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On the rapid manufacturing process of functional 3D printed sand molds

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Abstract

3D printing sand mold technology offers an opportunity for the foundry industry to rethink old casting approaches and to revive the manufacturing approach using computer models. One of the major concerns in sand molding using 3D printing is the functional characterization of the 3D printed molds as its mechanical and mass transport properties. This research paper discusses the effects of binder content on the mechanical strength and the permeability of 3DP sand molds at different curing conditions. The local permeability of the 3DP specimen was measured as a function of the injection flow rate in order to quantify the inertial pressure effects. The mechanical strength of the 3DP sand molds was characterized using traditional three-point bending strength measurements. The results show that the mechanical strength of the printed molds is deeply dependent on the amount of binder and the curing process. The 3PB strength was found to increase when cured at 100 °C and decrease when cured at 200 °C

23 for all binder contents. The 3PB strength attains its maximum when cured at 100 °C for 2
24 hours for all binder content. In contrast, no significant effect of the amount of binder on the
25 initial permeability of the samples before curing was observed within the functional range of
26 binder mass fraction (1.02 to 1.98 %). Maximum permeability is attained at the same
27 conditions as the 3PB strength. Therefore, the mechanical strength of the sample can be
28 optimized within the investigated range of binder contents without resulting in any significant
29 decrease in permeability.

30

31 **Keywords:** Additive manufacturing; 3D Printing; Mold characterization; Sand casting; Three-
32 point bending strength; Permeability.

33

34 **1. Introduction**

35

36 Sand casting is a cost-effective method adopted in the production of metallic parts and is an
37 excellent solution to manufacture low-to-medium runs of parts meeting standard dimensional
38 requirements. Three-dimensional printing (3DP) of sand molds uses Powder Binder Jetting
39 (PBJ) technology and overcomes some of the issues commonly encountered in traditional
40 production methods. Indeed, 3DP technology allows rapid production of high-quality sand
41 molds with complex geometry as required in many casting applications [1,2], and ensures
42 optimized design freedom for any castable alloys [1–3]. The layer-based Three-Dimensional
43 Printing (3DP) technology is an Additive Manufacturing (AM) technique which was invented
44 at MIT to produce 3D parts directly from computer-aided designs (CAD) [4–7] This
45 technology has been fully recognized as one of the most promising technologies for the

46 production of casting sand molds. Among the available AM techniques, the powder-based
47 ink-jet 3D printing, which is based on the basis of a chemical reaction between silica sand
48 powder and an acidic binder, is widely used to manufacture sand molds. An extensive
49 literature review in this area of research [8] and a few studies on the relationship between the
50 properties of the 3D printed specimen and processing parameters [9,10] have been recently
51 published.

52

53 Foundries encounter a wide variation in the physical properties of the 3DP resin-bonded sand
54 molds, e.g. three-point bending (3PB) strength and permeability, which depend on certain
55 variables such as moisture and binder content. Indeed, greater binder contents generally result
56 in higher values of mechanical strength, but also in more gas being produced during metal
57 casting. Also, an excessively high amount of binder makes the 3DP sand mold too rigid
58 impeding proper expansion and giving rise to hot tearing defects and high residual stresses
59 [11,12]. In contrast, low binder amounts reduce the off-gassing but affect negatively the
60 mechanical strength, which can lead to penetration of the molten metal into the large inter-
61 sand interstices producing enlarged, rough surfaces on the casting. On the other hand, the
62 process of mold filling requires consideration of air evacuation from the mold cavity driven
63 by the compression of the gas by the melt. In particular, the melt can entrap air and other
64 gases in the mold cavity, which is favored by turbulent filling. Consequently, it is necessary to
65 evacuate the gas in an efficient manner in order to obtain a sound casting product with a
66 minimum of defects. For these reasons, the success of this novel technology is strongly
67 conditioned by the production of sufficiently permeable sand molds with convenient
68 mechanical strength for their manipulation.

69

70 3DP furan resin-bonded sand is widely used in casting due to the high dimensional precision
71 and mechanical strength of the produced parts. Furan Binder (FNB) is composed of an acid
72 catalyst (Toluene Sulfonic acid) and furfuryl alcohol which generates a 3-dimensional
73 polymer chain network (furan resin bridges) through acid-hardening reaction, polymerization,
74 and condensation. The polymer bridges (H-C bonds) observed in furan resin bonded sand
75 mold provide extra cohesion and strength to the silica sand particles, which is necessary in
76 order to retain the shape of 3D printed sand molds when in contact with the melt. The furan
77 binder condensation reaction produces water (dehydration), which tends to slow down the rate
78 of curing and hence affects the strength and permeability [13,14] of the molds. The recent
79 research shows that there are many possible factors affecting the quality of 3DP sand molds,
80 including furan resin binder content, curing temperature, curing time, types of base sand and
81 sand grain size [10,15–20]. All these works point out the high variability of the 3DP sand
82 molds.

83

84 The effects of curing time and temperature on permeability and mechanical strength using
85 ZCast 501 powder and Zb56 resin binder system of the ZCorporation were investigated by
86 other researchers [21]. The effects of curing time and temperature on permeability and
87 mechanical strength using ExOne 3D printed sand mold was also investigated [10], where it
88 was shown that the permeability decreased with increase in curing temperature. In the latter
89 work, a mathematical model was proposed to predict an optimal curing time and temperature
90 for both permeability and compressive strength. Also, the curing cycle of parts fabricated with
91 ZCAST® was optimized by taking into account the potential casting defects due to off-
92 gassing of volatile binder components [22,23]. These works showed that using higher
93 amounts of binder (8-9%) than the standard values in casting sand (1.4%) results in more off-
94 gassing and incomplete filling of the mold [8,22,23]. The same aspects were also studied in

95 the case of an ExOneTM 3D printer, finding that the specimens had high mechanical strength
96 (~1.3 MPa) with less amount of binder than in ZCAST system, due to the well-controlled
97 distribution of silica sand and furan resin binder [23]. Recommendations on the orientation
98 and position of the samples in the job box can also be found in the recent literature in order to
99 minimize the anisotropic behavior of the molds produced with this technology [9].

100

101 ExOne S-Print is one of the latest machines for 3D printed porous sand molds using furan
102 binder system, and it requires curing (heat treatment) to remove the byproduct (water) from
103 the polycondensation (polymerization + condensation) of the furfuryl alcohol based
104 monomers (the furan resin), from the mold. This evolution of binder affects both the
105 mechanical and mass transport properties of the mold hence results in altered gas
106 permeability. In particular, the mass flow rate by which the air is evacuated from the molds is
107 directly related to pore size and binder percentage (microscopic characteristic length).
108 Therefore, there is a vital need for a suitable method for characterizing the permeability and
109 its relation to the curing temperature and time. The evolution of permeability and mechanical
110 strength of the 3DP sand molds during the curing stage was studied in a recent work using
111 traditional characterization methods for a unique value of binder content [10]. However, the
112 effects of binder content on permeability and 3PB strength have still not been studied to the
113 best of our knowledge. Such effects are expected to play a crucial role in the functionality of
114 the casted parts for the above-mentioned reasons. To fill this gap, the present study focuses on
115 the effect of binder mass fraction on permeability and mechanical strength of printed molds
116 for different curing temperatures and times.

117

118 **2. Theoretical background**

119

120 Three-point bending (3PB) tests are commonly used to characterize the mechanical strength
121 of brittle materials. These tests are comparatively easy to set up and interpret and are usually
122 performed on a rectangular bar, which is positioned over two roller pin supports while the
123 load is applied via a third roller pin typically mounted halfway between the pin supports. The
124 3PB bending stress is calculated using the measured load from Eq. 1:

125

$$\sigma = F \times \frac{3l}{2bd^2} \quad (1)$$

126 where F is the load at the middle section of the 3DP rectangular bar, l is the length between
127 the support span, b is the width of 3DP test bar and d is the thickness of the 3DP tested
128 sample.

129

130 Permeability can be defined as the ability of a porous medium to allow the fluids to pass
131 through it when driven by a pressure gradient. In the particular case of casting sands, the
132 standard method recommended by the American Foundry Society (AFS) consists in
133 determining gas permeability (GP), which is extensively used in foundry industries [24]. In
134 spite of the key advantages provided by the simplicity and rapidity of this traditional method,
135 GP is not an intrinsic porous-medium property and does not have permeability units [m²].
136 Indeed, GP depends on the dynamic shear viscosity of the injected fluid, which increases with
137 temperature and generates higher pressure losses at higher temperatures for similar injection
138 flow rates. Also, the standard method does not take into account the inertial pressure drops

139 and compressibility of the fluid. Consequently, the obtained permeability value is not accurate
140 when the pressure gradient within the interstices of the sand is moderate or high. Furthermore,
141 usual GP characterization is frequently based on a unique-point measurement, so the result is
142 strongly influenced by experimental uncertainty. For these reasons, a rigorous method aiming
143 to improve the accuracy of permeability measurements in 3DP molds will be used in the
144 present work.

