SULFONIC ACID COATING OF REFRACTORY SAND FOR THREE-DIMENSIONAL PRINTING APPLICATIONS

O. Dady[1], K. Nyembwe[2] and M. Van Tonder[3]

ABSTRACT

Rapid sand casting processes by additive manufacturing are predominantly based on furfuryl alcohol resin bonded sand catalysed with sulfonic acid. The prior coating of the refractory sand with sulfonic acid is a crucial process to ensure the suitability of the sand for three-dimensional printing applications. The present paper investigated the sulfonic acid coating process of a local silica sand, which was found to have potential for three-dimensional printing applications in previous studies. Experimental conditions included sulfonic acid catalyst addition and mixing time. Coated sand was assessed for flowability and mechanical properties of test specimens produced by three-dimensional printing using a Voxeljet VX 1000. The optimum catalyst addition ranged between 0.3 and 0.6% yielding to transverse strength in the order of 110 to 165 KN/m^2 and tensile strength ranging from 710 to 770 KN/m^2

[1] Department of Metallurgy University of Johannesburg, South Africa dnyembwe@uj.ac.za
[2] Metal Casting Technology Station University of Johannesburg, South Africa odady@uj.ac.za
[3] Vaal University of Technology Southern Gauteng Science and Technology Park, Sebokeng, South Africa malanvt@vut.ac.za

1. INTRODUCTION

Three dimensional printing (3DP) technology is nowadays successfully applied for the manufacturing of sand moulds and cores for casting applications. As with the conventional moulding and core-making methods, the refractory materials include siliceous and non-siliceous refractory materials such as silica sand, chromite sand, olivine sand, synthetic sand **[1]**.

Commercial 3DP processes for rapid sand casting applications in use are essentially based on the furfuryl alcohol resin bonded sand process [2]. The latter is a no bake process in which the sand self-setting at room temperature catalysed by an acid such as the sulfonic acid. The sand used for 3DP is coated with sulfonic acid. A printer head selectively dispensed the resin during the layer-by-layer manufacturing. Well-known 3DP systems working on this fashion include ExOne and Voxeljet [3].

The hardening mechanism of the furfuryl alcohol resin in the presence of the sulfonic acid catalyst is well-explained in the literature [4]. Essentially, the addition of an acid activator to a furan resin triggers an exothermic poly-condensation reaction, which hardens the binder. The condensation reaction produces water, which has a tendency to retard the cure rate (dehydration). The bond generating reaction is the further polymerisation of these chains with cross-connecting. Within the presence of strong acids, prepolymers of furfural and furfuryl liquor form polymer films that act as fasteners. The curing rate is specifically relative to the measure of acid and a two-part system can be detailed with a very much controlled curing time [5].

In the case of 3DP, the flowability of the sulfonic coated sand is an important property to be considered prior to the actual hardening of the resin as explained above. The flowability property is a measure of the ability of the sand to free flow during layer-by-layer manufacturing. This property of the coated sand will influence the recoating behaviour during three-dimensional printing process, which is required to be flawless in order to prevent glitches [6]. Experimentally, the flowability of a powder material is measured by calculating the angle of repose formed by the free flow of sand on a cylindrical support. Multiple images are taken by the use a camera focusing on the position of the interface sand/air. The angle of repose is therefore calculated determining the angle of the isosceles triangle, which has the same surface as the heap of granular materials [7]

Previous studies have investigated the importance and effect of sand properties including particles size, clay content, pH level, acid demand, refractoriness, surface morphology and angularity of local sands on the mechanical properties of 3DP sand specimens [8]. It was found that not all the local silica sands are suitable for three dimensional printing as the mechanical properties were inferior and recoating problem during additive manufacturing were encountered.

Three-dimensional printing is available in South Africa. However, due to the limited availability of suitable local silica sand and the complexity of the sulfonic acid coating, imported refractory sand from oversees is used, making the 3DP process expensive and unaffordable to the local foundry industry. This state of affair possibly prevents the full adoption of the AM technology by South African sand casting foundries [8].

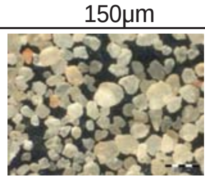
This research focuses on 3DP material preparation consisting of the coating of a local silica sand with sulfonic acid in order to determine the optimum sulfonic acid addition for required mechanical properties of sand parts. The overall aim of the study is to localize the manufacturing of silica sand for three-dimensional printing applications.

2. METHODOLOGY

2.1 Raw materials

The raw materials used in the study include silica sand and sulfonic acid produced locally. The properties of the silica sand are presented in table 1. The size distribution of the sand is shown in figure 1. This sand used by local foundries in the Gauteng region was found to have suitable properties for 3DP [9].

