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WITH SUPERIOR MECHANICAL PROPERTIES**

PROJECT

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<p style="text-align: center;">FIBRE REINFORCEMENT OF TRADITIONAL CERAMICS</p>

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Abstract

The possibilities of fibre reinforcing traditional clay based building ceramics (floor and wall tile and sanitaryware) have been experienced. The main results achieved are presented and discussed, and the main problems to be faced in view of industrial application are outlined. It is shown how commercially available fibres are not fully suitable for the reinforcing purpose under consideration. A scientific and technical base is achieved, and future research options are recommended.

1. INTRODUCTION

1.1 - Objectives of the research

The general objective of the project was that of verifying and experimenting the possibility of improving the mechanical characteristics and performance of selected ceramic materials for the building industry (ceramic floor and wall tile and sanitaryware) by applying the mechanism of fibre reinforcement.

This objective should have been pursued in the project under consideration using a technical approach which included:

- i) the identification of existing fibres which can be suitable for the reinforcing purpose, and
- ii) the experimentation, at both laboratory and industrial scale, of the reinforcing effect, achieved by adding fibres to the conventional bodies at present used for the products under consideration.

1.2 - General remarks on the composite theory

A limitation of ceramics in general is that they are strong but brittle. They require a high stress to initiate a crack (i.e. high modulus of rupture), but the energy required to propagate the crack is low (i.e. low toughness) .

The incorporation of fibres into the ceramic matrix has been found to improve the toughness of several ceramic and metallic materials . An essential feature of these composites is that when stressed they fracture in the matrix prior to the fibre. For this to occur the fibre must have a higher stiffness than the matrix. Thus fibres increase the energy for fracture, and reinforcement is observed. The mechanism by which this occurs follows the stages below:

- .deflection of the crack along the weak matrix/fibre interface;
- " pull-out of the fibre after it has been debonded from the matrix;
- .fibre bridging the crack and resisting its progress;
- .fibre fracture.

The fibre reinforcement mechanism has been the object of several studies [1÷7]. After these studies, the requirements for a successful composite can be summarised as follows:

a) **Fibres**

- i) having a strength of at least an order of magnitude greater than that of the ceramic matrix;
- ii) having a smooth surface;
- iii) with a similar thermal expansion to that of the ceramic matrix;
- iv) having a high Young modulus;
- v) being stable at the firing cycle of the ceramic matrix;
- vi) having a length which is significantly greater than the crystal phases or porosity in the ceramic matrix.

b) **Strength of fibre/matrix bond**

- i) if a weak fibre/ceramic bond is formed, the fibre must have a low sliding resistance and therefore the fracture surface must be smooth. Experimentation has shown that the

strength of the fibre/matrix bond should not exceed one quarter of the fibre fracture strength;

ii) if a strong fibre/matrix bond occurs, the fibre must have a high Young modulus for strengthening to occur.

In the field of advanced ceramics, several ceramic-ceramic composite materials have been developed, with different matrices (for example, Al_2O_3 , SiC, Si_3N_4), reinforced with both ceramic fibres (e.g. SiC) or whiskers. And outstanding toughness increases have been achieved. Some of these experiences have shown some interesting aspects, related also to the microstructure of the composite and the preparation procedure. For example:

- the higher the amount of fibre(or whiskers) added, the higher is the increase of both strength and toughness, but also the higher are the compaction difficulties [8]. Shorter fibres, and a more narrow length distribution - achieved subjecting the fibre additivated body to a prolonged milling - has been found as effective in this case;
- a correlation seems to exist between fibre addition and fibre length {or aspect ratio) [9] : qualitatively, the higher is the fibre addition, the shorter the fibres should be.

The application of these concepts to traditional, clay based ceramics was to be demonstrated, and this was the aim of this research project. The concepts above have represented the scientific base-line. Commercially available fibres have been used.

