RELATION BETWEEN THE MECHANICAL PROPERTIES OF CERAMIC GLAZES AND THEIR BEHAVIOUR ON SUBJECTING THEM TO EXTERNAL STRESSES.

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ABSTRACT

The mechanical properties (toughness, Vickers hardness, Young's modulus, index of rigidity, index of brittleness, etc.) of four ceramic glazes (two transparent, one matt and one opaque), obtained from frits commonly used in ceramic wall tile manufacture, were determined.

The values obtained were compared to each other, in an attempt to relate them to the mechanical behaviour of the glazes studied.

1.- INTRODUCTION

When an external force is applied to a solid material for a sufficient length of time, it can react in different ways. For low force values, the solid responds elastically, recovering its initial shape as soon as the applied force ceases. If it increases, the material may undergo deformation which will not entirely disappear when this force ceases (plastic behaviour). On crossing a certain applied force threshold value, fracture of the solid takes place.

A force-deformation graph is shown in Figure 1, in which the three stages described can be seen. The extension of the deformation interval each of them covers, depends on the nature of the naterial.

Certain characteristics of solid materials, such as deformability, wear resistance, ease of fracture, etc., on which their way of behaving depends in service, are closely related to some of their mechanical properties (1, 2), listed in Table I, together with the symbols normally used to designate them (1, 3, 4).

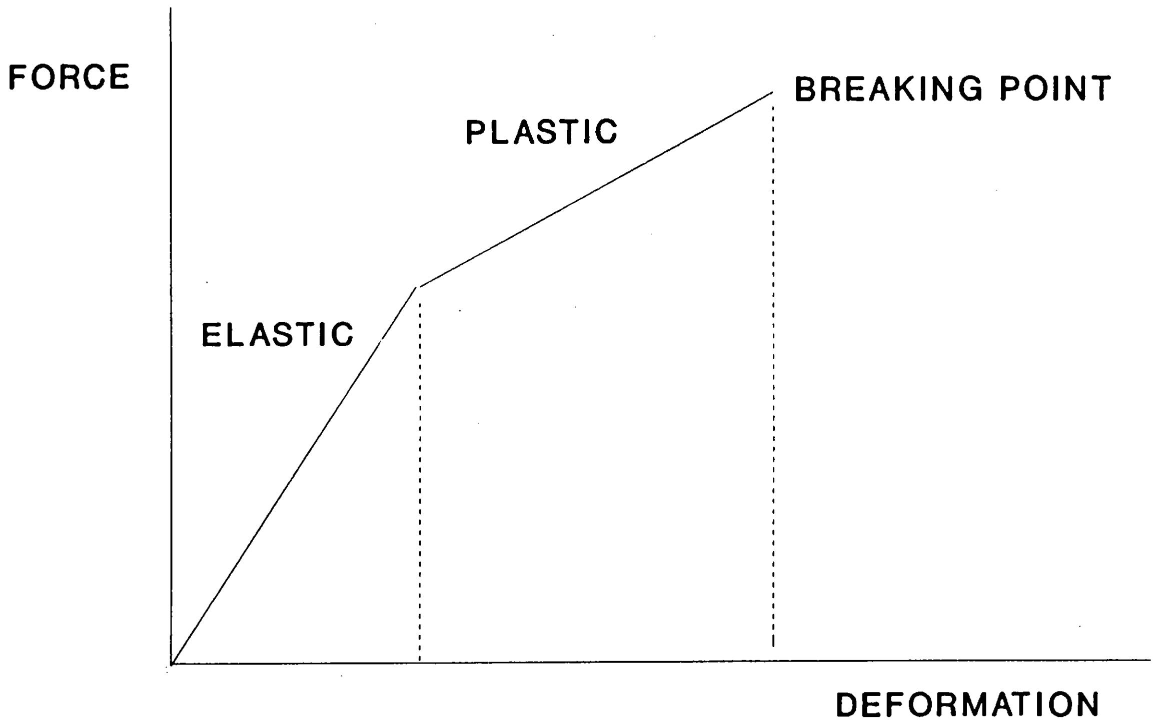

Figure 1. Mechanical behaviour of a solid.

