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Using statistical techniques to model the flexural strength of dried triaxial ceramic bodies

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Abstract

Due to the simplicity of experimental determination and sensitivity to raw materials and/or processing changes, bending strength is frequently used as a quality control parameter in the development and manufacture stages of floor and wall ceramic tiles. This configures the ideal scenario to apply the techniques of experiments design, often used in a lot of other areas, to model the dry bending strength of such ceramics bodies. In the present study, three different raw materials, namely a clay mineral, sodium feldspar and quartz, were selected and eight formulations thereof (triaxial compositions) were used to obtain the limiting conditions of the experiments design. Those formulations were then processed under conditions similar to those used in the ceramics industry: powder preparation (wet grinding, drying, granulation and humidification), green body preparation (pressing and drying) and characterization. The use of this methodology enabled the calculation of a regression model relating the dry bending strength with composition. After statistical analysis and a verification experiment, the significance and validity of the special-cubic model obtained was confirmed.

Keywords: Mechanical strength; Mixture experiments; Regression models; Tiles; Triaxial ceramics; Variance analysis

1. Introduction

In the industrial processing of ceramic bodies such as floor and wall tiles, handling of dried pieces requires a significant mechanical strength, which is often experimentally determined as resistance to rupture in bending. Given the simplicity of its laboratory determination, the bending modulus of rupture is also used as quality and process control parameter. This dry mechanical strength is mainly dependent on the ceramic composition, moisture content and compaction pressure.[1,2]

When the property of interest is basically determined by the combination (or mixture) of raw materials, an optimisation methodology specific to the design of mixture experiments can be successfully used.[3,4] Such procedure is common practice in the chemical industry [5–8] and is becoming popular in the field of glasses and ceramics.[9–12] It has proven, in all cases reported, to lead to greater efficiency and confidence in the results obtained, and to be less demanding in time and both material and human resources.

The design of mixture experiments configures a special case in response surface methodologies using mathematical and statistical techniques, with important applications not only in new products design and development, but also in the improvement of the design of existing products. The basic assumption is that there is a given mixture property which depends solely on the fractions (x_i, summing up to unity) of specific components, or ingredients, of the mixture, and not on the amount of the mixture; thus, the changes in (or the response of) the property is entirely determined by the proportions of those components. To this aim, it is necessary first to select the appropriate mixtures from which the response surface might be calculated; having the response surface, a prediction of the property value can be obtained for any mixture, from the changes in the proportions of its components.

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In a system with q independent variables (or components), there will be $(q-1)$ independent composition variables x_i, and the geometric description of the factor space containing the q components consists of all points on or inside the boundaries (vertices, edges, faces, etc.) of a regular $(q-1)$-dimensional simplex. The response function f can be expressed in its canonical form as a low degree polynomial (typically, first, second or third degree):[3,4]

$$\text{Linear } f=\sum_{i=1}^{q}\beta_i x_i \quad (1)$$

$$\text{Second degree} f=\sum_{i=1}^{q}\beta_i x_i+\sum\sum_{i<j}^{q}\beta_{ij}x_i x_j \quad (2)$$

$$\textit{Special cubic } f=\sum_{i=1}^{q}\beta_i x_i+\sum\sum_{i<j}^{q}\beta_{ij}x_i x_j+\sum_{i<}\sum_{j<}\sum_{k}^{q}\beta_{ijk}x_i x_j x_k \quad (3)$$

This polynomial equation has to be evaluated over a number N of points so that it can represent the response surface over the entire region and it is only natural that a regular array of uniformly spaced points (i.e. a lattice) is used. This lattice is referred to as a $\{q, m\}$ simplex lattice, m being the spacing parameter in the lattice. Then, a laboratory study consisting of N experiments ($N > q$) has to be carried out and the values of the property on those selected N lattice points evaluated. The observed or measured value, y_u, includes the theoretical response value, f, and the experimental error, ε_u, and is given by:

$$\mathrm{y_u}=\mathrm{f}+\varepsilon_\mathrm{u}, \quad 1\leqslant u\leqslant \mathrm{N} \quad (4)$$

A regression equation, such as Eqs. (1) – (3), is then fitted to those experimental values and the model is considered valid only when the experimental errors ε_u are uncorrelated and randomly distributed with a zero mean value and a common variance.