145

146 In the case of unconsolidated granular media as 3DP sand molds, permeability mainly
147 depends on the particle size distribution of the solids forming the bed, their shape, the liquid
148 saturation of the pore interstices and the packing structure (i.e. bed bulk porosity). When
149 dealing with casting processes, the pressure gradient is generated by the metallostatic pressure
150 during filling of the mold (to which an external pressure can be added) and the shrinkage of
151 the solidified alloy during cooling. Darcy's law (Eq. 2) is widely used to model the laminar
152 steady flow of Newtonian fluids through porous media (e.g. sand molds). This law relates the
153 volumetric flow rate to the pressure gradient through the viscosity of the fluid and the
154 permeability of the porous material.

155

$$\nabla P = \frac{\mu}{K} \frac{Q_v}{S} \quad (2)$$

156 In the preceding equation, Q_v is the volumetric flow rate, S is the cross-sectional area, μ is the
157 dynamic shear viscosity of the injected fluid, $\nabla P = \frac{\Delta P}{L}$ is the pressure gradient and ΔP is the
158 pressure drop throughout a porous sample of length L and intrinsic permeability K . In
159 unidirectional flow, K is usually measured by injecting fluid with known viscosity through a

160 sample of the investigated medium of known dimensions. During the tests, either Q_v or ΔP is
161 imposed and the other magnitude is measured.

162

163 The value of K may be overestimated when performing measurements with gases at very low
164 flow rates in porous media with low permeability. This is caused by wall-slip of the gas flow
165 and is known as Klinkenberg effect [25,26]. Klinkenberg effect depends on the relative size of
166 the gas molecule with respect to the diameters of the pore, becoming significant only when
167 pore diameter is close to the mean free path of gas molecules. This is not the case of
168 commonly used casting sands, which exhibit high permeability levels. However, special
169 attention should be paid to the measurements performed at medium-to-high values of pressure
170 gradient, due to inertial effects which result in extra pressure losses that are not taken into
171 account by Darcy's law. Indeed, Darcy's law only applies to creeping flow in which inertial
172 forces are negligible compared to viscous forces [27–30]. Nonlinearity of fluid flow stems
173 from inertial pressure losses generated by the repeated accelerations and decelerations due to
174 rapid changes in flow velocity and direction along the flow path. Both theoretical and
175 empirical models taking into account the extra pressure losses due to inertial effects were
176 presented in the literature [31].

177

178 Forchheimer's empirical law [32] is commonly used to model the nonlinear behavior
179 associated to inertial regime through addition of a quadratic flow rate term to Darcy's law:

180

$$\nabla P = \frac{\Delta P}{L} = \frac{\mu Q_v}{K S} + \rho \beta \left(\frac{Q_v}{S} \right)^2 \quad (3)$$

181 with $\nabla P = \frac{\Delta P}{L} = \frac{P_i - P_o}{L}$, P_i being the absolute pressure at the inlet, P_o being the absolute
 182 pressure at the outlet, ρ the density of the injected fluid and β the inertial coefficient.
 183 Forchheimer's law has been experimentally validated and has found some theoretical
 184 justifications [33–37].

185

186 The compressibility of the injected fluid is often neglected by the standard permeability
 187 measurements used in casting. However, Q_v is not constant throughout the porous medium
 188 when injecting compressible fluids, so Eq. 3 needs to be re-written in terms of mass flow rate

189 Q_m :

190

$$\bar{\rho} S \nabla P = \frac{\mu}{K} Q_m + \frac{\beta}{S} Q_m^2 \quad (4)$$

191 where $\bar{\rho}$ is the average density of the fluid in the porous medium and $Q_m = \bar{\rho} Q_v$. For the sake
 192 of simplicity, the left term of Eq. 4 will be named f ($f = \bar{\rho} S \nabla P$). If isothermal flow is assumed
 193 and the compressible fluid is considered to be an ideal gas, the following relationship can be
 194 used:

195

$$\frac{P}{\rho} = \frac{rT}{M} \quad (5)$$

196 where P is the absolute pressure, T is the absolute temperature, r is the universal gas constant
 197 ($\sim 8.31 \text{ J kg}^{-1} \text{ mol}^{-1}$) and M is the molar mass of the gas ($\sim 28.96 \text{ g/mol}$ for air). From Eq. 6,
 198 it can be deduced that $Q_m \sim 1.29 Q_v$ for air flow when both Q_m and Q_v are given in SI units
 199 and Q_v is taken as the volumetric flow rate in standard conditions of pressure and temperature.
 200 From Eq. 5, $\bar{\rho}$ can be calculated as:

$$\bar{\rho} = \frac{M}{rT} \bar{P} = \frac{M}{rT} \frac{(P_i + P_o)}{2} \quad (6)$$

201 with \bar{P} being the average pressure of the gas throughout the sample.

202

203 The criteria for transition from Darcian to non-Darcian flow regimes are commonly given in
 204 terms of the non-dimensional Reynolds number Re. However, as discussed by researchers
 205 [38], the definition of Re in granular unconsolidated porous media as casting sand is
 206 controversial. This is due to the diverse characteristic lengths used in the definition of Re by
 207 different authors: average grain size, pore constriction size, the square root of permeability,
 208 etc. The latter authors showed that the use of Forchheimer number F_o is more suitable for
 209 establishing the transition between creeping and inertial flows. F_o represents the ratio between
 210 inertial and viscous pressure drops and is defined from Eq. 3 as follows:

211

212

$$F_o = \frac{\Delta P_{\text{inertial}}}{\Delta P_{\text{viscous}}} = \frac{\Delta P_{\text{total}} - \Delta P_{\text{viscous}}}{\Delta P_{\text{viscous}}} = \frac{\Delta P_{\text{total}}}{\frac{\mu Q_m L}{K \bar{\rho} S}} - 1 \quad (7)$$

213

214 According to researchers [38], the transition to non-Darcian flow occurs at $F_o = 0.11$ (10% of
215 inertial pressure drop), independently of the type of porous medium.

216

217 An apparent permeability K_{app} can be defined as follows for every couple of Q_m - ΔP
218 measurements:

219

$$K_{app} = \frac{\mu Q_m}{\bar{\rho} S \nabla P} \quad (8)$$

220

221 The preceding definition can be derived from Eq. 8, by using $\beta = 0$. Therefore, the inertial
222 effects are not encompassed in K_{app} and it is expected to markedly differ from K at moderate
223 and high-pressure gradients. Standard permeability-characterization methods are based on the
224 measurement of K_{app} . This explains that these methods are extremely inaccurate unless the
225 flow rate used during the unique measurement is not meticulously selected, as will be shown
226 in subsection 4.3. Indeed, $K_{app} \sim K$ only at low flow rates ($F_o < 1$).

227

228 **3. Experimental setup and methods**

229

230 **3.1. Materials**

231

232 The raw materials used in the present experiments were quartz silica sand and a furfuryl-
233 alcohol-based binder (furan resin) of density (1.1-1.2) g/cm³. The silica sand grains had
234 regular spherical shape, with a mean diameter of 140 μm and a standard deviation of 25 μm,
235 which corresponds to American Foundry Society (AFS) size number 97. The furan binder was
236 a mixture of furfuryl alcohol (70-90 wt%), bisphenol A (5-15 wt%), resorcinol (1-10 wt%)
237 and 3-aminopropyltriethoxysilane (0.1-0.2 wt%) [39].

