Analysis of The Role of Ceramic Green Body Enhancer (C3h3nao2) N in Art Ceramic Molding

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Abstract. Using (C3H3NaO2) n as a dispersing agent, an alumina art ceramic slurry having good dispersibility and suspension stability is obtained. The effect of the addition amount of (C3H3NaO2) n on the viscosity of alumina art ceramic slurry and the influence of solid content on the blanking time, mold release performance and shrinkage of the green body were analyzed. The results show that (C3H3NaO2) n can effectively improve the forming strength of the art ceramic body and reduce the deformation rate of the green body. When the mass fraction of the reinforcing agent c is 0.6%, the drying strength of the green body increases by 167.5%. The deformation rate of the blank is reduced from 50% to 10%.

1. Introduction

In the current production of art ceramics, the phenomenon of missing corners is more serious due to insufficient green strength, which reduces the yield. The preparation of the blank is a very important part [1], and the dry strength of the blank is an important indicator, which has an important impact on the yield and quality of the product. Many factories in China, especially in the southern wall and floor tile production plant, have poor plasticity of the clay, which is limited by the process and the drying strength of the green body is poor. Even if the molding pressure is increased, it is difficult to meet the requirements. The addition of a green body reinforcing agent in production is an effective way to solve the above problems. The reinforcing agent is generally an organic high molecular polymer. After the addition, there should be no adverse effect on the various stages of the art ceramic production process. The art ceramic green body enhancers produced by the German Sima company and the Italian Imperial Company are effective, but the price is too high. In recent years, the relevant units in China have developed some art ceramic green body reinforcing agents with more obvious enhancement effects [2], and gradually formed a production scale. (C3H3NaO2) n has attracted much attention as an art ceramic green body enhancer [3]. (C3H3NaO2) n can be classified into three types according to the relative molecular mass, such as low relative molecular mass (<104), medium relative molecular mass (104-106), and high relative molecular mass (>106). Among them, the medium molecular weight (C3H3NaO2) n has the most obvious enhancement effect on the green body. Based on the relative molecular mass (C3H3NaO2) n in the self-made, the author developed the (C3H3NaO2) n composite art ceramic body reinforcement, studied its reinforcing effect on the art ceramic body and the effect on the production rate of the floor tile. The reinforcing mechanism of the art ceramic green body enhancer.
2. Experiment

2.1. Reagents and raw materials
Acrylic acid, sodium persulfate, polyacrylamide, calcium lignosulfonate is all CP; sodium hydroxide is AR; enhancer additive (surfactant) is CP; ceramic blank is industrial product.

2.2. Synthesis of (C3H3NaO2)n
(C3H3NaO2)n can be prepared by different methods, that is, first neutralizing the monomer acid, then performing aqueous solution polymerization, or first performing aqueous solution polymerization to form polyacrylic acid, and then neutralizing and phase-transforming into a (C3H3NaO2)n solution. In this experiment, the two methods were compared, and the latter method was finally selected. The process equipment is simple, the liquid phase reaction is easy to operate, the molecular weight is easy to control, and there is no three-waste treatment, the reaction formula is as follows, and the flow chart is shown in FIG. 1.

![Fig. 1 (C3H3NaO2)n synthesis flow chart](image)

A mixed solution of acrylic acid and isopropyl alcohol was dropped into a 250 mL three-necked flask containing sodium persulfate solution, and the temperature was controlled at 60 °C. After the polymerization is completed, the intrinsic molecular weight of the product is determined by a Ubbelohs viscosity meter and the relative molecular mass of the product is calculated according to the formula \( [\eta] = K_0 M^a \). Detailed preparation conditions can be found in the previous work report [3].

