(Online First) Studying clay formulations for porcelain ceramics using simultaneous thermal analysis (STA) techniques

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ABSTRACT

In this study, modern simultaneous thermal analysis instrumentation is employed to obtain valuable thermal response behavior of a three primary component porcelain ceramic formulation containing kaolinite, feldspar, and silica. The silica component consisted of both crystalline quartz and amorphous silica. The thermal analysis data obtained in this study provide information related to the behavior of the raw materials in the mixture during the firing of the formulation to produce the porcelain product. The types of thermal analysis data obtained in this study were differential thermal analysis (DTA), thermogravimetry (TG or TGA), and derivative thermogravimetry (DTG). These data were obtained experimentally in our laboratory using a single computerized simultaneous thermal analysis (STA) instrument.

Keywords: thermal analysis; STA; DTA; TGA; ceramic raw materials; porcelain ceramics

1. Introduction

The thermal analysis techniques are used in the ceramic industry for more than one application or reason. First, it is possible to quantify some of the individual components of the formulation to be used in the firing process. Second, valuable information relating to the processing of the mixture to the final product may be obtained by observing the thermal response of the formulation while it is submitted to a temperature, or heating, program, which is similar to that employed in the firing in a kiln. When using the technique of DTA to follow the heating profile of the raw material mixture, one may observe the temperature at which polymorphic crystalline transitions, dehydration, and decompositions, as well as crystallization events. All of these thermal transitions are endothermic in nature except for the crystallization (or organizational) transitions which are exothermic and liberate heat. Thus, the DTA instrument response, in this case, is an upward or positive peak while the endothermic transitions are observed as a downward (△T) response on the DTA thermal curve. Glass transitions (Tg) observed in the heating of amorphous materials are observed as a negative, or downward, baseline shift in the experimental DTA thermal curve. This (△T) shift is a result of the increase in heat capacity when heating the material (or substance) in a specified temperature range.

The technique of DTA is known to be a very valuable tool for the ceramic laboratory. These instruments are available from several commercial vendors and several of them are capable of reaching temperatures as high as 1600° C. In the DTA experiment, two matched thermocouples e.g., Pt, Pt (10%) Rh) are employed for measuring the difference in temperature (△T) between the analytical sample and an inert reference, such as calcined alumina, as both are heated at a programmed heating rate. The difference signal is continuously monitored in such a manner that endothermic activity in the sample cup causes a negative △T signal and an exothermic event would exhibit a positive △T response. These differential (△T) responses are displayed on the ordinate axis of what is known as a "DTA thermal curve." These △T values are displayed versus the temperature (or time) at which the ordinate (△T) value were measured.
The technique of thermogravimetry (TG), or thermogravimetric Analysis (TGA), monitors the mass of the sample material as it is heated in a controlled atmosphere at a programmed heating rate. The TG thermal curve displays the mass, or percentage of the original sample mass, remaining in the sample pan at a particular (measured) temperature in the TG experiment. Most TG (or TGA) instruments have associated software which allows the conversion of the "TG thermal curve" to a derivative thermal curve (DTG). The DTG thermal curve represents the rate of mass loss (mass loss per unit time) versus temperature. This DTG thermal curve is very valuable in distinguishing multiple decompositions in the same temperature region. It also allows the assignment of the temperature at maximum rate of weight loss for a particular thermal mass loss event.

It should be stated that mass loss values for the thermal decompositions obtained from TG data are the most accurate quantitative results obtained when using thermal analysis methods. Also, it is possible to use or purchase instruments which perform both DTA and TG (TGA) simultaneously on the same analytical specimen. Such instruments are referred to as "STA" or "simultaneous thermal analysis" instruments. Such a STA instrument was employed in obtaining all DTA/TG thermal curves which are presented in this study.

2. Porcelain clay analysis using simultaneous thermal analysis

Whether a porcelain clay formulation is being used in the production of a commercial product, or an artistic creation, the ceramicist needs to ensure the quality of the finished product, and this depends in part upon the chemical and physical behavior of the formulation during the firing process. For example, in the firing of a porcelain clay object, the physical and chemical properties of the clay formulation determines whether the structure slumps as it is fired, whether there is cracking around sharp edges, and whether the final product is bright and translucent. In a process known for millennia, clay is heated to yellow heat where the components transform in a series of processes, as the "mud" is transformed into a useful vessel, or a beautiful piece of art. Therefore, the following thermal analyses are an attempt to characterize a clay formulation and its behavior during the firing process. It should be mentioned that STA methodology has been employed to characterize raw materials from the Bikaner region of India for use in the production of (firing to) electrical porcelain ceramic products (2).