1.3 - Technical approach adopted

In general terms, the technical approach adopted can be summarised as follows:

- some reference bodies, representatives of the products under consideration (ceramic floor and wall tiles and

sanitaryware) , and several commercial fibres, identified as potentially suitable for reinforcement, have been selected;

- composites (fibre additivated test pieces) have been produced in different and predefine fabrication conditions, using the conventional forming methods for the products under consideration (in particular, dust pressing and slip casting) ;

- the possible reinforcing effects {in term of increased modulus of rupture or fracture toughness) have been studied and correlated to i) type, amount , dimensions of the fibres; ii) type of body; iii) firing temperature and other fabrication parameters ; iv) matrix and composite microstructure .

Experiments have been carried out at laboratory level. For some products, on the base of the results achieved, also industrial tests on pilot production lines have been carried out.

2. TECHNICAL DESCRIPTION

2.1 - Materials

BODIES : Reference bodies have been selected, in order to cover all the commercial products on which the fibre reinforcing experiments were scheduled, according to the project objectives. These bodies have been supplied by the industrial partners, with their respective technical and manufacturing specifications. In the following the bodies under consideration are identified with reference to the respective product. The technical and manufacturing specifications are not indicated here.

B1a: porcelain stoneware (Dust pressed tiles, Class B1a according to ISO 13006 [10], Water Absorption ≤ 0.5 %)

B1: single fired low porosity floor tiles (Dust pressed tiles, Class B1 according to EN 87, Water Absorption ranging from 0.5 to 3 %)

BII: single fired medium porosity floor tiles (Dust pressed tiles, Class BII according to EN 87, Water Absorption ranging from 3 to 10 %)

BIII: double fired high porosity wall tiles (Dust pressed tiles, Class BIII according to EN 87, Water Absorption \geq 10 %)

VCS: vitreous china sanitaryware

FIBRES : Several types of fibres have been considered, as from the following list:

.Alumina fibres: different types have been experienced, such as Saffil LA, Saffil RF, manufactured by ICI, containing around 96+97 % alumina, in the form of a wool (average length around 2.5 mm; average diameter 3 μ m), or supplied as milled (average length around 100 μ m). Also other particularly expensive types of alumina fibres have been experienced. In particular:

- Saffimax, by ICI, which has a similar composition to Saffil fibres, but is spun so that continuous fibres are produced;

"Saphikon", which is a pure alumina single crystal fibre, available as a continuous filament, having a 125 μ m diameter.

. Alumino-silicate fibres : different types have been experienced, such as Kertec 412, Kertec 432 and Zirlane, manufactured by S.E.P.R.-Kerlane, or Kaowool Bulk A Standard and Bulk A Zirconia, manufactured by Morgan Thermal Ceramics. (Zirlane and Bulk A Zirconia contain around 15-18% ZrO₂). All these fibres are available in the form of a wool (average length ranging from 200 to 600+750 μ m, average diameter around 2-3 μ m).

• Zirconia fibres, such as that manufactured by Zircar Products Inc., containing 92 % ZrO₂, in the form of a wool (average length 1.6 mm, average diameter 3-5 p.m.

.Glass fibres, such as E-glass and S-glass by Owens Corning. These fibres are available in continuous and

chopped strands. Different lengths can be made available (from 3 mm up).

2.2 - Methods for the preparation of fibre additivated test pieces

Without entering in a detailed description of the techniques used, for the specific purposes of this paper it is advisable to report only the basic principle of the methods adopted.

Method 1: Milling method. The fibres, as supplied, have been added to the body in the due proportions. The fibre additivated body has been wet milled in a laboratory mill (in general, a ball mill) for different times, in order to achieve both a suitable dispersion of the fibres and a suitable reduction of fibre length (when required). The slip has been either used as such, in the slip casting experiments, or dried and granulated, in the dust pressing experiments.