Table I

Intrinsic breaking strength (toughness)	K_{Ic}
Vickers microhardness	H
Young's modulus (MPa)	E
Threshold indentation size	a_c
Index of rigidity	H/E
Index of brittleness	H/K_{Ic}

In fact, deformability of any solid, is related to Vickers microhardness, Young's modulus, and the index of rigidity. On the other hand, its greater or lesser tendency to fracture depends on toughness, breaking load and brittleness index. The boundary between deformation and fracture can be determined from the value of the parameter a_c, which represents the bound beyond which the material is no longer deformable and breaks (4). Similarly, this all has to be applicable to ceramic glazes, to which the following may be associated in the case of these materials:

a) tendency of the glaze to craze and crack, as a result of curvature of the ceramic ware (*), with its toughness, brittleness index and mechanical strength.

b) wear resistance with its toughness and index of rigidity.

Therefore, if the value of the mechanical properties is known or determined, it will be possible to predict the response or behaviour of ceramic glazes in the face of external actions as described above.

On trying to obtain a qualitative or quantitative relation between the behaviour of ceramic glazes and the mechanical properties defined above, it should not be forgotten that ambient conditions (moisture and temperature) have a considerable effect on them (6). This circumstance must be taken into account on setting the conditions for experimentally determining these properties, so that comparisons can be set up between the mechanical property values found for different ceramic glazes.

(*) Curving of the ware may be due to differences between the coefficients of thermal expansion of the glaze and the body during firing, or to the expansion of the body as a result of moisture absorption after being installed (5).

2.- AIM AND SCOPE OF THE STUDY.

In view of the foregoing, a series of experiments was programed for development in sequent stages, in order to achieve the following aims:

i) Establishing optimal conditions for test piece preparation and trials, so that the values of the mechanical properties measured for a glaze will be reproducible.

ii) Attempting to relate the values of the mechanical properties corresponding to different ceramic glazes, to their behaviour in the face of different external workings acting upon them: impacts, wear by abrasion, pressure, body/glaze stress, etc.

3.- MATERIALS AND EXPERIMENTAL PROCEDURE

3.1.- Materials.

Four frits were used, chosen from among those commonly utilized in the ceramic wall tile sector. Their composition is listed in Table II.

	Glaze A	Glaze B	Glaze C	Glaze D
SiO_2	59.5	53.0	53.0	40.6
Al_2O_3	6.5	7.0	9.5	2.6
B_2O_3	3.4	5.5	---	32.0
CaO	13.5	9.0	6.5	8.4
MgO	---	3.0	1.0	1.1
Na_2O	0.5	0.5	2.5	15.0
K_2O	2.5	3.0	3.3	0.3
ZrO_2	---	10.0	---	---
BaO	5.5	---	7.9	---
ZnO	8.6	9.0	16.3	---

Table II.- Chemical composition of the frits used (wt%).

In Table III the experimentally computed values are detailed corresponding to the four tested frits: transformation temperature (Tg), softening point (Tr) and flow point (Th). In Figure 2, the curves for viscosity (μ) versus temperature of the frits tested are reported, obtained by fitting the experimental values for this property by means of the Vogel-Fulcher-Taman equation.

FRIT	Tg (°C)	Tr (°C)	Th (°C)
A	663	778	1218
B	647	748	1165
C	605	740	1147
D	540	589	823

Table III.- Characteristic temperatures of the tested frits.

