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Introduction of Glassy Spheres in an Acrylic Matrix: A New Solution for Low-Pressure Sanitaryware Moulds

A. Fortuna*[1], D. M. Fortuna[1], E. Martini[1], V. Tagliaferri[2], G. Rubino[3]

[1]SE.TE.C. Srl, via Enrico Fermi 6/18, 01033 Civita Castellana (VT), Italy
[2]Department of Business Engineering, University of Rome "Tor Vergata", Via del Politecnico 1, 00133 Rome, Italy
[3]Department of Economics and Business, University of Tuscia, Largo dell'Università, 01100 Viterbo, Italy

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Abstract

In this work we have conducted a study to improve the mechanical strength and abrasive wear of the moulds used for traditional casting in the sanitaryware industry. We replaced the beta gypsum commonly employed in low-pressure moulds with a mix of alpha plaster and acrylic resin (Poolkemie Ecoresin). This product greatly improves the mechanical properties of the mould, but does not enable adequate thickness formation owing to the low porosity of the compound. For this reason we introduced increasing amounts of Poraver glassy spheres (10 %, 20 %, 30 %, 40 %) with the goal of ensuring the same thickness formation as in the case of the beta plaster, but with higher values for flexural strength and abrasion resistance. We conducted a series of abrasion tests and obtained good values with all samples containing spheres. In the mechanical flexural test, the best result was obtained by the resin formulation, but we also obtained very good results for 10-% and 20-% samples. On the other hand, in the casting test the best thickness is obtained with the formulation using 20 % spheres. This mix is therefore the best compared to the beta plaster and can definitely be applied in low-pressure casting.

Keywords: Sanitaryware casting, thickness formation, beta plaster moulds, acrylic resin and glassy spheres, flexural strength and abrasion resistance.

I. Introduction

In low-pressure sanitaryware casting, beta plaster moulds are used owing to their high porosity [1–6]; the water contained in the vitreous china bodies is extracted as a result of the capillary action of the mould, allowing the formation of a solid thickness in a relatively short time (about 1 h and 30 min) [7–9]. Vitreous china bodies are prepared by dissolving the raw materials in water and then by casting them in plaster moulds to shape the final pieces. This technology currently uses beta plaster moulds (beta calcium sulphate hemihydrate): this material, after the completion of the reactions, forms a structure with open porosity. However, this type of mould can be used to make a maximum of 100 pieces as the mould suffers marked abrasion, which quickly leads to the loss of beta plaster, causing dimensional changes to the mould. Furthermore beta gypsum exhibits poor mechanical properties: this characteristic, combined with bad casting operation management, can easily lead to the formation of cracks in the mould and therefore to the loss of its functionality [10–14]. All this causes a deterioration in the final quality, leading to contours that are less defined with variable volumes: after approximately 100 castings, the piece quality is not acceptable and the mould therefore has to be replaced. For this study we decided to use Poolkemie Ecoresin, a mixture of alpha plaster and acrylic resin, to replace the commonly used beta gypsum. This non-toxic compound is normally used to form products for aesthetic purposes, and in particular to realize reproductions, statues and models. It is designed to last for a long time in the basis of its mechanical properties. Once hardened, this synthetic ecological resin forms a structure and a "sound" similar to ceramics. The detail obtained with acrylic resins faithfully reproduces the original model, without any deformation or shrinkage. Furthermore, various pigments and charges can be added to the Ecoresin. Unfortunately, this product is not good for low-pressure casting on account of its low porosity. In this work the goal is to increase the porosity of the Ecoresin with the addition of different percentages of Poraver glassy spheres (grain size of 0.04 – 0.125 mm). The application fields for Poraver glass spheres are tile adhesives, cementitious adhesives and concrete repair products. In this study we demonstrate how increasing amounts of glassy spheres influence the mechanical properties of the Ecoresin and its casting behaviour. As described, these materials do not have common application fields: in this work we mixed them for the first time to obtain a new formulation to replace the beta plaster. In this innovative composite material, Ecoresin is the matrix and it is introduced to obtain mechanical resistance. The Poraver glassy spheres are the fillers and they