2.3. Composite green body enhancer
A series of composite green body enhancers, referred to as composite reinforcing agent No. 1, were prepared by using the self-made relative molecular mass (C3H3NaO2)n as the main component and different proportions of polyacrylamide and calcium lignosulfonate as auxiliary components. No. 2,
No. 3 and No. 4, No. 5. In order to investigate the effect of the addition amount of \((\text{C}_3\text{H}_3\text{NaO}_2)_n\) on the strength of the green body, on the basis of the feasibility experiment, the addition amount of the five different relative molecular weights \((\text{C}_3\text{H}_3\text{NaO}_2)_n\) (calculated on a dry basis) was 0.2%, 0.4%, respectively, 0.6%, 0.8%, 1.0%, five sample numbers of \((\text{C}_3\text{H}_3\text{NaO}_2)_n\). Are: \(a_1, a_2, a_3, a_4, a_5\); the numbers of \(b, c, d, e\) samples are analogous.

| Tab. 1 Formulation of the blank (wt %) |
|----------------------------------------|
| Porcelain clay | Potash feldspar | quartz | clay | Calcium carbonate |
| 65            | 5               | 10     | 15   | 5               |

2.4. Determination of the strength of ceramic bodies
The \((\text{C}_3\text{H}_3\text{NaO}_2)_n\) or the composite enhancer is separately formulated into a solution according to different addition amounts and 50 mL of water, and then added to the blank by spraying, and then thoroughly mixed, and then passed through a 20-mesh sieve. The mass fraction of water in the billet is controlled to be 5% to 6%, and then the material is stuffed for 24 hours, and then formed by semi-dry pressing at a pressure of 18 MPa. After drying in an oven at 110 °C, a sample of 70 mm × 30 mm × 7 mm was prepared, and the strength was tested on a tcs-1000 type folding tester. Reinforcement ratio (\%) = \([\text{ceramic body strength after addition of reinforcing agent - strength of ceramic body without reinforcing agent]} / \text{strength of ceramic body without reinforcing agent}\] × 100. The Sanyang Kaitai body (about 77 cm in height and ca. 20 mm in diameter) was formed by grouting, and the degree of deformation of the body was determined by observation and comparison after drying at 110 °C.

2.5. Detection method

2.5.1. FTIR measurement. The functional group structure of the polymer was analyzed by a Perkin-Elmer (Generation one) Fourier transform infrared spectrometer, and the purified and dried sample was subjected to KBr tableting.

2.5.2. Determination of average molecular weight. The average molecular weight of the polymerized product was determined by the American Waters gel permeation chromatograph. Waters 1525 HPLC double pump, Waters 717 autosampler, Japan Tosoh TSKgel G-5000PWxl and G-3000PWxl, Waters 2414 refraction detector, mobile phase: 0.02 mol/L KH\(_2\)PO\(_4\), Flow rate: 0.6 mL/min, using dextran as a standard substance (molecular weight range 5200 to 1.400000), column temperature: 35 °C.

2.5.3. Determination of slurry viscosity. The ball-milled slurry after standing for 1 min was measured by Shanghai Fangrui Instrument Co., Ltd. NDJ-8S digital viscometer at room temperature, and the viscosity reduction was used to characterize the water-reducing and dispersing effects of the polymerized product. The test used a No. 3 rotor with a rotor speed of 60 r / s.

2.5.4. Zeta potential measurement. 9 different mass concentrations of dispersant (0, 0.05, 0.2, 0.35, 0.5, 1, 2, 4 and 6 g / L) were determined using a British Malvern ZS90 nanoparticle size analyzer. In a plastic bottle with 100 mL of deionized water and 0.2 g of fine powder, shake it and then sonicate for 10 min.

2.5.5. Bending strength test. The bending strength of the rough blanks was measured using a TZS-4000 digital ceramic tile bending tester, and each spline was tested 3 times and averaged. The bending strength is calculated as follows:

\[
\sigma = \frac{3LF}{2AH^2}
\]  

(1)
Where: $\sigma$ is the bending strength of the spline (MPa); $F$ is the maximum load (N) when the spline breaks; $L$ is the span of the spline (mm); $A$ is the spline width (mm); $H$ is the spline fracture surface the minimum thickness (mm) above.