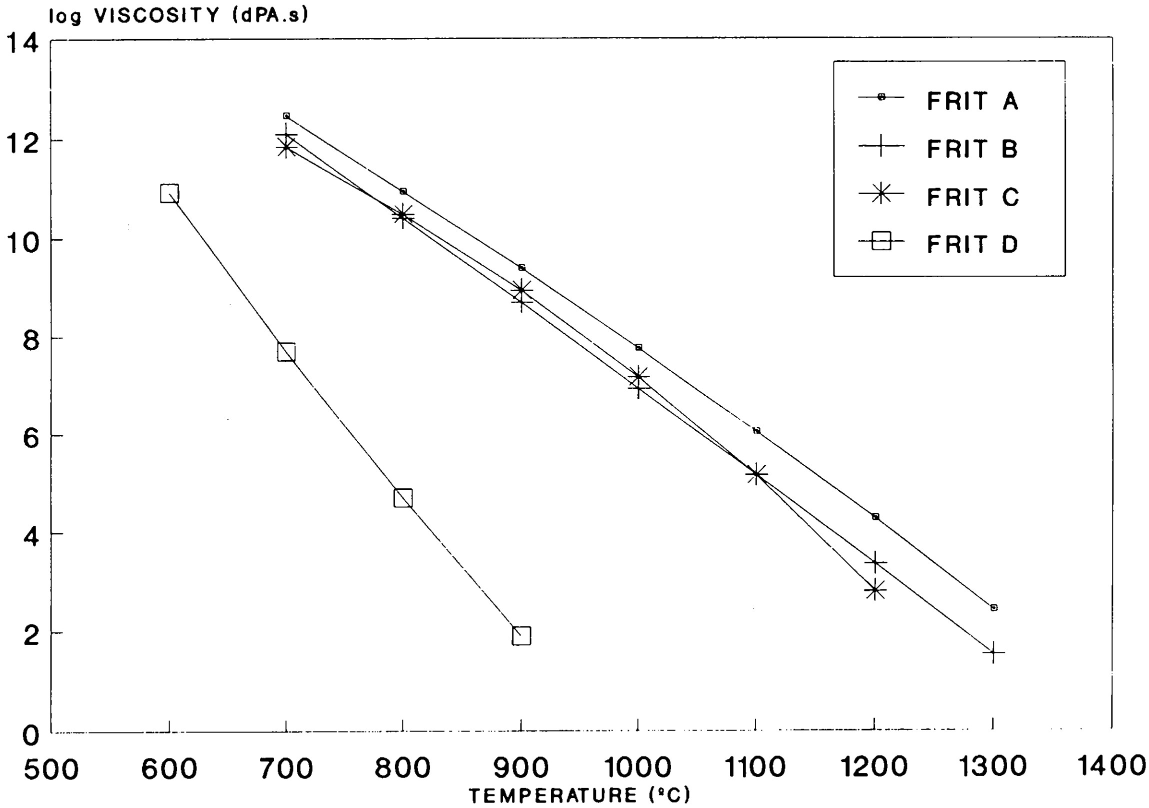

Figure 2. Viscosity-temperature curves.

3.2.- Experimental procedure.

3.2.1.- Sample preparation.

The frits were subjected to wet grinding in fast laboratory mills, with acetone. After drying the samples, they were wetted with an aqueous polyvinyl alcohol solution. Test pieces measuring 80x30x4 mm^3. were pressed, from the resulting powder of each frit, at a pressing pressure of 300 kg/cm .

3.2.2. Firing cycles used.

The shaped test pieces were fired according to the thermal cycles listed in Figure 3. The peak temperature used was different for each kind of frit tested, so that the resulting fired glaze test pieces would show under 5% porosity, while holding their dimensional characteristics. Table IV details these maximum temperatures.

