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Methodology to control the influence of processing factors during composite stone fabrication

Metodologia para controlar a influência de fatores de processo na fabricação de pedra composta

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Abstract

Composite stone is made of crushed materials bound by a polymer resin. A design of experimental techniques was used to evaluate the influence of factors (resin type, use of adhesion promoter, compaction pressure, vibration duration, use of a vacuum, and cure program) on the manufacturing of composite stone. The response variable was flexural strength. A 2_{IV}^{6-2} fractional factorial design with five replications was initially used, which showed that resin type, use of adhesion promoter, and a cure program were factors of significant influence, as well as the interaction between them and the interaction between the resin type and the use of adhesion promoter. The data was re-arranged into a full 2^3 factorial design with ten replications to calculate the influence of these factors. The lack of influence of the other factors suggests that lower pressures should be used to improve the process by employing the surface response methodology.

Keywords: composite stone, manufacturing, design of experiments, influence of factors

Resumo

A pedra composta é feita de uma mistura de materiais granulados ligados por uma resina polimérica. Técnicas de planejamento fatorial foram utilizadas para determinação da influência de fatores na fabricação da pedra composta. Seis fatores foram analisados: tipo de resina, uso de promotor de adesão, pressão de compactação, duração da vibração, utilização de vácuo e programa de cura. A variável de resposta foi a resistência à flexão. Foi, inicialmente, empregado um planejamento fatorial fracionário 2_{IV}^{6-2} com cinco réplicas, cujo resultado indicou a influência significativa dos fatores tipo de resina, uso de promotor de adesão e programa de cura, assim como da interação entre eles e da interação entre tipo de resina e promotor de adesão. Os dados foram rearranjados num planejamento fatorial 2^3 completo com dez réplicas para o cálculo da influência desses efeitos. A falta de influência dos outros fatores sugere que pressões de compactação mais baixas devem ser utilizadas para a otimização do processo, com o uso da metodologia de superfície de resposta.

Palavras-chave: *pedra composta, fabricação, planejamento fatorial, influência de fatores.*

1. Introduction

Composite stone, also known as engineered stone or polymer concrete, is made with crushed natural materials, which are responsible for 90 to 96% of its mass. It is obtained from particulates of silicic or calcareous materials of different granulometries (less than 10 mm). Fractions of these materials are blended with resin and additives to form a paste, which is molded and vibrocompacted under vacuum, followed by resin hardening (Tassone and Toncelli, 1995). Slabs of different dimensions can be obtained by this process.

This product is already largely commercialized in the USA and Europe. Its appearance is similar to natural stone, yet it is controlled and more uniform. Its hardness is comparative and it has no pores. The exploitation of natural reserves of raw materials is diminished because crushed materials are used in its manufacture. These characteristics are seen as advantageous by consumers and environmental agencies. Therefore, a prominent role is expected for composite stone in civil construction for use in wall coatings and paving. In Brazil, there is an interest in the production of composite stone using mining residues.

During the paste preparation, resin is used which should form a thin layer on the surface of each particle. The additives act as adhesion promoters or initiators and accelerators of polymerization. The resin acts as an organic bonding agent between the particles. An unsaturated polyesther resin is normally used. It is usually dissolved in a styrene monomer to reduce viscosity and facilitate the formation of cross-links, which are responsible for the hardening (Souza, 2010).

The mineral silicic particles contain many silanol groups (SiOH) on their surfaces. They are highly polar and hardly compatible with nonpolar resins. The weak interaction impairs the mechanical properties of the composite stone. Additionally, silanol groups tend to form hydrogen bonds with each other, which results in a relatively strong interaction between these particles. Since the resin concentration is low, the particles tend to form agglomerates, resulting in hardly any dispersion of mineral silicic particles in the resin. Silane adhesion promoters are used as additives to decrease interaction between particles and enhance their interaction with the resin, acting as a bridge between them. The organofunctional silanes have distinct endings on each part of their molecular chain. One of the endings is a Si-OR group (silanol). This ending interacts with the surface of silicic particles by means of hydroxyl groups. The other ending is a reactive organic functional group (e. g., epoxy or amine groups). This group is compatible with the resin, if it has adequate functionality and is able to participate in the polymerization reaction (Pizzitola, 2011). In summary, these adhesion promoters act as a bridge between the silicic particles and the resin, greatly enhancing the interaction between them.

