Properties of furfuryl alcohol resins for conventional sand moulding and binder jetting applications.

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Abstract. This paper compares two commercial acid-cured furfuryl alcohol resins. The first material is used for conventional sand moulding (CSM), while the second material was manufactured for the binder jetting process (BJP) using a Voxeljet VX 1000 printer. To that end, chromite sand test specimens were prepared following the American Foundry Society (AFS) procedures to assess various foundry properties, including flowability and flexural strength. The study provides valuable insight into furan resins' properties and differences. In addition, the investigation provides an understanding of the requirements for a suitable local furfuryl alcohol resin for the binder jetting process to produce quality three dimensional printed sand parts.

Key words: Furan; Voxeljet VX 1000; Binder jetting process; Flexural Strength; Flowability.

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1 Introduction

In recent years, metal casting as a production technique has been adjudged one of the shortest routes for component design and production. This is because nearly all ferrous and nonferrous metals that can be melted can also be cast, and the design of the casting can be both complex and flexible [1]. The furan-no-bake (FNB) acid cured system has become the preferred sand moulding system as it can produce high quality castings using minimum manual labour [2].

Furan resins, also known as furfuryl alcohol-based binders, are commercially classified according to their nitrogen and water content. The lower the amounts of these two components, the greater the monetary value of the resin [3]. FNB binders are slightly more expensive than other binders, however the decline in overall production costs resulting from improved sand reclamation properties gives them a distinct advantage over other binder systems.

Technically, furan binders use a two-part cold-set binder system which employs furfuryl alcohol as the resin and sulphonic acid as the catalyst. It has become the most popular organic binder. This FNB system is used in both conventional sand moulding CSM and binder jetting process (BJP), which is applied in additive manufacturing (AM) platforms with the Voxeljet VX1000 three dimensional printer. In the case of CSM binders, the resin amount is calculated based on the weight of sand (BOS) and the catalyst amount on the weight of resin (BOR), however for BJP both the resin and catalyst amounts are calculated based on the weight of the sand as is the accepted practice in both the foundry and AM industries.

The binder, which is made up of both catalyst and resin combined, of the two FNB acid cured sand moulding systems range between 0.9-2% furfuryl alcohol resin additions and 20-50% sulphonic acid catalyst additions for CSM, then 1-5% furfuryl alcohol resin additions and 0.1-0.5% sulphonic acid catalyst additions for BJP respectively. The catalyst and effectively the resin percentages for these 2 system are so different due to the fact that the BJP furan binder is uniquely and specifically designed for use together with a Voxeljet VX1000 3D printer with optimal functioning during the binder jetting process with little to no adjustments required in order to produce high quality printed components with no hiccups or issue.

The major difference between the two processes is the manner in which the acid catalyst is introduced into the system. In the CSM method both resin and catalyst are added into a mixer with the sand [4]. The catalyst is always added first to the sand and thoroughly mixed before the resin is added because once the resin is added the hardening process starts immediately due to it being a two-part system. If the polymerization reaction starts before the gang mould compaction or ramming process, it would result in significant decrease in the overall peak strength and reduced integrity of the prepared mechanical testing specimens or moulds and cores to be cast.

In 3D printing, the sand is first coated with the catalyst prior to it being placed in the printing machine, the resin is then automatically jetted onto the layered sand during the printing process. The binder jetting process is summarized in Fig. 1 below.