Table IV.- Maximum firing temperatures used

GLAZE	TEMPERATURE (°C)
A	925
B	960
C	850
D	680

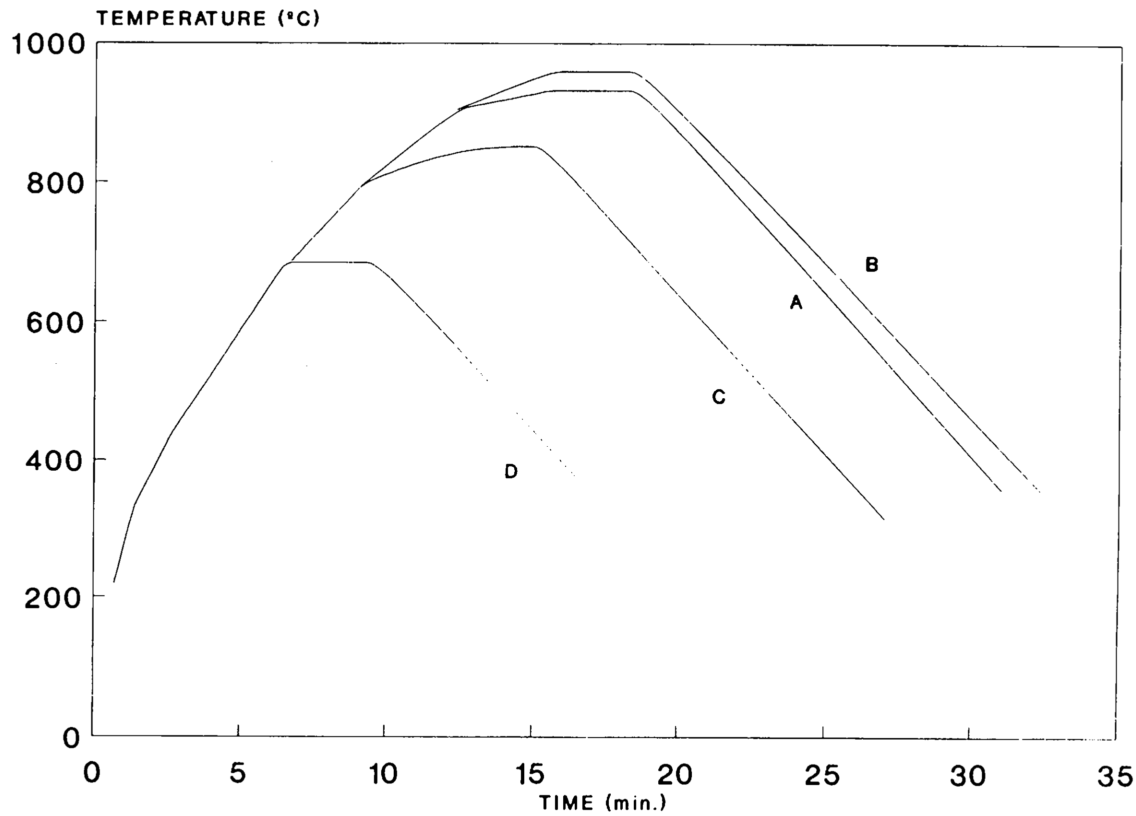

Figure 3. Firing cycles used.

3.2.3.- Determination of microhardness

The Vickers hardness of the glaze test pieces was determined by means of a LECO CORPORATION microdurometer, M-400, with a standard Vickers indenter and an adapted optical microscope, loading at 300, 500 and 1000 grams, with an application time of 15 s.

3.2.4.- Determination of mechanical strength and Young's modulus.

Young's modulus and mechanical strength were determined in test pieces previously indented with the microdurometer, by means of a 3-point cross-bending test (Figure 4), in which an INSTRON universal testing machine was utilized, deformation of the pieces being measured by a calibrated extensometer. The test pieces were horizontally placed in the measuring device, so that the previously indented surface remained face downwards. The distance between the supporting points (l) was 60 mm, and load application rate (c) was 1 mm/min.

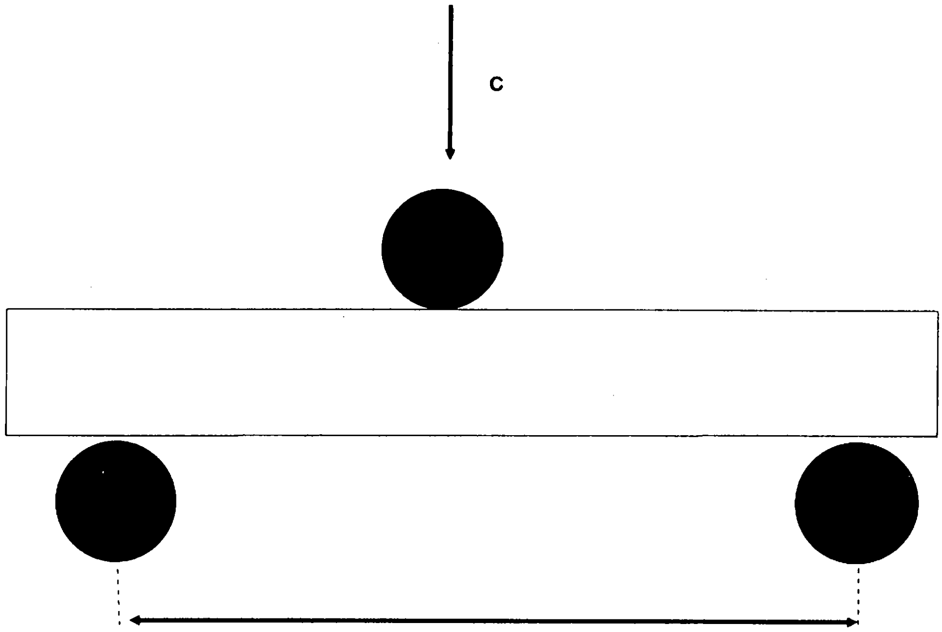

Figure 4. Scheme representing the position of the piece in the cross-bending test.

