading rate 300N/s (BS EN 13286-53:2004). All UCS tests were performed using between three and six replicates and the mean, standard deviation and 95% confidence interval calculated.

2.6. Microstructure

Scanning electron microscopy (JEOL JSM 5610) was used to examine the microstructure of gold coated polished surfaces of selected SBE monolithic samples.

3. Results and discussion

3.1. Characterisation of SBE

The specific gravity and loose bulk density of SBE samples were 0.6 g/cm³ and 0.4 g/cm³ respectively. The mean particle size of SBE was 140µm and 90% of the particles were below 810 µm (i.e. d₉₀=810 µm), the d₅₀ was 310 µm and d₁₀ was 75 µm.

Approximately 90% of the particles were larger than 75 μ m and this results from extensive agglomeration of primary spent bleaching earth particles due to the residual oil. The LOI of SBE samples was 47.0% with a standard deviation of 0.4 and the moisture content was 2.6% with a standard deviation of 0.3.

Differential thermogravimetric (DTG) analysis data is given in **Fig. 1**. This shows that the bleaching earth accelerated the thermal decomposition of the residual oil as compared with the thermal decomposition of the recovered oil. It was observed that decomposition of SBE began at around 100-110 °C which is 90-100 °C lower than the decomposition temperature of the recovered oil. The thermal analysis results show that the oil begins to decompose at around 200 °C and therefore temperatures below this can be used for polymerisation.

3.2. Characterization of residual oil

The organic fraction of SBE recovered using acetone extraction was much darker than the refined oil. The peroxide value and FFA content of recovered residual sunflower oil were 120.4 and 12.30% (w/w) respectively compared with 10.0 and 0.07 % for refined sunflower oil.

The FTIR spectra of refined and recovered sunflower oils both had similar sharp peaks between 2850-3000 cm^{-1} and 700-1700 cm^{-1} . This confirms the presence of typical triglyceride molecules consisting of esters of long chain carboxylic acids in both alkane and alkene forms. The peak at 3008 cm^{-1} corresponds to stretching vibration of the cis double bond, the disappearance of which is related to polymerisation reactions (Mallégol, 1999; Mallégol et al., 2000; Wang et al., 2008).

3.3. Polymerisation in SBE monolithic samples

3.3.1. Unconfined compressive strength (UCS) of samples heat treated at 60°C

Samples pressed at 1MPa and heat treated at 60 °C had low UCS below, typically below 1 MPa. Samples pressed at 5 MPa achieved a UCS of only 2 MPa after curing for 0.5 hour, which increased to approximately 3 MPa after curing for 48 hours. SBE surrogate samples pressed at 1 and 5 MPa achieved similar UCS values. Samples made using 100% bleaching earth without any oil addition had no strength, confirming that UCS

development in compacted SBE samples is associated with polymerisation of the residual oil.

3.3.2. Unconfined compressive strength of samples heat treated at 150°C

The UCS significantly increased for all samples cured at 150°C, as shown in **Fig. 2** and samples compacted at 1 MPa achieved compressive strengths of 8 MPa after 2 hours curing, which increased to a maximum of 11 MPa after 8 hours curing. This did not change on increasing the curing time up to 48 hours.

The UCS of the 5 MPa compacted samples was 21 MPa after 2 hours curing and 38 MPa after 16 hours curing after which time it remained constant. The samples prepared from 100% BE and heat treated at 150 °C did not gain any strength and the SBE surrogate samples only achieved ~28% of the UCS of SBE samples pressed at 1 and 5 MPa.

3.3.3. Effect of compaction pressure on UCS of polymerised SBE samples

Fig. 3a shows the UCS of SBE monolithic samples compacted at 1, 3, 5 and 7 MPa and cured at 150 °C for between 0.5 and 48 hours. The delaying effect of compaction is observed in the data for 7 MPa pressed samples which were the slowest to reach maximum UCS which for these samples was 54 MPa. The relationship between the maximum UCS and the applied compaction pressure is linear as shown in **Fig. 3b**, with an R^2 value of 0.994 in the range from 0 to 7 MPa. The results confirm that UCS increases with increasing compaction pressure and that increased compaction delays the rate of UCS development in compacted SBE.

