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ON THE MEASUREMENT OF THE ELASTIC MODULUS OF A VITREOUS COATING ON A TITANIUM SUBSTRATE BY THE RESONANCE METHOD.

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We have synthesized a biocompatible glass that, when used as a glaze, allows wetting and adhesion on a titanium substrate. The elastic modulus of this glaze cannot be measured isolately. It is possible to calculate the modulus of the vitreous coating by measuring the resonance frequencies of a titanium plate before and after the deposition of the glaze. The values obtained can be compared to the modulus of elasticity of bulk glass. The evolution and the dispersion of the calculated modulus values are followed in function of the density for three different coatings.

1. INTRODUCTION.

The measurement of the elastic modulus is essential in order to caracterize completely the mechanical behaviour of a coating. The residual stresses and the adhesion properties of the coating cannot be described quantitavively without precise modulus values.

The elastic modulus of a coating cannot be measured isolately unless the coating can be detached from the substrate. Different methods have been proposed in the literature : four point bending test with constrain gauges[1] or indentation tests[2,3]. The resonance frequency method[4,5,6] presents the advantage to be non-destructive and rapid.

However, the calculation of the modulus of a thin coating by the resonance frequency is not so evident because this method is all the more sensitive to the thickness of the coating. The problem is worsened when the elastic modulus of the substrate and that of the coating have close values. We compared the moduli calculated by two different models proposed by List & McKee[5] and Chandra & Clyne[4] for three different kinds of coatings presenting moduli of the order of 70, 45 and 30 GPa.

In the present orthopaedic practice, the hip prosthesis is attached to the femur by means of a tail covered with a plasma-sprayed hydroxylapatite overlayer aiming at favouring bone ingrowth. The adhesion between sand-blasted titanium and the ceramic is essentially of mechanical nature. We have synthesized a glass which wets both titanium and hydroxylapatite and exhibits chemical adhesion to titanium. The work of Pask[7] indicates that a glass wets a metal if it is saturated by the metal oxide. Thus, in order to obtain good wetting of the titanium substrate, the composition of our glass is based on SiO_2, B_2O_3, Na_2O and TiO_2, with a minimum content of 10 wt % TiO_2. Adhesion between glass and titanium is obtained after enameling if the substrate is preoxidised during 1 hour at 700 °C. It is due to the diffusion of the oxide layer into the glass during thermal treatment, as previously described[8,9].

2. MATERIALS AND METHODS.

The glass was synthesized by fusion of a mixture of SiO_2, $Na_2B_4O_7$, Na_2CO_3 and TiO_2 powders in an electric furnace at 1100 °C during 6 hours. This hot glass was then poured in water and crushed in a planetary ball mill to obtain a fine powder. After sieving, the fraction of powder with particle size less than 50 µm was retained. The dimensions of the titanium plates used as substrates are 60 x 10 x 1 mm. The plates are preoxidized in air during one hour at 700 °C so that an oxide layer of 1 to 2 microns thick is formed on the surface. The glass powder was dispersed in methylethylketone (MEK) and the green coatings were obtained by sedimentation during 12 hours on the preoxidized titanium plates. After drying, the samples were fired.

The first kind of coating (A) is obtained with a fluid glass that gives dense coatings after enameling in air during 5 minutes at 700 °C. The second kind of coating (C) is fired in N_2 atmosphere at 700 °C without preoxidation of titanium substrate and resulting to this treatment, it is very porous. The third kind of coating (B) of intermediate porosity is obtained with a less fluid glass which presents a higher transition temperature (Tg) and is fired in air at 730 °C. This glass, made from the same oxides, is of higher B_2O_3 and SiO_2 contents and lower Na_2O content than the glass used for coatings A and C.

The thicknesses of titanium plates and of composite beams (plate + coating) were measured with a micrometer and by the Archimedean method. The density of the titanium substrate and of the coating were determined by the Archimedean method. On some samples, several layers of glass have been deposited successively to determine the influence of the coating thickness on composite resonance frequency. We measured also the modulus and density of the first glass composition on a beam prepared by sintering glass powder at 700 °C.

To assess the accuracy of the calculated modulus, we glued together titanium and glass plates (slides for microscopy) of 1 mm thickness whose moduli had been measured isolately. We used a cyanocrylate glue whose thickness is about 20 μm and can thus be neglected.

The resonance frequency in bending of the titanium substrate before preoxidation and of the composite beam was measured by means of a "Grindo-Sonic" equipment developed by Lemmens n.v.