3.2.5.- Computation of K_{Ic}.

K_{Ic} was computed by using the equation (9):

$$K_{Ic} = \delta \left(\frac{E}{H} \right)^{0.125} (\sigma P^{1/3})^{0.75} \qquad [1]$$

where:

δ = cte = 0.59
σ = mechanical strength (MPa)
P = indenter load (N)
K_{Ic} = intrinsic breaking strength ($MPa{\cdot}m^{1/2}$)

E and H have already been defined.

Using this equation circumvents the difficulty of having to measure crack lengths appearing on indenting the sample in the microdurometer, as crack length size is to be determined prior to computing K_{Ic}, when other correlations are used (3, 4, 8). The accuracy and reliability of the above equation for computing K_{Ic} has been demonstrated by different workers in different studies (3, 8).

4.- RESULTS AND DISCUSSION

4.1.- Preliminary tests.

As K_{Ic}, according to Eq. [1], depends on the value of the product ($\sigma P^{1/3}$), an attempt was made first of all, to determine the possible variation of this product on modifying the indentation load (P), in order to establish suitable conditions for using the microdurometer. Figure 5 reports the values of ($\sigma P^{1/3}$) obtained, versus the values corresponding to the tested indenter load. As may be observed, this product hardly varies with the indenter load in the load interval ranging from 0.3 to 1 kg, in the specific case of the glazes obtained from frits A and B.

As the product ($\sigma P^{1/3}$) remained virtually invariable in the indenter load interval studied, on interpreting the findings throughout this study, all the measurements conducted with the micodurometer were considered valid, as long as the load applied to the indenter remained within the indicated interval.