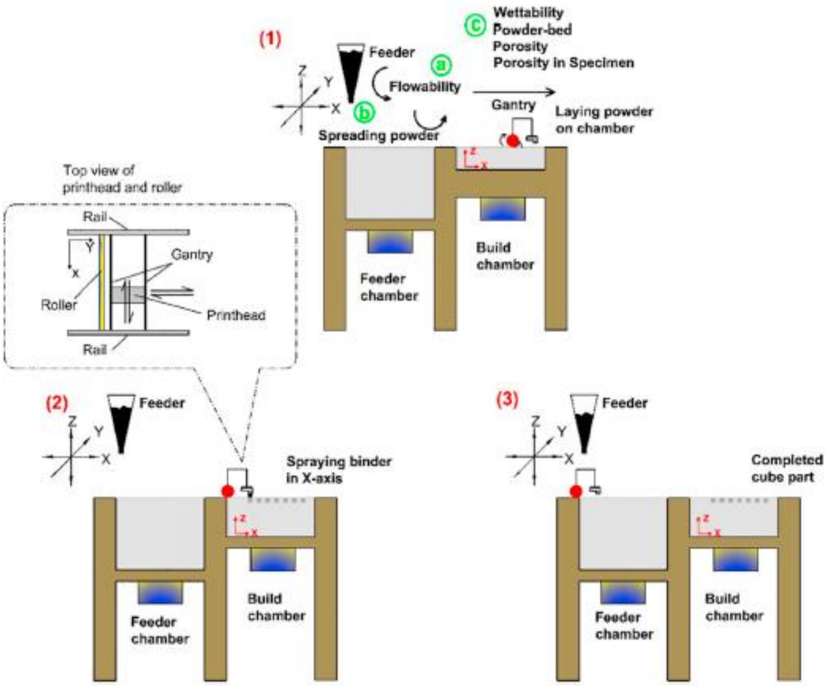

Fig. 1. Schematic diagram showing binder jetting procedure as used in 3D printers ***[5]***.

Studies have been undertaken in 2021 by Tshabalala et al. [6] and Chauke et al. [7] on the utilisation of local chromite sands as alternative refractory materials to silica sand imported from Voxeljet in Germany for rapid sand casting have been evaluated using the VX1000 3D printer as a result of chromite sand having certain technical advantages over silica sand, which include high refractoriness and metal permeation resistance, exceptional chilling ability and better dimensional strength [3].

The coated sand recoating performance via pH and flowability and foundry sand properties via flexural strength were analysed, 4 weight % and 0.3 weight % for both additions based on sand weight for resin and catalyst amounts respectively. The studies also concluded that four out of five of the locally sourced chromite sands from major South African suppliers could be used for rapid sand casting.

In sand moulding, the refractory raw materials that are commonly used are silica, chromite, zircon and olivine sands. The criteria commonly considered in the selection of refractory materials for moulds and cores are generally based on the availability of raw materials, cost of tooling, the metals to be used for casting as well as, to a lesser extent, the geometry of the parts to be made, particularly when measured against permanent moulding techniques [8]. In his study regarding the development of a quality assurance framework, van Tonder, 2019 outlined the critical quality attributes (CQA) to be considered when dealing with chemically coated sand for 3D printing purposes [9].

These CQAs that were described and thoroughly discussed in that paper were useful in the evaluation of the suitability of locally sourced chromite sand for being compatible with FNB sand system as well as their application in BJP. In this research, a comparative study was performed to assess the curing properties of different furan resins with a local chromite sand for both commercially available and Voxeljet FNB-acid-cured systems.

2 Methodology

The following section presents the procedure of the study as shown in Fig. 2 below. The raw materials used in this research were local chromite sand, CSM and BJP furan binders.

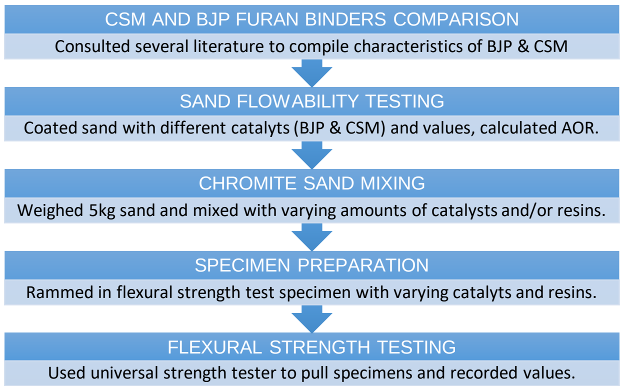

Fig. 2. Flow diagram showing methodology followed.

2.1 CSM and BJP binder comparison

The different FNB acid cured binder systems, namely conventional sand moulding and binder jetting process, are compared to each other based on some characteristics/traits that they have in common based on data collected from different sources.

2.2 Sand flowability testing

The flowability of the chromite sand coated only with the two sulphonic acid catalysts for both CSM and BJP systems was determined using the HMK Flow 329 powder flowability angle of repose tester, as per ASTM C1444-00 standard, the apparatus are shown below in Fig. 3(b). The chromite sand was acid coated with equipment shown below in Fig. 3(a) according to the combinations shown in Table 1 below.