238

239 **3.2. Printing stage**

240

241 The specimens were first designed with the commercial software NetFabbTM [40], and were
242 then converted to .stl format. The bar specimens for 3 PB test were designed with length 172
243 mm, breadth 22.4 mm and height 22.4 mm. And the cylindrical specimens for permeability
244 test were designed with diameter = 35 mm and height 75 mm. The dimensions chosen were
245 according to the requirement by the machine for experimental testing of 3DP specimen.
246 Then, the samples were 3D-printed by means of an ExOne S-Print Furan machine [41], with a
247 job-box size of 800 × 500 × 400 mm³. The printing process began by mixing sulfonic acid
248 (0.18 wt% of the sand) catalyst with 8 kg of silica sand grains inside the mixing chamber of
249 the 3D printer. The mixture was subsequently transferred to the re-coater. Successive layers of
250 280-μm thickness (i.e. 2 times the mean diameter of the sand grains) were spread over the
251 build platform and a compacting force was applied over the sand bed by means of a re-coater
252 head. Then, the print head nozzle injected the furfuryl alcohol binder on top of these sand
253 layers to bind them. As the droplets of furan resin binder were injected over the layer of acid-
254 activated silica sand bed, a coating layer was formed on top of each individual sand grain. The
255 surface of this resin-bonded sand grains crosslink with each other, forming a bridge of resin

256 binder between the sand particles formed by capillarity and gravitational forces immediately
257 after application of the binder. Then, and a hardening mechanism progressively occurs during
258 curing, making the sand particles bond closer as a result of surface tension and forming a
259 strong resin binder-particle bridge. The process continued until the last slice of the sample
260 was printed and the final two sand layers spread.

261

262 Previous experiments were performed to evaluate the effect of printing speed on the quality
263 and part integrity [42]. It was concluded that an increased printing speed would influence not
264 only the dimensional accuracy but also the mechanical strength of the 3DP parts due to
265 enhanced inertia forces. It is to be noted that a higher recoating speed also leads to non-
266 uniform spreading of sand over the job-box and low compaction of sand bed, generating
267 lower packing densities and high porosities. On the other hand, it is known that low recoating
268 speed leads to high sand packing density, and consequently to greater flexural strength [43].
269 The recommended process parameters for minimal variation in 3PB strength and permeability
270 along the job-box were selected according to Ref. [9,10,44] and are listed in Table 1. The
271 recoating speed was kept constant throughout the printing process and only the printing
272 resolution (furan drop spacing) was altered to achieve different binder percentages. It was
273 highlighted in previous works that loose sand does not provide a good support for the 3D
274 printed parts to build higher up in volume, and results in specimen sinking over the powder
275 bed during compaction [45–47]. Therefore, the specimens were printed over a thick sand layer
276 of 1.4 mm (around ten layers of sand) in order to avoid sinking, sub-layer displacements [45]
277 and sticking of the resin-bonded sand to the job-box.

278

279 A total of 180 (60×3 different binder content) cylindrical specimens were printed for
280 permeability tests. Also, 90 (30×3 different binder content) rectangular bars were printed for

281 the 3PB tests and (6×3 different binder content) 18 specimens were produced for loss on
282 ignition (LOI) tests. The initial dimensions of the 3D printed parts (bars) were measured using
283 a Vernier caliper, with length, breadth and height of 22.3 ± 0.02 mm, 22.2 ± 0.02 mm and
284 171.9 ± 0.07 mm, respectively (the uncertainty corresponds to 95% confidence interval). The
285 initial dimensions of the 3D printed parts (cylinders) were also measured using a Vernier
286 caliper, with length of 74.9 ± 0.01 mm and diameter of 34.8 ± 0.02 mm with 95% confidence
287 interval. The temperature of the printing room was 25 ± 3 °C and the relative humidity $40 \pm$
288 10%. After printing, the samples were then de-powdered, cleaned and taken out of the job-
289 box.

290

291 To go further, Scanning electron microscope (SEM) images were obtained using 3DP
292 specimens of 5mm in diameter and height, to verify the furan resin bridges between sand
293 particles. SEM images were obtained with a scanning electron microscope JEOL JSM-7001F.
294 Micrographs of 3DP samples were obtained in low vacuum (0 - 40 Pa) with an acceleration
295 voltage of 5 kV at a 100 μ m working distance for different magnifications. The scans were
296 acquired and the obtained images were subsequently analyzed and processed using median
297 filter with the open-source platform for image analysis Fiji-ImageJ [48], in order to
298 differentiate between the sand particles, the pores, and the furan resin bridges. Samples of
299 SEM images are presented in Figure 1, showing the morphology of the furan resin bridges
300 within a cross-section of the 3D printed sample.

301

302

303 **3.3. Curing stages**

304

305 Despite providing superior mechanical strength to the 3DP parts, high binder amounts can
306 also generate a decrease in permeability, as the pores get filled with liquid. Also, more binder
307 leads to more off-gassing of the 3DP sand mold and the molds suffer from excessive moisture
308 generated from polycondensation reaction (dehydration) after printing. Therefore, samples
309 with usual mass fractions of binder require initial curing in order to remove excess moisture
310 content which affects their 3PB strength and permeability. For this reason, oven curing was
311 performed up to 60h at low temperatures to investigate its effect on the mechanical properties
312 of the 3DP mold [10]. The binder percentage was measured after this initial curing stage by
313 means of LOI test.

314

315 After the pre-curing stage 25 °C, 100 °C and 200 °C were chosen as curing temperatures to
316 investigate the curing mechanisms. The choice of these temperatures is motivated by the
317 boiling points at room conditions of water and furfuryl alcohol, which are 100 °C and 180 °C,
318 respectively. Three curing times were considered: 0h, 2h, and 14h. Here the 0h conditions
319 represents the initial conditions of the specimen after printing. As observed in the previous
320 work [10], there is a rapid change in 3DP mold properties after 2h curing and approach a
321 constant value after 12h. Therefore, 0h, 2h, and 14h were chosen for the experiments. Images
322 of a set of heat-treated specimens are shown in Figure 2. One may note that the color of the
323 samples evolves during curing due to the progressive evaporation of binder and water. The
324 binder content, curing times and curing temperatures of the printed samples are listed in Table
325 2.

326

327 **3.4. Loss on Ignition tests**

328

329 The Loss-On-Ignition (LOI) test is used to measure the amount of volatile materials present in
330 a sample. In the case of the investigated 3DP sand samples, it was used to measure the mass
331 of binder, i.e. the combined mass of water, resin, catalyst, and volatile impurities. To do so,
332 the initial mass of the printed specimens was first measured, obtaining values close to 30g
333 (initial mass) in all cases. The specimens were then put into ceramic crucibles which had been
334 pre-heated at 100 °C for 1 h in an oven to extract moisture and organic residues. Once in the
335 crucibles, the 3DP specimens were heated at 900 °C for 45 min so as to burn-out and expel
336 the binder and moisture. After that, the crucible was removed from the oven and the mass of
337 the burnt-out specimen (final mass) was weighted. Images of the crucibles containing the
338 tested samples at the different stages of the LOI tests are provided in Figure 3. From the
339 results of the LOI, the binder contents of the samples were determined using Eq. 9:

340

$$\text{Binder content} = \frac{\text{initial mass} - \text{final mass}}{\text{initial mass}} \times 100 \% \quad (9)$$

341

342 The remaining binder content at each stage of curing was calculated using this procedure, for
343 all curing temperatures and initial binder contents. 6 repetitions were performed for each
344 different binder specimens during the LOI test in order to estimate the experimental
345 uncertainty of the measurements.

346

347 **3.5. Porosity measurements**

348

349 The porosity of the samples was determined with the oven-dry method. The particle density
350 was considered as being the density of SiO₂-quartz (2648 kg.m⁻³), which constitutes 99.1% of

351 the sand used by the printer. A laboratory precision balance was used to weight the printed
352 specimens after drying in a hot-air oven at 105 °C for 24 hours, and the bulk density of the
353 3DP specimen was calculated as the mass of sample per unit bulk volume. It is worth
354 reminding that both the volume of solid and the volume of pores were taken into account for
355 the calculation of bulk density. In contrast, the particle density was equal to the mass of
356 sample per unit volume of silica sand particles. From the bulk density and particle density, the
357 total porosity of the 3DP specimens was calculated as:

$$\text{Porosity} = 1 - \frac{\text{mass of the sample after LOI}}{\text{density of silica} \times \text{volume of the sample}} \quad (10)$$

358

359 The experimentally measured porosity values were close to 50% for all tested samples, with
360 an estimated standard deviation of 0.2%. 6 repetitions were performed with 6 analogous
361 specimens for each measurement in order to evaluate the uncertainty related to the
362 repeatability of the porosity tests.