When some or all the proportions x_i are restricted by either a lower bound and/or an upper bound (i.e. the proportion is not allowed to vary from 0 to 1.0 and only a sub-region of the original simplex is of interest), which is frequently the case, the concept of pseudo-component [3,4] can be used to define another simplex of new components present in the proportions x_i' and to which the $\{q, m\}$ simplex lattice is applied. The proportions x_i' are first calculated from the original x_i (by $x_i'=(x_i-L_i)/(1-L)$, where L_i is the lower bound for the ith component and $L<1$ is the sum of all the lower bounds) and, once the regression equation is obtained, they are reverted back to the original components, so that the mixture can be prepared and the property experimentally determined.

In the particular case of ceramic mixtures with three components or ingredients (triaxial mixtures), such as clay, feldspar and quartz,[13] an equilateral triangle can be used ($q=3$) to represent the composition of any such ceramic mixture; a property axis can then be used, perpendicular to the triangle plane, to represent the response function (property prism).

This work describes the use of the design of mixture experiments methodology to mathematically model the dry bending modulus of rupture (MoR) of triaxial ceramic compositions, as a function of the proportions of the clay mineral, feldspar and quartz present, under constant processing conditions (wet processing, moisture content, compaction pressure). The resulting statistical analysis involves fitting of mathematical equations to the experimental results (i.e. measured modulus of rupture), to get the entire response surface, and the validation of the model through the analysis of the variance and residue behaviour.

2. Experimental procedure

The raw materials used were a clay mineral (containing 45.6 wt.% kaolinite, 10.9 wt.% muscovite, 41.6 wt.% quartz and 1.9 wt.% other minor constituents), sodium feldspar (99.5 wt.% albite) and quartz sand (99.5 wt.% α-quartz), all supplied by *Colorminas* (Criciúma-SC, Brazil).

A modified {3,2} simplex-lattice was used to define the mixtures of these raw materials that should be investigated. The selected mixtures were wet processed, following the conventional wall and floor tile industrial procedure: wet grinding, drying, moisturizing (6.5 ± 0.3 wt.%, dry basis), granulation and uniaxial pressing (*Servitech* CT320, 30 ton hydraulic press). For each mixture, seven flat specimens ($126\times56\times8$ mm) were produced, using 90 g of material for each specimen and a compaction pressure of 30 MPa. After compaction, the test specimens were oven dried at 110 ± 5 °C, until constant weight, and cooled to ambient temperature before mechanical testing.

The mechanical strength of dried specimens was determined in three-point bending tests, using a digital EMIC test machine with 10 kN capacity, with a 2 mm/min cross-head speed until rupture (in accordance with the Brazilian standard ABNT 13818).[14] For each mixture, the test result was taken as the average of the MoR of the seven specimens, affected by the corresponding standard deviation.

To these values, the regression Eqs. (1) – (3) were fit to obtain the best response surface relating the dry bending modulus of rupture with the proportions of the clay mineral, feldspar and quartz present in the mixtures (the calculations were carried out with *STATISTICA*—StatSoft Inc., 2000).

3. Results and discussion

3.1. The simplex-lattice mixture compositions

Based on their distinctive roles during ceramic green body processing, the independent components considered, to define the composition equilateral triangle, were clay, feldspar and quartz. Those roles were also used to establish the lower bound limits of 20 wt.% for the clay, 10 wt.% for the feldspar and 30 wt.% for quartz. Bearing this in mind, the quartz sand and the sodium feldspar were considered to be pure, whereas the clay mineral was divided into its alumino-silicate fraction (kaolinite + mica) and quartz fraction (i.e. a point on the clay–quartz side of the composition triangle). All mixtures of these three raw materials must lie within the triangle they define. Hence, only a part of the composition triangle will be used (Fig. 1).

New pseudo-components were defined, based on the lower bound limits imposed on the independent components,[3,4] to create a restricted composition triangle on which a {3,2} simplex lattice (six points) was set. To these original six points, a central point was first added (centroid simplex), followed by three more (augmented {3,2} simplex lattice), as shown in Fig. 1. The compositions of the resulting 10 mixtures (M_i, $i = 1, 2, \ldots, 10$), in terms of the independent components, are listed in Table 1. Fig. 1 also shows the intersection area containing all compositions that fulfil those restrictions.

