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Rheological behavior of aqueous polymer-plasticized γ-LiAlO$_2$ pastes for plastic forming

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Abstract

The rheological properties of aqueous methylcellulose (MC) plasticized γ-LiAlO$_2$ pastes with high solid loading were investigated.

A power-law model was applied to characterize torque–shear rate relation of the paste system. The results demonstrated that the power-law model fits well for the aqueous γ-LiAlO$_2$ paste. Thixotropy behavior of the paste was found during shearing, mainly due to linkage break of particle–polymer and polymer–polymer. The rheological study showed that the change of components content has large influence on the thixotropy phenomena and plastic deformation behavior of γ-LiAlO$_2$ pastes. And the rise of temperature caused gelation of MC, leading to the climb of torque value.

Keywords: γ-LiAlO$_2$; Ceramic paste; Rheology; Thixotropy

1. Introduction

γ-LiAlO$_2$ is a promising solid tritium breeder in the fusion energy reactors due to its favorable tritium contribution after neutron irradiation [1–3]. γ-LiAlO$_2$ is also a potential substrate material for GaN semiconductors because of its optimal structure for GaN epitaxy [4]. Besides, γ-LiAlO$_2$ is a common material in use for matrix production in molten carbonate fuel cell and for composite electrolytes in lithium polymer battery [5,6].

In our research, γ-LiAlO$_2$ ceramics are expected to be tube with uniform microstructure and favorable mechanical properties. Plastic forming, such as extrusion, is an effective process to produce hollow products with uniform cross-section. An understanding of rheological behavior of γ-LiAlO$_2$ plastic pastes is helpful to plastic forming processing.

Ceramic pastes for plastic forming are usually composed of ceramic powders, liquid and polymers. The additives, i.e. liquid and polymers, are introduced into the batch as solvent, wetting agent, binder, plasticizer or lubricant to optimize the particle dispersion and flow behavior for forming [7]. The properties of polymer thin-film in the submicron space between particles in ceramic pastes differ in significant ways from those of polymer solutions, due to degradation, conformation, adsorption, mechanical phase separation, slippage between microscopic particles and surface tension [8]. The rheological behavior of extrudable ceramic pastes is not only controlled by polymers and liquid phase, but also solid loading, shape and size distribution of the particles, surface chemistry and packing density [9].

With the specialty of high solid loading and low moisture, ceramic pastes have different rheological behavior from solutions and suspensions, which is hard to be characterized by common viscometer, in terms of relation between shear stress, τ, and shear rate, γ (or viscosity, η, and γ). Beeaff and Hilmas investigated the rheological properties of barium titanate (BaTiO$_3$) pastes for coextrusion, using the parameters torque M and shear rate R recorded by a Brabender high-shear mixer [10]. They pointed out that the Hershel-Bulklely model

$$\tau = \tau_0 + K\gamma^n \tag{1}$$

is suitable to describe the rheological property of those BaTiO$_3$ pastes with 40–60 vol.% ceramic powders. More recently, Xu and Hilmas found that the power law relation between torque

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and shear rate defined as (2) fits well for both pure polymer and ceramic/polymer mixtures for coextrusion [11].

$$M = C(n)KN^n \quad (2)$$

where M is torque, $C(n)$ is a constant, N is the roller speed in revolutions per minute (rpm).

The objective of this study is to investigate the rheological properties of aqueous polymer-plasticized γ-$LiAlO_2$ pastes, searching the relation between torque and shear rate fitting for the ceramic pastes with high solid loading for plastic forming and investigating the influence of temperature and paste components in the rheological behavior of γ-$LiAlO_2$ pastes.