363

364 **3.6. Three-Point bending tests**

365

366 The 3PB strength of the 3DP specimens was determined through destructive tests, as
367 commonly done with traditionally manufactured sand molds. The tests were performed using
368 a universal strength test machine (Simpson-Electrical PFG type) [49]. The bars were fixed to
369 the testing machine by means of two supporting pins separated 150 mm from each other. The
370 load was applied by a third pin at the mid-length of the 3DP bar, with a load rate of 0.1
371 MPa.s⁻¹, until the specimens broke. The maximum load capacity of the machine was 12.8
372 MPa and the uncertainty of the pressure gauge was ± 0.05 MPa. 4 repetitions were performed

373 with 4 analogous specimens for each measurement in order to assess uncertainty. For each
374 binder, the initial 3PB strength was measured using 4 distinct specimens. And the 0h
375 condition for each binder content specimen is same as of their initial 3PB strength for
376 different curing temperature.

377

378 **3.7. Permeability tests**

379

380 The permeability of the printed samples was measured using the experimental setup shown in
381 Figure 4, (Vinci TechnologiesTM perm-meter [50]). The experimental procedure started by
382 inserting the cylindrical 3DP sample into a Viton sleeve and mounting it in a Hassler-type
383 core holder. After that, the core was confined with pressurized oil surrounding the sleeve in
384 order to avoid lateral leaks during flow. This oil was provided by an auxiliary confining pump
385 (Enerpac company). Then, air coming from a pressurized cylinder was continuously injected
386 through the cores at a controlled mass flow rate. A set of steeply increasing values of mass
387 flow rate was imposed by means of two mass flow rate regulators (Brooks Instrument B.V,
388 Accuracy: $\pm 0.7\%$ of flow rate), with working ranges of 0 - 1 NL/min and 0 – 30 NL/min,
389 respectively. The corresponding steady-state pressure drop ΔP between the inlet and the outlet
390 of the core ($L = 75$ mm) was measured by a membrane-type differential pressure sensor
391 (DP15 Variable Reluctance Pressure Sensor, Validyne Engineering, Accuracy: $\pm 0.2\%$ of
392 flow rate). The outgoing air was released to atmospheric pressure, so P_o was assumed to be
393 0.1 MPa and $P_i = P_o + \Delta P$. Each measurement was repeated four times in order to evaluate
394 uncertainty related to the repeatability of the pressure. For each binder, the initial permeability
395 was measured using 4 distinct specimens at a low flow rate (0 - 1 NL/min) and 4 distinct
396 specimens at a high flow rate (1 – 30 NL/min). Therefore the 0h condition for each binder

397 content specimen is the same as of their initial permeability for different curing temperature.
398 A total of 10 flow rate (low flow rate + high flow rate) vs. pressure drop measurements were
399 performed for each case; covering the mass-flow-rate range from 0.01 NI/min to 10 NI/min.
400 The temperature of the core-holder was maintained at 23.0 ± 2 °C by using a temperature
401 control subsystem consisting of an electric heating thermostat. The dynamic shear viscosity of
402 air at this temperature was taken as 1.81×10^{-5} Pa s. 4 repetitions were performed with 4
403 analogous specimens for each measurement in order to evaluate the uncertainty related to the
404 repeatability of the tests.

405

406 **4. Results and discussion**

407

408 The effects of binder content on mass loss, permeability, and 3PB strength for uncured and
409 cured samples were experimentally investigated from the results of the measurements
410 presented in the preceding section.

411

412 **4.1. Evolution of binder content during curing as a function of the initial binder content**

413

414 The mass loss during curing, as measured by the LOI tests, are represented as a function of
415 curing time and temperature in Figure 5 for the three different values of binder content. All
416 the testing results were the mean value of six measurements. It is noted that loss of binder
417 mass by evaporation was negligible at the room temperature of 25 °C, even after 14h of
418 curing. This was expected given that 25 °C is far below the boiling temperatures of the water

419 and alcohols present in the binder. In contrast, a significant decrease in the mass of binder is
420 observed for the three initial values of binder content at both 100 °C and 200 °C. This
421 decrease is more pronounced within the first two hours of curing.

422

423 It is reminded that the furan binder (FNB) is a mixture of furfuryl alcohol and acid catalyst
424 [51]. FNB's condensation reaction produces water, which tends to slow down the rate of
425 curing (dehydration) affecting the mechanical properties of the 3DP mold [13,14]. A closer
426 look to Figure 5 reveals that the rate of mass loss when during curing at 200 °C is roughly
427 similar to the one at 100 °C, leading to analogous values of remaining binder content after 2h
428 and 12h in both cases. One may expect a higher evaporation rate at 200 °C, as this
429 temperature is greater than the boiling temperature of both alcohol and water. However, it
430 must be borne in mind that water is released only after polycondensation, which is
431 conditioned by the reaction of the acid catalyst with alcohol. Consequently, less water should
432 be released at 200 °C as the polycondensation reaction is interrupted by the early evaporation
433 of alcohol. Therefore, it can be concluded from Fig.8 that the mass of water being evaporated
434 at 100 °C is equivalent to the sum of the masses of water and alcohol being evaporated at 200
435 °C.

436

437 **4.2. 3PB strength as a function of the initial binder content for different curing** 438 **conditions**

439

440 Figure 6 shows the 3PB strength test results of 3DP sand specimens in the uncured and cured
441 conditions. All the testing results were the mean value of four measurements. It was found

442 that 3PB strength increases with binder content for all curing times and temperatures.
443 Moreover, 3PB strength increases when curing at 100 °C and decreases when cured at 200 °C
444 for all binder contents. When curing at 100°C, the 3PB strength experienced an increase of
445 20% for 1.02% binder, 16.7% for 1.46% binder and 28% for 1.98% binder. However, when
446 curing at 200 °C, the 3PB strength experienced a decrease of 41.6% for 1.02% binder, 40%
447 for 1.46% binder and 22% for 1.98% binder.

448

449 It is of crucial importance to manufacture 3DP sand molds meeting the requirements in terms
450 of gas evolution during metal casting (low binder content) and optimum 3PB strength. In this
451 regard, 3PB strength should be above 1.5 MPa so that the mold can resist the impact of liquid
452 metal. Therefore, 1.46 wt% of sand can be selected as the optimum furan resin binder content
453 to print 3DP molds for metal casting with the present technique. Indeed, when the initial furan
454 resin binder content is 1.46 wt%, the 2 h and 14 h strengths are above 2 MPa, satisfying
455 standard production requirement for casting melted alloy. It is also observed in Figure 6 that
456 3PB is unaltered by curing at 25 °C. The 3PB strength attains its maximum for all binder
457 content when curing at 100 °C for 2 hours. The reason is that the low roasting temperature
458 (100 °C) provides secondary hardening of furan resin bridges which increases the 3PB
459 strength, while the resin bonding bridges of 3DP sand mold burn at high curing temperature
460 (200 °C), resulting in reduced 3PB strength.

461

462 The 3PB strength of 3DP sand mold has a direct influence on the strength of the furan resin
463 bridge between sand grains in the sample (adhesion of binder between sand and cohesion of
464 the furan resin binder). This furan resin bridge is formed by capillary action after the binder is
465 dropped by the print head (X-resolution) and strengthens gradually. The intermolecular resin

466 bond strength depends on the physical state of the binder and its interaction with the
467 surrounding sand particles. When the 3DP specimen is cured, the furan resin binder hardens
468 by polycondensation (polymerization and condensation), forming a network furan resin
469 bridges which hold the sand particles together. The strength of the resin bridge greatly
470 depends on the amount of the binder content. The volume of the bridge corresponds to the
471 printed furan binder content minus the evaporated solvent (mixture water and alcohol). This
472 resin bridge strengthens gradually and affects the 3PB strength of the sample. The strength
473 increases more rapidly at 100 °C (cured by heat treatment) than at 25 °C (cured at room
474 temperature). However, this resin bridge hardening and strengthening mechanism have a
475 limit, leading to reduced strength and loss of ductility for prolonged heating at 100 °C or
476 when heating at high temperature (200 °C). These results facilitate the choice of the optimum
477 binder content, curing time and temperature to obtain the functional values of 3PB strength.

478

479 The mechanical and the mass transport properties of the cohesive granular materials depend
480 on their microscopic structure and their composition. A scheme of the resin-bonded bridges
481 between sand particles with simple cubic compaction density is displayed in Figure 7, where
482 R_{sand} is the radius of the silica sand particle and T_{binder} is the thickness of the furan resin
483 bridge. Considering that the binder is evenly distributed over the sand particles, the thickness
484 of the resin bridge is expected to increase when the binder content is increased. This leads to
485 improved cohesion strength of the bonding bridges and higher 3PB strength, in agreement
486 with the experimental results.