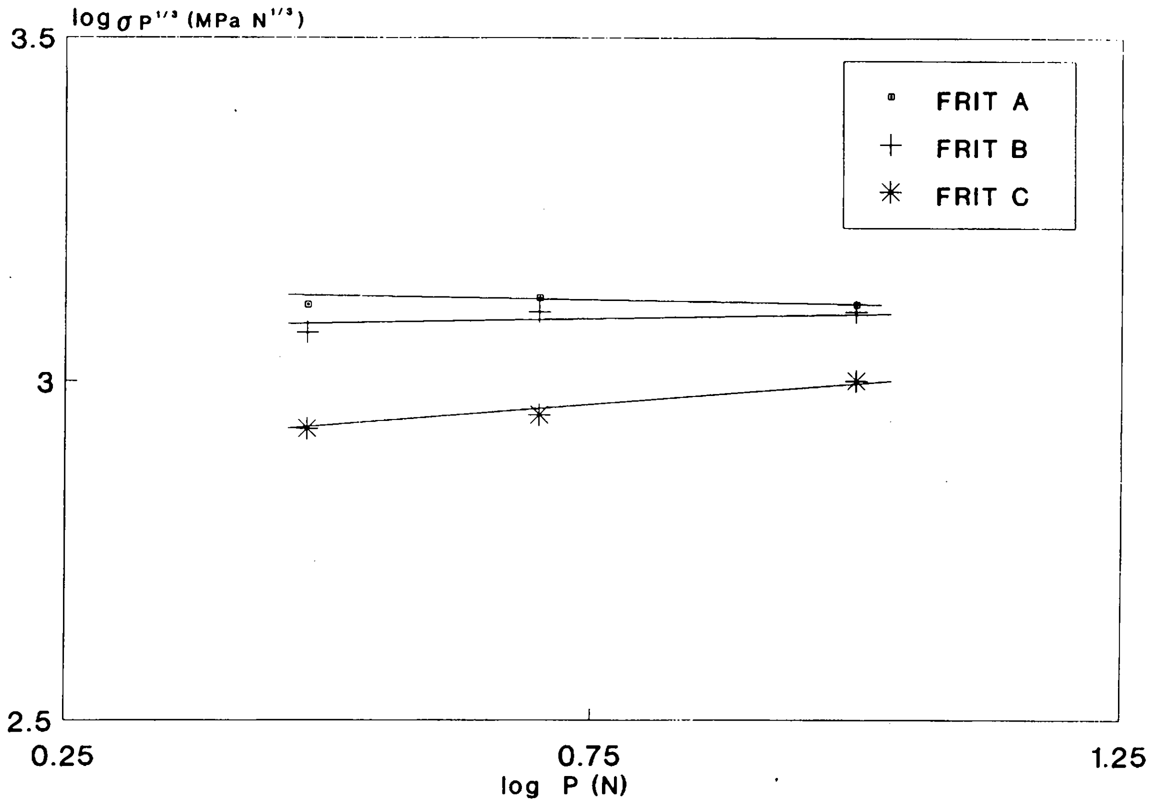

Figure 5. Relation between the product $\sigma P^{1/3}$ and the indenter load.

4.2.- Influence of ambient conditions on the value of the mechanical properties.

A set of experiments was carried out with a view to studying the possible influence hydration of the glaze has on the value of its mechanical properties.

With this aim, four different tests were carried out by using the fired test pieces prepared from frit C, modifying in each the conditions to which the glaze test piece was subjected prior to experimentally determining its mechanical properties. The sequential treatment the fired test pieces underwent in each test is described below:

Test 1 - Oven dried at 110°C, indentation, exposure to ambient for 15 minutes and cross-bending test.
Test 2 - Oven dried at 110°C, indentation, immersion in oil for 15 minutes and cross-bending test.
Test 3 - Immersion in water at 25°C, indentation, exposure to ambient for 15 minutes and cross-bending test.
Test 4 - Oven dried at 110°C, indentation, immersion in water at 25°C for 15 minutes and cross-bending test.

Table V details the values of K_{Ic} and σ found in each test for identical test pieces. In all these tests, microhardness was determined with an indenter load of 500 grams.

Table V.- Influence of ambient conditions on mechanical property measurements.

Test conditions	σ(kg/cm)	K_{Ic} (MPa$^{1/2}$)
1	623	0.82
2	739	0.93
3	574	0.77
4	582	0.78

As may be observed, the treatment to which the glaze test pieces were subjected prior to experimentally determining their mechanical properties, considerably influences the values obtained. On remaining in contact with ambient atmosphere or on wetting (tests 1, 3 and 4), the glaze test pieces yielded lower mechanical strength (σ) and toughness (K_{Ic}) values than when the dry test pieces were immersed in oil. It should be pointed out, that a drop of 30% in mechanical strength took place in the conditions in which tests 3 and 4 were carried out (with a stage involving immersion of the test piece in water), compared to the conditions in which test 2 was run. Likewise, toughness fell considerably (about 15%). This behaviour might be explained by the fact that the mechanical properties of glasses undergo considerable modifications on hydrating (6). In view of the findings, it was decided to carry out measurements in accordance with test-2 conditions, in order to eliminate the influence of any possible glaze hydration on the values of the properties to be determined. By conducting all the measurements according to a perfectly reproducible procedure, the values which were determined were guaranteed not to be influenced by ambient conditions.

4.3.- Mechanical behaviour and properties of the glazes studied.

Table VI details the values of the mechanical properties obtained for the four glazes studied, as well the values of the moduli (H/K_{Ic}), (H/E) and a_C defined above.

The value of the modulus a_C was determined from the graph $a_c=f(K_{Ic})$ proposed by Marshall and Lawn (4), based on utilizing the equation:

$$a_C = \beta \left(\frac{K_{Ic}}{H} \right)^2 \qquad [2]$$

where ß α E/H

The values of the mechanical properties of three other different materials, also of a vitreous nature, a Pb/Na glass, another Si/Al glass and a glass-ceramic product, taken from the literature (8), have also been included in the same table for comparative purposes.

