The rheological performance of aqueous ceramic ink described based on the modified Windhab model

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Abstract
The good stability is the pre-requrement for ceramic ink in ink-jetted printing technology. The aqueous ceramic ink owning a significant shear-thinning effect is proposed using guar gum as additive agent. Due to the shear-thinning effect, the ink in static state has a high viscosity, which contributes to keep the ink stable. At the same time, the ink in spray state has a very low viscosity to meet the requirement of spraying. To describe this rheological performance, the Windhab model is modified, in which the correction term $\eta_\alpha$ is added into $\eta_\infty$. The term $\eta_\alpha$ is related to the concentration of guar gum and the solid content of the aqueous ceramic ink. A slip model is proposed to understand the interaction between pigment particles and guar molecules.

1. Introduction
Ink-jet printing is the mainstream technology for printing images onto ceramics without patterning or etching processes [1, 2]. The used ceramic ink is usually the suspension of ceramic powder. The good stability of the ink is pre-required in ink-jetted printing.

Currently, to increase the stability of ceramic ink, organic solvent with a low surface tension and dielectric constant is usually chosen. However, volatile organic solvent brings to the risk of combustion and toxicity. The aqueous ceramic ink is inclined to accept by markets [3, 4].

However, the obstacles of the aqueous ceramic ink are the stability performance and the spreading on tiles [5]. As it is well known, little dispersants or stability reagents have a good solubility in water because water has a large surface tension and dielectric constant, which is detrimental to the stability of ceramic ink [6, 7]. Moreover, water-based ceramic inks are prone to spread on glaze surface, which decreases the resolution of printing image. According to the Stocks equation (equation (1)), the settling velocity is inversely proportional to viscosity. In another word, the stability of inks may be increased through increasing viscosity. However, the high viscous ink loses its flowability which cannot be printed and easily clog the nozzles [8]. Now, it is proposed that the stable aqueous ceramic ink has the different viscosity depending on the flow state in ink-jetted printing process. It requires that the prepared ink has the high shear thinning rheological properties.

$$V_s = \frac{2r^2(\rho - \rho_0)g}{9\eta}$$

Where $V_s$ is settling velocity, $r$ is particle radius, $\rho$ is dispersed phase density, $\rho_0$ is dispersion medium density, $g$ is gravity acceleration, $\eta$ is viscosity of dispersion medium [9].

The well-known Windhab model [10] (equation (2)) were used to fit the shear stress-shear rate data to describe the rheology of the GG solutions [11]:

$$\tau = \tau_0 + \eta_\infty \dot{\gamma} + (\tau - \tau_0)[1 - \exp(-\gamma/\dot{\gamma}^\kappa)]$$

The rheological description of the model is based on the measurable physical parameters which affect the flow/textural characteristics in ‘structured’ multi-phase system [12]. It incorporates the yield point $\tau_0$ and the
shear stress at the y-axis crossover point $\tau_1$. The difference between $\tau_0$ and $\tau_1$, i.e. $(\tau_1 - \tau_0)$, is considered to represent the 'shear induced structural change' [13]. $\eta_\infty$ is the slope value of the flow curve at high shear rates and the point of the curve where the final viscosity. These parameters are all extrapolated from the data. The constant $\eta_\infty$ can be calculated from $\tau_0$ and $\tau_1$. This parameter corresponds to the shear thinning character of the flow curve at low shear rates [14–16].

As a natural macromolecular natural hydrocolloid, guar gum aqueous solution has the high good shear thinning rheological property [17–20]. However, the addition of pigment will change the rheological behavior of the guar gum aqueous solution [21]. In the present work, the rheological behavior of the ceramic ink is studied based on Windhab model.