487

488 **4.3. Permeability as a function of the initial binder content for different curing**
489 **conditions**

490

491 The relationships between f ($= \bar{\rho}S\nabla P$) and Q_m obtained during permeability measurements for
492 uncured samples with different levels of initial binder content are shown in Figure 8. All the
493 testing results were the mean value of four measurements. It is noted that f increases
494 nonlinearly with increasing mass flow rate deviating from the linear relationship predicted by
495 Darcy's law (Eq. 3 with $\beta = 0$). As explained in section 2, Darcy's law is only valid for
496 creeping flow at low Reynolds numbers. Therefore, the non-linear behavior observed in
497 Figure 8 reveals that the flow is no longer creeping at moderate and high mass flow rates and
498 the inertial pressure losses are not negligible. The same figure shows that all f vs. Q_m curves
499 collapse for uncured samples, independently of the binder content. Therefore, similar values
500 of permeability and similar inertial pressure drops are expected for the three investigated
501 binder contents when curing is performed at room temperature (25 °C). The f vs. Q_m
502 measurements for all the considered binder contents and curing conditions are represented in
503 Figure 9, showing that the curves also collapse for all curing conditions in the case of 1.02%
504 and 1.46% initial binder contents. Indeed, significant differences depending on the curing
505 time and temperature were only observed for 1.98% initial binder content, which will be
506 interpreted below in terms of permeability variation.

507

508 K_{app} was calculated using Eq. 8, as traditionally done with the standard permeability
509 characterization methods, for different values of the injection flow rate. The experimentally
510 obtained Q_m vs. K_{app} relationship for uncured samples with different binder contents is
511 presented in Figure 10. These results show that K_{app} is monotonically decreasing as Q_m
512 increases for all the specimens, which is explained by the inertial pressure drops which are not
513 taken into account in the calculation of K_{app} . Moreover, it is observed that the K_{app} tends to a

514 constant value within the low flow rates region in which the flow is viscous-dominated and
515 the inertial deviations are negligible. Therefore, $K_{app} \sim K$ at the lowest flow rates and K was
516 considered to be equal to the plateau value.

517

518 Darcy's law (Eq. 3 with $\beta = 0$) was then fitted to the f vs. Q_m measurements obtained during
519 permeability tests, as illustrated in Figure 11a for the uncured 1.02% binder content sample.
520 Similar results were observed for all considered curing conditions. From this figure, it can be
521 deduced that the flow regime is creeping only at the lowest flow rates in which Darcy's law
522 predictions are accurate. However, the deviations from Darcy's law become larger as Q_m is
523 increased due to additional inertial pressure drops. Therefore, it is confirmed that both
524 creeping and inertial flow regimes were covered by a wide range of Q_m imposed during the
525 measurements. Furthermore, F_o (Eq. 7) was also calculated as a function of Q_m so as to
526 quantify the relative importance of the inertial pressure drops, as presented in Figure 11b. The
527 critical value of $F_o = 0.11$ (10% of inertial pressure drop) marking the transition from
528 Darcian to non-Darcian flow occurs at Q_m close to 3×10^{-6} kg/s. Accordingly, for the given
529 sample dimensions and experimental conditions, it can be concluded that flow rates close to 3
530 $\times 10^{-6}$ kg/s must be used to characterize permeability in this type of casting sands. Non-
531 dimensionalization of this criterion is challenging given the compressibility of the injected
532 fluid and will not be addressed in the present work.

533

534 Following the procedure presented above, the permeability of the samples was calculated for
535 all the investigated binder contents, curing times and temperatures. The results are presented
536 in Figure 12. It can be observed that no significant evolution of K over time was obtained for
537 the samples cured at 25 °C. This was expected, given the low evaporation rate at room

538 temperature in agreement with previous results [21] and the mass loss measurements
539 presented in Fig. 5. Moreover, the permeability of these samples is very close for all binder
540 contents. This may be explained by the combined effect of two mechanisms with opposed
541 effects on permeability: 1) the generation of thicker resin bridges through polymerization at
542 higher binder amounts tend to separate of the grains, which enhances porosity and
543 permeability; and 2) higher binder amounts lead to a higher saturation of the interstices,
544 resulting in a decrease in permeability. However, these mechanisms need further verification,
545 for example through specifically dedicated X-ray micro-computed tomography (μ -CT)
546 experiments, which will not be presented here.

547

548 It can also be observed in Figure 12 that the permeability of the 1.02% binder content samples
549 remains roughly constant throughout the 14h of curing at the three considered temperatures.
550 This may be explained by the thinness of the liquid layer between the sand grains which
551 produces only a very weak reduction in permeability. Also, the polymerization reaction
552 (transformation of the liquid binder into resin bridges) is expected to conclude earlier than for
553 higher amounts of binder, so the liquid saturation is lower and the effects of remaining
554 alcohol and water evaporation are minimum. A stronger effect of evaporation on permeability
555 is observed at 1.46% and 1.98% binder contents, which is potentially due to the higher
556 amount of remaining alcohol and water blocking air flow through the pores. Also, a decrease
557 in permeability is observed after 14h of curing, which could be explained by the shrinkage
558 effect produced by the burning of the resin bridges [52]. The permeability attains its
559 maximum in the case of the specimen with the highest binder content when heat-treated at
560 100°C for 2h. It is to be noted that higher amounts of binder would generate more toxic gas.

561

562 **5. Conclusion**

563

564 The quality of the parts produced by casting in 3DP molds is strongly conditioned by the
565 careful choice of suitable binder content. Motivated by the vital role of this process parameter,
566 the effects of binder content on the permeability and the mechanical strength of 3DP sand
567 molds has been experimentally evaluated for different curing times and temperatures. The
568 following conclusions are drawn from the present work:

569

- 570 ✓ Binder content has a profound influence on the 3PB strength of 3DP sand molds.
571 Higher binder amounts lead to increased mechanical strengths. Moderate curing
572 temperatures and times (100 °C, 2h) are recommended in order to optimize 3PB
573 (avoiding degradation of the resin bridges, excessive off-gassing, and hot tearing).
- 574 ✓ Mass-loss measurements performed during LOI tests allow the evaluation of liquid
575 evaporation rates, which can be subsequently used in the analysis of the physical
576 mechanisms governing the changes in permeability and 3PB strength during the
577 curing stage.
- 578 ✓ The effect of binder content on permeability is not significant when curing at room
579 temperature (25 °C). However, liquid evaporation and binder shrinkage significantly
580 affect permeability. Maximum permeability is attained at the same conditions as the
581 optimum 3PB strength.
- 582 ✓ The porosity of the 3DP sand molds is very high, leading to inertial-dominated flows
583 at moderate values of air flow rate. Consequently, permeability measurements must be
584 performed at sufficiently low injection flow rates in order to achieve creeping flow.

585

586 The present experimental results facilitate the characterization of printing process parameters
587 by quantifying the effects of binder content on the functionality of 3DP molds. These criteria
588 are most valuable for the production of casting molds meeting the requirements of aerospace
589 and automotive industries.