Dimethylaniline (DMA) is used to stimulate initiation of the polymerization of unsaturated polyester resins. It is a reducing agent, decomposing the organic peroxides and generating free radicals which initiate the polymerization. Another additive used is the cobalt accelerator. It is a 6% solution of cobalt salts in aliphatic solvent, which acts as a strong reductant. By means of a redox reaction, it provides great amount of energy for the catalysis of the polymerization reaction of unsaturated polyester resins. It is used in curing processes where the reactivity is controlled.

After mixing, the paste is molded for vibrocompaction under vacuum. The goal of vibrocompaction is to achieve a high packing of the mineral particles, where the smaller particles fill the voids between larger ones. The combination of vibration and the correct use of particle size fractions are very important for obtaining high-density matrices. The role of the compaction pressure is to improve the settlement of particles and increase the adhesion between them. Therefore, high compaction pressures are unnecessary (Biazzo, 2009). The vacuum is necessary because air bubbles may be trapped during vibrocompaction and later become pores after the cure of the resin. Moreover, the existing drag forces of the ambient air pressure have significant effects on the porosity and uniformity of the pressed mold (Xiang, 2009).

Finally, the curing of the resin is carried out to complete polymerization and promotes its adhesion to mineral particles, so as to achieve a monolithic piece of high mechanical strength and hardness. The piece may then be subjected to grinding and polishing, as is usually done for marble and granite. Because of industrial protection, there are few published papers in literature about this product.

There are several factors in the manufacturing process of composite stone that may influence its characteristics. The objective of this paper is to present a methodology for studying the influence of six factors, as well as the interactions between them, so as to introduce changes aimed at optimizing the process, both technically and economically. The factors studied were resin type, use of adhesion promoter, compaction pressure, duration of vibration, use of vacuum, and cure program.

2. Materials and methods

The following materials were used: granular minerals (quartz supplied by Ecoart in three grain sizes and residue from the iron ore concentration process supplied by Samarco Mineração), unsaturated orthophthalic polyester resins (a commercial resin from Fibercenter and another special one whose manufacturer claims it avoids the use of adhesion promoter, taken as a blind experiment), organofunctional silane (Dynasylan, 3-aminopropyltriethoxysilane, Evonik), dimethylaniline (Fibercenter), and 6% cobalt accelerator (Fibercenter).

The fractions of quartz granules and residue were mixed based on Ecoart's recipe, as well as the quantities of resin and adhesion promoter used. The three grain sizes and amount used were 8.91µm (7.13 g), 283.62 µm (6.45 g) and 638.88 µm (11.4 g). They were mixed with 2.25 g of resin and 0.225 g of adhesion promoter. These ingredients were mixed by hand with a spatula in a glass container until a paste was obtained. Then, the DMA (0.045 g) and cobalt accelerator (1 drop) were added, with an additional mixing step.

The vibrocompaction under vacuum was performed in a 70 mm x 25 mm x 8 mm mold, where the paste was placed. The vacuum was created using a pump which draws air from the mold through an orifice in the wall of the mold after the start of pressing. A German Pfeifer Vacuum DUO 2.5 pump was used. The compaction was performed with the aid of a manual hydraulic press with a 15-ton capacity. A Netter Vibration, NTP 25 B+C pneumatic vibrator was installed under the platform of the mold. This vibrator produces the vertical movements of the mold, operating at 200 kPa with 2600 vibrations per minute and a force of 190 N. After vibrocompaction, the mold was removed from the press and placed in an electric oven (Icamo, Model 3) and air-cooled. After cooling, the composite stone samples were removed from the mold. No unmolding agent was used.

Flexural strength was used as the response variable. The three-point test was used, performed in an American Instron 5882 universal test machine with a load cell of 5 kN and a cross-head speed of 70 mm/min. Flexural strength measurements were taken from five samples for each run.

A 2_{IV}^{6-2} fractional factorial design was initially conducted, which required 16 experiments. In this experimental design, the main factors are confounded with interactions between three factors that probably have little influence, and interactions between the two factors are confounded with each other. Table 1 shows the six factors studied. Table 2 shows the design matrix and the aliases for the main factors of the 2_{IV}^{6-2} fractional factorial design. Both, tests for obtaining the samples and the flexural tests, were performed in random order with five replicates.