2. Material and methods

2.1. Preparation of ceramic ink
Vanadium-Zircon blue pigment with mean particle size of (d50 = 1 $\mu$m) was used in the experiment whose. The SEM image of the pigment is shown in figure 1. The pigment particles are irregular in shape and most of them are in flakes. Some fine particles are adhered on the coarse particles. The irregular shape originates in not the grinding in the mixing of ceramic ink but the preparation of vanadium-zircon blue pigment. The carboxylate dispersant and Guar Gum (GG) are commercially available from Sinopharm Chemical Reagent Co., Ltd

In a special preparation process, 85.71 g of pigment and 0.8571 g of dispersant were added to 100 ml of deionized water. And then, 2 g of guar gum was added 100 ml of deionized water. Finally, the pigment suspension and GG solution were mixed by ball milling for 5 h.

2.2. Characterization
A MCR02 rheometer (Anton Paar, Austria, Germany) was used for the rheological measurement experiments. Unless otherwise noted, the shear stress was measured while increasing the shear rate continuously from 0.5 to 500 s$^{-1}$. All rheological measurements were tested three times and averaged.

3. Results and discussion

3.1. Rheology of guar gum solution
To better illustrate the Windhab model, an example fitting of the Windhab model for the 1% guar gum solution sample is shown in figure 2.

The three regions of the fitting line can be identified in figure 2. The change of the line represents the reflects the different structural changes of the GG molecule that the material undergoes during shear process: Region 1 represents the measured yield value; Region 2 represents the intermediate flow region which describes the shear induced structure; and Region 3 represents the flow function in the high shear region, which is similar to the flow of normal Newtonian fluids [14].
The fitting parameters for guar gum (GG) solutions with different concentrations shown in figure 2 where are given in table 1 based on Windhab model. The variance squares $R^2$ for different concentrations of GG solution are shown in figure 3. As it can be seen, $R^2$ is around about 0.99, which indicates that the Windhab model can basically describe the rheological data performance of guar gum solution is basically consistent with the Windhab model.

As it can be seen from table 1, the values of the yield point $\tau_0$, $y$-axis crossover point $\tau_1$, and shear induced structural change (SISC) $\tau_1 - \tau_0$ increase with the concentration of GG solution. It can be imaged that the more

| Concentration (wt%) | $\tau_0$ (Pa) | $\tau_1$ (Pa) | $\tau_1 - \tau_0$ (Pa) | $\dot{\gamma}^*$ (s$^{-1}$) | $\eta_\infty$ (Pa·s) |
|---------------------|--------------|--------------|------------------------|-----------------|-----------------|
| 1                   | 6.838        | 44.286       | 37.448                 | 21.40           | 0.058           |
| 1.5                 | 7.035        | 125.024      | 117.989                | 11.44           | 0.082           |
| 2                   | 7.457        | 198.800      | 191.343                | 5.07            | 0.091           |
| 2.5                 | 8.083        | 342.463      | 334.380                | 3.14            | 0.144           |
| 3                   | 20.591       | 479.766      | 459.175                | 4.91            | 0.138           |
complex the cross-linking of GG molecule, the higher the concentration of GG solution. This means that as the GG concentration increases, the cross-linking of GG molecules in solution is hard to break [22]. Specially, the values of the parameter $\tau_0$, $\tau_1$ and $(\tau_1 - \tau_0)$ increase sharply when the GG concentration is in the range of 2.5% to 3%. It reflects that the cross-linking of GG undergoes the drastic change under the action of shear forces, such as from in tangle to in discreteness. The parameter $\dot{\gamma}^*$ reaches the minimum value at the GG concentration of 2.5%. $\dot{\gamma}^*$ indicates the different behavior between the solution and the normal Newtonian fluid [9]. Correspondingly, $\eta_\infty$ reaches the maximum value at a concentration of 2.5%. Both $\dot{\gamma}^*$ and $\eta_\infty$ indicate the entanglement degree of the GG molecule. In a given space, GG molecular is in serious entanglement state in the high concentration GG solution, which requires the greater shear stress to break.