3.3.4. Physical properties of polymerised SBE samples

The apparent porosity of the 5 MPa compacted samples after 48 hours curing was approximately 17%, compared to 27% for the 1 MPa compacted samples. The porosity of the 1 and 5 MPa samples are sufficiently high for polymerisation to occur. The reduced porosity of the 5 MPa pressed samples may have reduced the rate of oxygen diffusion into the sample and this has extended the time required for complete polymerisation compared to the 1 MPa compacted samples. No significant change in porosity was observed during

48 hours of curing, with only a slight decrease in the apparent porosity occurring in the first 4 hours.

The bulk densities of SBE samples heat treated at 150 °C are shown in **Fig. 4**. The density of the samples cured at 150 °C increased with increasing curing time, reaching a maximum of 1.05 g/cm³ for the 1 MPa samples after 8 hours of curing and 1.26 g/cm³ for the 5 MPa samples after 16 hours of curing.

The relationship between the bulk density and UCS of samples cured at 150 °C is linear, as shown in **Fig. 5**. The UCS has increased with the increase in the bulk density and stabilises when the maximum density has been achieved. Achieving maximum density therefore indicates complete polymerisation of monolithic samples and this was 1.05 g/cm³ and 1.26 g/cm³ for 1 MPa and 5 MPa pressed samples respectively.

3.4. Micro-structural analysis of polymerised SBE samples

The surface of heat treated monolithic samples pressed at 5 MPa and heat treated at 150 °C for 48 hours is shown in **Fig. 6**. This shows a densely compacted sample that contains some residual porosity formed during compaction that is likely to limit the strength of polymerised SBE samples.

Polymerisation of the residual oil in SBE occurs with high efficiency due to the combined effect of four polymerisation catalysts that are naturally present. The high surface area of bleaching earth increases the area of oil exposed to oxygen and this accelerates oxidation reactions. The catalytic and acidic properties of bleaching earth accelerate the decomposition of hydroperoxides and the production of free radicals. In addition, trace heavy metals present in the bleaching earth and also in the residual oil accelerate the rate of oil oxidation and this reduces the temperature needed for oxidative polymerisation (Mallégol et al., 2000). The presence of FFA also increases the rate of oxidation because these oxidise more rapidly than the corresponding triglycerides.

The rate of polymerisation of the SBE monolith is expected to be similar to an oil film if all the SBE particles in contact with residual oil in the monolith are exposed to the same amount of oxygen. Particles in the compacted monolithic sample will bond together at different rates because this will depend on oxygen availability with regions close to the monolithic sample surface expected to more rapidly polymerise.

The local temperature of particles is also affected by position in the monolith. Particles close to the surface are initially heated more rapidly than particles in the sample core.

However, with increasing time the monolith core will store more heat due to the reduced rate of heat loss at the sample centre compared to the surface. The temperature of the core increases and this accelerates polymerisation and may cause spontaneous combustion and decomposition of the residual oil.

The strength gain during heat treatment is mainly controlled by the porosity of the compacted sample, which controls the rate of oxygen diffusion into the sample and the rate of heat loss during polymerisation. Porosity is controlled by the applied compaction pressure which is therefore a key processing factor determining the polymerisation of SBE monolithic samples. In addition, the heat treatment temperature and curing time are key process variables.

The high peroxide value of the recovered oil indicates the presence of significant concentrations of hydroperoxides which are formed by oil oxidation during bleaching and storage. The high FFA may be due to oil hydrolysis caused by the water content in the bleaching earth or this may have resulted from the adsorption of FFA remaining in the unbleached oil. The characterisation results indicate that the recovered oil oxidises more rapidly than refined oil and this is because FFA are known to oxidise more readily than triglycerides (Formo, 1979a). The presence of high concentrations of peroxides shows that the recovered oil is already in an advanced oxidation state, which may be near the end of the induction period after which hydroperoxides begin to decompose, causing cross-linking at free radical sites.

4. Conclusions

Compacting and heat treating spent bleaching earth (SBE) forms monolithic blocks with significant compressive strengths due to polymerisation of the residual oil. The oxidation reactions are catalysed by the high surface area, the acidic properties of the bleaching earth and the presence of free fatty acids. Compaction pressure influences the rate of strength development because this controls oxygen diffusion and polymerisation reactions. Increasing the curing temperature from 60 °C to 150 °C significantly increased the maximum strength achieved. SBE has limited options for disposal and it has been demonstrated that this waste has potential to be used for low energy production of novel clay/vegetable oil polymer blocks for use in construction products. This represents an important contribution to developing new waste management options for this problematic material.