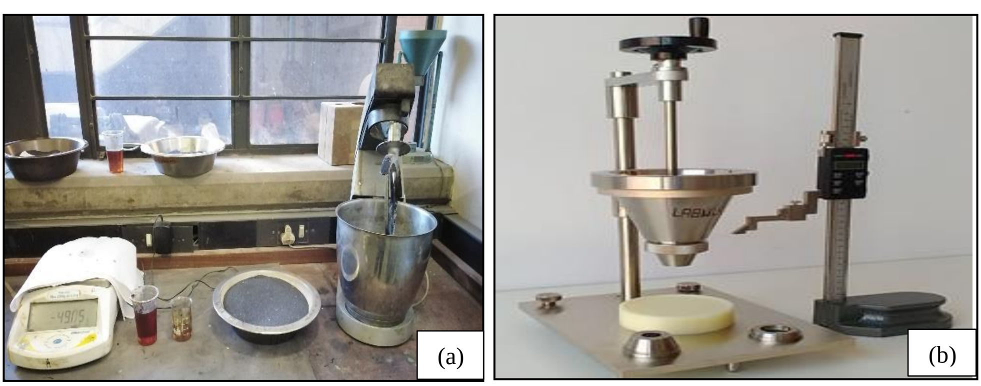

Fig. 3. (a) Experimental setup in the laboratory and (b) HMK Flow 329 powder flowability apparatus available at the University of Johannesburg.

Flowability can be defined as the ability of powders/grains/sand to flow readily. It is an important factor in BJP as it prevents faults in the final printed part or issues with the sand recoating process during printing [10]. Other factors that have an effect on flowability include powder surface area, roughness of the surface, the layer thickness that is printed as well as size of the particles. As the chromite sand flows through the funnel opening onto the base plate as shown in Fig.3(b) above, the height of the sand cone formed together with the width of the base are measured after each pour. The rate of flow of the sand is affected by the size of the opening on the funnel orifice.

The consistency of the flow of the sand was examined for different compositions of sulphonic acid-coated chromite sand mixtures for both BJP and CSM systems. However, should the sand not readily flow, then additional blending of the sand with catalyst is essential in order to achieve optimal flowability prior to it being used in the Voxeljet VX1000 3D printer. Conversely, if the powder reaches the desired flow, it is utilized for the printing of flexural strength testing specimens, moulds and/or cores [5].

2.3 Chromite sand mixing

Table 1 shows the total weight of furfuryl alcohol resin and sulphonic acid catalyst. The experimental setup used in this experiment is shown in Fig. 3(a) above.

Table 1. Total weight of furfuryl alcohol resin and sulphonic acid catalyst used.

Sample No.	Sand (kg)	Alcohol (%)	Acid (%)	Resin (g)	Catalyst (g)
1	5	0.9	20	45	9
2	5	1.5	20	75	15
3	5	2	20	100	20
4	5	0.9	35	45	15.75
5	5	1.5	35	75	26.25
6	5	2	35	100	35
7	5	0.9	50	45	22.5
8	5	1.5	50	75	37.5
9	5	2	50	100	50

2.4 Testing specimen preparation

Flexural strength testing specimens, each measuring 25.4 x 25.4 x 203.2mm in dimensions as per ASTM standards [11], were made using the hand-ramming method, in relation with the different combinations of furfuryl alcohol and sulphonic acid as specified in Table 1 above using 5kg of sand with each mix/blend. After mixing the test specimens were shaped using a flexural strength gang mould core box as shown in Fig. 4(a) below. The universal strength tester used in the laboratory is shown in Fig. 4(b) below as well.

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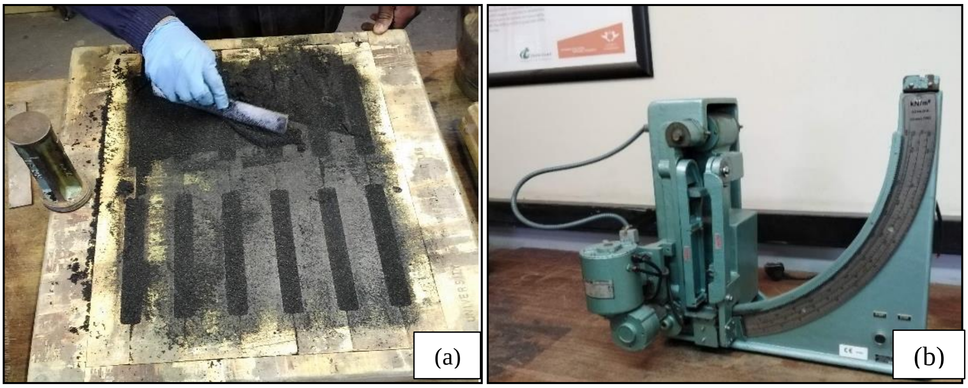

Fig. 4. The (a) Gang mould flexural strength core box and (b) universal strength tester both available at the University of Johannesburg.