3.2. Rheological model of GG
The applied shear stress to GG solution is through the rotation of the rotor, as shown in figure 4(a). If the shear stress $\tau < \tau_0$, the stress is too small to form the shear deformation, there is no shear thinned behavior in solution at this time; When $\tau = \tau_0$, the stress reaches the yield value. At this point, the entanglement GG molecules start to unravel. The closest molecules to the rotor begin to move toward the rotor rotation, the system begins to shear deform. The shear stress increases with the increase of shear rate, the driven GG molecules by rotor start to drive the next molecules layer to move. The shape variables reach the maximum until $\tau = \tau_1$, the speed of unlock entanglement catches faster than the rate of reentanglement, two type molecules driven by the rotor directly or indirectly form the large velocity difference, thus the boundary layer is formed, which is called slip layer. In this process, the solution shows the shear thinning effect.

When $\tau_1 \leq \tau \leq \tau_\infty$, with the increase of shear rate, the velocity difference between guar gum molecules that close to rotor in each layer decreases, then the slip layer migrate to the next layer with bigger velocity difference, as shown in figure 4(b), the sliding layer of GG solution will not fixed, but offshore gradually with the increase of shear rate. Besides this, there is no the other forces in the whole process of offshoring, therefore, the applied stress in high shear area of the system keeps the constant. The slip layer spreads to the outermost part when the shear rate changes very high. Under this condition, the entanglement is destroyed, and new tangles cannot be formed at the same time, the apparent viscosity keeps the constant. The viscosity is the final viscosity $\eta_\infty$. As a result, $\eta_\infty$ by intermolecular guar gum is the viscosity affected by the entanglement between GG molecules.

3.3. Rheology of water-based ink
The fitting of rheological data of water-based ink based on Windhab model is shown in figure 5(a), in which the solid content of the pigment keeps the constant of 30 wt% and the GG concentration is in the range of 1% and 3% by weight of the dry pigment. Figure 5(b) shows the fitting of rheological data of water-based ink with different solid contents when the GG concentration is 2.5% by weight of the dry pigment.

Figure 5(a) shows that the water-based ink has the similar rheological behavior to that of the GG solution when the guar concentration is less than 2.0% even if the solid content is 30 wt%. However, the shear stress has a sharp decrease as the shear rate beyond a certain value. The variance square $R^2$ also decreases to 0.777, which
implies that the ceramic ink has the different rheological behavior with that of GG solution. The similar behavior occurs when the GG concentration is 2.5% and the solid content 30 wt.%, as shown in figure 5 (b). Comparing figures 5(a) to 3, it is found that the $R^2$ value of the ink is smaller than that of the GG solution due to the addition of the pigment. The rheological curve of the ink deviates dramatically from Windhab model. A new model should be proposed or a modification should be given based on Windhab model for the ceramic ink.

3.4. A slip model of water-based ink

Compared with the pure guar gum solution, the variance of the ink rheology curve fitted based on the Windhab model (equation (2)) is $R^2 < 0.99$. It shows that the traditional Windhab model is no longer suitable for describing the rheological behavior of ink after adding pigment. Therefore, the recommend adding modifications are made based on the original Windhab model. As shown in figure 5, the major changes in the curve are reflected in the high-shear region, so the correction term should be added to this region of the model. The new Windhab rheological model is shown in equation (3), which is called slip model.

$$
\tau = \tau_0 + (\eta_{\infty} + \eta_p) \dot{\gamma} + (\tau - \tau_0)[1 - \exp(-\dot{\gamma}/\dot{\gamma}^*)]
$$

(3)

In which, $\tau$ is shear stress, $\tau_0$ is yield stress, $\tau_1$ is maximum shear induced stress, $\dot{\gamma}$ is shear rate, $(\eta_{\infty} + \eta_p)$ is final viscosity, $\eta^*_\infty$ is the viscosity influenced by GG molecules after adding powder, $\eta_p$ is the viscosity affected by forces between GG molecules and powder particles after adding powder, $\dot{\gamma}^*$ is a constant.