Fig. 1 clearly shows that mixture M_1 (simplex left apex) lies outside the restricted composition area (the clay mineral already contains far too much quartz). Mixture M_3 (simplex top apex) also had to be eliminated, due to processing difficulties. Thus, only the remaining eight mixtures were considered and experimentally investigated.

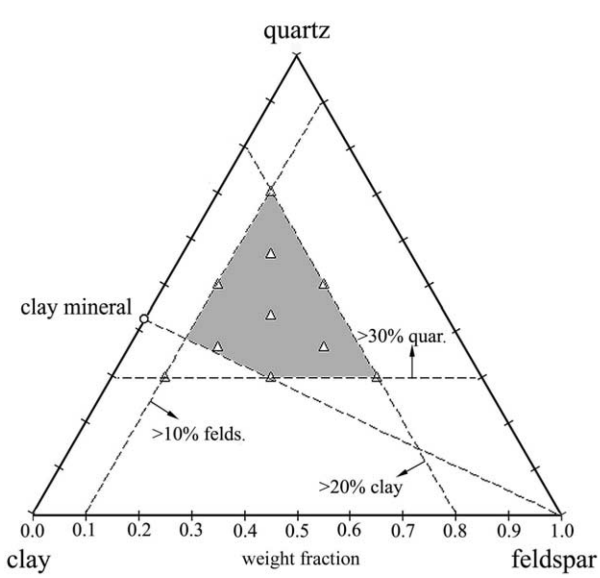

Fig. 1. The ternary system clay–quartz–feldspar, showing: the raw materials triangle, the restricted pseudo-components triangle and simplex points, and the intersection area containing all compositions that fulfil those restrictions.

3.2. Variance analysis and calculation of the MoR model

Table 2 shows the MoR results obtained for the selected eight mixtures.

Having a measured value for the response property at specific coordinates, a regression equation can be sought. Three regression types were evaluated, viz. Eqs. (1) – (3), subjected to a significance level of 5%. Table 3 gives the various statistical properties of the regressions, using the nomenclature commonly found in the relevant texts.[3,4]

Using the P-value approach to hypothesis testing (i.e. P-value $\leqslant$ significance level), Table 3 shows that the linear model ($P = 0.3108$) and the second degree model ($P = 0.6095$) do not reach the stipulated significance value. Only the special cubic model ($P = 0.0378$) is statistically significant at that level. For this model, the adjusted coefficient of multiple determination, R^2_A, is 0.9928, meaning that the model presents a very small variability. The final equation, relating the MoR with the proportions of the independent components, is:

$$\begin{aligned} \text{MoR} = & -32.61x_1 - 29.18x_2 - 12.26x_3 \\ & + 163.03x_1x_2 + 101.97x_1x_3 + 95.98x_2x_3 \\ & - 355.53x_1x_2x_3 \end{aligned} \quad (5)$$

In Eq. (5), x_1 is the clay fraction, x_2 is the feldspar fraction and x_3 is the quartz fraction. Eq. (5) shows that each component alone or the three together have an antagonistic effect on MoR (negative coefficients in the equation), whereas their binary mixtures act synergistically on MoR (positive coefficients in the equation).

Eq. (5) can be further rearranged to relate the MoR with the weight fractions of the original raw materials (X_1 = clay mineral, X_2 = feldspar and X_3 = quartz). Eq. (6) is the final result:

$$\begin{aligned} MoR = & -56.61X_1 - 29.18X_2 + 11.74X_3 + 283.02X_1X_2 \\ & + 177.02X_1X_3 - 24.01X_2X_3 - 617.20X_1X_2X_3 \\ & + 261.67X_2X_3^2 - 75.05X_3^2 \end{aligned} \quad (6)$$

3.3. Testing the adequacy of the model

Before the model can be considered adequate, it is necessary to analyse the residuals. Fig. 2(a) is a plot of the MoR raw residuals (i.e. difference between the experimentally determined value and the calculated estimate) as a function of the predicted MoR values, and shows that the errors can be considered randomly distributed around a zero mean value, hence are uncorrelated, which suggests a common constant variance for all the MoR values.

