Effect of Palygorskite on the Sintering Process and Kinetics of Bone China

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ABSTRACT: The sintering process of bone china bodies containing 0, 2, 4, and 6 wt % palygorskite was studied by X-ray diffraction (XRD), differential scanning calorimetry and thermogravimetry (DSC/TG), and dilatometric tests. According to the XRD and DSC/TG results, the increment of palygorskite increased the content of the amorphous phase and reduced the formation temperature of the early liquid phase in the bone china bodies. The shrinkage data showed that the starting sintering temperature and maximum shrinkage temperature of bone china bodies in the stage of liquid-phase sintering decreased by 20 and 15 °C via adding 6 wt % palygorskite, respectively. Also, the maximum shrinkage rose with increasing amount of palygorskite. Moreover, the kinetic analysis of shrinkage data was conducted by the Salem model. The value of the mechanism-characteristic exponent, m, rose from 0.62 to 0.91 by adding 6 wt % palygorskite. In addition, with increasing palygorskite, the value of activation energy, $E_a$, linearly reduced, and the value of rate constant $A$ increased.

1. INTRODUCTION

Bone china is one of the world’s most attractive and expensive types of tableware due to its characteristics, including high degree of whiteness, unique translucency, the highest strength value among whitewares, and high glaze decoration quality. However, its insufficient mechanical properties make it break easily during machine washing, which limits its application to homes and upscale restaurants. Therefore, the improvement of the mechanical properties, including flexural strength, fracture toughness, and thermal shock resistance, is a sustained focus in the area of bone china. Zhang et al. improved the flexural strength and the thermal shock resistance of bone china from 120 to 150 MPa and from 140 to 180 °C by the addition of 1 wt % corundum powders, respectively. Mukhopadhyay et al. discovered that the modulus of rupture of bone china was increased by 10% via adding 12% fired scraps in commercial bone china composition.

A general method to toughen ceramics is adding fibers to the matrix, such as zirconia fibers, quartz fibers, carbon fibers, and SiC fibers. However, the high cost of the above fibers limits their wide utilization in ceramic manufacturing. Palygorskite is a nanofibrous phyllosilicate with a 2:1 ribbon-layer structure composed of two continuous tetrahedral sheets and one discontinuous octahedral sheet. The nanofibrous morphology, abundant resource, and low cost endow it with inherent advantages to be utilized as reinforcing agents in several matrices, including plastics, rubber, membranes, coatings, and synthetic fibers. In our previous study, the strengthening effect of palygorskite fibers on mechanical properties of bone china was systematically investigated. After reinforcing with moderate palygorskite fibers, the three-point flexural strength and fracture toughness of bone china increased by 10.9 and 4.7%, respectively. It was also found that the optimum sintering temperature was decreased from 1260 to 1240 °C with the addition of 4 wt % palygorskite. Clearly, palygorskite not only improves the mechanical properties of bone china but also promotes the sintering process. On the above basis, this work focused on the impact of palygorskite on the sintering process and kinetics of bone china.

In general, the reactions that occurred in the bone china body in the sintering process include dehydrations of hygroscopic, bound, and structural water of kaolin, decomposition of hydroxyapatite into $\beta$-tricalcium phosphate and lime, formation of anorthite from lime and metakaolin, and fusing of fluxing agents. Among them, sintering after the fusing of fluxing agents is the most important stage in which the bone china body undergoes rapid densification due to the diffusion of the liquid phase into the pores between the particles. After the sintering in the presence of the liquid...
phase, a relatively loose mass of compacted particles transforms into a denser body. On the other hand, bone china bodies shrink obviously during the liquid-phase sintering process, which affects the dimensional stability and mechanical performance of final products. The vitreous phase flows and causes rapid shrinkage until the sealing of open pores. After that, the closed pores expand with the temperature as a result of “bloating”. To avoid the expansion of closed pores, the investigation of shrinkage by the dilatometry technique becomes indispensable during the design of the firing cycle. A theoretical model was proposed by Frenkel to predict the sintering shrinkage of compacted glass particles.\(^3\)\\n\\n\[
S = \frac{3\gamma t}{2a\eta}
\]  
(1)\\n
where \(S\) is the shrinkage of the sample, \(a\) is the diameter of glass particles, \(t\) is the isothermal sintering time, \(\gamma\) is the surface tension of the liquid phase, and \(\eta\) is the viscosity of the liquid phase. According to this model, the shrinkage of the sample is in direct proportion to the surface tension/viscosity ratio, \(\gamma/\eta\). Bone china goes through a liquid-phase sintering process in which the surface tension of the liquid phase provides the driving force, and the viscosity of the liquid phase creates resistance of viscous flow.\(^33\) The above model is not applicable to estimate the sintering shrinkage of the porcelain body in the liquid-phase sintering process, which is shown in Section 5.\(^1\)\\n
Another way to investigate the sintering process is based on the shrinkage measurement technique. The experiential model is generally presented by Orts et al.\(^34\)\\n\\n\[
S = kt^b
\]  
(2)\\n
where \(k\) is a constant, \(t\) is the sintering time, and \(b\) is a parameter that depends on the dominant sintering mechanism.