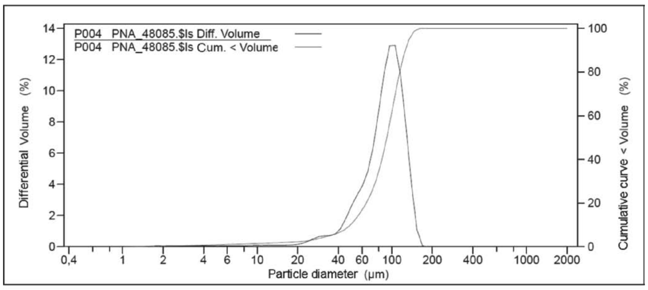
* Corresponding author: afortuna@setecsrl.it

are used to create porosity at the interface with the matrix. In fact there is no chemical bond between the Ecoresin and Poraver.

II. Experimental

(1) Materials

Siniat 101 beta gypsum (Via G.G. Winckelmann, 2 – 20146 – Milan, Italy), Poolkemie Ecoresin, (Via Plava, 40, Turin TO, Italy), has a hardening time of 15 – 20 min. Poraver glassy spheres, (Dennert Poraver GmbH, Gewerbegebiet Ost 17, 92353 Postbauer-Heng, Germany), grain size 0.04 – 0.125 mm, with a PSD (Particle Size Distribution) as shown in Fig. 1 and dry loose bulk density of (530 ± 70) kg/m^3.



Volume Statistic (Arithmetisch) P004 PNA_48085.$ls

Calculation of 0,375 µm to 2000 µm

Volume: 100%
Average: 89,09 µm
Median: 91,80 µm
Average /Median: 0,970
Maximum: 105,9 µm

d_{10}: 49,16 µm d_{50}: 91,80 µm d_{90}: 126,2 µm

<10%	<25%	<50%	<75%	<90%	<97%		
49,16 µm	70,66 µm	91,80 µm	110,1 µm	126,2 µm	140,8 µm		
>1 µm	>2 µm	>5 µm	>20 µm	>40 µm	>50 µm	>63 µm	>100 µm
99,998%	99,7%	99,1%	97,7%	93,6%	89,5%	81,1%	38,3%

Fig. 1: Particle size distribution of Poraver glassy spheres.

(2) Formulations utilized

Ecoresin is the base material for the new formulations. To this, we added increasing amounts of Poraver glassy spheres to obtain the following compounds:

- **A**: 100 % ECORESIN; solid/water ratio = 3.25.
- **B**: 90 % ECORESIN, 10 % PORAVER; solid/water ratio = 2.93.
- **C**: 80 % ECORESIN, 20 % PORAVER; solid/water ratio = 2.60.
- **D**: 70 % ECORESIN, 30 % PORAVER; solid/water ratio = 2.27.
- **E**: 60 % ECORESIN, 40 % PORAVER; solid/water ratio = 1.95.

It is important to note that it is necessary to add more water when the amount of glassy spheres is increased. This choice is obviously not arbitrary but is required to maintain the same working conditions of the A formulation. In particular, we have to keep the reaction time (20 min at 25 °C) as the standard reference as it is the most important parameter from a technological point of view. The reactions that lead to the solidification must only occur when the material has already been cast into the matrix, which gives the mould the desired shape; indeed if the material hardens during mixing it becomes unusable. The change in the solid/water ratio, used in the various formulations, is necessary because glassy spheres have a finer particles size than Ecoresin, making it necessary to add more water. To perform a comparison, we also made 101 beta plaster samples (product by Siniat). This material is normally used for low-pressure casting. The formulation used for the beta gypsum, in accordance with sanitaryware standard references, is the following:

- **F** : 100 % 101 beta gypsum; solid/water ratio = 1.30

(a) *Experimental tests*

With the different formulations mentioned in paragraph 1.2, we obtained samples to perform:

- 3D Maps on the samples obtained with different formulations (4 x 4 mm^2, spacing 2 µm, Gauss filter 0.8) with a *Taylor-Hobson TalySurf* CLI 2000 profilometer (see Fig. 2), and Table 1 reports all the parameters (Ra, Rz, RSm and RΔq) obtained with the profilometer for the samples tested.