Method 2: Mixing method. Shorter fibres as supplied ("milled" fibres, as indicated above) or fibres previously cut at the required lengths have been used with this method. A stirrer or a shearing mixer have been used in this case, to improve fibre dispersion in the body slip. Also in this case, the slip has been either used as such, in the slip casting experiments, or dried and granulated, in the dust pressing experiments.

In all the experiments, reference not additivated bodies have been prepared, subjected to the same operations as the fibre additivated bodies. The purpose of such a procedure was to identify in a more reliable way the effects of fibre additions, separated by the effects of the actual preparation method.

Test pieces have been then formed either by dust pressing (at specified pressures) or pressureless slip casting in

plaster moulds. The test pieces have then been dried in laboratory drier, and fired (at specified temperatures and firing schedules) in laboratory or industrial kilns.

Also industrial trials, with production of actual components (tiles or sanitaryware articles) have been carried out in the framework of the project.

2.3 - Characterisations carried out on both unfired and fired test pieces:

Several measurements have been carried out on both slips and unfired and fired test pieces. Attention is focused, in the following, on the specific methods adopted to measure and characterise the properties more directly related to the reinforcing effects.

Fibre length distributions in the fibre additivated slips have been determined with a light microscope connected with an image analyser.

The following measurements have been performed on unfired test pieces:

- Modulus of Rupture (MOR), 3-point loading test.
- Work of Fracture (WOF), calculated from the load-displacement curve obtained in a 3-points loading test.

Finally, the following measurements have been performed on fired test pieces:

- Water Absorption (WA) (EN 99)
- pore size distribution - mercury porosimeter
- Modulus of Rupture (MOR), 3-point loading test (EN 100 test conditions)
- Work of Fracture and/or Displacement at rupture (see above) ;
- Fracture toughness, K_{IC} - SENB technique;

- Microstructure has been examined using light microscope and scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1 - **Fibres and fibre reinforcement mechanism**

A review has been made of the fibres available worldwide, and attempts have been made to identify fibres that may be suitable for ceramics. The properties considered were strength, thermal expansion, dispersibility in water, probable reaction with the glassy phase of the ceramic, stability at the peak firing temperature of the ceramic, resistance to oxidation, etc.

Alumina fibres (Saffil, in particular) were identified as having the best possibility of success. Saffil LA fibre was selected for study. This is regarded as the best fibre produced (with the exception of single crystal fibre, which is prohibitably expensive} . It has the disadvantage that it is only available as a wool.

Experiments were undertaken to separate the fibre into filaments. Techniques used were milling, sieving and pressing. All had the disadvantage of potentially damaging the fibre.

Attempts were made to classify the length of the fibre by hydrocyclone, aircyclone and precipitation techniques. None of the methods were effective.

Starting from several negative results achieved in the experiments on fibre reinforced bodies (as discussed in the next sections) , a fundamental study of fibre reinforcement has been undertaken. This identified reasons for the poor reinforcement of the fired. bodies. This theoretical study was tested using Saphikon single crystal fibre . Reinforcement was obtained using this fibre (Table 1), and thus confirmed the hypothesis.

Table 1 - Unfired and fired mechanical properties of composites with Saphikon fibres

Body: BIII; Fibre: Saphikon, 3 mm length; Fibre addition: 5% w/w; Body preparation: Method 2: Mixing method; Forming method: dust pressing at 300 kg/cm²; Firing temperature: 1150 °C

[BCR]

	MOR (MPa)	WOF (J.m ⁻²)	Bulk Density
Unfired sample			
Standard	1.1	3.2	1.72
.5% Saphikon	0.7	18.8	1.73
Fired sample			
Standard	12.7	45.0	1,61
.5% Saphikon	10.9	107.7	1.62

It was concluded that fired ceramics could not be reinforced to acceptable levels (from the technical and economic points of view) by any of the fibres which are currently commercially available. The possibility of producing a purpose-made fibre has been experienced. A test sample of a zirconia fibre has been produced and tested, but the expected reinforcement levels have not been achieved.