2.1 Experimental

All STA thermal curves of this study were obtained using a Perkin-Elmer STA 8000 Simultaneous Thermal Analyzer. All DTA thermal curves were obtained using the DSC (differential scanning calorimeter) mode of the STA 8000 software. Thus, the ordinate scale is in heat flow, Watts per gram (W/g), units when using this data handling mode of the instrumentation. The instrument was calibrated with aluminum and gold standards using ASTM standard methods[6,13]. The mass measurement of the STA was calibrated using a NIST Class F 100 milligram standard weight. All data given were obtained using a heating rate of either ten or twenty degrees Celsius per minute. The sample size for these studies ranged from 50 to 150 milligrams and the atmosphere used in the analysis chamber was dynamic air diluted with high purity nitrogen. For optimum accuracy, an empty pan baseline was obtained for the instrument, prior to the sample analysis runs, and then subtracted from the sample data to minimize instrumental baseline effects.

2.2 Kaolinite clay raw material

The thermal characterization of kaolinite clays dates back to the first reported thermal analysis experiment which was performed by Le Chatelier (I) in 1887. Although the experimental method used only one measuring thermocouple embedded in the sample, the major thermal events that occurred were detected as the clay was heated to elevated temperatures. The features of a DTA thermal curve depend somewhat on the related physical properties of particle size distribution and degree of crystallinity of the kaolinite specimen being analyzed. Kaolinite specimens of small particle size and low crystallinity will have a larger amount of adsorbed surface water. This means that a dehydration endothermic peak is often observed at 100-160 degrees Celsius in the DTA thermal curve for kaolinite specimens of low crystallinity [9,10,11]. For this reason, both the refined kaolinite component, as well as the porcelain clay formulation, were dried at 140 degrees Celsius prior to analysis in the STA analyzer.

2.3 Dehydroxylation of kaolinite clays

The major endothermic peak in the DTA thermal curves at, or near, the range of 500 to 550 degrees Celsius, is also
affected by particle size distribution of the kaolinite clay. The smaller the size distribution, the narrower the width of the DTA peak. This endothermic dehydroxylation event will take place at lower temperatures for smaller particle size specimens than for those of larger particle size. Since smaller particles of the kaolinite will dehydroxylate during the transition at a faster rate than larger particles, the peak amplitude is increased somewhat with increasing fractions of the smaller particles.

2.4 STA thermal curves for kaolinite and porcelain clay formulation

A typical analysis by STA of a dried porcelain clay formulation can be seen in Figure 1, which shows the TG weight loss change on one axis, and on the other axis the DTA ordinate values, using the conventional DTA convention of endothermic (energy absorbing) activity in the downward direction. The initial endothermic weight loss on heating to temperatures near 500°C, of a previously dried specimen, is due to the dehydroxylation of kaolinite to form amorphous metakaolinite. This is described by the equation given below:

\[ 2\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow 2\text{Al}_2\text{Si}_2\text{O}_7 + 4\text{H}_2\text{O} \]  

Using the DTA thermal curve obtained for this porcelain clay mixture, the strong endothermic peak\(^3,4\) obtained for
the dehydroxylation allows for determination of the quantity of kaolinite present in the test sample. Kaolinite clay mineral is the primary component in the porcelain clay formulation employed in this study. This analytical calculation is done by comparison of the peak area obtained for the porcelain formulation to a similar analysis of commercially refined kaolin used in the preparing the formulation. The STA curve of the purchased kaolinite raw material looks very similar to that shown for the formulation in Figure 1. The corresponding TG thermal curve for the kaolinite sample (in Figure 2) gives a weight loss of 12.7%. From the two weight loss calculations, we can determine that the percent kaolinite for the material in Figure 1 is 50.5%. Although the theoretical percentage mass loss given by equation 1 is near 14.0 %, the experimental value of 12.5 % was used because it was the same kaolinite specimen used in the formulation. Alternatively, we can determine the percent kaolinite in the formulation by comparing the DTA dehydroxylation peak areas using calorimetric values (J/g). From the ratio of the normalized DSC peak areas, the kaolinite analysis yields 51.9%. For these calculations an instrumental baseline was subtracted after having been obtained by repeating the experiment with only empty sample capsules in the STA.