Elastic modulus of titanium substrate is readily calculated from the classical expression of Spinner and Tefft[6] : $E = 0{,}94642\ (\rho\ L^4\ f^2\ \Gamma / h^2)$ where ρ is the density, L and h are specimen length and thickness, f is the resonant frequency and Γ is a dimensionless shape factor.

We used two models for calculating the coating modulus.
First, the method of Chandra and Clyne[4] (model 1) is based on the displacement of the neutral axis due to the presence of the coating and on the composite beam stiffness. A quite complex expression allows the calculation of the coating modulus. Secondly, the formula proposed by List and McKee[5] (model 2) expresses the coating modulus directly in function of resonance frequency, thickness and density of the substrate and of the composite beam :

$$E_g = \frac{1}{3}\left\{ \frac{2(f_c - f_{Ti})}{f_{Ti}} \frac{h_{Ti}}{h_g} + \frac{\rho_g}{\rho_{Ti}} \right\} E_{Ti}$$

3. RESULTS.

Precise measurement of the coating thickness is the major problem. The thickness of the coating is of the order of 50 to 80 microns. The layers obtained by sedimentation are thinner on the edges of the samples. The thickness values obtained by the Archimedean method and by the micrometer can differ by up to 20 %. The micrometric measurement overestimates the thickness because of the slight roughness of the glass surface. The Archimedean method supposes that the thickness of the coating is perfectly homogeneous, which is not the case. It gives thus an underestimation of the thickness.

Densities of the three kinds of coating are different. The mean values are around 2,45 g/cm^3, 2,10 g/cm^3 and 1,7 g/cm^3 for coatings A, B and C, respectively.

Elastic moduli were calculated with the two models and the results were compared. For each sample, we calculated the moduli corresponding to the minimum and maximum coating thicknesses, which were obtained by the Archimedean and micrometric measurements, respectively. The mean value of the modulus was then deduced.

Figure 1 shows the evolution of this mean modulus value as a function of the density of the three coatings according to model 1. The error bars give the minimum and maximum values of the calculated modulus. The same graph was obtained with model 2, but we observed that the mean value calculated with model 2 is systematically higher than that obtained by model 1. The dispersion of the results is quite important, but decreases with the modulus value.

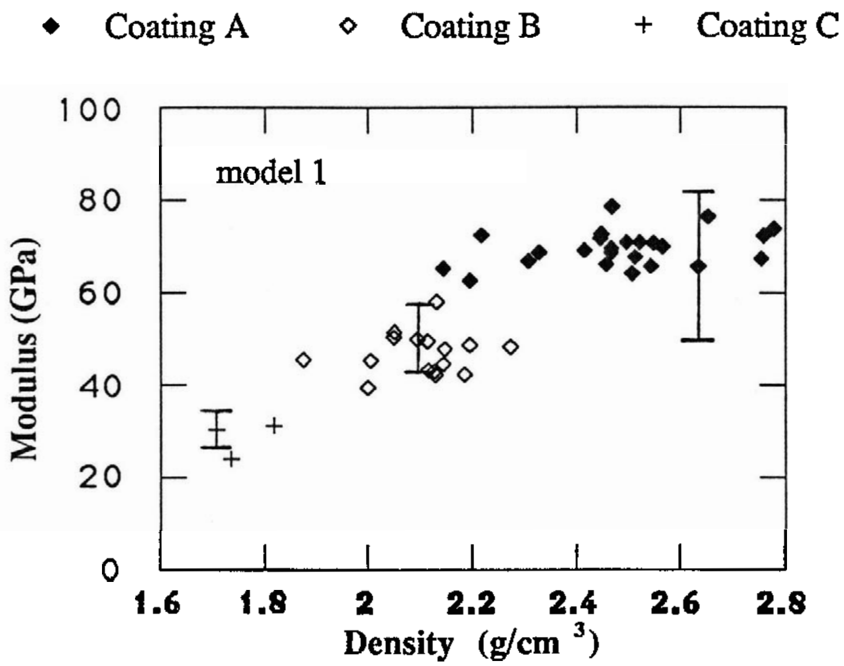

FIGURE 1
Mean value of modulus in function
of density of the coatings (model 1)

Figure 2 shows for the coating A that the difference between the two extreme values of the moduli is proportional to the difference between the maximum and the minimum values of the thickness. The formulations of model 2 seems to be less sensitive to thickness dispersion than that of model 1.