Table 1
Composite stone manufacturing factors studied in this paper

Factor	Level	
	low (-)	high (+)
A. Resin	commercial	special
B. Adhesion promoter	without	with
C. Compaction pressure	16 MPa	33 MPa
D. Duration of vibrocompaction	2 minutes	4 minutes
E. Vacuum	without	with
F. Cure program	80 °C/30 min + 120 °C/120 min	90 °C/30 min + 110 °C/120 min

Table 2
Design matrix for the 2_{IV}^{6-2} fractional factorial design

Run	A	B	C	D	E = ABC	F = BCD
1	-	-	-	-	-	-
2	+	-	-	-	+	-
3	-	+	-	-	+	+
4	+	+	-	-	-	+
5	-	-	+	-	+	+
6	+	-	+	-	-	+
7	-	+	+	-	-	-
8	+	+	+	-	+	-
9	-	-	-	+	-	+
10	+	-	-	+	+	+
11	-	+	-	+	+	-
12	+	+	-	+	-	-
13	-	-	+	+	+	-
14	+	-	+	+	-	-
15	-	+	+	+	-	+
16	+	+	+	+	+	+
Aliases for the main factors		A = BCE + DEF + ABCDF			B = ACE + CDF + ABDEF	
		C = ABE + BDF + ACDEF			D = AEF + BCF + ABCDE	
		E = ABC + ADF + BCDEF			F = ADE + BCD + ABCEF	

Density was also measured by helium picnometry.

3. Results and discussion

In this experiment a new lab scale assembly was used to obtain the samples of composite stone. Table 3 shows the results obtained for flexural strength. Minitab 16 software was used to calculate the effects, whose results are presented in Table 4. Figure 1 shows the normal plot of the effects. The significant factors are A (resin), B (adhesion promoter), and F (cure program), and the A×B and A×B×F interactions. The factors C (compaction pressure), D (duration of vibrocompaction), and E (vacuum) had no significant effect.

The flexural strength values were much lower than the values usually obtained for composite stone. This suggests problems in the process of obtaining the samples.

Run	Flexural strength in MPa				
1	6.53	7.86	6.42	7.05	6.06
2	2.45	3.53	3.08	2.36	2.82
3	8.92	8.02	6.75	8.93	7.15
4	2.27	2.51	2.52	7.46	2.34
5	7.78	6.80	6.24	2.80	5.39
6	2.62	2.93	2.30	3.57	4.38
7	9.00	8.59	9.82	6.64	8.20
8	4.02	3.57	6.16	5.31	3.17
9	7.29	2.06	7.71	1.25	7.29
10	2.47	2.54	1.85	6.66	2.05
11	9.68	10.93	11.18	7.65	9.47
12	3.54	3.22	5.98	8.54	3.62
13	8.00	10.41	8.52	8.00	6.88
14	3.21	1.88	1.91	2.97	0.73
15	10.94	12.39	10.97	9.02	8.76
16	2.92	2.16	3.44	0.69	3.53

Table 3
Results of flexural strength tests of the composite stone samples

Factor	Effect in MPa	t	p-value
A. Resin	-4.51	-12.50	0.000
B. Adhesion promoter	1.83	5.07	0.000
C. Compaction pressure	0.16	0.45	0.652
D. Duration of vibrocompaction	0.45	1.24	0.219
E. Vacuum	0.05	0.13	0.899
F. Cure program	-0.79	-2.18	0.033
A×B	-0.80	-2.21	0.030
A×C	-0.68	-1.88	0.064
A×D	-0.72	-2.00	0.050
A×E	-0.23	-0.64	0.523
A×F	0.24	0.67	0.503
B×D	0.42	1.16	0.252
B×F	-0.05	-0.13	0.899
A×B×D	-0.31	-0.87	0.390
A×B×F	-1.41	-3.17	0.002

Standard deviation = 0.36 MPa

Table 4
Results of the effect calculations ($t_0 = t_{64;0.05} = 2.00$)

This result allows us to rearrange the data in Table 2 in a 2^3 full factorial design with 10 replicas (runs 1+13: A-, B-, F-; A+, runs 2+14: B-, F-; runs 7+11: A-, B+, F-; runs 8+12: A+, B+, F-; 5+9: A-, B-, F+; runs 6+10: A+, B-, F+; runs 3+15 : A-, B+, F+ and runs 4+16: A+, B+, F+). Table 5 shows the results of the effects according to the 2^3 full factorial design, which are practically the same as those in Table 4.