Table 1
Compositions of the triaxial mixtures created by the augmented {3,2} simplex

Raw material (wt.%)	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8	M_9	M_{10}
Clay	60.0	20.0	20.0	40.0	40.0	20.0	46.7	26.7	26.7	33.3
Feldspar	10.0	50.0	10.0	30.0	10.0	30.0	16.7	16.7	36.7	23.3
Quartz	30.0	30.0	70.0	30.0	50.0	50.0	36.6	56.6	36.6	43.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 2
Average values of MoR and corresponding standard deviation

Mixture	M_2	M_4	M_5	M_6	M_7	M_8	M_9	M_{10}
MoR (MPa)	1.37±0.2	2.17±0.2	2.51±0.3	2.31±0.4	1.27±0.3	2.25±0.3	2.15±0.2	2.16±0.3

Table 3
Analysis of variance for significance of regression models[a]

Model	SSR	df	MSR	SSE	df	MSE	*F*-test	*P*-value	R^2	R^2_A
Linear	0.5306	2	0.2653	0.8904	5	0.1781	1.4897	0.3108	0.3734	0.1227
2nd degree	0.4757	3	0.1585	0.4147	2	0.2074	0.7646	0.6095	0.7081	0.0000
Special cubic	0.4133	1	0.4133	0.0015	1	0.0015	282.1750	0.0378	0.9990	0.9928
Adj. total	1.4210	7	0.2030							

[a] SSR: regression sum of squares; df: degrees of freedom; MSR: regression mean squares; SSE: error sum of squares; MSE: error mean squares; R^2: coefficient of multiple determination; R^2_A: adjusted R^2.

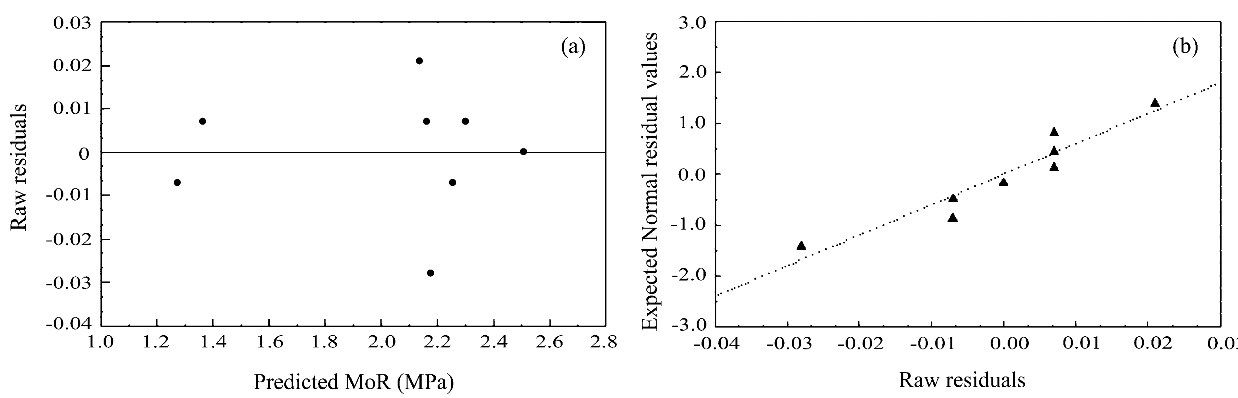

Fig. 2. (a) Raw residuals vs. predicted MoR values; (b) normal probability curve for the MoR residuals.

Fig. 2(b) shows that a straight line can be considered to relate the residuals with the expected normal values, meaning that the distribution is normal.[3,4] Thus, a good estimate of the property under consideration (MoR) can be obtained, using Eq. (5) and the fractions of the independent components.

Fig. 3 shows the projection of the calculated response surface (in pseudo-components) onto the composition triangle, as constant MoR contours (contour plot). It can be seen that the highest dry bending strength (MoR $\geqslant$2.3 MPa) is reached within a reasonably forgiving composition area, for clay contents of 30–36 wt.%, feldspar contents of 10–17 wt.%, and quartz contents of 50–60 wt.%. It is interesting to note that high dry MoR values correspond to high contents of non-plastic materials. This can be explained by a better particle packing effect, since both quartz and feldspar contain larger particles and the clay mineral will have a dominant role as a binder.