3.2 - Fibre reinforcement experiments on tiles

Several types of fibres have been experienced with all the relevant bodies. Glass fibres have found to be quite unsuitable for any reinforcement in the fired state, since they are dissolved in the liquid phase at the firing temperature. The most interesting results have been achieved using the alumina fibres (Saffil) ; this has been attributed to the better quality' of these fibres, which, compared to the commercial alumino-silicate fibres, have no blobs of shot, and are characterised by a more uniform diameter. Therefore, despite the high cost (which represents, however, a heavy obstacle for the industrial application) , the attention has been focused on Saffil

fibres . Fibres additions ranging from 5 to 15 % w/w have been experienced [11].

Any fibre addition has always lead to increased porosity levels, i.e. to higher water absorption values, compared to the reference body. Fibres have been found to introduce pores and flaws into the body, and bad microstructure are sometimes obtained, especially when longer fibres are used.

With BIa body the objective of achieving fibre additivated pieces with $WA \leq 0.5 \%$ - a basic requirement for porcelain stoneware tile - has been pursued through a prolonged milling of the fibre additivated body. In this way also fibres have been milled and reduced in length: fibre length distributions have been achieved with more than 90 % of fibres shorter than 20 μm , and a large amount, more than 20 %, with an aspect ratio (length to diameter ratio) lower than 3 (the fibres under consideration have an average diameter of 3 μm , as reported above) . Thus, a lot of alumina "particles", rather than fibres, are produced in this way. The water absorption of a 10 % fibre additivated body pressed at 500 kg/cm^2 and fired at 1220 °C was 0.07 % (against 0.04 % of the reference body, processed in the same way) , but the effects on mechanical **characteristics** were rather limited: MOR is increased from 55.5 to 60.0 MPa (+ 8.1%), while K_{IC} is increased from 1.28 to 1.33 (+3.9 %)

For BI body, fibre additivated test pieces with the same WA as reference body have been produced increasing both pressing pressure (from 300 to 400 kg/cm^2) and firing temperature (from 1190 to 1230 °C) . The results achieved, in terms of MOR increase, are reported in Figure 1. The strengthening result is interesting (note that the reference material, although produced in different

conditions, nevertheless has the same porosity. Therefore the observed strengthening can be attributed to fibres).

Figure 1- Strengthening effect in fibre additivated bodies, with the same WA as the reference bodies.

Body: BI; Fibre: Saffil LA Milled; Fibre addition: 5% w/w; Body preparation: Method 1: Milling method; Pressing pressure: reference body: 300 kg/cm²; fibre additivated body: 400 kg/cm²; Firing temperature: reference body: 1190 °C, fibre additivated body: 1230 °C
[Société Française de Céramique]