Figure 2 shows the cube plot of the significant effects. The resin is the factor with the greatest influence. The flexural strength decreases when using the special resin on average 4.51 MPa compared to the commercial resin. The adhesion promoter has the second greatest influence. Its use increases the flexural strength, on average 1.83 MPa. There was a small, but significant interaction between the resin and the adhesion promoter. The value of this interaction was negative (-0.80 MPa). This shows that the adhesion promoter has a smaller effect on the special resin.

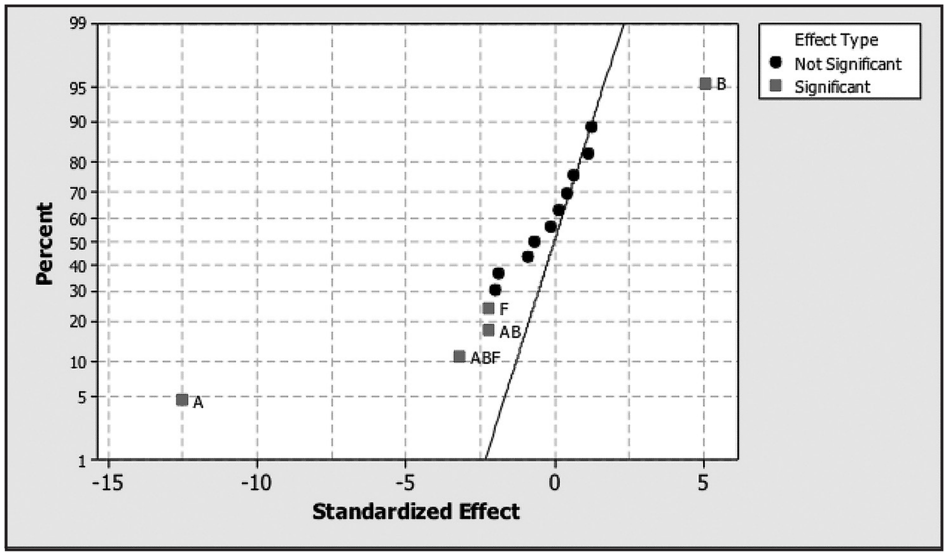

Figure 1
Normal plot of the effects (response is flexural strength, alpha = 0.05).

Table 5
Results of the effect calculations ($t_0 = t_{72;0.05} = 1.99$) for the 2^3 full factorial design
Standard deviation = 0.36 MPa

Factor	Effect in MPa	t	p-value
A. Resin	-4.50	-12.16	0.000
B. Adhesion promoter	1.83	4.95	0.000
F. Cure program	-0.78	-2.11	0.038
A×B	-0.80	-2.16	0.034
A×F	0.24	0.65	0.520
B×F	-0.05	-0.13	0.898
A×B×F	-1.14	-3.07	0.003