3. Results and discussion

3.1. Effect of $(C_3H_3NaO_2)_n$ on the strength of the green body

The effect of $(C_3H_3NaO_2)_n$ on the strength of the green body is shown in Fig. 1. As can be seen from the figure, the drying strength of the green body increases with the increase of the amount of $(C_3H_3NaO_2)_n$. When the addition amount reaches 0.6%, the strength of the five samples reached the maximum, especially the strength increase rate of the $c_3$ body reached 167.5%. When the applied amount of $(C_3H_3NaO_2)_n$ exceeds 0.6%, the strength increase rate of $a_i$, $b_i$, $c_i$ sample does not change significantly, while the strength increase rate of $d$, $e$ sample decreases, and the $e_5$ sample is in $(C_3H_3NaO_2)$. When the amount of $n$ added was 1.0%, the strength of the green body was lower than that of the sample to which $(C_3H_3NaO_2)_n$ was not added. The reason why the strength of the sample varies with the type and addition amount of $(C_3H_3NaO_2)_n$ is that $(C_3H_3NaO_2)_n$ has a relatively large molecular weight and has a long single chain. When the blank is not added with a reinforcing agent, the combination of the green body is purely a particle. The combination of $(C_3H_3NaO_2)_n$ when the amount of $(C_3H_3NaO_2)_n$ is ≤0.6%, the $(C_3H_3NaO_2)_n$ added to the green body can bridge between the green body particles, causing cross-linking to form an irregular network structure, tightly the ceramic particles are wrapped to increase the strength [5-6].

![Fig. 2](image)

**Fig. 2** Relationship between the amount of $(C_3H_3NaO_2)_n$ added and the strength of the green body

When the amount is more than 0.6%, the surface of the particles is completely encapsulated by $(C_3H_3NaO_2)_n$ molecules, and the coating layer is thicker, and the distance between the particles is increased, which in turn reduces the capillary force between the particles, so that the strength increase tends to be gentle. The experimental results show that if the relative molecular mass of $(C_3H_3NaO_2)_n$ is too low or too high, the enhancement effect is weaker, especially in the case of too high molecular weight, the strength of the green body is more significant, such as $c_i$, $d_i$ sample. This is because the
relative molecular mass is too low \((C_3H_3NaO_2)_n\) has a short molecular chain (such as a, b), which does not form a network structure well in the green body, and acts to wrap the ceramic particles, thereby making the green body. The increase in strength is not obvious; when the relative molecular mass of \((C_3H_3NaO_2)_n\) is too high (such as d, e), the molecular chain is too long to be dissolved into the slurry, resulting in most \((C_3H_3NaO_2)_n\) molecules in the billet. The body can only exist in the form of a cluster, and the ceramic particles cannot be wrapped in the body, but instead acts as a barrier, resulting in a decrease in the strength of the body. The \((C_3H_3NaO_2)_n\) molecule has a moderate chain length, can form a cross-linking action to form an irregular network structure, and tightly encloses the ceramic particles, thereby increasing the strength thereof.

According to the literature, \((C_3H_3NaO_2)_n\) can be divided into three categories according to its relative molecular mass, such as low relative molecular mass (<10000), medium relative molecular mass (104-106) and high relative molecular mass (>107). The relative molecular weight of \((C_3H_3NaO_2)_n\) is most effective in enhancing the green body. The molecular mass distribution range of the five \((C_3H_3NaO_2)_n\) prepared in the experiment is shown in Table 2. It can be seen from the table that a and b \((C_3H_3NaO_2)_n\) belong to the low molecular weight range, d and e \((C_3H_3NaO_2)_n\) is in the range of high relative molecular mass, c \((C_3H_3NaO_2)_n\) is in the range of relative molecular mass, which further demonstrates that only the proper chain length of \((C_3H_3NaO_2)_n\) molecules can enhance the green body.

Table 2 Relative molecular weight range of 5 species \((C3H3NaO2)_n\)

| a | b | c | d | e |
|---|---|---|---|---|
| 10^3-10^6 | 10^6-10^7 | 10^7 |

In addition, after the addition of the reinforcing agent, the bonding of the green body particles also has the effect of hydrogen bonding. The body particles contain moisture, and in the absence of a reinforcing agent, their combination is only the van der Waals force and the capillary force between the particles [4]. After the addition of \((C_3H_3NaO_2)_n\), in addition to the above effects, since the surface of the particles is surrounded by \((C_3H_3NaO_2)_n\), hydrogen bonds can be formed between the particles. The \((C_3H_3NaO_2)_n\), which has a high surface charge density on the molecular chain, enables it to form strong hydrogen bonds, thereby greatly enhancing the strength of the green body.