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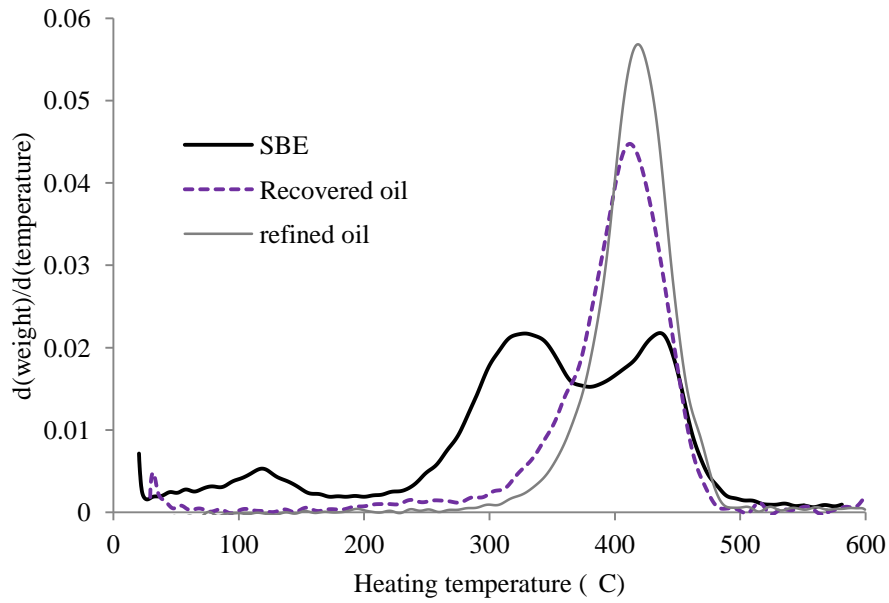


Fig. 1. Differential thermogravimetric (DTG) analysis data for SBE compared with recovered and refined oils, under a N_2 atmosphere showing the reduced temperature required to induce weight loss when the oil is present in SBE.

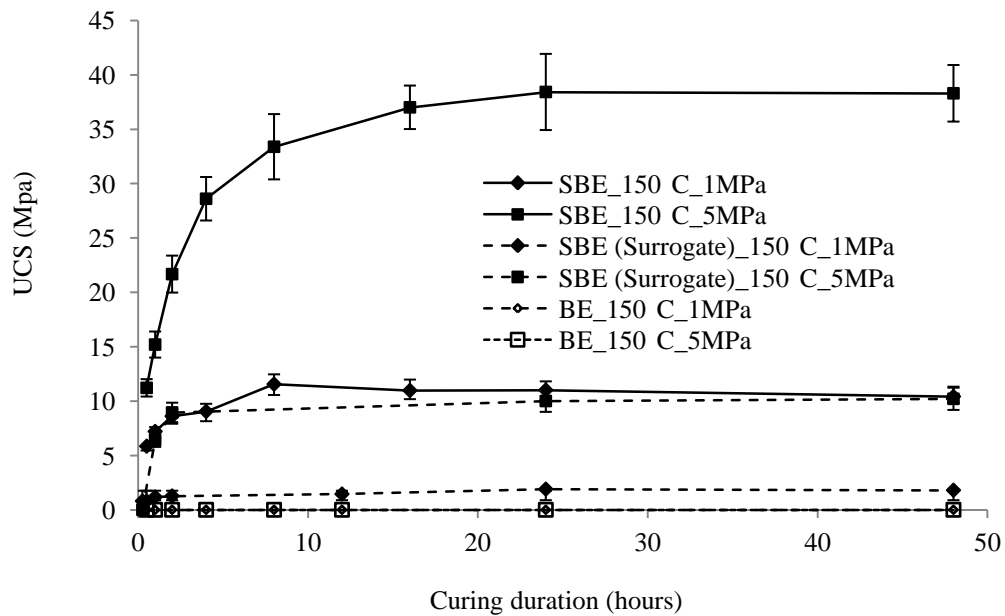


Fig. 2. Effect of curing time at 150 °C on the UCS of SBE, SBE surrogate samples and 100% BE samples compacted at 1 and 5 MPa. The results are the mean \pm standard deviation of at least four independent measurements.