	Glaze A	Glaze B	Glaze C	Glaze D	Pb/Na glass(*)	Si/Al glass(*)	Glass-ceramic(*)
H (GPa)	5.6	5.7	6.3	5.2	4.9	6.6	8.4
E (GPa)	49.5	64.8	57.8	58.8	65.0	89.0	108
σ (Kg/cm^2)	527	874	738	651	-	-	-
K_{Ic} (MPam$^{1/2}$)	0.71	1.13	0.95	0.86	0.68	0.91	2.5
(H/E)	0.11	0.09	0.11	0.09	0.08	0.07	0.08
(H/K_{Ic}) (m$^{-1/2}$)	7778	5000	6663	6093	7206	7253	3360
a_C (μm)	0.490	1.488	0.954	1.056	0.819	0.822	3.645

(*) Values found by G. R. Anstis et al. (8)

Table VI.- Mechanical property values.

Firstly, in Figure 6, log (H/K_{1c}) vs. log a_c were plotted in accordance with Eq.[2] for the four frits tested and the other three above-mentioned glassy materials. As was to be expected, all values fit a straight line quite well, with negative slope (-1/2), a result confirming what was found for glasses and glass-ceramics by Anstis et al. (8).

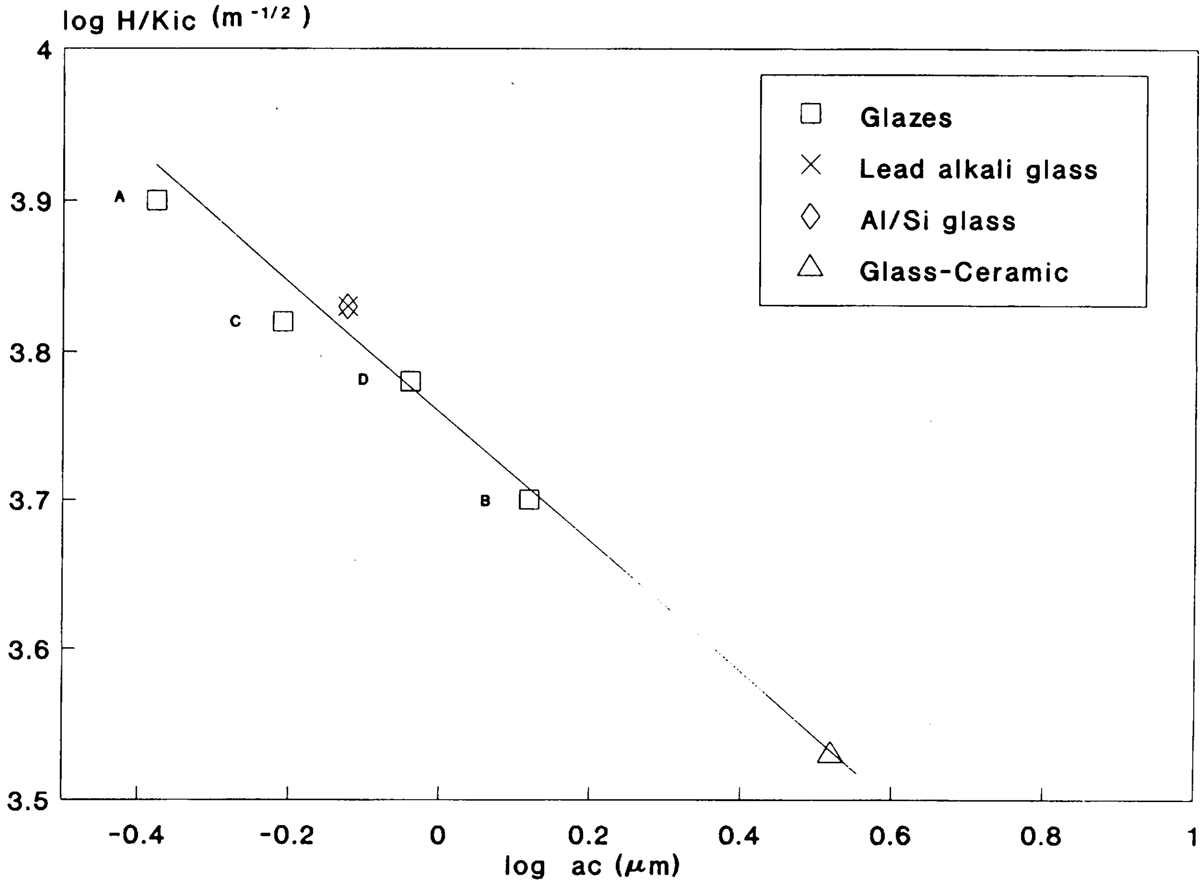

Figure 6. Relation between the ratio (H/K_{1c}) and ac.