Table 1: Data values obtained with a *Taylor-Hobson TalySurf* CLI 2000 profilometer for the samples tested.

Sample	Formula	Ra (GS 0.800 mm) ± SD (µm); (n≥ 3)	Rz (GS 0.800 mm) ± SD (µm); (n≥ 3)	RSm (GS 0.800 mm) ± SD (µm); (n≥ 3)	RΔq (GS 0.800 mm) ± SD (°); (n≥ 3)
100 % Ecoresin	A	0.59 ± 0.014	4.3 ± 0.15	68 ± 2.4	5.0 ± 0.20
10 % Poraver glassy spheres	B	0.61 ± 0.011	3.8 ± 0.16	59 ± 2.8	5.8 ± 0.26
20 % Poraver glassy spheres	C	0.79 ± 0.022	5.1 ± 0.18	64 ± 3.3	5.2 ± 0.19
30 % Poraver glassy spheres	D	0.83 ± 0.025	6.5 ± 0.24	99 ±4.1	6.8 ± 0.29
40 % Poraver glassy spheres	E	1.62 ± 0.053	8.1 ± 0.30	105 ± 5.2	9.7 ± 0.43
100 % Beta plaster	F	0.54 ± 0.011	4.1 ± 0.12	58 ± 2.8	4.9 ± 0.15
Ra = (Arithmetical Mean Roughness); Rz = (Maximum Height); RSm = mean spacing of profile elements; RΔq = root mean square slope of the assessed profile.					