590

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592

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597

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599

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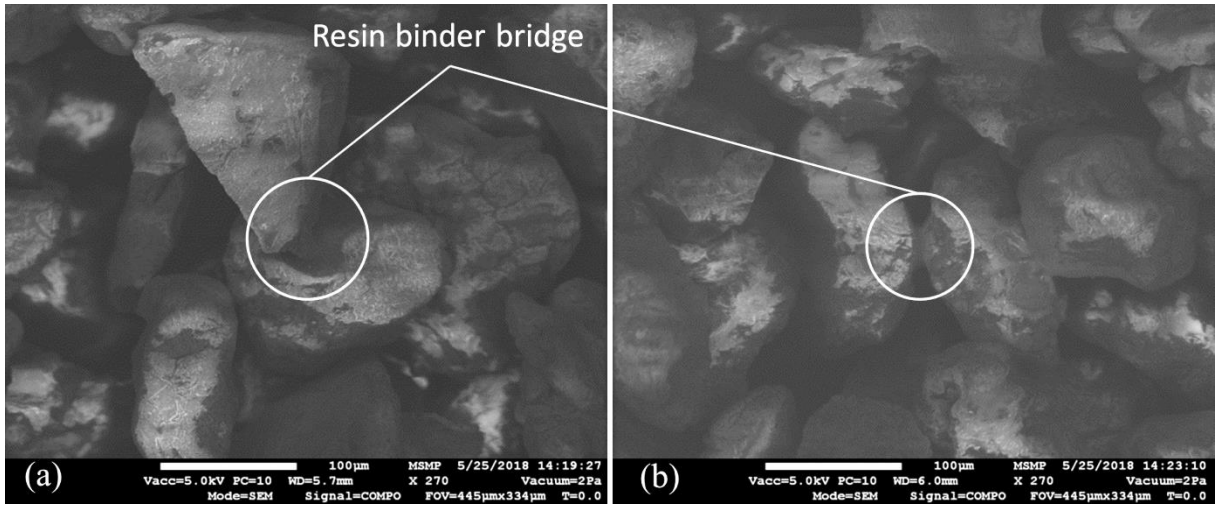
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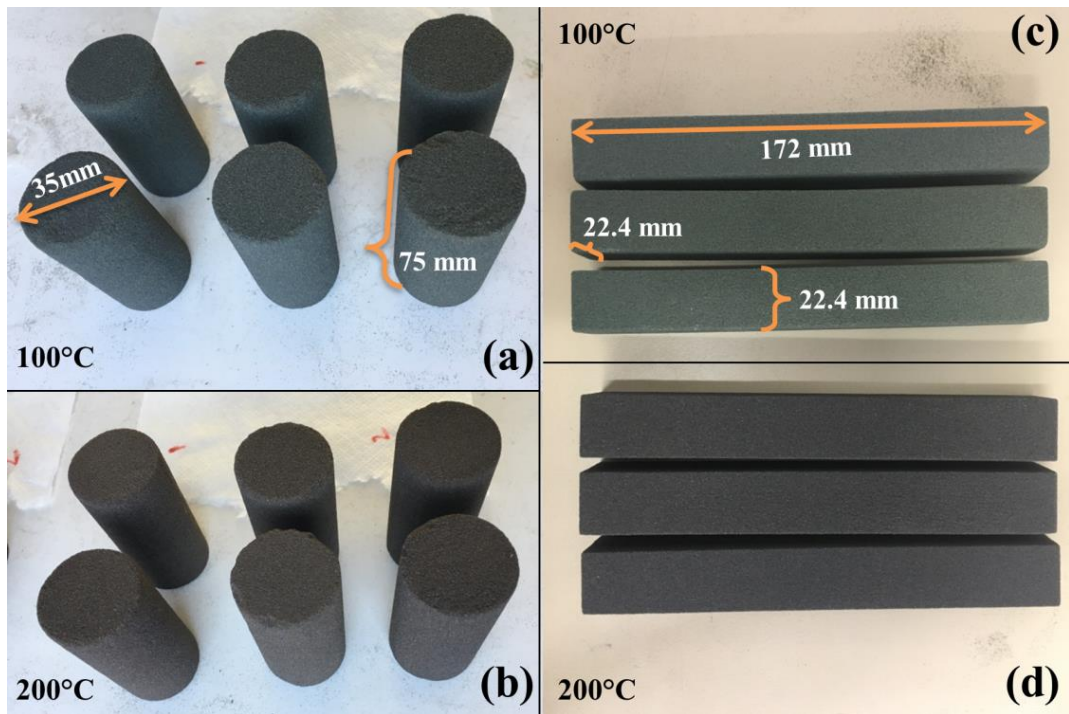


732

733 **Figure 1.** Scanning electron microscope (SEM) image of the 3DP sample, (a, b) zoom
 734 showing the resin bridges

735

736



737

738 **Figure 2.** Heat-treated 3DP samples with 1.45% binder, (a,b) cylinders and (c,d) bars

739

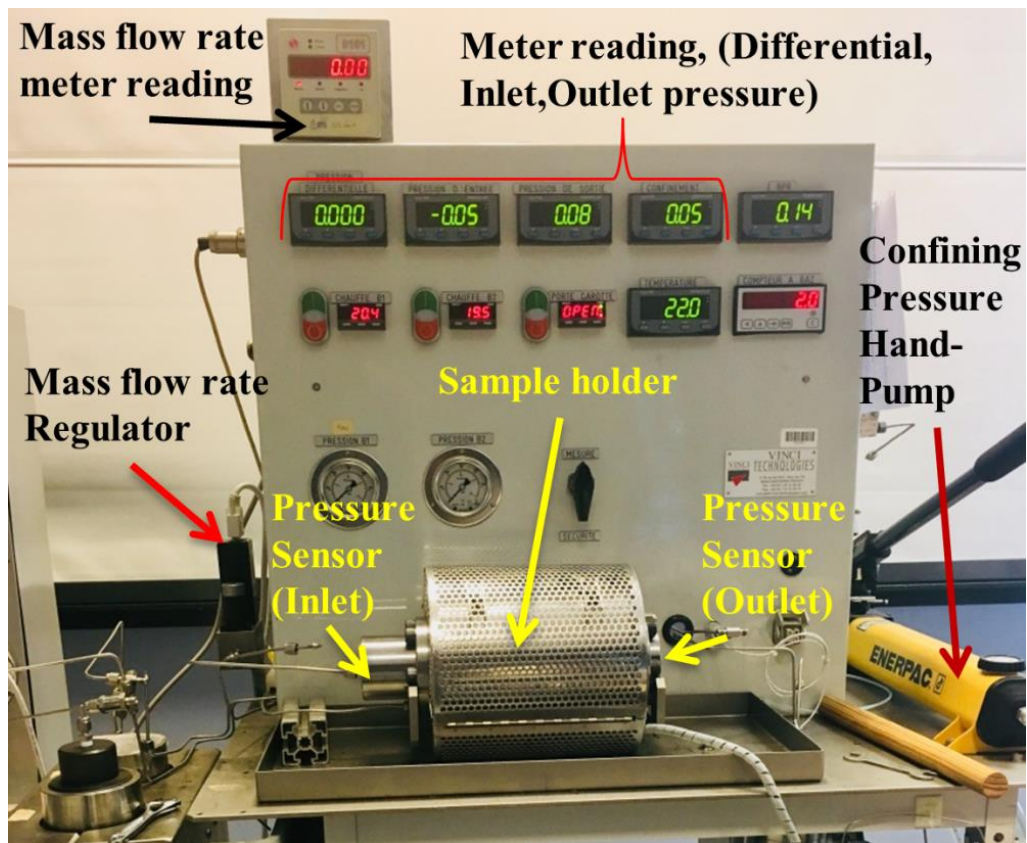


740

741 **Figure 3:** LOI test with (a) 3DP specimens, (b) immediately after taking out of the oven at
 742 900 °C

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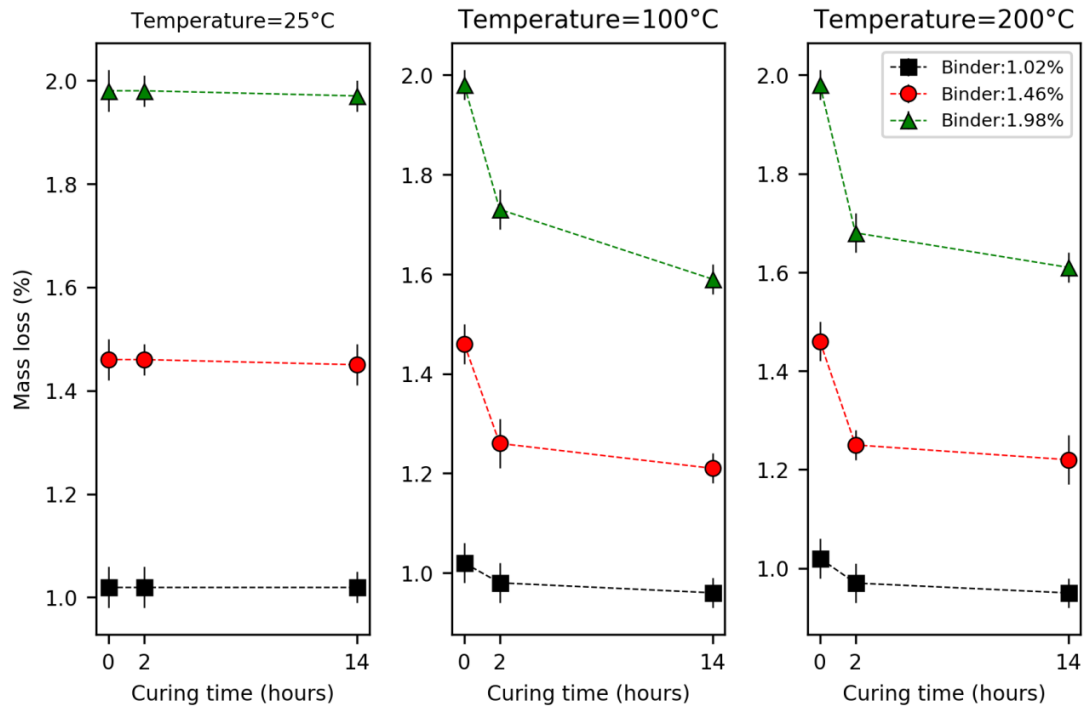
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Figure 4. Perm-meter setup