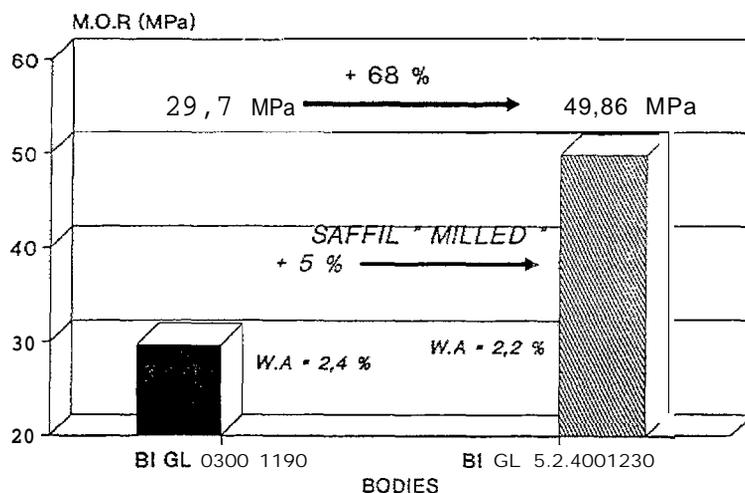
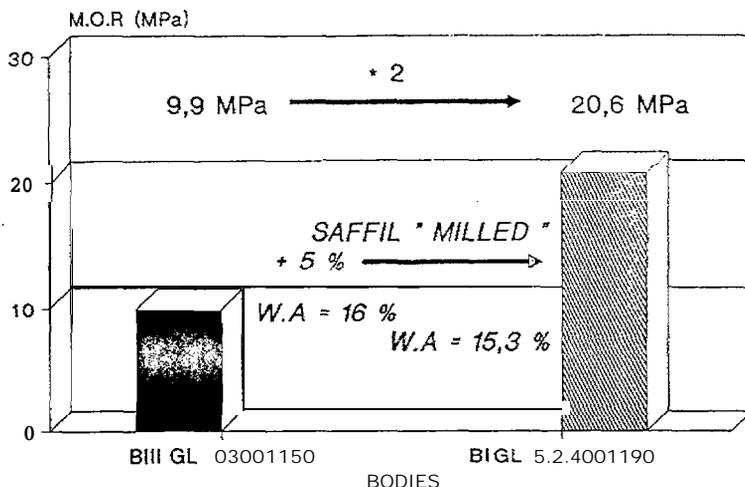


Figure 2 - Strengthening effect in fibre additivated bodies, with the same WA as the reference bodies.

Body: BIII; Fibre: Saffil LA Milled; Fibre addition: 5%w/w; Body preparation: Method 1: Milling method; Pressing pressure: reference body: 300 kg/cm²; fibre additivated body: 400 kg/cm²; Firing temperature: reference body: 1150 °C; fibre additivated body: 1190 °C
[Société Française de Céramique]



Similar results have been achieved with the BIII body (Figure 2) . However, in both fibre additivated bodies no appreciable variation in fracture behaviour has been observed.