Based on the slip model, figure 6 presents the fitting of the data of different GG solution concentrations and different solid contents, respectively. Table 2 shows that firstly under the same concentration of GG, the values of the system’s yield point after adding powder, the intersection of y axis and the shear induced structure changes (SISC) increase along with the increase of GG concentration. When GG concentration rises from 2.5% to 3%,
Table 2. Parameters for slip model analysis of ceramic inks with 30 wt% solid content and different concentrations of GG.

| Concentration (%) | τ₀ (Pa) | τ₁ (Pa) | τ₁ − τ₀ (Pa) | ηₘ (s⁻¹) | (ηₘ + ηₘ) (Pa·s) | ηₘ (Pa·s) | ηₘ (Pa·s) | R² |
|-------------------|---------|---------|--------------|----------|------------------|-----------|-----------|---|
| 1                 | 7.336   | 64.401  | 56.865       | 13.65    | 0.064            | 0.064     | 0         | 0.994 |
| 1.5               | 7.692   | 169.213 | 161.521      | 5.01     | 0.041            | 0.041     | 0         | 0.993 |
| 2                 | 7.693   | 268.167 | 260.475      | 3.16     | 0.045            | 0.045     | 0         | 0.988 |
| 2.5               | 10.961  | 397.036 | 386.075      | 2.38     | −0.062           | 0.193     | 0.131     | 0.985 |
| 3                 | 20.831  | 581.560 | 560.729      | 3.10     | −0.394           | 2.004     | 1.61      | 0.921 |

Table 3. Parameters for Windhab model analysis of ceramic inks with different solid content keep the constant of GG concentration 2.5% by weight of dry pigment.

| Solid content (wt.%) | τ₀ (Pa) | τ₁ (Pa) | τ₁ − τ₀ (Pa) | ηₘ (s⁻¹) | (ηₘ + ηₘ) (Pa·s) | ηₘ (Pa·s) | ηₘ (Pa·s) | R² |
|----------------------|---------|---------|--------------|----------|------------------|-----------|-----------|---|
| 0                    | 8.083   | 342.463 | 334.380      | 3.14     | 0.144            | 0.144     | 0         | 0.989 |
| 20                   | 8.135   | 377.708 | 369.573      | 2.76     | 0.054            | 0.054     | 0         | 0.994 |
| 30                   | 10.961  | 397.036 | 386.075      | 2.38     | −0.062           | −0.193    | 0.131     | 0.985 |
| 35                   | 18.009  | 458.189 | 440.180      | 4.05     | −0.256           | −1.506    | 1.25      | 0.921 |
| 40                   | 24.496  | 502.889 | 478.393      | 4.82     | −0.324           | −1.649    | 1.325     | 0.937 |

these parameters change almost twice as much, these are consistent with the changing rule of the GG solution. Secondly, when GG concentration increases from 2.5% to 3%, the parameters change from positive to negative. The similar change tendency also occurs in table 3. When GG concentration is 2.5% and the solid content ≥30 wt.%, the parameter ηₘ changes into the negative, which is believed caused by the rearrangement of powder particles and GG molecules in the system. GG solution has the typical shear rheological behavior of polymer macromolecules. The movement resistance of GG macromolecules can be described by parameter ηₘ.

Table 1 shows that for normal GG solution, parameter ηₘ only is related with the entanglement and free movement of GG molecules, whose value is in direct proportion to the GG concentration. After adding the powder, the solid particle not only hinder the movement of the GG macromolecules, but also compress inevitably the space of GG itself due to the addition of micron pigment particles. The parameter ηₘ is related to the squeeze of the GG except for the entanglement and free movement. Moreover, the interaction between pigment particles and guar gum molecules can affect the viscosity and rheological behavior of ceramic ink. According to equation (3), the rheological behavior in high shear zone is determined by (ηₘ + ηₘ). As shown in tables 2 and 3, after adding powder, the values of parameter (ηₘ + ηₘ), parameter ηₘ and parameter ηₘ are related to the GG concentration (GG number of molecules) and the solid content of pigment, besides the parameters (ηₘ + ηₘ) and ηₘ are inversely proportional to them as the parameter ηₘ is proportional to them.