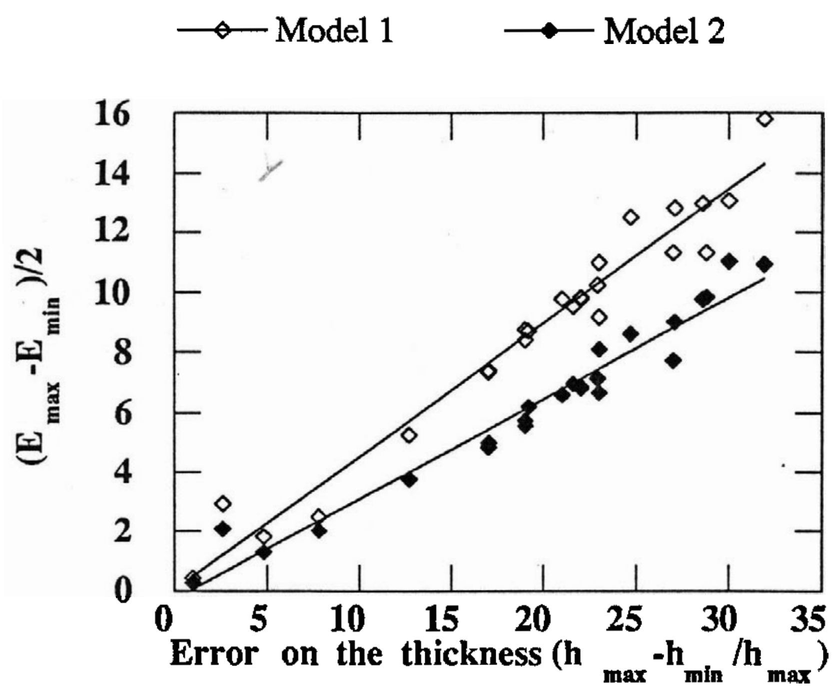

FIGURE 2
Comparison of the dispersion on values of moduli
vs the thickness error with the two models.

We compared the modulus of the vitreous coatings A with the modulus measured on beams of the same glass composition obtained by sintering of glass powder. This modulus was also calculated by means of the resonance frequency method. We obtained a value of 71 GPa for a density of 2,54 g/cm^3. This value is close to the mean value obtained for the vitreous coatings A of comparable density.

According to model 2, the evolution of the frequency of a composite beam as a function of the coating thickness is linear :

$$f_c = f_{Ti} + \frac{f_{Ti}}{2h_{Ti}}\left(\frac{3E_g}{E_{Ti}} - \frac{\rho_g}{\rho_{Ti}}\right)h_g$$

Samples were prepared by sedimentation and firing of successive glass layers on the same plates. As shown on figure 3, the two slopes corresponding to Archimedean and micrometric thickness measurements give two extreme values of modulus. The modulus mean value and the difference between the lower and the higher values of the moduli are of the same order as if they were calculated on each layer separately. The mean value calculated with model 1 is still lower than that calculated by use of model 2.