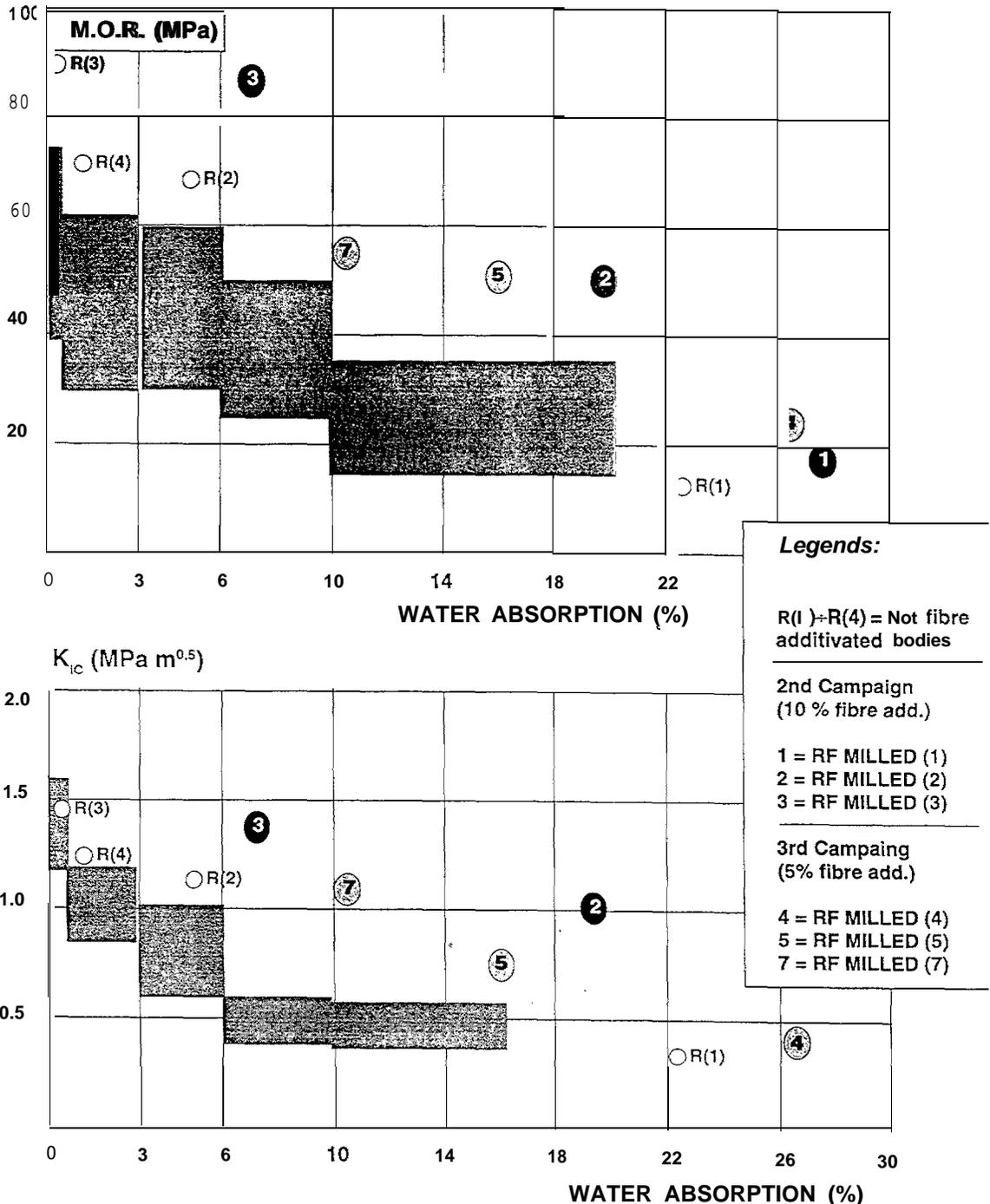
For BII body, the effect of fibre addition on porosity is confirmed. For the same fabrication conditions (pressing pressure: 350 kg/cm²; firing temperature: 1050 °C), a 7% fibre addition has increased WA from 10.6 to 12.2 %, while a 10 % addition brings WA to 15.9 %. But, despite these appreciably increased porosity levels, the fibre additivated products have a higher strength and a higher deflection at fracture.

The most promising results have been obtained in experiments of fibre addition., by the Method 2 - Mixing method, to bodies for medium-high porosity tiles produced by slip casting.

A suitably modified composition of the BIa body has been used for these experiments. Test pieces containing 10 % and 5% Saffil RF milled fibres have been prepared with the "Mixing method", cast in plaster moulds, dried and fired at different temperatures, ranging from 1080 to 1220 °C.

Any fibre addition leads to porous products for any firing temperature : composites have been produced with water absorption ranging from around 7% to over 26 %. As a consequence, the composites are characterised by lower values of both MOR and K_{IC} , compared to the lower porosity reference test pieces, fired at the same temperature.

Figure 3 - Mechanical properties (MOR and K_{Ic}) of composites vs Water Absorption, compared to conventional products (represented by the shaded areas)
 Body: B1a; Fibre: Saffil RF Milled; Fibre additions: 5 and 10% w/w; Body preparation: Method 2; Mixing method; Forming method: slip casting; Firing temperatures: as specified
 [Centro Ceramico]



However, these decreases are in part counterbalanced by the effect of fibres (in particular, by the bridging effect brought about by fibres) .

In Figure 3 the main results achieved are summarised as a function of water absorption, and compared to the mechanical characteristics of conventional, commercially available products (ceramic floor and wall tiles), represented by the shaded areas. Interesting increases of both MOR and KIC have been observed, with respect to conventional products with the same porosity, and the materials developed have, in effect, innovative levels of mechanical performance, compared to the conventional products at present available. These reinforcement levels can be considered interesting and worth of further development from an industrial point of view.