3.4. Response trace plots

The response trace is a plot of the estimated property values as the composition moves away from a reference point, along lines that go through each apex in turn (i.e. it is a vertical section through the property prism in which the fraction of one of the components is changed while the proportion between the other two is kept constant). In this case, the reference composition used was the simplex centroid, which corresponds to 33.33% clay, 23.33% feldspar and 43.34% quartz (by weight).

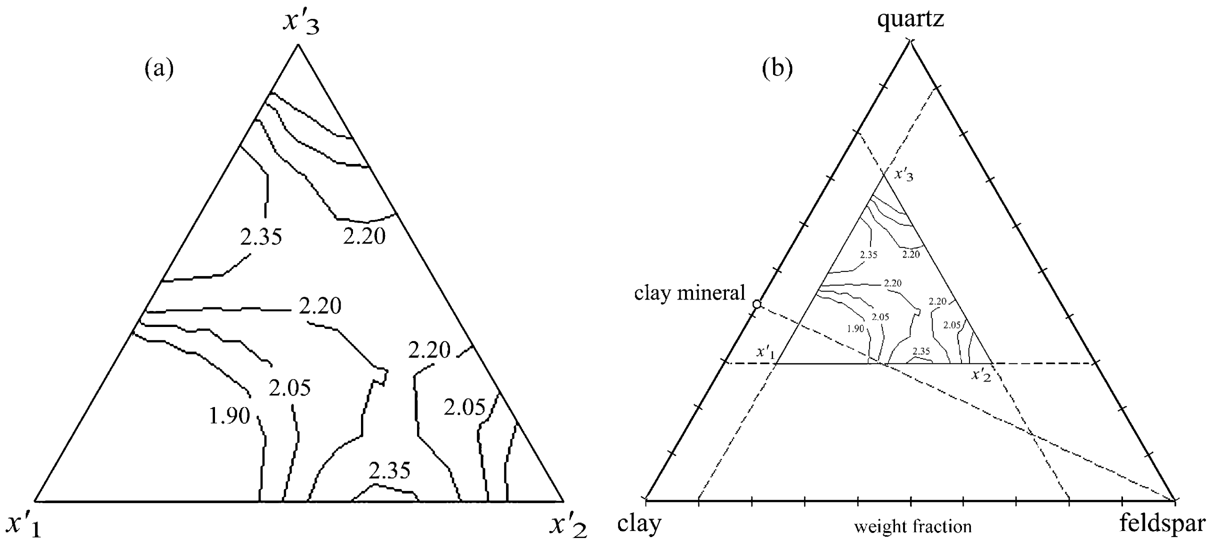

Fig. 3. (a) Constant dry MoR contour plot vs. composition, expressed in terms of pseudo-components; (b) location in the composition triangle.

Thus, the response trace for each pseudo-component shows the MoR values as the weight fraction of that component varies from zero to unity while the fractions of the other pseudo-components, present in equal amounts, vary from 0.5 to zero.

Fig. 4 shows the MoR trace plots for each pseudo-component (the diagram on the right side shows the lines along which the composition changes). There are three auxiliary axes in Fig. 4, to help in the conversion of weight fractions from pseudo-components into components. For example, the pseudo-quartz fraction that maximizes the MoR is 0.58 (read directly from the relevant trace plot), which means that the fractions of the other two pseudo-components are 0.21. These values are used to obtain the corresponding components fractions on the relevant component axis: quartz 0.532 (starting from 0.58), clay 0.284 (starting from 0.21) and feldspar 0.184 (starting from 0.21).

Fig. 4 shows that the dry bending strength is particularly sensitive to the changes in the clay mineral content. A smooth decline of MoR can be observed while the clay content increases from 20 wt.% (zero pseudo-clay fraction) to circa 34 wt.% (0.35 pseudo-clay fraction), followed by a sharp drop from then on. Thus, for these raw materials, processed as they were, compositions containing more than 34 wt.% clay (corresponding to 61 wt.% original clay mineral) should be avoided. This