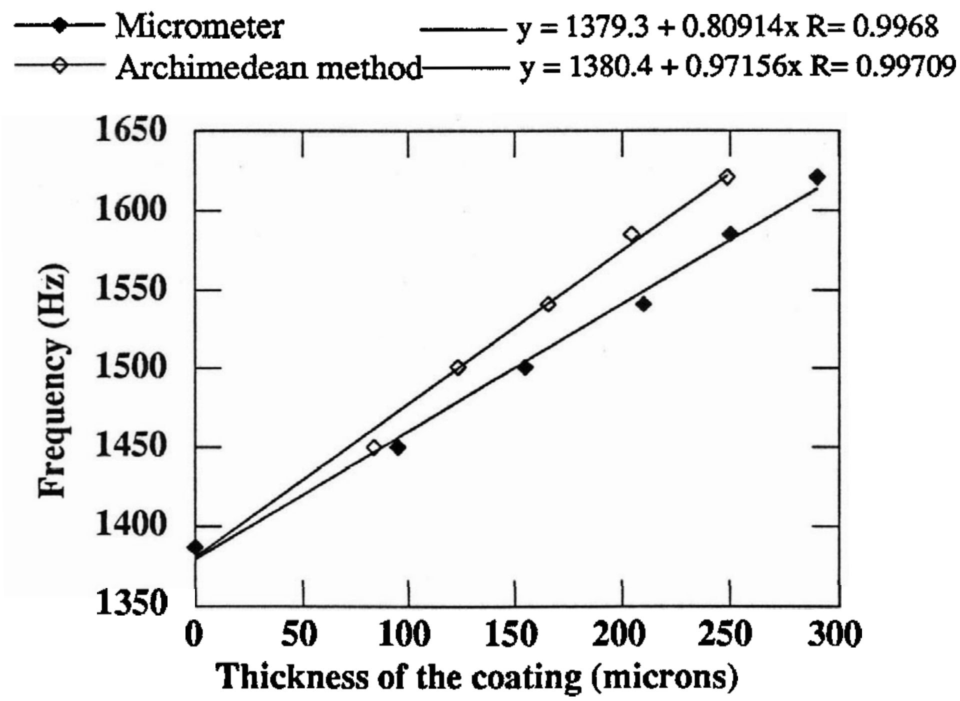

FIGURE 3
Evolution of the composite beam frequency
in function of the coating thickness.

4. DISCUSSION.

As expected, modulus value decreases with density of the coatings. This evolution is evident between the three kinds of coatings, but less obvious inside the same group of coatings.

We can wonder which formula gives the more accurate value of the modulus. If we compare the modulus measured on the glass beams and on the coatings of comparable densities, if seems that the model 1 gives more accurate values. To verify this conclusion, we measured separately the resonance frequency of titanium and glass plates both 1 millimeter thick and we calculated moduli of 105 GPa and 69 GPa respectively using the classical formula for the bending of plates[6]. The two plates were then glued together with a cyanocrylate glue. We calculated the modulus of the glass plate, considered as an unknown coating, using the same formula as previously. The model 2 gives a value of 92 GPa and the model 1 a value of 69 GPa.

The lack of precision on thickness measurement gives dispersion on modulus values calculated by the two models. The difference between the lower and the higher values of the moduli decreases, for the same error on thickness, when the mean value of modulus decreases (figure 4).

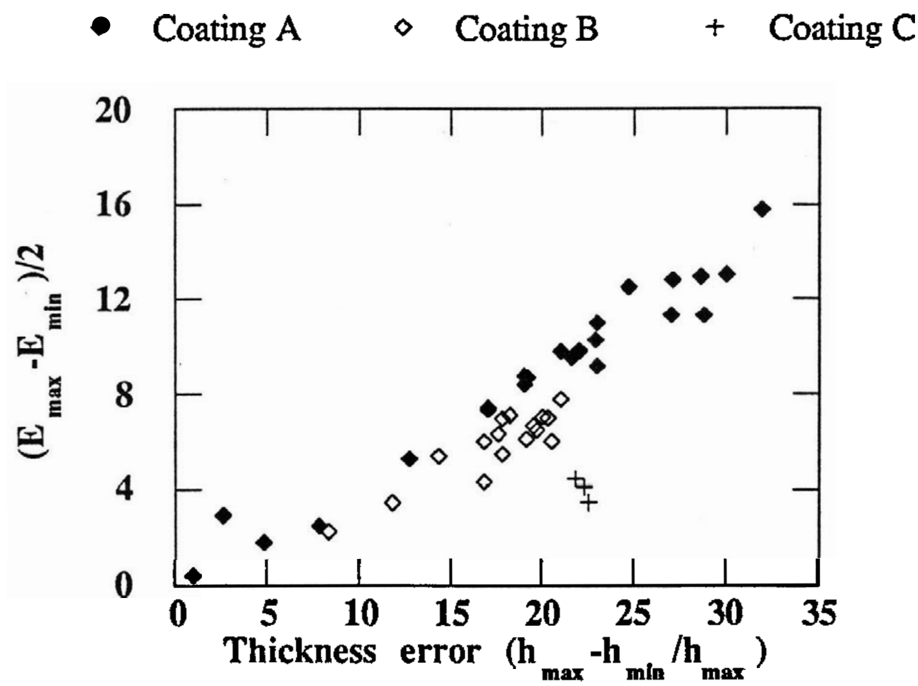

FIGURE 4
Evolution of the error on modulus value
for the three kinds of coatings.

This means that the absolute error on modulus decreases, but that the relative error is constant as the modulus value becomes lower.

5. CONCLUSION.

The accurate measurement of the thickness is the most influent factor which affects the precision of calculated modulus value with both formulas. Model 1 gives systematically a lower value of elastic modulus than the model 2. Moreover, model 1 seems to give more accurate value of modulus.

The sensitivity to thickness errors increases when the difference of moduli between the substrate and the coating decreases.

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