Based on the above two models, Salem and Salem proposed a new semitheoretical model to accurately describe the shrinkage of the porcelain body in the liquid-phase sintering process, which is shown in Section 5.\(^3\)

The aim of this work is to investigate the impact of palygorskite on the sintering process of bone china. XRD, DSC/TG, and dilatometric tests were utilized to analyze the sintering process. The Salem model was adopted to study the sintering kinetics of bone china bodies using shrinkage data, and the impact of palygorskite on kinetic parameters was evaluated. In addition, the validity of the model was also studied.

2. RESULTS AND DISCUSSION

2.1. Properties of Raw Materials. The different particle size distributions of the bodies result in diverse pore radii, which dramatically changes the viscous flow of liquid, thus affecting the shrinkage behavior in the process of sintering. As indicated in Figure 1, the particle size distribution shows a bimodal distribution consisting of two main peaks centered at 1 and 10 \(\mu\)m. The arrangement of the coarse and fine particles in the pressed body is suitable for efficient particle packing. The fine particles could fill the gaps between the coarse particles due to the large size difference, which can favor better mechanical performance of final products.\(^36\) A small peak centered at 500 \(\mu\)m is observed on the particle size curve, which is caused by the agglomeration of particles during measurement. Because the powders of the green bone china bodies were obtained after wet ball-milling the raw material and sieving through a 75 \(\mu\)m sieve, particles with a size of 500 \(\mu\)m could not pass through a 75 \(\mu\)m sieve.

2.2. Phase Composition Analysis. The fired bone china bodies were analyzed by the X-ray diffraction technique in order to investigate the impact of the palygorskite on the phase composition of the bone china bodies, and the XRD patterns of these samples are shown in Figure 2. An examination of the reflections of different samples leads to a conclusion that these bone china bodies contain \(\beta\)-tricalcium phosphate (\(\beta\)-TCP, JCPDS #09-0169), anorthite (JCPDS #76-0948), and quartz (JCPDS #46-1045) phases labeled as T, A, and Q, respectively. This result is in agreement with the previous studies.\(^3,4,6\) No reflections of the palygorskite are observed in the XRD patterns due to the decomposition of palygorskite into enstatite in the process of sintering. As a matter of fact, the reflections of enstatite are unobservable in all the samples containing palygorskite owing to the small proportion of palygorskite and the fusion upon firing.\(^4\)

The phase composition of the bodies is listed in Table 1. The main crystal phases of the four samples are consistent. Among them, the proportions of anorthite and quartz decrease with the increment of the palygorskite; conversely, the

| sample | \(\beta\)-TCP | anorthite (wt %) | quartz | amorphous |
|--------|--------------|-----------------|--------|-----------|
| P0     | 38.36        | 28.33           | 8.62   | 24.69     |
| P2     | 38.87        | 27.63           | 7.43   | 26.07     |
| P4     | 38.14        | 28.18           | 6.37   | 27.31     |
| P6     | 39.06        | 26.52           | 5.98   | 28.44     |

Figure 1. Particle size distribution of the green bone china body.

Figure 2. XRD patterns of the bone china bodies.
proportion of amorphous phase increases. This result indicates that the composition and amount of amorphous phase change by dissolving palygorskite, anorthite, and quartz with increasing palygorskite. The surface tension and viscosity of the liquid phase would change with the variation of composition in the sintering process. The changes in the composition of the liquid phase have a significant impact on the surface tension and viscosity in the sintering process. According to eq 11, the rate constant, \( A \), is in direct proportion to the surface tension/viscosity ratio, \( \gamma/\eta \). Thus, the sintering behavior changes with the addition of palygorskite.

