Preparation of engineered stones

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Abstract. Engineered Stones were produced in a laboratory using polyester resin and domestic quartz stones. Selection of these particle sizes were based on packing theory and simple Stroke’s law. From combination of both scenario, three different sizes of quartz were calculated and selected. In this scenario, the smallest size was calculated to be 6 \( \mu \)m while the other size ranges were calculated based on the 7x factor. To test the idea, another two sets of samples were also prepared for comparison. The samples were fabricated by vibration or uniaxial pressing. It was found that all the sample sets fabricated by pressing offered better density and Vickers hardness due to the better packing and higher solid loading of the composite. However, the sample set which strictly followed the calculation did not provide the best density and hardness suggesting that the simple model may not be fully correct and some missing parameters may be required. The best sample set belonged to one which followed 7x factor but with a larger starting quartz size. Sample set with the best properties was comparable to the commercial products.

1. Introduction

Natural stones have been used as decorative construction materials due to their aesthetic qualification, accessibility and strength [1]. However, they are often regarded as hard but fragile so combination with other materials to adequately offer more desirable qualities have been addressed [2, 3]. This new composite material is quoted as “engineered stone or “agglomerated stone” as according to BS EN 14618:2009. Engineered stone is thus defined as a composite material made from stone particles packed together by polymer resin or cement to obtain mechanical properties closed or superior to natural stones. Engineered stone typically contain 90-94\% natural stones and other minerals [3]. Applications of engineered stones in construction industry may be ranged from exterior cladding to table or bench slabs for interior use applications. For use as exterior cladding, properties such as light weight, low thermal conductivity was achieved by using aggregate of low density was reported [4]. In this patent, crushed limestone, silica sand, and ground calcium carbonate were used as the aggregate while the unsaturated polyester resin binder was improved by adding 1:1 mix of polypropylene (PP) and polyethylene (PE), and about 1\% methyl ethyl ketone peroxide catalyst. However, the product showed low thermal resistance and low resistance to staining. Low porosity engineered stones offered a variety of applications especially those required high mechanical properties, surface maintenance free and resistance to chemical attacks. These products found their use in diverse places such restaurants, homes, hospitals, laboratories, and in many more, so different sets of thermal properties
might be needed for different purpose of use. The work in ref 3 showed that when heated up to 100 °C, commercial engineered stones showed superior flexural strength than natural lime stone and granite. After being submitted to rapid cooling rom 200 °C down to 20 °C, engineered stones continued to show higher values of flexural strength as compared to the natural stones.

Various processing methods with have been discussed in literatures [4, 5]. Compaction vibration in a vacuum environment was used to compact engineered stone slab whose main solid components were waste glass and fine granite aggregate. The final product showed high compressive strength of 148.8 MPa, water absorption < 0.02%, and flexural strength of 51.1 MPa which were superior to those of natural construction slabs [5]. The research results revealed that vibration was the key processing step required to adjust the orientation of aggregates to become more closely compacted so densified product could be obtained. Only pressing failed to give the slabs with so desirable properties. A similar method so-called “vibro-compression under vacuum” was patented in the USA [US 7,815,827 B2]. Autoclave polymerization of polymeric resins mixed with stone gravels for production of synthetic marble slab was patented in 2014 [US 2012/0196087 A1]. In the study by Khater and Ezzat [2018], engineered stone was prepared using geopolymer resin instead of polymer resin [2]. To obtain minimal porosity, packing of gravel particles used is essential. In packing of monosize spherical particles, the highest density could be obtained was only 74%. With irregular shaped-particles, packing of monosize particles would bring down the number to only 56% [6]. To achieve higher packing density, particles of multi-sizes must be employed. However, according to Stroke’s law preparation of engineered stones is performed in liquid polymer resin, where dragging force acting on particles depends on viscosity of the liquid, density and particle size of the solids [7]. In this research, particle packing was designed and quartz particles of mixed sizes were selected and used for preparation of engineered stones. Size selection was based on Stroke’s law. Density and hardness of the slab was the main focus of our present study.

2. Experiments

2.1. Packing design of particles

Size selection for particle packing was designed based on particle packing theory and also based on Stroke’s law [7]. In packing theory, triangular packing of iso-spherical size particles would leave an interstitial site with the size ratio of about 0.155 or 7 times smaller than the large particles. This is the smallest size that can fit into the interparticle voids and was selected following Stroke’s law. From Stroke’s law, the resistant force (F) acting on a falling particle in a liquid as it is sinking under the influence of gravity is a function of its size and viscosity of the liquid as follows:

\[ F = \rho V g = 6\pi r \eta v \]  

where \( r \) is radius of the spherical particle, \( \eta \) is viscosity of the liquid, \( v \) is velocity of the sinking particle, \( \rho_s \) is density of the solid while \( \rho_l \) is density of the resin, \( V \) is volume of the particle which is equal to \( \frac{4}{3} \pi r^3 \). Eq. 1 can then be re-written as:

\[ r = 3 \times \frac{\eta v}{2(\rho_s-\rho_l)g} \]  

Where \( \eta \) was measured viscosity of the resin while velocity of the sinking particles was calculated based on the falling distance and the curing time of the resin.

From Eqn. 2, size of the smallest particles was thus calculated to 5.18 µm. It must be kept in mind that there are parameters omitted in this simple model. Those parameters are such as variation of viscosity of the resin with time, true morphology of the particles, Brownian motion. The packing of 3 sized-particles was designed to be 3 sets as follows:
Set 1: The biggest size was chosen to be in the range of 500-1,000 µm while the medium and smallest particles were selected to be smaller by 2-5x factor so they were 250-500 µm and 75 µm respectively. This sample set was used as a compared set.

