THEORETICAL APPROXIMATION OF GLAZE MECHANICAL STRENGTH FROM INFRARED SPECTROSCOPY MEASUREMENTS

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ABSTRACT

Infrared spectroscopy (FT-IR) is a widely used technique for glass characterisation. The immense majority of the studies performed by IR have focused on the structure of glasses and its variation with composition or treatment. However, the IR spectra also allow predicting other glasses properties like the modulus of elasticity (Young's modulus) using the Einstein model which relates bond vibration frequency to elastic properties.

In this study IR spectroscopy has been used to analyse the structure of ceramic glazes and predict their moduli of elasticity. The glazes studied have been of the Si-Ba-Ca-Mg-Al-K system in which the relations Si/Ba, Al/Ba, Mg/Ba and K/Ba have been varied. The resulting FT-IR spectra have been deconvoluted, obtaining the bands necessary to make the mentioned calculations. The results show the influence that each element has on the elastic properties, the variation being greatest for those elements that are glass structure formers like Si and Al.

1. INTRODUCTION

In recent years the number of frits required for the different demands of new types of tile glazes has grown significantly. In many such cases it is sought to achieve better mechanical properties for which it is necessary to perform long and tedious sample preparations and measurements to obtain representative values. In this study, it is attempted to demonstrate how FT-IR spectroscopy enables predicting mechanical strength values, in particular Young's modulus of ceramic floor and wall tile glazes.

2. THEORY

The elastic modulus (E) can be determined from measurements of the resonance frequencies of materials according to the following equation:

$$E = C\ M\ \nu^2 \qquad (1)$$

where C is a constant dependent on the size and form of the sample and on Poisson's ratio, M is the mass of the solid and ν the normal mode of vibration of the bond determined by FT-IR. The resonance frequency in absence of stresses is found from the following equation [1]:

$$\nu = k\ (t\ /\ L^2\ )\ (E\ /\ \rho\ )^{1/2} \qquad (2)$$

where k is a constant, t the thickness of the sample and L the length between the fixing points of the sample for the determination of the modulus. This expression is slightly different when a given stress σ is applied.

On the other hand, the relation has been described between the vibration frequency ν and thin film thickness in terms of the simple harmonic oscillator:

$$\nu = n\ /\ 2\ d\ c\ (E/\rho)^{1/2} \qquad (3)$$

where d is bond distance and n the vibration mode [2]. Therefore, we can express the relation between the longitudinal vibration frequency and E in the following way:

$$\nu = k\ (E\ d\ /\ \mu)^{1/2} \qquad (4)$$

where μ is now the reduced mass of atoms involved in the bond vibration. The longitudinal vibration mode is the most appropriate mode for the determination of E, since it is parallel to the direction of the infrared radiation wave, so that it reproduces on a small scale the classic determination of the mechanical properties of solids. The local configuration of the bonds is very important in the determination of E, since the distance of the Si-O bond and the Si-O-Si angle varies with the number of components of the silica ring [3,4] and in addition, it is necessary to consider the influence of the porous structures in the infrared spectrum of silica [5].

3. EXPERIMENTAL

The glazes analysed by FT-IR were prepared from frits using an industrial firing cycle. A glaze has been used of reference composition: SiO_2=55, Al_2O_3=5, CaO=20, BaO=3, MgO=10, K_2O=7. Four types of modifications were performed on this glaze, varying the concentration of Ba with regard to Si, Al, K and Mg in percentages between 0 and 15%; the corresponding glazes have therefore been referenced Ba-Si, Ba-Al, Ba-K and Ba-Mg, respectively.

The FT-IR spectra were obtained on powder samples of the corresponding glazes by means of the dilution technique in KBr. An IR Perkin-Elmer 1760 X spectrophotometer was used, in the intermediate infrared, with a resolution of 2 cm^{-1}.

4. RESULTS

Figure 1 shows the FT-IR spectra of different glazes with respect to the reference Base. All the spectra are observed to be quite similar, as they contain similar concentrations of the network former. A very wide band appears at 1020 cm^{-1} and two small ones at 740 and 480 cm^{-1}. The band with the highest frequency corresponds to stress vibrations of the Si-O-Si bonds in the glassy network, whereas the other two bands correspond to bending vibrations inside and outside the plane [6]. The shift of these bands towards lower frequencies than those which correspond to silica or other classic glasses is due to the great number of network modifier elements existing in the glazes.

The values of E have been obtained with the position of the most intense band and equation (4). Figure 2 shows the evolution of E as a function of the BaO content in each studied glaze. It shows that E decreases when the content in SiO2 (Ba-Si) is diminished or when BaO is replaced with MgO (Ba-Mg); it remains constant when Al_2O_3 is replaced with BaO, and increases when BaO is replaced with K_2O. The evolution found is analogous to that expected for glasses with different modifier elements [7].

Figure 1. FT-IR of glazes. a) 15Ba/45Si ;
b) 15Ba/0Mg ; c) 8Ba/0Al ; d) 7Ba/3K

Figure 2. Values of E in the glazes.

5. CONCLUSIONS

In this work it has been shown that FT-IR spectroscopy enables obtaining quite similar values of the ceramic glaze modulus of elasticity to the ones determined by means of mechanical measurements. In addition variations are observed that are consistent with the glaze composition.

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