2.5 Flexural strength testing

A universal strength testing machine, Fig. 4(b) above, was used to determine the flexural strengths of the different compositions of CSM and BJP binders as depicted in Table 1 above.

3 Results

3.1 CSM and BJP binder comparison

Table 2 below shows the comparison of the different characteristics for FNB acid cured systems used for the two sand moulding systems, namely CSM and BJP [12], [13], [14], [15].

Table 2. Comparison of different furan binder systems.

Parameters	CSM	BJP
Binder system	Two-part self-set binder system (resin and acid catalyst)	
Strength development cycle	Air drying for 4-12 hours	Oven baking at 110 ºC for 2 hours.
Ingredients	Resin (furfuryl alcohol) + Catalyst (sulphonic acid)	
% Nitrogen	3.0 – 4.0%	–
% Resin	0.9-2% BOS	1-5% BOS
Resin introduction into system	Mixed in with the sand and sulphonic acid.	Automatically jetted onto sulphonic acid pre-coated sand.
Resin composition	Furfyryl Alcohol, Formaldehyde and 3-Aminopropyltriethoxysilane	Furfuryl Alcohol, 4,4-Isopropylidenediphenol and 3-Aminopropyltriethoxysilane
% Catalyst	20-50% BOR	0.1-0.5% BOS
Catalyst composition	Xylene Sulphonic acid, Methanol, Sulphuric acid, Dimethyl Sulphate	Toluene Sulphonic acid / Xylene Sulphonic acid
Dimensional accuracy	Good	
Surface finish	Excellent	
Shelf Life	1 year after production date	

*The shelf life represents the period during which the product will remain fit-for-purpose.

According to the information gathered in the above table, it was observed that the major differences between these two sand moulding processes are the (1) actual compositions of the furfuryl alcohol resin and sulphonic acid catalyst used, (2) the strength development process modelled using either air drying for 4-12 hours or baking at 110ºC for 2 hours in an air ventilated oven, as required by Voxeljet original equipment manufacturer (OEM) post process heat treatment protocol, in order to remove any remaining moisture after the polymerisation reaction. This was observed to have improved overall flexural strength of the printed parts considerably [7, 12] as well as the manner in which the resin and catalyst compositions are calculated, whether based on sand or resin weight (BOS/BOR) respectively depending on which moulding system you decide to use.

3.2 Sand flowability testing results

Fig. 6(a) shows the flowability results of CSM sulphonic acid catalyst coated chromite sand, assessed immediately upon mixing and again after 24 and 48 hours respectively. This was carried out in order to determine how storage time affects the flowability of a CSM FNB sand moulding system catalyst in terms of angle of repose (AOR). Fig. 6(b) and Fig. 6(c) show the flowability test results for BJP and CSM with different catalyst additions.