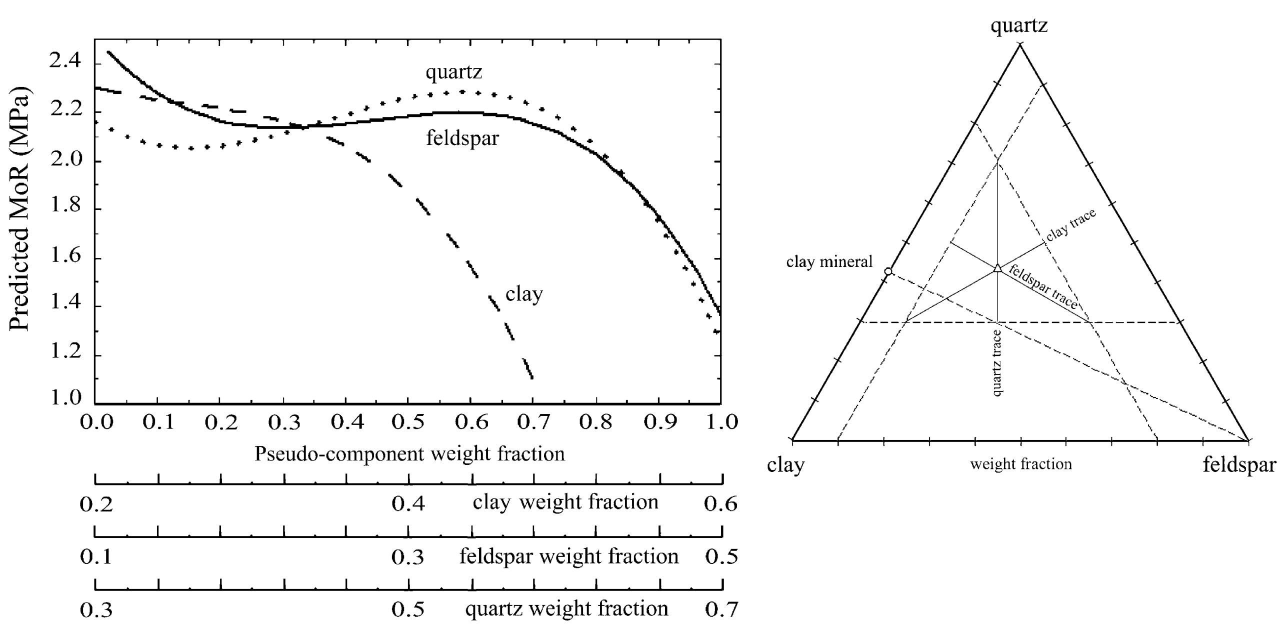

Fig. 4. Predicted dry bending strength trace plots (the composition moves away from the simplex centroid along lines that go through the apex, as shown in the diagram on the right).

suggests that the processing routine used is no longer adequate for this excessive content of plastic material and the MoR is being sacrificed due to defects introduced, most likely, during a non-optimised drying stage.

3.5. Validation of the experiments

To counter-check the calculated statistical model, which gives an estimate for the dry MoR as a function of the clay mineral, feldspar and quartz contents, mixture M_8 was used to evaluate the relative error involved. The calculated MoR value, through Eq. (5), is 2.14 MPa. The measured experimental value (Table 2) is 2.16 MPa. Thus, the estimate error introduced by the model is 0.93% relative to the experimental value, which validates the special cubic model obtained.

4. Conclusions

The use of the design of mixture experiments methodology to mathematically model the dry bending modulus of rupture (MoR) of triaxial ceramic compositions, under constant processing conditions (wet processing, moisture content, compaction pressure), was found to be coherent. A special cubic equation was found to significantly relate the dry MoR with the proportions, in the mixture, of the particular raw materials considered (viz. clay mineral, feldspar and quartz). This was investigated through statistical analysis, adequacy testing and experimental validation of the model.

The constant contour and response trace plots obtained show that, with the particular raw materials used, high dry MoR values correspond to high contents of non-plastic materials and that the dry bending strength is particularly sensitive to the changes in the clay mineral content. This can be explained by a better particle packing effect for those compositions, since both quartz and feldspar contain larger particles and the clay mineral will have a dominant role as a binder.

Still, even within the high MoR region, the values do not reach the level usually recommended by the floor and wall tile industries (dry MoR $\geqslant 3.0$ MPa). These results throw a strong light onto the role of the hidden variables (i.e. those that were kept constant throughout the work). Particle size distribution and particle packing on one hand, and processing conditions on the other, seem to be especially relevant and their effect will be investigated in future works.

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