Furthermore, with reference to Figure 1, it can be seen from the DTA thermal curve that an exothermic peak associated with a crystallization process which leads to the formation of a spinel. The sharp exothermic event is shown to occur at an onset temperature of 993.2°C by extrapolation of the leading edge of the peak back to the intersection of the pre-transition DTA thermal curve baseline. The temperature of the peak maximum is assigned by the STA software to be 1005.0°C. The exothermic heat of transition was determined, from the integrated peak area, to be 46.55 Joules per gram of ceramic formulation analyzed in the STA instrument. The spinel is formed from the combination of amorphous silica and metal oxides in the STA sample cup at this temperature (ca. 1000°C). The types of metal oxides will vary in different kaolinites as well as different ceramic formulations. It is well established[9,10,11] that this characteristic exothermic transition will differ in both temperature and amplitude with both crystallinity of the kaolinite specimen , as well as the types of metal oxides involved in the spinel formation. It should be noted that the peak temperature is somewhat dependent upon heating rate. This analysis was made at 20°C per minute. At slower heating rates, the peak temperature for this exothermic transition will be a little lower.

The other major components of this dried porcelain clay formulations includes silica, SiO₂, known in its most common crystalline form as quartz, and its amorphous (non-crystalline form) , such as that found in glass. An additional component in the formulation is another mined family of minerals, feldspar, which has the chemical composition X-Si₃O₈ where X is usually sodium or potassium. However, calcium, barium and lithium can sometimes serve as the alkaline cations. The usual content ranges from 5 to 15% Na₂O or K₂O. The primary function of the feldspar ingredient is to supply fluxes to the formulation. They also provide additional alumina and silica to the mixture. Figure 2 shows the relevant STA data for the three refined components (not of reagent purity) that, together with low composition additives, make up the porcelain clay formulation. Although the TG thermal curves are not shown in this plot, from these analyses it was found that both the silica and feldspar show no weight loss on heating other than that from adsorbed water. The high temperature endothermic activity observed above 1100°C in the feldspar DTA thermal curve corresponds to melting. The exothermic events shown in the DTA thermal curve for kaolinite at temperatures above 1200°C are due to the formation of orthorhombic mullite (Al₂Si₂O₇) and crystobalite. These two important high temperature species are not discussed very much in this study because they are so stable and the focus here is on porcelain ceramics formulations.

2.5 Component of the formulation

The characteristic "inversion" peak for crystalline silica specimens is well studied [5,10,11] and is usually observed in DTA thermal curves at (or near) 573 °C. This endothermic event corresponds to the crystal lattice change from the trigonal ("alpha") form to the hexagonal ("beta") form. This transition is also accompanied by a change in volume and as a result, cracking is often associated with this lattice transition. The heat of transition for this energetically weak conversion is reported to be in the range of 13.1 J/g [5]. This endothermic event in silica is usually not observed in the STA thermal curve when analyzed in the presence of substantial quantities of kaolinite clay. This is due to the overlap of the much stronger dehydroxylation endotherm. However, the polymorphic inversion transition in the crystalline silica component of a clay formulation can be observed by using the DTA cooling curve. It may also be observed by repeating
the DTA analysis after previously heating it to sufficiently high temperature to allow the dehydration reaction to go to completion. Some analysts prefer to simply use a programmed cooling curve immediately following the initial heating run. In this case, the transition will be seen as an exothermic DTA peak on cooling.

**Figure 3** shows the DTA thermal curve obtained from heating a crystalline silica specimen as well as a clear cone 10 glaze, after previously heating each to 800°C to eliminate the endothermic effect of any dehydroxylation. Both samples were heated at 20°C per minute. By making certain assumptions, one can use the normalized peak area energy values in Joules per gram (J/g), of this solid-solid transition to estimate the relative amount of silica in the formulation. This is accomplished by comparison to the peak area to that obtained for the analysis sample of silica. As can be seen in **Figure 3**, the normalized peak area of the transition for this silica specimen was determined to be 8.36 J/g while the integrated area of the cone 10 clear glaze endotherm is only 1.96 J/g. By dividing the enthalpy change observed for the glaze specimen by that found for the silica, the calculation estimates 23% silica in the glaze material. This calculation makes the assumption that both silica components are of the same degree of crystallinity. Therefore, it is imperative that the analyst be knowledgeable of the identity and properties of the silica used to prepare the glaze specimen in order to make such a calculation.

![Figure 3. Inversion of SiO2 in commercial Silica and in a Cone 10 clear glaze after heating to 800°C](image-url)
Figure 4. STA heat flow comparing the transition in glass to silica inversion

Figure 4 shows the DTA thermal curves obtained by heating four materials containing amorphous silica. The thermal curves given in this figure show that the glass transition (Tg) is detected by the change in the observed heat capacity, as a DTA baseline shift, in the temperature region of the glass transition, where the amorphous solid softens. However, as can be seen in Figure 4, the temperature range of the glass transition observed from the heating of a sample of window glass closely overlaps the endothermic crystalline quartz inversion temperature of the DTA thermal curve. Therefore, it is concluded that the separation between the two thermal transitions exhibited by the amorphous and crystalline content of the silica is not possible using the thermal analysis technique (DTA) used here.