Table I: Sands characterisation results.

Properties	*New silica sand*
pH	6.91
Size distribution	57.0
Relative density	2.62g/cc
Bulk density	1.52g/cm^3
Average grain size	150µm
Grain Morphology	

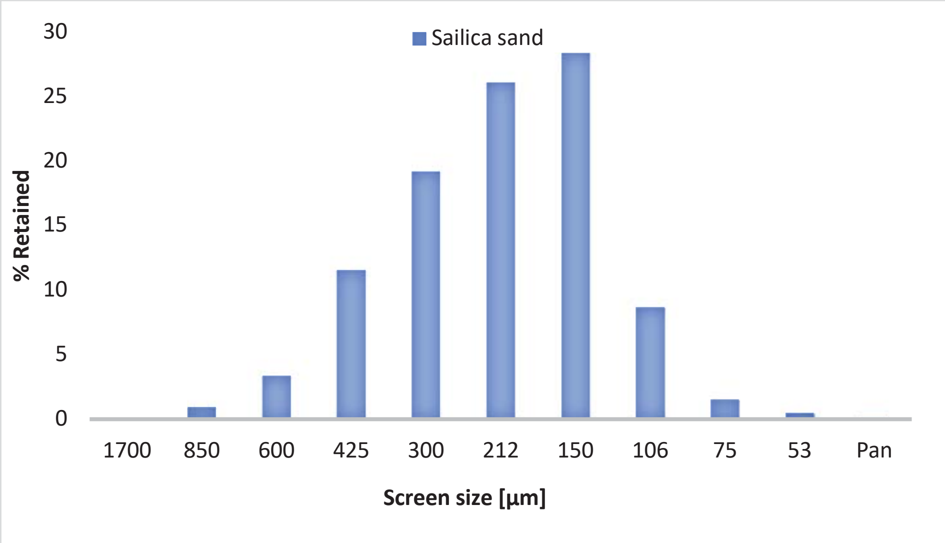


Figure 1 shows the sands grain size distributions obtained with a particle size distribution analyser (Filta).

2.2 Experimental Procedure

The followings steps were conducted in the experimental procedure:

2.2.1 Sand coating

The sand coating consisted of addition sulfonic acid to 50 kg of silica sand in a foundry batch sand mixer. The sulfonic acid addition was determined at 0.3, 0.6 and 0.9% per weight of the sand. The mixing time was maintained constant at 5 minutes per batch of sand. The prepared coated batches of silica sands were then stored in sealed plastic buckets prior to additive manufacturing in order to prevent them from acid evaporation and moisture pick up.

2.2.2 Flowability measurement

The sand flowability was measured immediately after mixing, after 24 hours and 48 hours to determine the influence of storage time on the flowability. Figure 2 schematically illustrates the determination of the flowability in terms of angle of repose.

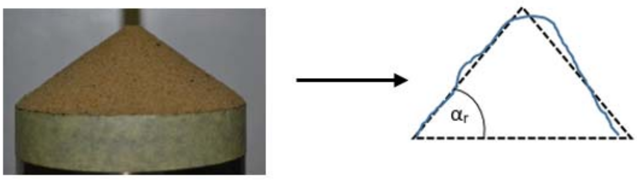


Figure 2: Illustration of sand granule on a cylindrical support displaying an angle of repose α_r.

2.2.3 Three dimensional printing

The manufacturing of transverse and tensile test specimens were produced on a Voxeljet VX 1000 three-dimensional printer. The geometries and dimensions of specimens were according to the AFS standards [10]. The standards specimens were then oven cured at 105-110^{0}C to allow complete bond sand particles.

2.2.4 Testing

The mechanical properties of the test sand specimens produced by 3DP were assessed in terms of tensile and transverse strengths. A universal strength test machine was used for strength determination following the American Foundry Society mould and core test procedures [10].

3. RESULTS

3.1 Coated sand pH

Figure 3 shows the variation of the coated sand pH for the different addition of catalyst as a function of the storage time after mixing and prior to the three-dimensional printing. It appears that the pH for the different batches of sand in terms of catalyst addition increases as time elapsed. This variation of pH over time could possibly suggest a loss of sulfonic content in the sand with time. This could be due to evaporation of the catalyst at room temperature.

The above phenomenon could affect the effectiveness of the catalyst in hardening the furfuryl alcohol resin bonded sand during three-dimensional printing, resulting in the production of weak sand parts.