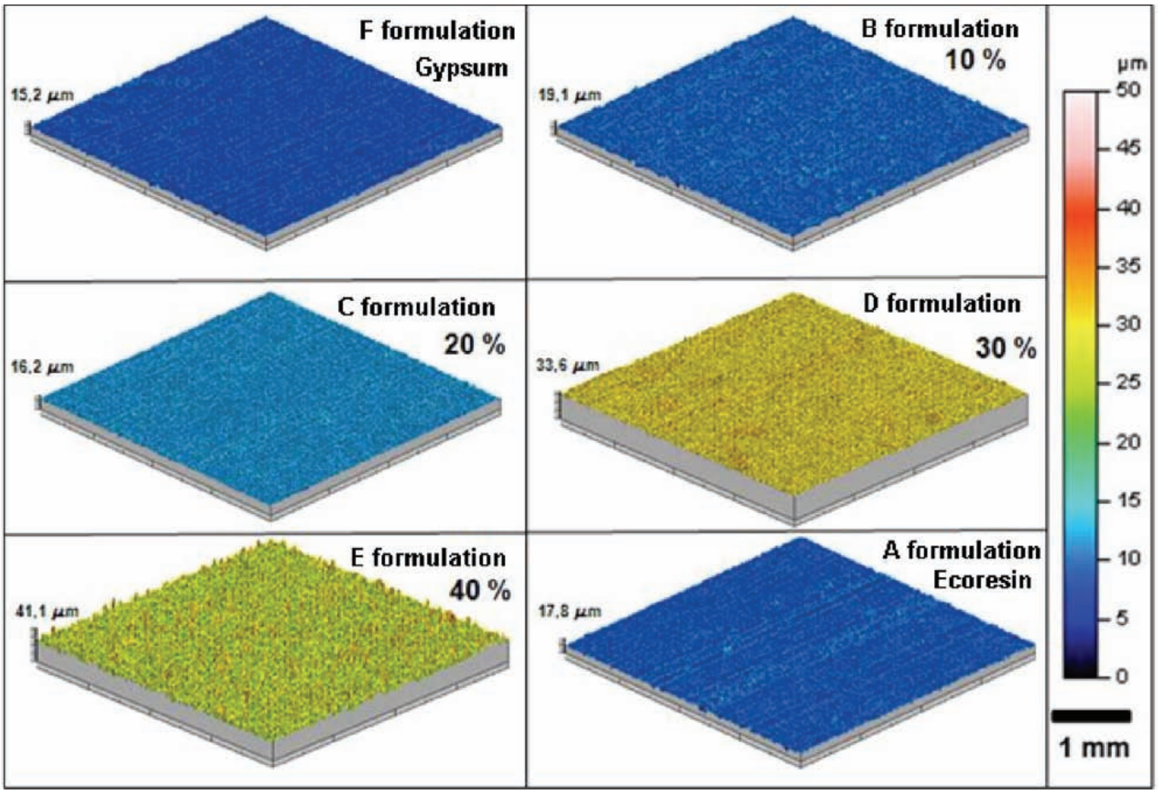


Fig. 2: 3D maps of the samples obtained from different formulations (4 x 4 mm^2, spacing 2 µm, Gauss filter 0.8) with a *Taylor-Hobson TalySurf* CLI 2000 profilometer.

- Tribological testing by means of a Micro Combi tester (the tribological parameters used are listed in Table 2) (sampling points: x = 2 µm; y = 5 µm); Fig. 4 shows the results of the test on samples obtained with different formulations after a path of 10 m, while Tables 3 and 4 show the values for the wear volumes.
- 3-point flexural testing [15]: strain rate = 0.25 mm/min, samples dimension: l = 100 mm; b = 26 mm; h = 26 mm. In Fig. 5, the flexural strength values obtained with samples of different formulation are shown.
- Thickness testing after 90 min with the following vitreous china body (see Fig. 6):
  - Specific weight: 1.815 kg/l
  - Viscosity: 300 °Gallenkamp
  - Thixotropy: 30 °Gallenkamp
  - Temperature = 25 °C

Table 2: Tribological test parameters used.

Geometry of the static counterparty	Sphere
Geometry of the static counterparty	6.00 mm
Geometry of the static counterparty	Al_2O_3
Speed	5 cm/s
Radius	3 mm

Table 3: Wear volumes (mm^3) measured after the abrasion resistance test on samples obtained from different formulations. Paths 10 m.

Sample	Formulation	Wear volumes (mm^3) at 10 m
100% Ecoresin	A	0.289
10 % Poraver glassy spheres	B	0.000
20 % Poraver glassy spheres	C	1.280
30 % Poraver glassy spheres	D	3.760
40 % Poraver glassy spheres	E	5.910
100% Beta plaster	F	33.900

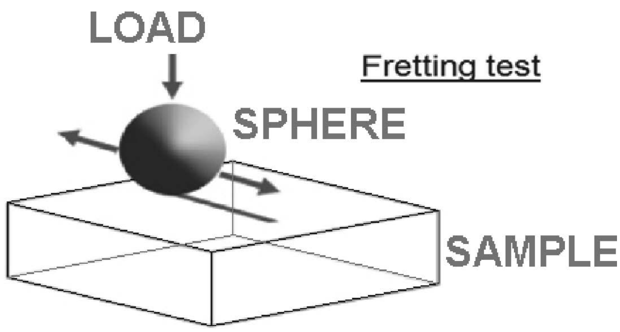


Fig. 3: Tribological testing with the Micro Combi tester (sampling points: x = 2 µm; y = 5 µm), when a load of 1 N is applied for a path of about 10 m and 100 m.