3.5. Rheological model of ceramic ink

The sandwiched-plate structure is assumed in the new model because the ceramic vanadium zirconium blue powder particles in the experiment are micron size and much larger than the molecular size of guar. Thus, the GG molecules are sandwiched between colored particles in the ink, which is equivalent to GG molecule sandwiched between two plates, as shown in figure 7. When the distance between molecules and pigment particles is small enough, GG molecules will move with the pigment particles under the action of shear stress. During this process, the molecules need to overcome the entangled forces between them and the forces between the molecules and powder particles. With the increase of shear rate, powder particles and GG molecules begin rearrange. Because all orientation is consistent, the yield stress τ₀ and the maximum shear stress τ₁ increase.

There are only van der waals forces among GG molecules, however, there are other forces between molecules and powder particles except the van der waals force. In another word, the forces between GG molecules and powder particles are far outweigh the entanglement forces between GG molecules. Therefore, under the action of shear stress, it can only solve the entanglement forces preferentially. At this point, the guar gum and pigment particles together can be seen as a whole.

When τ = τ₀, the system start to generate the shear deformation with the increase of shear rate. The molecule-particles combination near the rotor side moves faster in shear direction. The untangling among GG molecules does not start. When τ = τ₁, the first slip layer is formed and the shear thinning flow behavior occurs. When τ₁ < τ < τₘ, the moving velocity difference between molecules-particles combination in each layer will increase consecutively. New sliding layer is generated and the number of the slid layer increases with the increase
of the shear rate. With the increase of shear rate and the number of the slip layers, the shear stress required by
system will decrease. The system shear stress reaches the lowest if the outermost slip layer is formed.

The final viscosity of water-based ink system is \( \eta_a + \eta_\infty \) , the parameter \( \eta_a \) is the viscosity affected by
the reaction between powder and GG. Meanwhile, the plate structure constrains the free movement of GG. And
during the shearing process, especially under the condition of high solid content or high guar concentration, the
guar molecules between the plates are easily squeezed, which causes the guar molecules to deform. Therefore,
the inter-plate structure will exacerbate the shear-thinning rheological behavior and lead to a decrease in
viscosity, so the parameters \( \eta_a + \eta_\infty \) both will decrease.

When the solid content keeps the constant, the spacing between the two colorant particles (the plate
distances) is decided at the same volume. If the concentration of GG in the system is relatively low and the
distance between GG molecules and colored particles is large, there is no interaction between GG molecules and
colored particles. The system only shows the typical rheological behavior of macromolecules. With the increase
of solution concentration, the distance between GG molecules and pigment particles will be small enough to
generate forces among them. The interaction forces between molecule and particles would enhance, and the
deformation of GG molecules will be larger as their compressed space become smaller. Therefore the parameter
\( \eta_a \) is proportional to the concentration of GG, while the parameter \( \eta_\infty + \eta_a \) and \( \eta_\infty \) are inversely proportional
to it.

Similarly, when the amount of GG keeps the constant, the higher the content of solid, the narrower the
spacing between the two pigment particles (plate distance) and the fewer guar molecules there are between two
plates. Therefore, when the solid content is relatively low, also the distance between the two plates is far, there
is no interaction between GG molecules and colored particles. With the increase of solid content and the distance
between the two plates get closer, their force get enhanced, the deformation of GG molecules become bigger as
the compressed space is reduced. Thus the parameter \( \eta_a \) increases, while the parameter \( \eta_\infty + \eta_a \) and \( \eta_\infty \) decrease.

4. Conclusion

The rheological curve of GG solution accords with Windhab equation. It was found that the rheological curve of
the previous ink still conformed to the Windhab equation after the pigment was added. But as the solid content
of the pigment and the GG concentration increase, the rheological curve of the ink changes. It started to deviate
from the Windhab equation. Therefore, on the basis of Windhab model, this paper build a new slip model by
introducing a correction term \( \eta_a \). The model can be used to describe the rheological behavior of aqueous ceramic
ink system.

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Declaration of interest statement

The authors declare that they have no conflict of interest.

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