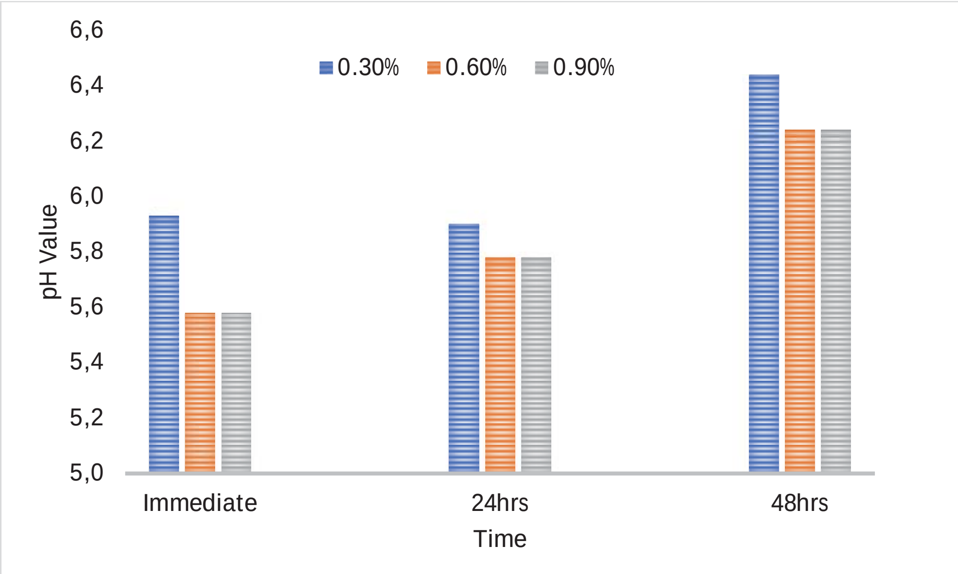


Figure 3: pH changes as function of time.

3.2 Flowability measurement

Figure 4 shows the variation of the angle of repose for the different addition of catalyst as a function of the storage time after mixing and prior to the three-dimensional printing. It appears that:

- The flowability of the sand decreases (higher angle of repose) as the percentage of sulfonic acid addition increases. This suggest that too much addition of catalyst could cause recoating problems during the additive manufacturing process. The coating could be serving as a glue preventing mobility of the sand grains.
- The flowability of the coated sand appears to improve (lower angle of repose) as time elapses. As the sulfonic acid content decreases with time, the flowability of the coated sand evolves towards the flowability of the uncoated sand, which is better (lower angle of repose)

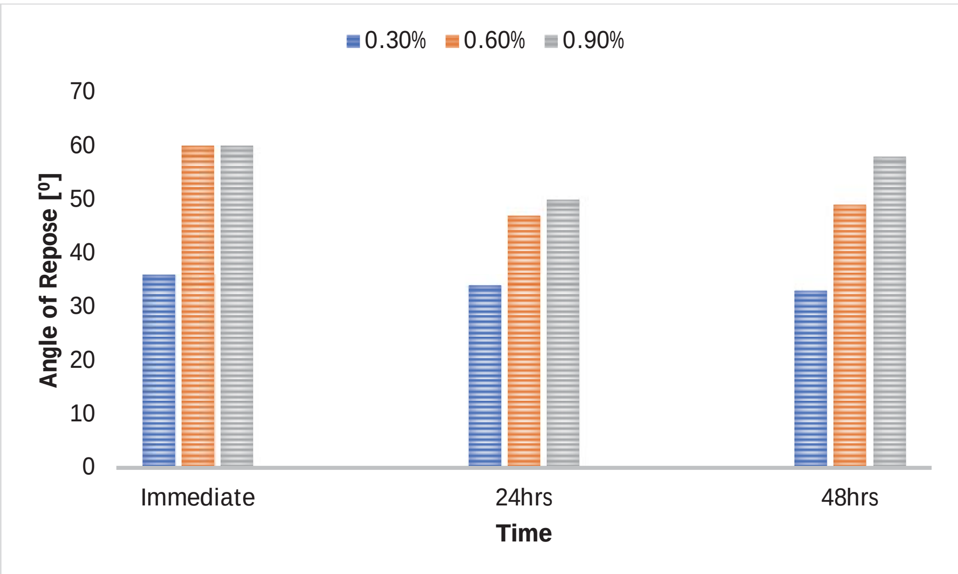


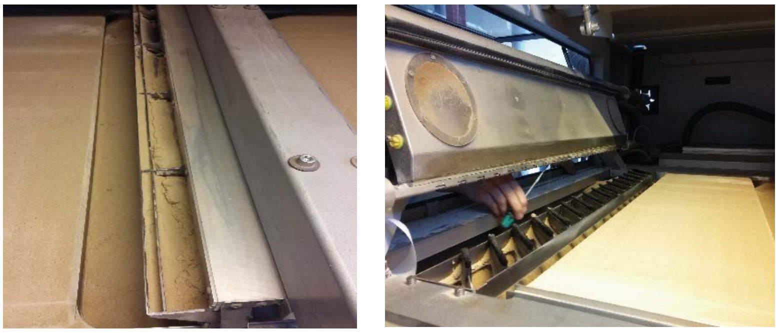
Figure 4: Flowability results as factor of time variations.