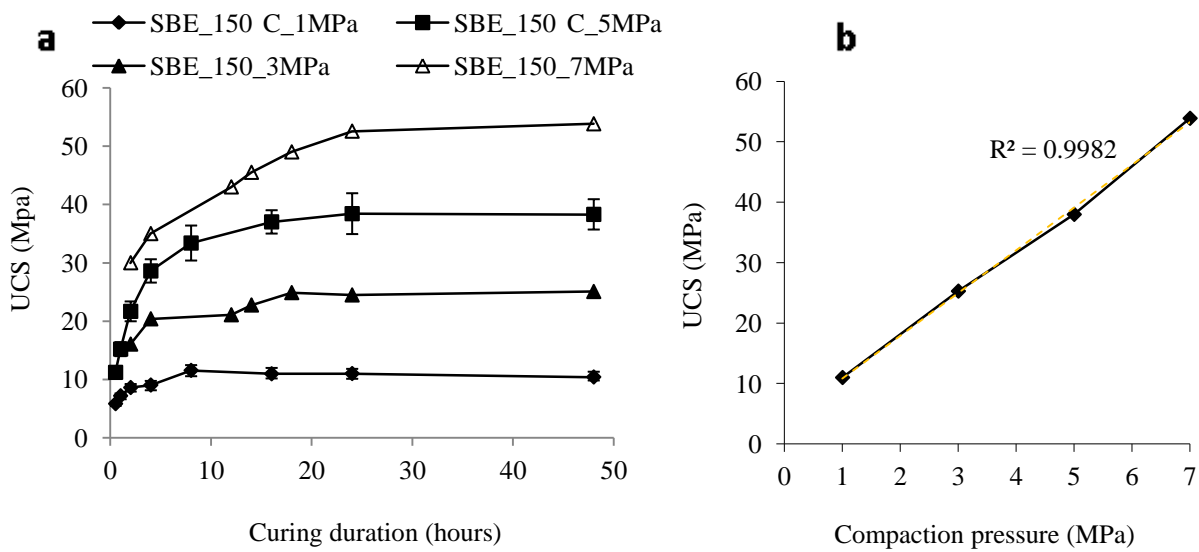


Fig. 3. a) the effect of curing duration at 150 °C on the UCS of SBE monolithic samples compacted at 1, 3, 5 and 7 MPa and b) the linear relationship between the maximum UCS achieved and the applied compaction pressure.

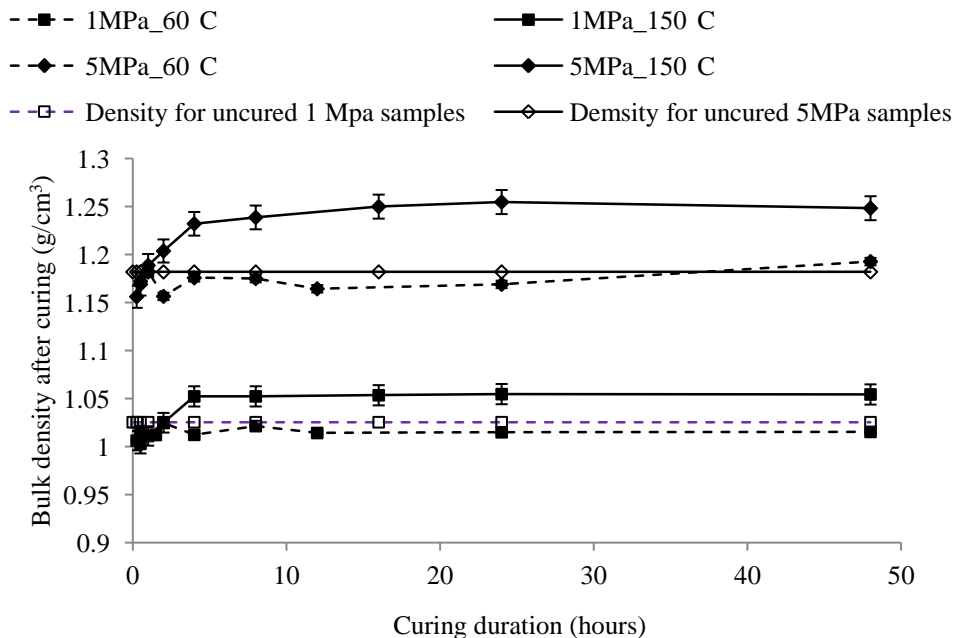


Fig. 4. Bulk density of SBE monolithic samples pressed at 1 and 5 MPa and cured at 60 and 150 °C, cured for different times. The results are the mean \pm standard deviation of at least four independent measurements.