2.6 Detection of the vitreous component

For a clear glaze and for a translucent ceramic porcelain piece one would expect that a primary component would be amorphous and crystallites are not reflecting incident light. Figure 5 shows two STA heat flow curves for the first and second heat of the glaze sample that was used in Figure 3. On the second heating of this glazed specimen, after the sample has been heated to 1300°C (roughly corresponding to cone 10 to set the glaze, i.e., to allow the components of the glaze to react and produce the amorphous phase desired for the ceramic finish), one sees an event which is the glass transition. The softening point of the vitreous component is indicated by the increase in the specific heat capacity as an endothermic shift in the DTA thermal curve as the post-fired material is reheated in the STA. It was confirmed that this is a glass transition, and its associated softening point, by subjecting the sample to thermomechanical analysis (TMA) using the penetration mode of the instrument.

For the ceramic artist a "thrown piece" with a high amorphous content sitting in the kiln at a temperature above the glass transition temperature is likely to "slump"; i.e., slowly flow under the force of gravity. Another piece with the same nominal content but a different thermal history, a different time-temperature profile, may have a lower amorphous content or a higher glass transition temperature. The piece would then be less likely to slump. It is possible to detect a glass transition in a ceramic clay using the STA to heat the ceramic after it has been previously fired. To demonstrate this, a clay that was known for producing translucent porcelain was "fired" in the STA and the results analyzed. Figure 6 shows the STA heat flow of the first and second heat with an indication of a glass transition at 872°C. Notice that the glass transition is quite different from that for the glaze material. It is well known in potting circles that the glaze must be matched to the clay body to avoid crazing. This can be understood by the fact that the coefficient of thermal expansion changes going through the glass transition region, and a change in the differential expansion of the two layers could certainly lead to stresses in the ceramic piece. One could then assume that matching the glass transition temperatures (Tg) of both the clay and glaze would lead to a more compatible combination.
3. Summary of results

The results of this study describe several important uses of simultaneous thermal analysis techniques for studying porcelain clay formulations. The percentage kaolinite clay component was successfully achieved in the presence of the two other primary components of the formulation (silica and feldspar). This was demonstrated by using components of the formulation (silica and feldspar). This was demonstrated by using both the DTA peak area as well as, the observed percent mass loss associated with the dehydroxylation of the clay component in the 500°C to 600°C temperature region. As was expected, the DTA thermal curve for the dried three primary component porcelain clay formulation was very similar qualitatively to the refined kaolinite clay component in Figure 2. The characteristic spinel crystallization was observed as a sharp exothermic DTA peak having a peak maximum of 1005°C. The onset of this transition was calculated by the DTA software to be 993°C. The effect of particle size and metal oxide content was mentioned in the discussion given. Good results for the weak endothermic inversion transition of crystalline quartz were obtained and this was utilized to quantify the percentage crystalline component in a previously heated clear glaze. Glass transition assignments were shown to be successfully performed with the DTA thermal curves obtained on the second heating of both clear and translucent glaze materials. However, it was found to not be possible to separate, and hence distinguish, both the crystalline component (inversion) peak and the glass transition (heat capacity) shifts of the amorphous silica component in the same sample using the thermal analysis technique of DTA.

![Figure 5. Glass Transition in Clear Glaze after heating to firing temperature](image)

![Figure 6. STA Heat flow data of a translucent porcelain product showing an apparent Tg on the reheat data](image)

4. Conclusions
From the results obtained in this study, as well as in other published studies\textsuperscript{[2,13]}, it has been shown that STA is a very valuable tool for the ceramic industry for analyzing porcelain clays. The choice of a STA instrument, rather than the use of individual DTA and TGA instruments, is often made due to the fact that the thermal analysis measurements are obtained on the same specimen, rather than two different samples of the same formulation or material. This eliminates the possibility of differences in the results resulting from inhomogeneity of the sample material. Another advantage of the STA technique is that the temperature axis of the TGA thermal curve is more accurately measured in the STA instrument. This is because the temperature measuring transducer (usually a thermocouple) is in contact with the sample cup and in most “stand-alone” TGA instruments it is not. This technique is a viable tool for commercial ceramics manufacturers to better understand their processes and control the quality of their raw materials. Moreover, thermal analysis of clay formulations offers an overlap between the art and science of the ceramic firing process.

References

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