From the above, it appears two competing phenomenon are at play: the loss of the catalyst with time and the increase of flowability with time. The first phenomenon will impact on the hardening process of the three-dimensional printing, while the second phenomenon will affect the layer by layer manufacturing.

3.3 Three Dimensional printing

Figure 5 shows the 3DP sand specimens produced on the Voxeljet VX 1000 printer after baking only for 0.3% and 0.6% addition of sulfonic acid in the silica sand. The 0.9% sulfonic acid coating could not be used for three-dimensional printing of sand specimen due to clogging of the printer's recoater as shown in figure 6. The 0.9% sulfonic correspond to the lowest flowability of the coated silica sand. The effect of storage could not improve the flowability for this sand to make usable for the 3DP.

Figure 5: Transverse bars and tensile specimens.



(a) (b)

Figure 6: Image (a) shows sand lumps formed in the re-coater and image (b) shows clogging of the sand feeder.

3.4 Moulding properties assessment

Figure 7 shows the mechanical properties of the 3DP sand specimens in terms of tensile and transverse strengths. Strength appears to increase slightly with sulfonic acid content. An increase of 8.7% was obtained for the tensile strength while and increase of 5% was found for the transverse strength from 0.3 to 0.6% addition of sulfonic acid. No data were reported for the 0.9% sulfonic acid due to unavailability of sand specimens as explained in the sections above.

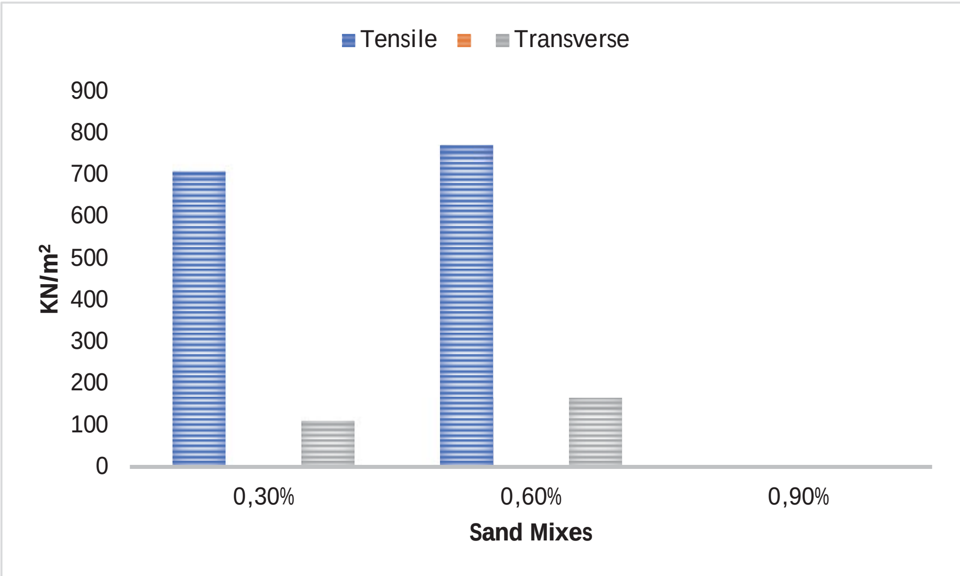


Figure 7: Tensile and transverse strengths data - 48 hours storage time.

4. CONCLUSION

The study attempted to understand the sulfonic acid coating of silica sand for three-dimensional printing applications based on furfuryl alcohol resin bonded sand. The study showed that the sulfonic acid content in the sand and the storage time of the coated sand after preparation are important factors in determining the manufacturability of the coated sand and the final mechanical properties of 3DP sand parts. In this study, it was possible to successfully coat a locally available silica sand, which could produce 3DP sands specimens meeting the requirements of mechanical properties with acceptable addition of sulfonic acid in the range of 0.3 to 0.6% addition. Further work will investigate the performance of different types of refractory sands including chromite sand and ceramic sand.

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