2.3. DSC/TG Results. Figure 3a presents the DSC/TG curves of sample P0. As shown in Figure 3a, there were four endothermic changes in the DSC curve and three steps of mass loss in the TG curve. The first endothermic peak occurring at below 300 °C with a mass loss of 1.22% is attributed to the loss of absorbed water. The endothermic reaction taking place at 400−600 °C with a dramatic mass loss of 3.67% is ascribed to the decomposition of carbonate and the dehydroxylation of kaolin to form metakaolin.37 The endothermic peak ranging from 860 to 1000 °C with a mass loss of 0.44% is due to the decomposition of hydroxyapatite into \( \beta \)-tricalcium phosphate, lime, and water. Simultaneously, the released lime reacts with metakaolin to form anorthite.30 The last endothermic change above 1100 °C is due to the appearance of the liquid phase. An abnormal mass gain of about 0.6% occurs above 1000 °C. This phenomenon can be explained by the buoyancy effect. In TGA analysis, buoyancy is the upward force on the sample produced by the surrounding atmosphere, which will affect the apparent mass during the TGA experiment. The buoyancy effect occurs as the density of the atmosphere decreases with increasing temperature, resulting in an apparent mass gain.

The DSC curves of samples P0, P2, P4, and P6 in the temperature range of 800−1200 °C are shown in Figure 3b. The peak temperature of hydroxyapatite decomposition in the four samples is 935 °C and does not change with increasing palygorskite. Meanwhile, the introduction of the palygorskite up to 6 wt % gradually reduces the temperature of liquid formation from 1114 to 1100 °C. This result indicates that the palygorskite contributes to the formation of the early liquid phase in the bone china bodies.

2.4. Dilatometry Results. The thermal behaviors of four bone china body mixtures were further analyzed using the dilatometric technique in non-isothermal mode from room temperature to 1250 °C. The linear shrinkage and the shrinkage rate of P0 as a function of temperature are plotted in Figure 4a. If no reaction occurs, the body expands with the increase of temperature due to thermal expansion of the samples. In the shrinkage curve of P0, the maximum expansion was lower than 0.31%, below 865 °C. In this region, the slight shrinkage in the temperature interval from 480 to 560 °C is due to the dehydroxylation of kaolinite.37 At 865 and 1165 °C, the body shrinks to the size before each expansion, which may represent the beginning of new reactions. The first shrinkage stage that takes place from 865 to 990 °C with a shrinkage of 0.98% is related to the gradual decomposition from hydroxyapatite to \( \beta \)-tricalcium phosphate, lime, and water.30 This process can be distinguished on DSC and TG curves as well (Figure 3a). The second shrinkage stage that occurs in a temperature interval from 1165 to 1250 °C with a shrinkage of 7.00% is caused by the liquid-phase sintering of bone china. In both shrinkage stages, the second one is much more important because it determines the physical and mechanical properties of final products.
The shrinkage curves of samples P0, P2, P4, and P6 in the second shrinkage stage are shown in Figure 4b, and the technical properties are given in Table 2. The curves presented in Figure 4b show that the shrinkage curves shift to lower temperature with increasing amount of palygorskite, indicating the enhanced sintering rate of bone china bodies. The presence of 6 wt % palygorskite in the composition leads to early-liquid-phase formation, which decreases the starting sintering temperature by 20 °C. Also, the temperature at which sample P6 reaches the maximum shrinkage is 15 °C lower than that of sample P0. By dissolving palygorskite, anorthite, and quartz, the surface tension and viscosity of the liquid phase change with the variation in composition. According to eq 11, the rate constant, \( A \), is in direct proportion to the surface tension/viscosity ratio, \( \gamma/\eta \). That is to say, the variation trend of \( \gamma/\eta \) with increasing temperature is the same as that of the \( A \) factor. As shown in Figure 7, the rate constant, \( A \), increases with the increment of palygorskite. It means that the surface tension/viscosity ratio, \( \gamma/\eta \), increases, and the densification process is promoted. In addition, the maximum shrinkage of sample P6 is 0.74% higher than that of sample P0, which is caused by the increase of the liquid phase (Table 1).

**2.5. Kinetic Study.** The shrinkage curves of the studied samples in the liquid-phase sintering stage were fitted by eq 15 to determine the temperature dependence of the shrinkage. The Salem model was adopted to associate the experimental data, revealing a shrinkage increment along with temperature. The fitting results and experimental data are compared in Figure 5, and the kinetic parameters of eq 15 including \( A_0 \), \( E_a \), and \( m \) are summarized in Table 3. For the studied cases, the values of \( m \) are found to be between 0.62 and 0.91 and gradually rise with increasing amount of palygorskite. The parameter \( m \) is the mechanism-characteristic exponent that is dependent on the mass transport process and determines the sintering rate. Specifically, for \( m = 1 \), the sintering shrinkage takes place by homogeneous first-order kinetics, and for \( m = 1/2 \), the process is controlled by diffusion and phase boundary reactions, respectively.38

The sintering activation energy values of the samples are listed in Table 3 and plotted in Figure 6. Results showed that activation energies of samples linearly reduce with the increase of palygorskite addition. As is well known, sintering can be considered as a heating activation process. The activation energy is thus explained as the required energy for starting a reaction. The surface tension of the liquid phase provides the driving force for sintering, and the surface tension/viscosity ratio controls the mass transport during sintering. The reduction of activation energies can be interpreted by the variations in the surface tension/viscosity ratio of the liquid phase caused by the dissolution of palygorskite, anorthite, and quartz with increasing palygorskite.