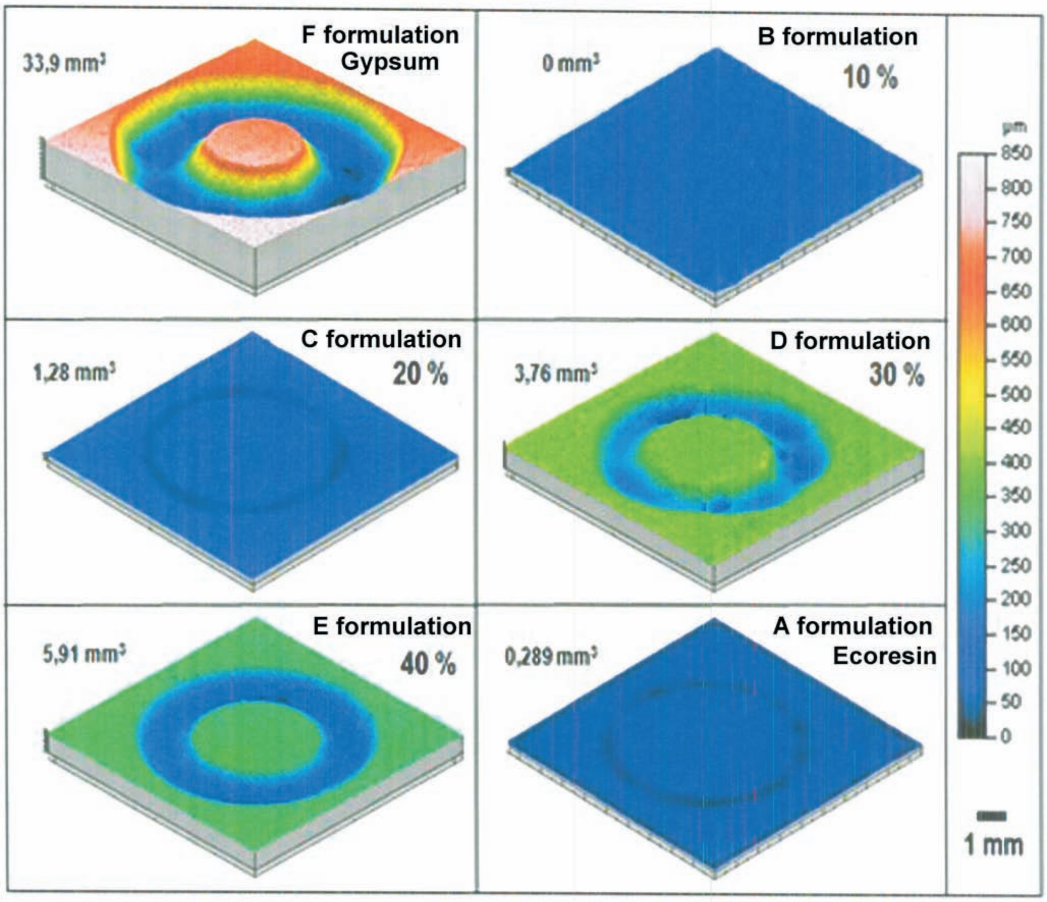


Fig. 4: Abrasion resistance test on samples obtained from different formulations after a path of 10 m.

Thickness was measured with a micrometer (Ceramic instruments); results are reported in Table 5.

Table 4: Wear volumes (mm^3) measured after the abrasion resistance test on samples obtained with different formulations, repeated by lengthening the path to 100 m on the samples that proved harder than the others in the test to 10 m.

Sample	Formulation	Wear volumes (mm^3) at 100 m
100% Ecoresin	A	1.690
10 % Poraver glassy spheres	B	0.000
20 % Poraver glassy spheres	C	6.240

III. Results and Discussions

Surface roughness: this test is interesting to see how the glass balls are distributed on the surface. Before measurements of each group, the profilometer was calibrated. All profilometer records were made as close as possible to the sample centre. For each specimen, three measurements were taken and the mean was calculated to obtain the general surface characteristics of the specimens. There are many surface roughness parameters that can be used to analyse a surface. The most common surface roughness parameter used in industry is the average roughness Ra (arithmetic mean deviation of the assessed profile) and Rz (maximum height of the profile). The real surface geometry is so complicated that a finite number of parameters cannot provide a full description. If the number of parameters used is increased, a more accurate description can be obtained. Parameters used to describe surfaces are largely statistical indicators obtained from samples of the surface tested. Other parameters, described in literature and the standards [16, 17], are: RSm (RSm, mean spacing of profile elements) and RΔq (root mean square slope of the assessed profile, defined on the evaluation length). These parameters are important because they provide information on the morphology of the surface texture. Three-dimensional maps show that increasing the content of the spheres raises the surface irregularities. This is in line with what was expected because the balls represent discontinuity elements in respect of the acrylic matrix. In any case micro-irregularities are uniformly distributed over the entire sample surface and so this fact confirms the good mixing of the resin-spheres system. As mentioned earlier, this is very important for technological purposes: if the Poraver spheres are not uniformly distributed, zones with higher porosity than others result. This would lead to different thicknesses in the ceramic pieces – obviously a defect that could not be tolerated, so it would not be possible to replace the beta plaster with new formulations.