However, if the reinforcement levels achieved are compared to the predictable cost of the fibre additivated product (on the basis of fibre cost and fibre addition envisaged), it must be concluded that the conditions to pass to the pilot industrial experimentation did not exist, since the cost/benefit ratio of the proposed technology was unacceptable from an industrial point of view.

3.3 - Fibre reinforcement experiments on sanitaryware

In the framework of the sub-task "Laboratory experimentation" , ceramic bodies were prepared using the Saffil fibres and evaluated both in their fired and unfired state. No significant reinforcement was achieved in the fired state.

The study on the commercially available fibres presented above lead to the conclusion that fired sanitaryware bodies

could not be reinforced by any of the fibres which are currently commercially available.

The possibility of reinforcing sanitaryware in their unfired state, through the addition of glass fibres cut at a specified length, has been considered (as a means to prevent or reduce production losses during drying) .

The results achieved in laboratory and little pilot industrial experiments using conventional casting were encouraging. A summary of these laboratory results, when conventionally casting a sanitaryware body containing S-glass fibres in different amounts and lengths, is as follows:

- the fibres were readily dispersed in the sanitaryware slip provided that a suitable sizing was used (sizing is a coating applied to the fibre to aid dispersion) ;
- the fibres did not affect the long term stability of the rheology of the slip;
- small additions of fibre considerably increased the work of fracture of an unfired sanitaryware body (Table 2);

Table 2 - Unfired mechanical properties of composites with S-glass fibres, for different lengths and fibre additions

Body: VCS (sanitaryware) ; Fibre: S-glass; Body preparation: Method 2: Mixing method; Forming method: slip casting
[Ceram Research]

Body	Work of Fracture (MPa)	MOR (MPa)
Standard	16	3.6
•0.1%, 1 mm fibre	44,44,53	4.1, 4.1, 4.4
•0.2%, 3 mm fibre	47	3.0
•0.5%, 6 mm fibre	23	2.9

- the fired strength of the composite was similar to that of the standard body ;
- increasing the amount or length of the fibre decreased the slip viscosity. There is a minimum slip viscosity required to avoid loss due to draining the excess slip from the cast. Further experiments have shown that the maximum

addition of fibre that could be used without compromising the slip viscosity was 0.5% 1.5mm fibre and 0.1% 3mm fibre; the fired composite did not contain any evidence of microstructural disturbance.

Since the laboratory findings were encouraging, a pilot plant scale evaluation of the composite containing 0.5% 1.5mm long S-glass fibre was conducted.

Two pilot industrial experiments have been carried out, using pressure casting. It has been found that the composite had increased cracking losses. This may be due to using unsuitable casting parameters for the composite: in other words, the composites developed are unsuitable for the pressure casting procedure. However, further experimentation is required to verify this conclusion.

4. CONCLUSIONS

The objectives of developing fibre reinforced traditional ceramics have not been achieved at a satisfactory level: in particular, the industrial objectives, represented by the development and the industrial production of such reinforced products (floor and wall tiles and sanitaryware) have failed.

However, in front of this disappointing situation, important experiences have been gathered, and basic concepts have been discovered and understood, which ensure a significant progress with respect to the state-of-the-art, from the scientific and technical point of view.

In fact, the laboratory experimentation carried out in the framework of this research project led to a deeper comprehension and awareness about several basic concepts regarding fibre reinforcement of traditional ceramics.

All the results achieved, even the negative results, lead to a coherent picture of the basic role of fibres and of

their properties: fibres are the "controlling factor", with respect to the objective of mechanical reinforcement of traditional ceramics.

On the basis of the experiences developed in the framework of this project, and in particular of the results discussed in this paper, it can be concluded that the main problem is not to adapt the ceramic technology to the fibre addition, but rather that of developing suitable fibres for the reinforcement of traditional ceramics. The results achieved represent a sound basis for facing this problem, i.e. the development of suitable fibres for the reinforcement of traditional ceramics in the fired state.

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