It may be deduced from this plot and from the values in Table VI, that the mechanical properties corresponding to the glaze obtained with frit B are those which most approach those of the glass-ceramic material. This finding is not surprising, as zirconium silicate and oxide crystal formation has taken place in the glaze obtained in frit B, which was rich in zirconium oxide, in the vitreous phase, a structure like that shown by a glass-ceramic material, although this has a greater amount of crystalline phase.

In Table VI, the glazes obtained from frits A and B may be observed to yield the same Vickers hardness, but show different indices of brittleness and rigidity, so that their mechanical behaviour will differ noticeably. It may be concluded from this, that the simple comparison of Vickers hardness in these two glazes is not enough to predict their mechanical behaviour.

Glaze B (opaque), is the toughest of all, so that in principle it should undergo less deformation on loading and be able to withstand a greater force before fracturing than the other three. Similarly, due to its lower index of brittleness and greater mechanical strength, it should show less tendency to develop crack formation and crack growth, this being a phenomenon related to wear by abrasion.

These predictions have been confirmed on an industrial scale, as opaque zirconium glazes, like the B glaze studied, have been seen to yield quite high abrasion resistance and breaking strength values, showing little tendency to develop crazing, for a specific body/glaze stress.

On comparing the mechanical properties of the opaque B glaze studied to those of the transparent glazes (A and D), the latter are observed to yield considerably lower toughness values than glaze B and higher brittleness index values, for almost identical Vickers hardness values. This finding suggests that the transparent glazes have less abrasion resistance, impact resistance and breaking strength than opaque zirconium glazes, which has also repeatedly been shown in practice.

Finally, glaze C (matt) yields mechanical properties halfway between those of transparent and those of opaque glazes, as is to be observed in Table VI, so that their mechanical behaviour should be halfway between both. This is due to similar crystallization development taking place in matt glazes to that which develops in opaque glazes and in glass-ceramics, although the crystalline phases formed are of a different nature, less hard and resistant. Moreover, the crystalline phase which forms is found in smaller amounts than in opaque glazes and glass-ceramics materials.

On comparing the properties of the Pb/Na and Si/Al glasses to each other, they are observed to yield similar values for the indices of rigidity and brittleness, whilst values for microhardness, toughness and Young's modulus, differ substantially. In this case, the Si/Al glass, on being tougher with higher Young's modulus, will show better performance with regard to deformation, as it is more elastic than the Pb/Na glass.

From the foregoing it may be concluded that predicting the behaviour of a glaze with regard to deformation and fracture requires its fullest possible characterization, determining all the mechanical properties highlighted in this study, as knowledge of only some of them will provide insufficient data and can lead to mistaken conclusions.

5.- CONCLUSIONS.

A series of mechanical properties were determined as well as the moduli related to the mechanical behaviour of four ceramic glazes obtained from four frits, chosen among the ones most commonly used in the ceramic wall tile subsector. On analyzing the findings, the following may be concluded:

- The great influence that ambient conditions, specifically moisture, have on the values of mechanical properties, has been clearly demonstrated.

- The glaze obtained with frit B (opaque, made of zirconium), bears different mechanical properties to those of the glazes obtained from the remaining frits tested, with values approaching those of a glass-ceramic product.

- The mechanical properties of glazes obtained from the other three frits (two transparent and one matt) yield values quite close to those found in the literature for glasses with different compositions.

- A qualitative relation has been observed between the mechanical properties of the glazes and their behaviour in the face of the external stresses to which they were subjected.

- The values of all the mechanical properties described in this study are to be determined, in order to dispose of enough data to be able to predict the mechanical behaviour of glazes. Knowledge of only some of them is not enough.

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