3.2. Influence of \((C3H3NaO2)_n\) on the deformation of the blank

The experimental results of the influence of \((C_3H_3NaO_2)_n\) on the deformation of the green body are shown in Table 3. It can be seen from the table that the Sanyang Kaitai body without the reinforcing agent has been deformed after drying, and 50% of the product has been deformed; after adding 0.6% \((C_3H_3NaO_2)_n\), the Sanyang Kaitai body, the product the dry deformation rate is only 10%, which effectively improves the yield of the product. From the dry billet situation, the wet and dry billets formed by the 60 wt% solid phase slurry are slightly deformed, and the deformation is obvious after sintering, indicating that the internal stress is present in the dry billet due to the large displacement during the drying process. The total shrinkage of the sample was measured and the deformation was observed. The solid content of the slurry is from low to high, the total shrinkage is gradually reduced, and the sample changes from easy deformation to no deformation.

Table 3 Relationship between solid content of slurry and shrinkage deformation of product

| Solid phase content (wt%) | 54 | 58 | 62 | 66 | 70 | 74 | 78 | 82 |
|--------------------------|----|----|----|----|----|----|----|----|
| Total shrinkage (%)      | 14.37 | 13.93 | 13.75 | 13.51 | 13.38 | 13.15 | 12.93 | 12.67 |
| Deformation Variability  | Small deformation | Basically, not deformed |
4. Discussion
The reason why the reinforcing agent can increase the drying strength of the green body is because the relative molecular mass of \((C_3H_3NaO_2)_n\) is large and has a long single chain. When the billet is not added with reinforcing agent, the combination of the blank is purely the combination between the particles; after the reinforcing agent is added, the polymer \((C_3H_3NaO_2)_n\) can bridge between the green particles to form cross-linking to form an irregular network. The structure is tightly wrapped with ceramic particles to increase its strength. The experimental results show that if the relative molecular mass of \((C_3H_3NaO_2)_n\) is low, the enhancement effect is weak. After the addition of the reinforcing agent, the bonding of the green body particles also has the effect of hydrogen bonding. The green body particles contain moisture, and in the absence of the reinforcing agent, their combination is only the capillary force between van der Waals force and the particles. After the addition of \((C_3H_3NaO_2)_n\), in addition to the above effects, since the surface of the particles is surrounded by \((C_3H_3NaO_2)_n\), hydrogen bonds may be formed between the particles. The \((C_3H_3NaO_2)_n\), which has a high surface charge density on the molecular chain, enables it to form strong hydrogen bonds, thereby greatly enhancing the strength of the green body. The composite enhancer also contains polyacrylamide, which helps to form stronger hydrogen bonds\(^5\), which makes the reinforcement better. However, the reinforcing mechanism of the ceramic green body reinforcing agent is complicated and cannot be considered only from a single factor. For example, the composite reinforcing agent No. 1 also contains polyacrylamide, but its reinforcing effect is not as good as \((C_3H_3NaO_2)_n\). Therefore, how to design a composite enhancer formula to further enhance the overall enhancement effect is the most critical.

5. Conclusion
(1) \((C_3H_3NaO_2)_n\) has obvious reinforcing effect on the strength of dry body of art porcelain body, and it is an ideal enhancer; the relative molecular weight \((C_3H_3NaO_2)_n\) enhances the strength of the body better than too small or too large Relative molecular mass \((C_3H_3NaO_2)_n\).
(2) When the addition amount of \((C_3H_3NaO_2)_n\) is 0.6%, the drying strength of the art porcelain body is increased by 167.5%, and the deformation of the product is reduced from 50% to 10%.
(3) The enhancement of \((C_3H_3NaO_2)_n\) is due to the formation of an irregular network of highly elastic polymer chains in the body and the formation of hydrogen bonds between the ceramic particles.

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