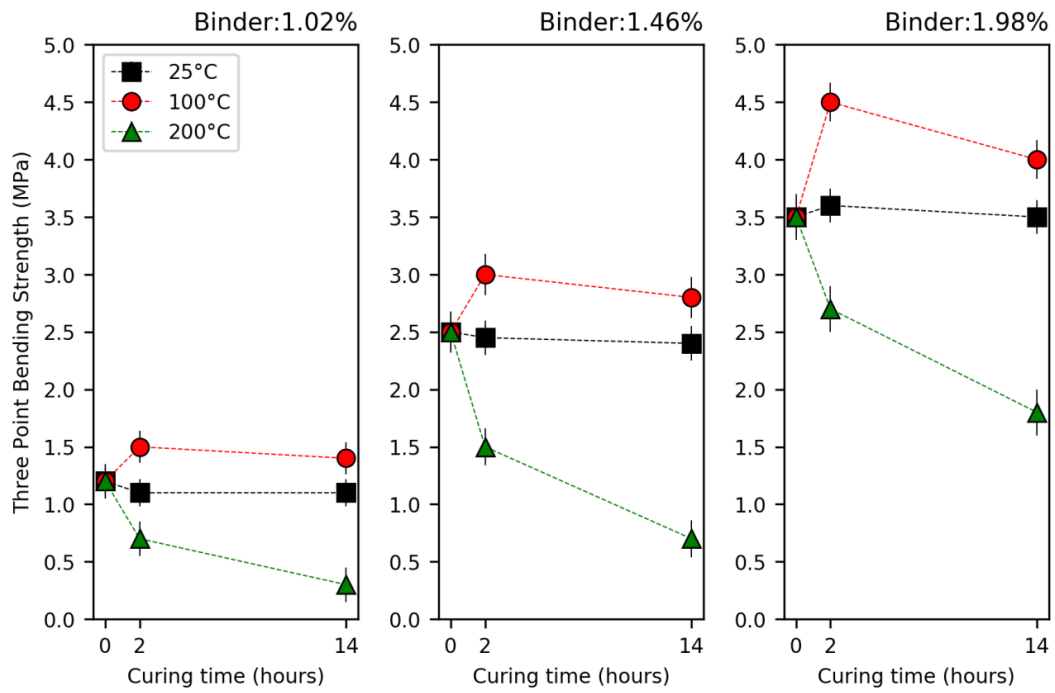


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Figure 5. Mass loss as a function of curing time for three curing temperatures

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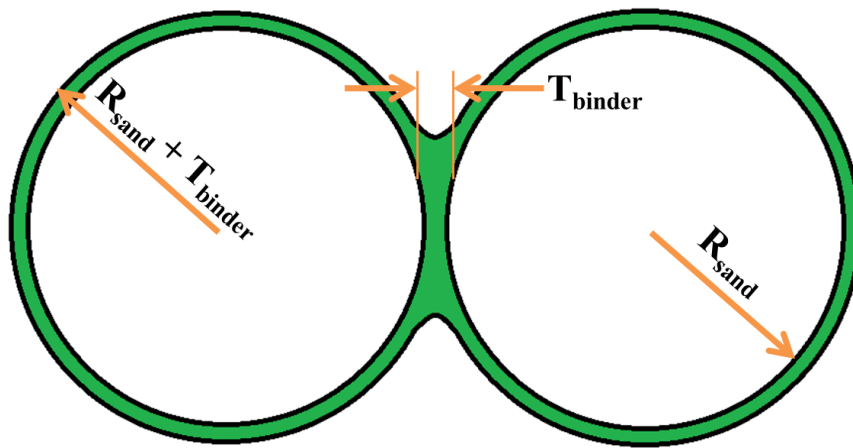


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Figure 6. Effect of curing parameters on 3PB strength

752

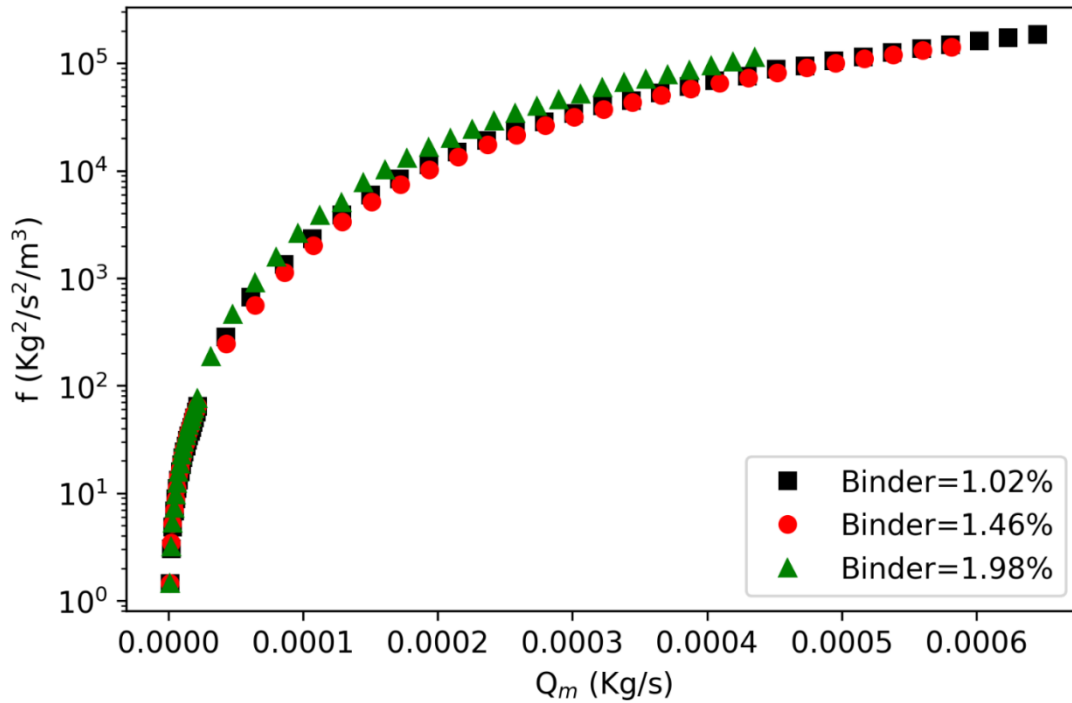


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Figure 7. Resin bonding bridge of adjacent sand particles

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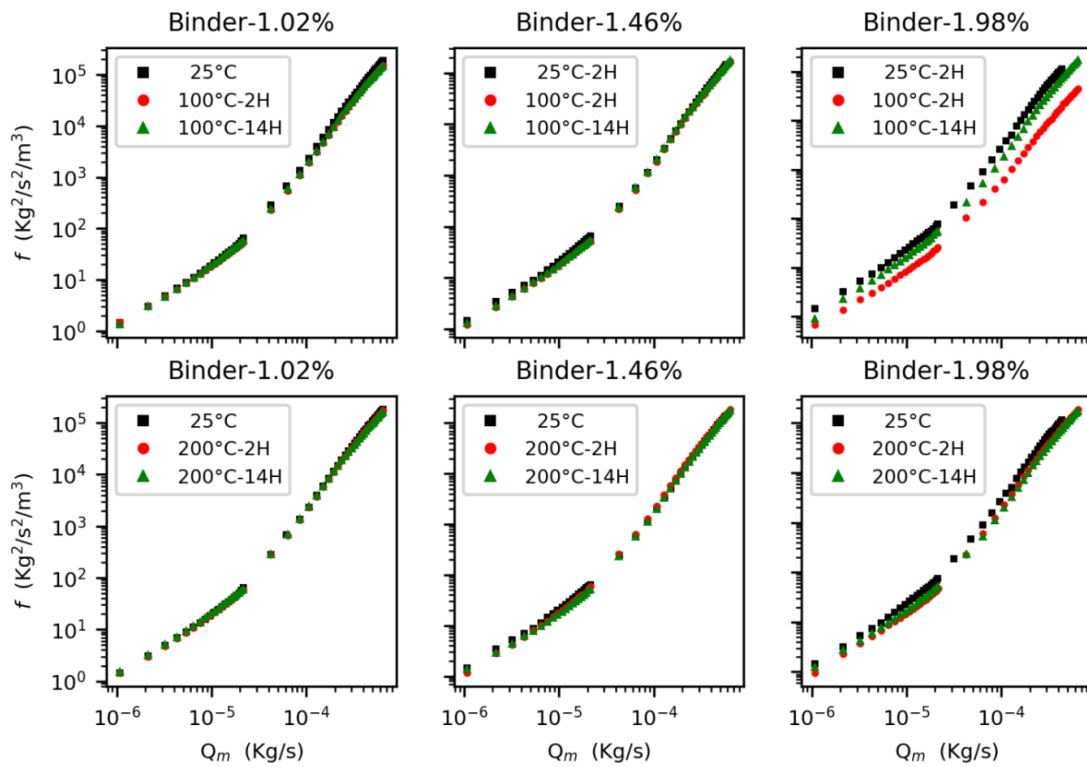


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Figure 8. Effect of binder content on f vs. Q_m rate for uncured samples at 25°C.