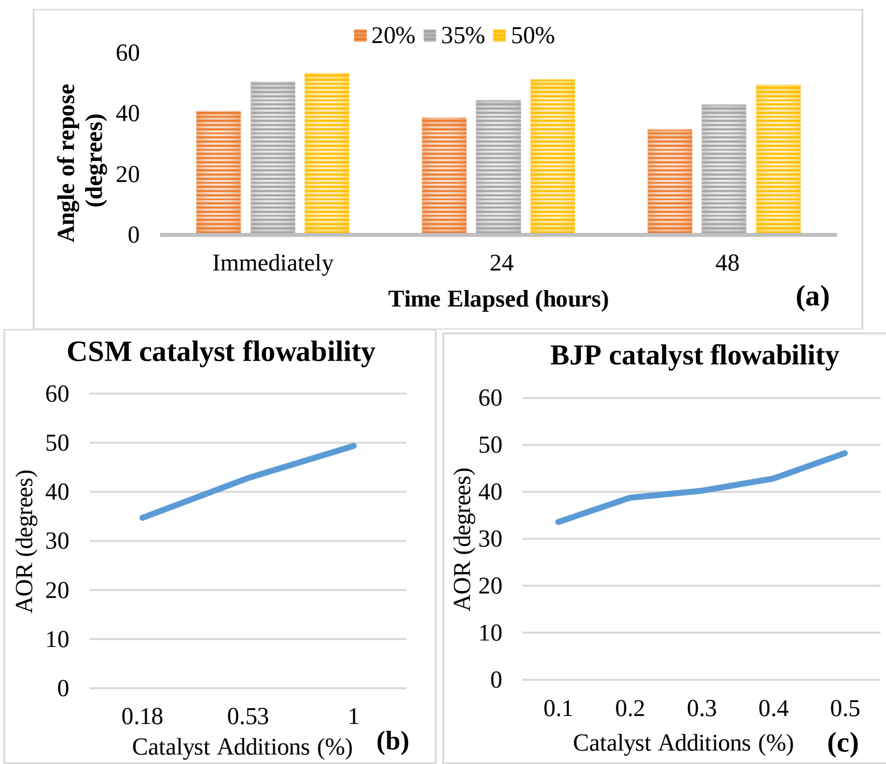

Fig. 5. Flowability curves for (a) CSM resin chromite sand at different compositions (b) CSM of acid coated chromite sand after 48 hours and (c) BJP of acid coated chromite sand after 48 hours.

Fig. 5(a) shows the flowability shows that increasing the CSM sulphonic acid catalyst in the chromite sand, in other words using higher amounts, the angle of repose (AOR) increases which in turn decreases the flowability of the sulponic acid coated sand as the two phenomena are inversely proportional to each other. In previous studies by Tshabalala et al. [16] and Chauke et al. [7] it was observed that when increasing the amount of BJP sulphonic acid catalyst in the chromite sand, the AOR also increased. A high AOR means a low/poor flowability of the sand during printing which is not a desired outcome in BJP.

Furthermore, they also concluded that storing the sulphonic acid coated sand for a period of two days, as is a recommended storage time by OEM and other literature source prior to doing any printing with the VX1000, improved flowabililty of the sand which also resulted in the AOR decreasing to a more desired value. The recommended storage time enhances the flowability of the sand as it allows for water, a by-product produced during the polymerization process which results in the curing of the coated sand to evaporate and reduce capillary forces thus allowing for improved flowability of the sand [17], [9].

In this research, the same phenomenon was observed with the CSM sulphonic acid catalyst after 48 hours of storage time, as can be seen in Fig. 5(b) where the lowest AOR value of 34.71^0 with 0.18% and the highest AOR of 49.36^0 with 1% catalyst respectively. As can be seen in Fig. 5(c) above, after 48 hours of storage time, the lowest observed AOR was 33.66^0 when 0.1% sulphonic acid catalyst was used and the highest AOR observed was 48.25^0 when 0.5% was used. A lower AOR gives the best flowability which will be most accepted as a good flowing sand is known to have an AOR which lies between 31^0 and 35^0 [1], [18], [14].

Moreover, there are also instances in the literature of formulations with an angle of repose in the range of 40° to 50° that were manufactured satisfactorily. When the angle of repose exceeds 50° the flow is rarely acceptable for manufacturing purposes.

3.3 Mechanical testing results

Figs. 6, 7 and 8 show plotted results for flexural strength tests of all compositions for different CSM sand mixtures, outlining the effect of resin on flexural strength while the sulphonic acid (catalyst) was kept constant. The specimens were tested in their cured state after 4, 24 and 48 hours as is common practice within the foundry industry to monitor or determine the rate of curing of the mixed/reacted sand after curing so as to find the optimal combination of catalyst and resin giving the most desired mechanical properties.

The values were averaged from 3 specimens produced per composition. It appears that by increasing the amount of resin and catalyst, the maximum/peak flexural strength obtained was obtained after two days for all compositions of CSM binders used.

Fig. 6 below shows the effect of different amounts of resin on flexural strength while the catalyst was maintained at 0.18%. The peak flexural strength of 31.04 MPa was obtained with the resin at 1.5% after 48 hours of curing.