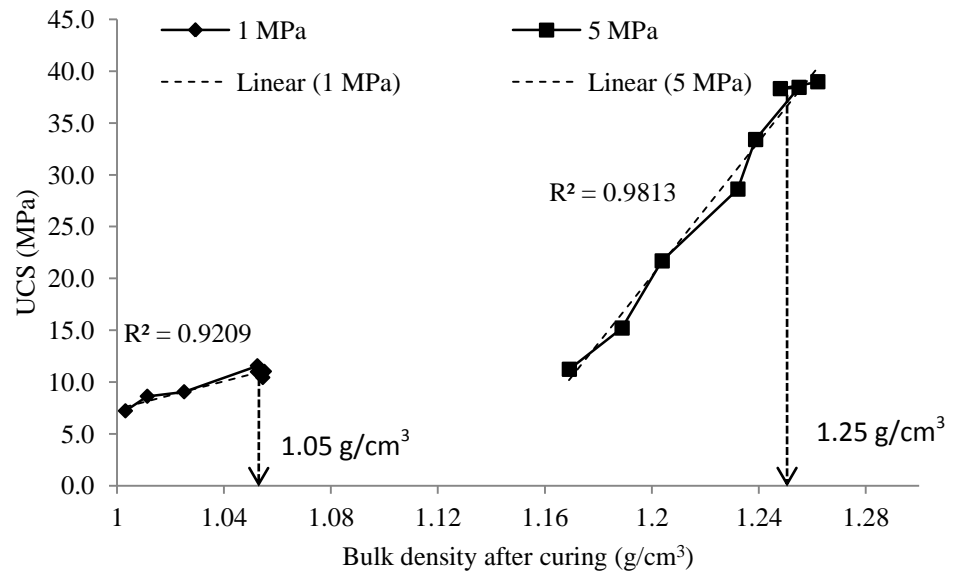


Fig. 5. Relationship between the bulk density and the UCS for the 1 and 5 MPa pressed SBE samples after heat treatment for 48 hours at 150°C.

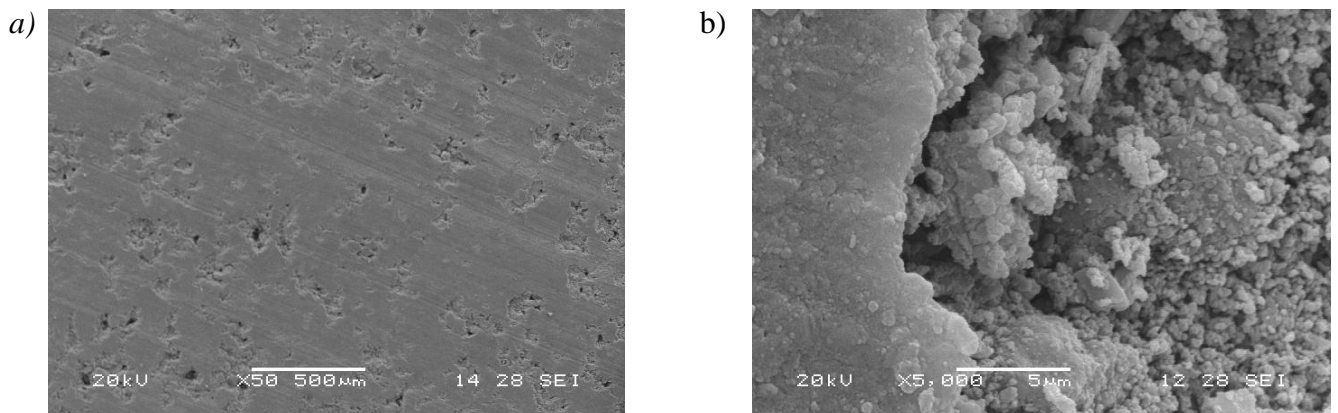


Fig. 6. SEM images of SBE monolithic compacted samples pressed at 5 MPa and heat treated at 150°C for 48 hours. a) low-magnification image of the surface and b) high-magnification image showing the polymerised SBE particles in a surface pore.