Set 2: The biggest size was chosen to be in the range of 500-1,000 µm, while the medium and smallest particles were selected in accordance with the 7x factor. The smallest particles were about 16 µm in size while the medium and large particles were in the size range of 108-125 µm. This sample set was used as a compared set.

Set 3: The smallest particles were about 6 µm in size while the medium and large particles were, as in accordance with the 7x factor, in the range of 37-44 µm and 250-350 µm respectively. This sample set follows the calculation’s guidelines exactly in both size ratio factor and the starting size range.

To obtain the required size, domestic quartz stones were crushed, ground and finally sieved through metal sieves.

2.2. Processing and characterisation

Polyester resin was first mixed with a hardener prior to addition of the ground quartz. Two shaping methods, vibration casting and compression, were compared so the mixture recipe was selected appropriated to the method. For the vibration casting, quartz to polymer resin ratio was 75 to 25 by weight. The mixture was vibrated at 25 Hz for 2 min before being cured at 80 °C for 30 min. In another shaping method, the mixture was pressed at 5 MPa for 1 min before being cured at the same condition. The mixture ratio was selected to be 90 to 10 by weight. The samples shaped by the vibrational method was coded as Set x-a while the samples shaped by pressing were coded as Set x-b.

Apparent density was measured following the International Organization for Standard (ISO 10545-3) as shown in Eq 3 [8].

\[ \rho = \frac{m_{\text{dry}}}{m_{\text{dry}} - m_{\text{susp}}} \]  

where \( m_{\text{dry}} \) is weight of the sample dried at in oven at 110±5 °C for 24 hr, \( m_{\text{susp}} \) is the suspended mass in water. The ideal density of the engineered stone was calculated based on the composition of the composite with quartz and resin density of 2.65 and 1.20 g/cm³ respectively. The calculated ideal density of Set x-a was 2.28 g/cm³ while that of Set x-b would be 2.50 g/cm³.

Vickers hardness was measured using micro-hardness. A square-based pyramid indenter whose opposite sides meet at the apex at an angle of 136° was employed. Hardness in Vickers was calculated using a formula in Eq 4;

\[ H_V = 1.854 \frac{F}{d^2} \]

where \( d \) is diagonal length of the indented surface and \( F \) is the applied load.

A scanning electron microscope (SEM) LEO/1450 VP at an accelerating voltage of 10 kV was used for microscopical observation.

3. Results and discussion

Apparent density of the Set x-a and Set x-b samples are graphically displayed in Fig. 1. The calculated ideal density for Set x-a is 2.28 g/cm³ while that of Set x-b is 2.50 g/cm³. In general samples of the same composition in Set x-a had slightly lower density than those in Set x-b. The maximum density was found in both Set 2-a and -b suggesting the best packing of the particles. From our hypothesis, the best packing of moving particles according to both closest packing principle and Stroke’s law should belong to Set 3. However, our results showed that Set 2-a and -b whose packing was based on 7x ratio, showed the best packing efficiency amongst the samples of the same shaping method. Set 1 showed relatively similar or slightly higher density than Set 3.
Figure 1. Apparent density of the two quartz stone sample sets.

Vickers hardness results are shown in Fig 2. Vickers hardness results for Set 1-a and 1-b and Set 2-a and 2-b showed a similar trend to the density i.e. the higher the density, the higher the hardness. Set 3-a, however, showed the poorest hardness, possibly due to the deeper sinking of particles below the resin surface. It was noted that Set 3-b sample was too crumble so measuring hardness was not possible. In good agreement with the density results, samples in Set x-b showed better hardness than those in Set x-a. The best Vickers harness was found in Set2-b due to its best packing efficiency according to the related density result. To compare the result, some commercial products were selected and tested. The average density and Vicker hardness were 2.31±0.01 g/cm³ and 833.21±27.10 HV.

Microstructure of the Set X-a and Set X-b samples are shown in Fig 3 and 4 respectively. Set 1-a (Fig. 3a) showed relatively larger space between particles while space filling with particles of 3 different sizes seems to be more effective in Set 2-a (Fig. 3b). Space filling in Set 3-a (Fig. 4c) was mainly occurred by two size of particles. Set 1-b (Fig. 4a) sample showed similar particle arrangement similar to Set 1-a but with a better space filling scenario. Set 2-b (Fig. 4b) showed existence of 3 particle sizes with a relatively smaller distance between particles. This sample showed the greatest density in good agreement with its microstructure.

Figure 2. Vickers hardness results of the quartz stone samples sets. Noted that Set3-b was too crumble so measuring hardness was not possible.
Figure 3. Back scattered electron microscopical pictures for (a) Set 1-a, (b) Set 2-a and (c) Set 3-a.

Figure 4. Back scattered electron microscopical pictures for (a) Set 1-b and (b) Set 2-b.

4. Conclusion
From our results, it was suggested the closest packing model gave satisfactory result as seen in both Set 2-a and –b. Set 3-a and –b had adopted the closest packing model along with the simple Stroke’s law for the drag force. This model was, however, cancelled off many parameters so in practical it may not be best fit. Practical parameters such as variation of viscosity of the resin with time, morphology of the particles, Brownian motion, and the falling distance may be needed to put together in calculation, though this will make it extremely complex.
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