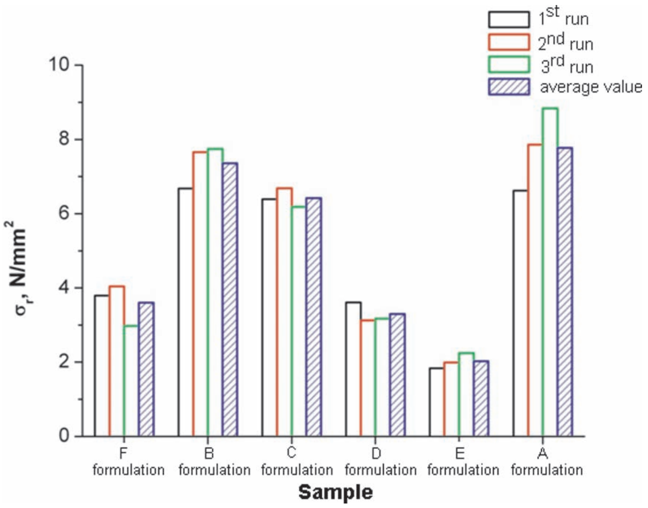


Fig. 5: Flexural strength values obtained on samples from different formulations in the 3-point flexural strength test.

Tribological test: this test permits estimation of the wear volumes caused by the relative movement between the sample and an alumina ball. The experimental details are shown in Table 2 while the obtained results are summarized in the figures and tables that follow. Wear tests at 10 m (distance travelled by the ball) show the significant improvement in all the samples compared to the beta plaster (see Fig. 4 and Table 3). Regarding the effect of the spheres, in general we noted a deterioration in the abrasion resistance with an increasing content of Poraver. However, it is important to underline that, when we introduce only 10 % spheres, there is an improvement compared to the sample containing only resin. This fact is very interesting and it was also confirmed by a further test at 100 m. The test in fact was repeated by lengthening the path to 100 m on the samples that proved harder than the others in the test to 10 m (results are reported in Table 4).

Flexural test: this test is particularly important because it allows evaluation of the mechanical properties. In fact beta plaster moulds very often break even during the opening-closing operations owing to the poor mechanical strength of the material. The test results are very interesting: the resin is the best material and presents values approximately double of those of the plaster, but the addition of spheres negatively affects the mechanical properties (see Fig. 5). In any case it is important to underline that samples with 10 % and 20 % exhibit very good values and for this reason they are an evident improvement in respect of the beta gypsum.

Casting and formation thickness test: this test is certainly the most important because they directly affect the production process. This test is therefore crucial to understand if new formulations are suitable to replace the plaster in mould production. In this test, we made moulds with the shape of a cup from each formulation (see Fig. 6). We cast a vitreous china body into each of these moulds: the body is left inside the shaped cup mould and a solid thickness is formed on the mould walls. After 90 min, the excess vitreous china is removed and it is finally possible to measure the thickness. The casting test shows that the best results are obtained with the beta plaster. However, all the other formulations, and in particular that with 20 % porous spheres, have significant casting behaviour. The introduction of Poraver spheres improves resin thickness formation but this beneficial effect reaches its maximum when the spheres content is 20 %. In fact, for larger quantities (30 %, 40 %), there is progressive deterioration (see Table 5).