The rate constant, \( A \), shows the shrinkage as a function of temperature, which is determined based on the modified Arrhenius equation, as presented in eq 13. The increment of palygorskite has a positive effect on \( m \) and a negative effect on \( A_0 \) and \( E_a \), as shown in Table 3. The changes in kinetic parameters including \( A_0 \), \( m \), and \( E_a \) have a significant impact on rate constant, \( A \), and as a result, the densification process considerably changes. The rate constants of studied bodies are calculated according to eq 13 and presented in Figure 7. The results show that the rate constant of sample P0 is the lowest one, and it increases with increasing amount of palygorskite. For example, the values of rate constant for samples P0, P2, P4, and P6 are about 0.011, 0.012, 0.014, and 0.015 min\(^{-1}\) at 1200 °C, respectively. The noticeable increment in the rate constant improves the sintering rate and, as a result, promotes the densification process.

The values of shrinkage calculated by eq 15 have been plotted versus those determined experimentally in Figure 8. These points should be located on the diagonal of the graph if the predicted values are consistent with the experimental ones. Good agreement can be observed between the experimental data and calculated values, as shown in Figure 8.

![Figure 5. Fitting results of experimental data to eq 15.](Image)

![Figure 6. Variation of sintering activation energy as a function of palygorskite addition.](Image)

| Table 3. Parameters of the Kinetic Model |
|-----------------------------------------|
| sample | \( A_0 \) (kJ/mol) | \( E_a \) (kJ/mol) | \( m \) | \( R^2 \) | RMS (%) |
|--------|------------------|------------------|------|--------|--------|
| P0     | 25               | 120.3            | 0.62 | 0.984  | 12.3   |
| P2     | 5.7              | 114.8            | 0.83 | 0.993  | 14.3   |
| P4     | 2.3              | 103.6            | 0.86 | 0.997  | 15.4   |
| P6     | 1.2              | 98.3             | 0.91 | 0.992  | 15.9   |

3 and 1/2, the process is controlled by diffusion and phase boundary reactions, respectively.38

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The overall percent root mean square (RMS) was calculated to compare the differences between experimental data and theoretical predictions by the following equation:

$$\text{RMS} = \sqrt{\frac{\sum_{i=1}^{N} D_v^2}{N}}$$

where $N$ is the number of experimental data, $D_v$ is the percent deviation, and it was calculated as follows:

$$D_v = \left( \frac{S_{\text{exp}} - S_{\text{cal}}}{S_{\text{exp}}} \right) \times 100$$

where $S_{\text{exp}}$ is the experimental shrinkage value and $S_{\text{cal}}$ is the calculated shrinkage value. The values of RMS deviations reported in Table 3 show good agreement between experimental data and theoretical predictions, further substantiating the validity of the kinetic model.

### 3. CONCLUSIONS

In this investigation, the bone china bodies containing different contents of palygorskite exhibited different sintering processes and final products. With the addition of 6 wt% palygorskite, the proportion of the amorphous phase in the final products increases from 24.69 to 28.44 wt%, and the formation temperature of the liquid phase decreases from 1114 to 1100 °C.

The sintering process of bone china bodies contains two obvious shrinkage stages. The first stage in the temperature range of 865–990 °C is related to the gradual decomposition from hydroxyapatite to β-tricalcium phosphate, lime, and water, and the second one from 1165 to 1250 °C is caused by liquid-phase sintering of bone china bodies. The increment in palygorskite promotes the liquid-phase sintering of bone china bodies. With the increase of palygorskite, the starting sintering temperature and maximum shrinkage temperature decrease, and the maximum shrinkage rises. This may be interpreted by the increase in the surface tension/viscosity ratio of the liquid phase caused by the dissolution of palygorskite, anorthite, and quartz.

The sintering kinetics of bone china bodies with and without palygorskite was investigated using the Salem model. The experimental and calculated values are of good consistency. The mechanism-characteristic exponent, $m$, gradually rises with increasing amount of palygorskite. In addition, with increasing palygorskite, the value of activation energy, $E_a$, linearly reduces, and the value of rate constant, $A$, increases.