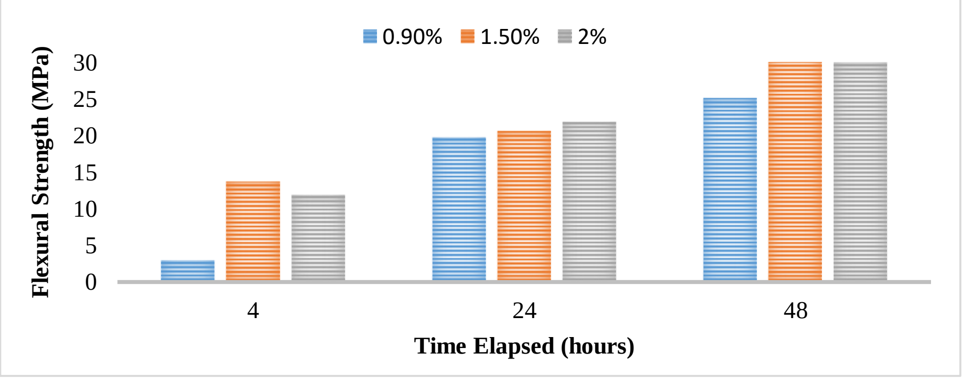

Fig. 6. The effect of 0.18% catalyst on flexural strength**.**

Fig. 7 below shows the effect of the different amounts of resin on flexural strength while the catalyst was maintained at 0.53%. The peak flexural strength obtained was 22.81 MPa with the resin at 2% after 48 hours of curing.

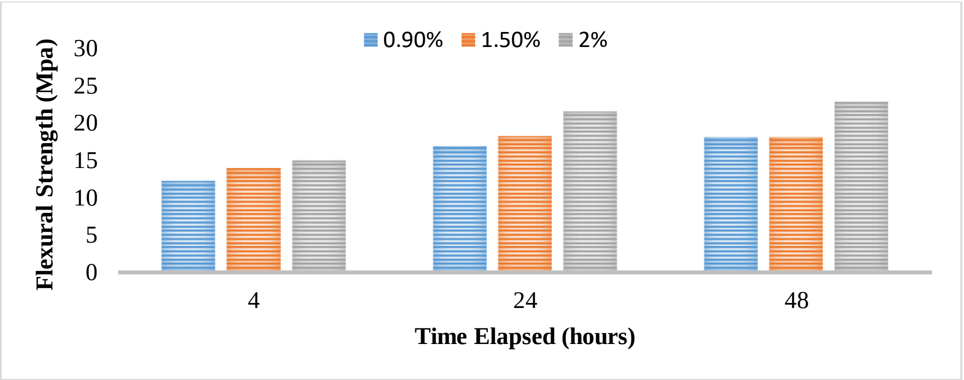

Fig. 7. The effect of 0.53% catalyst on flexural strength.

Fig. 8 below shows the effect of the different amounts of resin on flexural strength while the catalyst was maintained at 1%. The peak flexural strength of 17.97 MPa with the resin at 2% after 48 hours of curing.

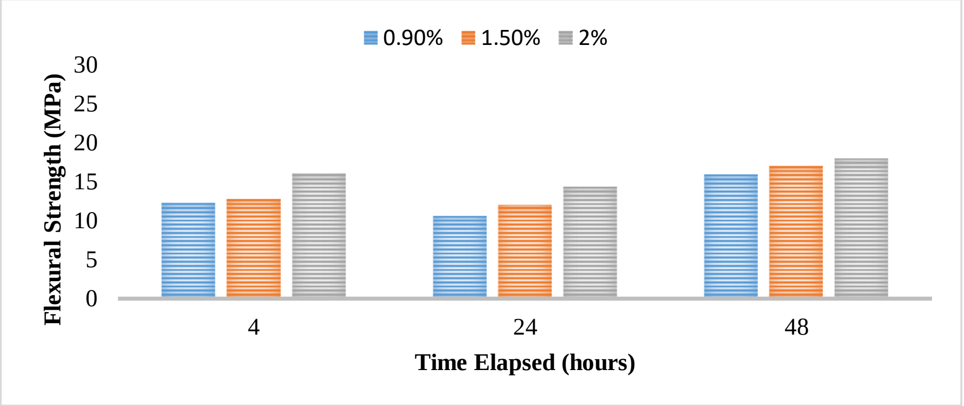

Fig. 8. The effect of 1% catalyst on flexural strength.

The peak flexural strength of 31.04 MPa was obtained with the resin at 1.5% after 48 hours of curing. It should be noted that even after 24 hours the flexural strengths in specimens that had sulphonic acid catalyst added were lower than the specimens to which 0.18% sulphonic acid had been added. This means that 0.18% was able to achieve the maximum strength for all compositions of 0.53 and 1% respectively as confirmed by Fig. 9(a) below.