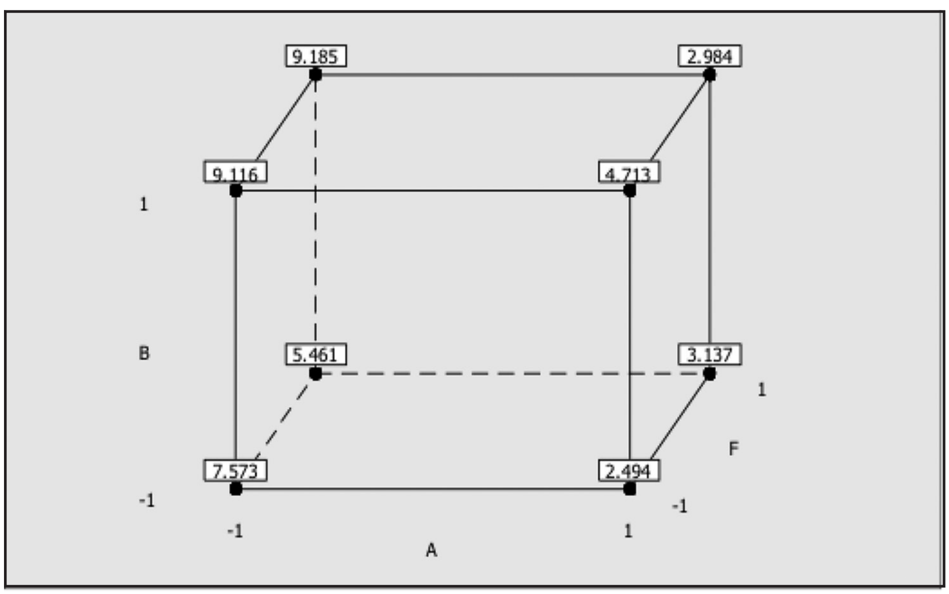

Figure 2
Cube plot for flexural strength

In fact, Figure 2 shows that the adhesion promoter increases the flexural strength in average 2.63 MPa using the commercial resin, while such an increase is only on average 1.04 MPa with the special resin. Although smaller, the effect of the adhesion promoter with the special resin is still significant. The cure program has a small, but significant effect on flexural strength. Its effect is on average -0.78 MPa. The interactions of the cure program with the resin or the adhesion promoter are not significant. However, the interaction between these three factors is significant, with a negative value of -1.14 MPa. That is, a temperature increase from 80 to 90 oC in the cure program decreases the flexural strength. Differential scanning calorimetry (DSC) was used to determine the degradation temperature of the resin in composite stone. The degradation takes place for temperatures higher than 300°C. Therefore, the cure program does not affect the polymeric resin properties.

There was no significant effect from the compaction pressure. This fact may be due to the use of very high pressures, which also prevented the effect of the vibrocompaction duration, which was also not significant. It suggests that lower pressures should be investigated. The fact that the vacuum did not cause a significant effect also merits an analysis of the design of the vacuum mechanism through a hole in the wall of the mold. Another possibility is that the use of very high pressures may have entrapped air bubbles in the samples, preventing the action of the vacuum. Without the vacuum effect, the presence of pores in the samples is expected, caused by the entrapment of air bubbles. In fact, the average density of the samples was 2.53 g/cm^3, slightly below the expected range of 2.54 to 2.56 g/cm^3. This lower density may have contributed to the low flexural strength values.

The analysis presented above considers that the data of Table 5 can be described by a normal distribution. A more rigorous approach should consider the Weibull distribution, shown in Table 6, where σ50 is the average flexural strength, Δσ50 is the standard deviation and R^2 is the correlation coefficient. The highest flexural strengths were achieved in runs (7+11) and (3+15), confirming the results obtained above (use of commercial resin and adhesion promoter).

Runs	Flexural strength, σ_{50}, in MPa	Standard desviation, $\Delta\sigma_{50}$, in MPa	R^2
1 + 13	5.787	0.440	0.769
2 + 14	2.981	0.125	0.549
7 + 11	8.972	0.132	0.955
8 + 12	4.036	0.225	0.788
5 + 9	7.115	0.257	0.897
6 + 10	2.605	0.138	0.917
3 + 15	9.546	0.155	0.942
4 + 16	3.519	0.243	0.788

Table 6
Flexural strength tests of the composite stone samples according to Weibull statistics.

4. Conclusions

A methodology for the simultaneous study of the effects of process factors for obtaining samples of composite stone was presented by using a fractional factorial design. This methodology helps to optimize the process, both technically and economically.

A new lab assembly was used to obtain samples of composite stone. The effects of the following parameters were studied: type of resin, use of adhesion promoter, compaction pressure, duration of vibrocompaction, use of vacuum, and cure programs. Flexural strength was the response variable. Within the range of values of the factors analyzed, it was determined that the resin type exerts the greatest effect on flexural strength. The use of a special resin caused a decrease in flexural strength. The use of the adhesion promoter had the second greatest influence, causing an increase in flexural strength. Although the adhesion promoter is more efficient with the use of commercial resin, its influence with the use of a special resin was still significant. The cure program had a small, but significant influence on the flexural strength value.

The compaction pressure, duration of vibrocompaction, and use of vacuum had no significant influences on flexural strength. This fact suggests that it is necessary to investigate new value ranges for these factors by means of the surface response methodology. The negligible influence of the vacuum shows that the samples must have had residual porosity, which was later confirmed by density measurements. This residual porosity may have contributed to the low flexural strength values of the composite stone samples.

In order to optimize the process, lower compaction pressures should initially be tested. The efficiency of the vacuum system of the experimental assembly should also be reviewed.

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