### 4. EXPERIMENTAL SECTION

#### 4.1. Materials and Characterizations

The powders of green bone china bodies used in this study were purchased from Zhenbei Porcelain Co. Ltd. (Shandong, China). The composition of the body was 40–50 wt% bone ash, 30–40 wt% kaolin, 5–10 wt% K-feldspar, 5–10 wt% quartz, and 0–5 wt% plasticizer. Bone ash containing mainly hydroxyapatite was produced by the reaction of the sea shell and phosphoric acid. The chemical compositions of green bodies and the raw materials for the bodies are shown in Tables 4 and 5, respectively. The particle size distribution of the green bone china body was measured by laser diffraction using a Mastersizer 2000 (Malvern, U.K.), and the resultant distribution curves are shown in Figure 1.

Palygorskite was produced from Guanshan Mine located at Mingguang City of Anhui Province in China, and its chemical composition is given in Table 6. According to our previous study, the phase composition of palygorskite contains palygorskite and small amounts of quartz, and the micro-morphology shows fibrous crystals with a length of 0.5–2 μm.

#### 4.2. Experimental Procedure

Four different body mixes containing 0, 2, 4, and 6 wt% palygorskite were prepared and marked as P0, P2, P4, and P6. The obtained body mixes were wet milled in a planetary ball mill with a ball-to-powder mass ratio of 3:1 for 30 min at a rotation speed of 300 r/min. Subsequently, the resultant slurry was dried in an oven at 110 °C for 24 h and ground into powders using a corundum mortar. The granulation process was conducted by adding 1 wt% polyvinyl alcohol solution to the powders while mixing them with a corundum mortar. The granulation was continued until all the granules were retained on the 250 μm sieve. Then the obtained granules were shaped to a rectangular prism (40 × 6 × 4 mm) under a uniaxial pressure of 250 MPa (TYE-300B, Wuxi Jianyi Instrument & Machinery Co., Ltd., China) and a holding time of 5 min.

### Table 4. Chemical Composition of the Green Bone China Body (wt %)

| Constituent | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | K$_2$O | Na$_2$O | P$_2$O$_5$ | LOI |
|-------------|---------|-------------|-------------|-----|-----|--------|---------|---------|-----|
| Green body  | 35.13   | 14.61       | 0.21        | 23.18 | 0.58 | 2.12   | 0.80    | 17.41   | 5.62|

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For the compact powder, the shrinkage depends on temperature, and the factor may be represented by the Arrhenius model as follows

\[
A = A_0(T - T_0)^m \exp\left(-\frac{E_a}{R g T}\right)
\]

where \(T\) is the absolute temperature, \(T_0\) is the temperature in which shrinkage is zero, \(A_0\) is a frequency factor, \(E_a\) is the activation energy of the ceramic matrix in the sintering process.

By substituting \(z^3/(1 + z^3) = (\epsilon_0^{1/3} - S/1 - S)^3\), eq 10 can be summarized as

\[
F(z) - F(z_0) = \int_0^t A dt = F(T)
\]

where \(F(z)\) is the shrinkage function and \(F(z_0)\) is the value of \(F(z)\) when \(S = 0\). Also, \(\epsilon_0\) is the initial total porosity of the ceramic body. \(F(T)\) is the absolute temperature, \(T\), dependency function.

For the compact powder, the shrinkage depends on temperature, and the A factor may be represented by the modified Arrhenius model as follows

\[
A = A_0(T - T_0)^m \exp\left(-\frac{E_a}{R g T}\right)
\]
activation energy, $R$ is the gas constant, and $m$ is an adjustable constant depending on the sintering mechanism.

The left part of eq 12 can be presented as

$$F(z) = \frac{1}{2} \ln \left( \frac{z^2 + 1}{z + 1} \right) - \sqrt{\frac{1}{3}} \tan^{-1}\left( \frac{2z - 1}{\sqrt{3}} \right)$$

(14)

F(T) can be presented by

$$F(T) = \frac{A_0(T - T_0)}{6\beta} \left( T - T_0 \right)^m \exp \left( -\frac{E}{R_g T} \right)$$

$$+ 2(T - T_0)^m \exp \left( -\frac{2E}{R_g (T + T_0)} \right)$$

(15)

where $\beta = (T - T_0)/t$ is the heating rate. The evaluation of the above kinetic parameters can be performed via nonlinear regression analysis (Origin Software Version 9.5) for each set of shrinkage data.

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### Notes

The authors declare no competing financial interest.

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