These lower flexural strengths could have been as a result of excess moisture in the sand which could have caused reaction retardation of the curing process, resulting in low readings being recorded as increased sulphonic acid could have inadvertently introduced more moisture in the sand mix thereby decreasing overall peak strength.

The results show the change in flexural strength as the amount of sulphonic acid (catalyst) increases while the furfuryl alcohol (resin) kept constant at 2% for both the BJP and CSM FNB acid cured binders. Fig. 9(a) shows that increasing catalyst addition for CSM binder leads to a decrease in flexural strength, with the opposite observed for the BJP binder as can be seen in Fig. 9(b) as increasing catalyst additions increase the overall flexural strength.

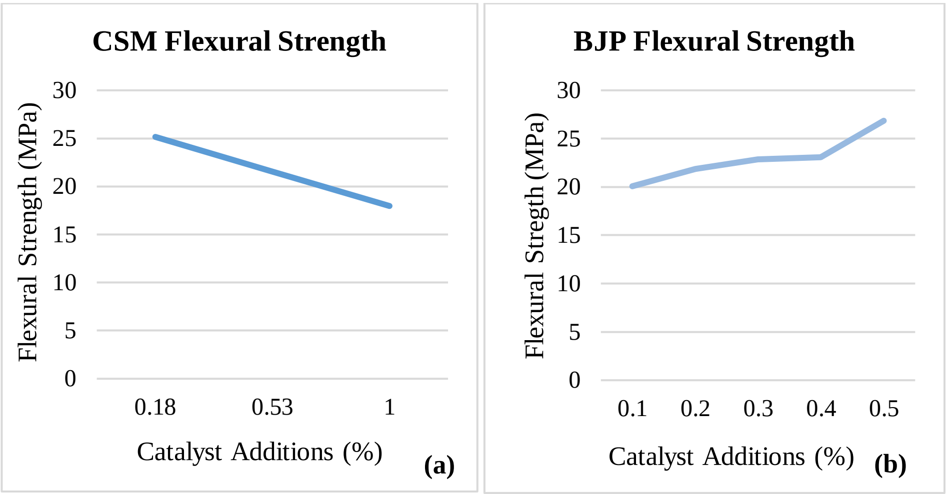

Fig. 9. Flexural strength curves after 48 hours for (a) CSM of acid coated chromite sand and (b) BJP of acid coated chromite sand.

This could have been as a result of post heat treatment of the printed parts which involved the heating of the specimens to 110ºC for 2 hours in an air-ventilated oven as a post treatment process. It is a requirement for all printed specimens with Voxeljet in order to achieve moisture free printed components that give the highest flexural strength possible as seen in Fig. 9(b) above. This process allows for the evaporation of any excess moisture that might have remained in the specimens during the printing process as result of the polymerization reaction.

Other factors that are known to compromise strength readings in foundry sand are acid demand value, mixing time, ambient temperature and mixing speed [1], [3]. The mixing time for the prepared specimens was subsequently decreased with increasing catalyst additions of both BJP and CSM furan binders. The mixing time is crucial for FNB systems and it becomes incrementally important with increasing sulphonic acid catalyst additions in the sand and resin mixture.

Increasing the catalyst enables a faster polymerization reaction, which means that the work time and the strip time for both CSM and BJP binders would also need to be decreased as well. If the polymerization starts before the compaction or ramming process, it would significantly decrease the strength and reduce the integrity of the prepared specimens. Hence a decrease in CSM flexural strength readings are seen in with 0.53 and 1% respectively. However, this phenomena is off-set in the case of BJP due to heating to 110^{0}C after stripping of the specimens.

Hence using high catalyst additions runs the risk of compromising the flowability of the sand which will lead to poor mould filing as has occurred in this experiment. It proved difficult to properly fill the gang mould core boxes as a result of the higher amount of catalyst which caused the sand mixture to quickly harden. Which could explain the lower strength values seen with CSM flexural strength readings.

4 Conclusion

The investigation results indicate that the sand specimens' achieved flowability was the same for the two types of furan resins. On the other hand, the peak flexural strength was higher in the binder jetting case than in the conventional sand moulding. However, the maximum flexural strength values obtained for the two furan resins were acceptable for three dimensional printing applications. The study has therefore demonstrated that the difference between the two resin types is not critical. Hence the CSM's resin could be explored for three dimensional printing applications. Future work will therefore investigate the effectiveness of using the CSM resin on the Voxeljet VX 1000 3D printer to produce the sand parts.

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