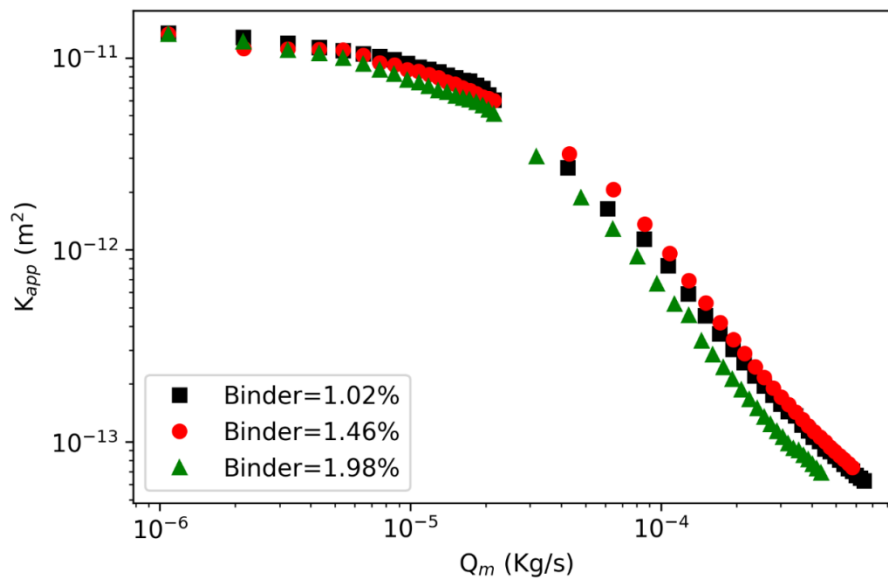


759

760 **Figure 9.** Effect of curing time on the relationship between f and Q_m at different temperatures

761 and binder contents

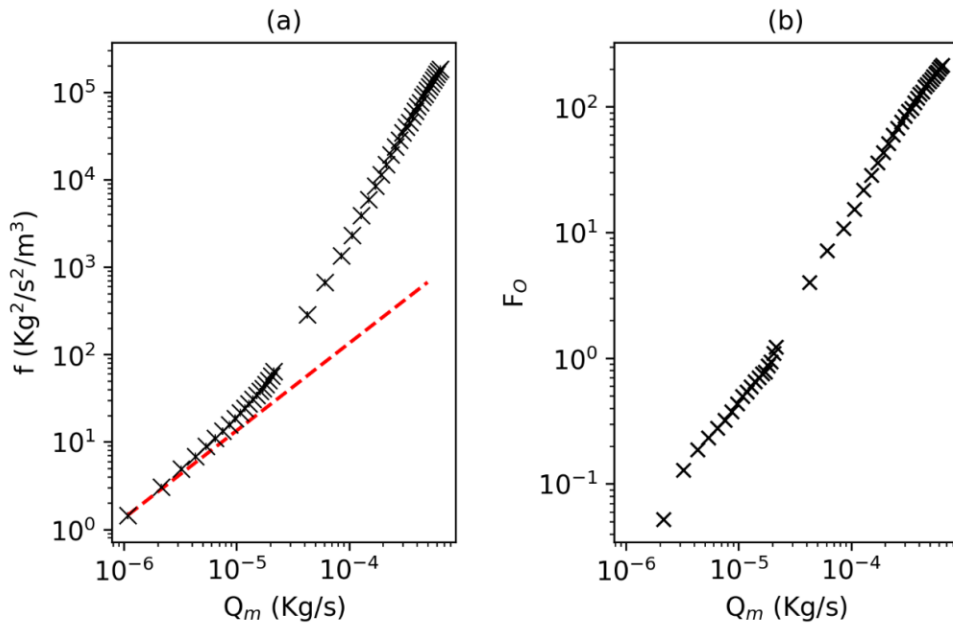
762



763

764 **Figure 10.** Relationship between apparent permeability and mass flow rate for uncured

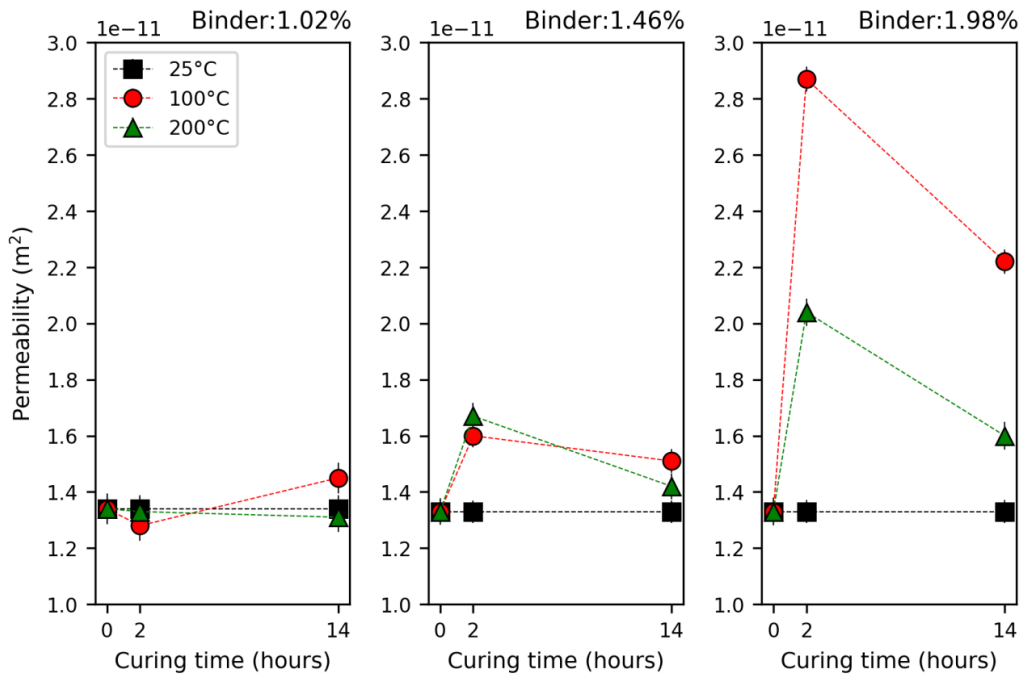
765 samples at 25°C.



766

767 **Figure 11.** Evaluation of the inertial effects for uncured samples at 25°C and a binder content
 768 of 1.02%: (a) Darcy's law fit. Black symbols represent experimental measurements. The red
 769 dashed line represents Darcy's law fit; (b) Forchheimer number at different flow rates.

770



771

772 **Figure 12.** Variation of permeability with binder content, curing temperature and time

773

Table 1. Printing process parameters used with ExOne S-Print furan machine

Average sand grain diameter	140 μm
American Foundry Society (AFS) number	97
Recoating speed	0.182 m/s (14%)
X Resolution	80 μm , 120 μm and 140 μm
Y Resolution	101.6 μm
Z-resolution/Layer thickness	280 μm
Print head voltage	78 V
Activator content(sulfonic acid)	0.18% of the weight of sand
Infrared heating temperature	32°C

774

775

776

777

Table 2. Experimental parameters

Parameters (Unit)	Category 1	Category 2	Category 3
Binder (wt%)	1.02 \pm 0.03	1.46 \pm 0.02	1.98 \pm 0.02
Curing time (hours)	2 and 14	2 and 14	2 and 14
Curing temperature (°C)	25, 100 and 200	25, 100 and 200	25, 100 and 200

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