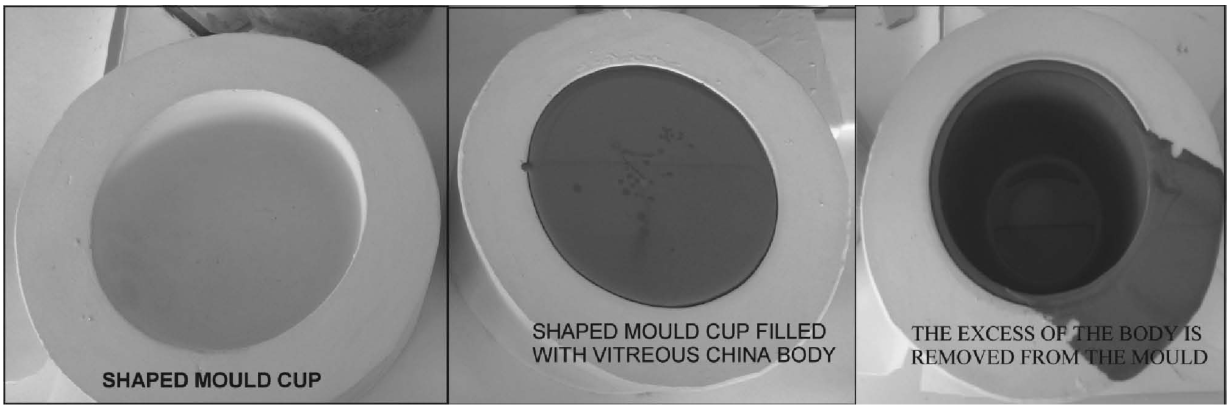


Fig. 6: Shaped mould cup used for thickness test measurement.

Table 5: Thickness after 90 minutes obtained on the samples tested.

Sample	Formulation	Thickness Mean value (mm) (n > 3)	Standard deviation SD (mm)
100% Ecoresin	A	7.4	± 0.1
10 % Poraver glassy spheres	B	7.9	± 0.4
20 % Poraver glassy spheres	C	8.2	± 0.1
30 % Poraver glassy spheres	D	8.0	± 0.3
40 % Poraver glassy spheres	E	7.4	± 0.1
100% Beta plaster	F	9.1	± 0.2

IV. Conclusions

In this work we investigated the behaviour of Ecoresin-Poraver glass spheres mixtures to replace beta plaster in the production of sanitaryware moulds. The goal was to find the best compromise between the mechanical resistance and the casting behaviour. In this composite material Ecoresin was the matrix and was introduced to ensure flexural strength and abrasion resistance. Poraver glass spheres were the fillers used to form porosity at the interface with the matrix. There is no chemical bond between Ecoresin and Poraver. To optimize the amounts of Poraver, we prepared different formulations on which we conducted tests to evaluate mechanical properties, roughness and casting behaviour.

The tests conducted confirm that the introduction of Poraver glass spheres worsens the mechanical and abrasion resistance of the Ecoresin; in any case there is an improvement compared to the beta plaster. The exception was the sample containing 10 % spheres: in fact in this case the volume loss owing to wear is lower than in the simple Ecoresin samples.

The casting test shows a beneficial effect associated with the introduction of the Poraver spheres. However, thickness formation reaches a maximum when the content of Poraver is 20 %. For higher volumes (30 %, 40 %), the situation worsens and there is no advantage associated with its use. To summarize, the 20-% mix is definitely the best compromise between casting behaviour and mechanical properties; for this reason it is considered the candidate to replace beta plaster. Indeed it enables a considerable increase in the useful life of the moulds, leaving all the other technological parameters almost unchanged. In any case this work is only the beginning of our research in this field, the next step is to apply these new formulations in an industrial application. Results are encouraging and confirm that this mixture will be able to replace beta plaster. In any case, it is not yet possible to quantify the improvements owing to the new formulation because we have to wait until the end of the industrial trial. At the same time we are working to evaluate the effect of the spheres' grain size and we are also testing other inorganic fillers. We shall present these results in future publications.

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