2. Experimental

2.1. Starting materials

γ-$LiAlO_2$ powders were prepared by a high temperature solid state reaction. Reagent-grade lithium carbonate (Li_2CO_3) and α-Al_2O_3 were used as lithium and aluminum sources. A stoichiometric amount of Li_2CO_3 and α-Al_2O_3 with the atomic ratio of Li:Al = 1:1 were mixed and then sintered at high temperature to prepare homogeneous fine crystalline γ-$LiAlO_2$ powder. Particle size distribution data (measured by Mastersizer 2000, Malvern) of the γ-$LiAlO_2$ powder obtained is shown in Table 1.

Commercial methylcellulose MC (M450, Sinopharm Chemical Reagent Co., Ltd.) was chosen as the plasticizer and binder in the aqueous system because of its several properties beneficial to ceramic pastes such as water soluble, surface active, nonionic, water retention, thermal burnout and thermal gelation [12,13].

2.2. Measurements of rheological parameters

Rheological properties were characterized with torque at variable shear rate. An XSS-300 torque rheometer (KECHUANG MACHINERY, Shanghai) with a Roller-cone mixer (HL 200) was applied to measure the rheological parameters of ceramic pastes. With the instrument, we can control the rotation speed N of Roller-cone, modify the temperature T of paste and measure the torque M. The rheological parameters measured in shearing situation are useful to practical ceramic extrusion processing.

The rheological property of MC solution was characterized by viscosimeter (Brookfield RVDVIII+, USA).

2.3. Mixing and testing program

The mixing of ingredients was processed at room temperature. Ceramic powders and binder of the ratio indicated in Table 2 were initially blended for about 5 min at 30 rpm in the Roller-cone mixer. Then de-ionized water was added slowly into the ceramic/binder mixture. The pastes were blended until the torque value was stable.

Table 1
Particle size distribution of γ-$LiAlO_2$ powder.

D10 (μm)	D50 (μm)	D90 (μm)
0.584	2.845	12.627

Table 2
Paste formulations in this study.

Paste no.	γ-$LiAlO_2$ (wt%)	MC (wt%)	H_2O (wt%)
1	69.70	2.50	27.80
2	64.10	3.85	32.05
3	68.18	3.41	28.41
4	72.14	2.98	24.88
5	76.31	2.54	21.15
6	74.10	2.48	23.42
7	74.10	2.75	23.15

To determine the relation between torque M and shear rate N, the roller speed was changed from 30 to 100 rpm with step of 10 rpm.

To observe the influence of shearing time and shear history in the rheological behavior of the ceramic pastes, the tests were taken at 30 and 50 rpm after the pastes were blended uniformly.

After mixing, pastes 2–5 were sheared at 50 rpm to investigate the effects of content of paste components on rheological properties. Pastes 3, 5 and 6 were taken as samples for stress–strain test, observing the differences in plastic deformation. Paste 7 was sheared at different temperatures to investigate the influence of temperature in aqueous methylcellulose plasticized γ-$LiAlO_2$ paste.

3. Results and discussion

3.1. Relation between torque and sheer rate

According to Beeaff and Hilmas [10], the relations between shear stress τ and torque M, shear rate γ and mixer rate are given by the following equations:

$$M = \tfrac{3}{2}V\tau \quad (3)$$

$$\gamma = \frac{d\pi R}{60h} \quad (4)$$

where V, d, h and R are constants related to the mixer. Based on these equations, the power law relation between shear stress τ and shear rate γ in Eq. (1) can be substituted by power law relation between torque M and mixer shear rate, given by Eq. (2). The relation can be further simplified as:

$$\log M = n \log R + C_{\mathrm{m}} \quad (5)$$

where C_{m} is a rheological mixing constant.

To examine whether this model fits for the ceramic pastes with high solid loading (around 70 wt%) for extrusion, the torque M of paste 1 was tested at various roller speeds below 100 rpm. The raw data was used to plot the logarithm of torque vs. the logarithm of roller speed. Fig. 1 presents the raw data of torque vs. mixer rate for the paste 1 recorded by the torque rheometer. From this graph, it was found that the torque value climbed with the increase of roller speed. To evaluate the

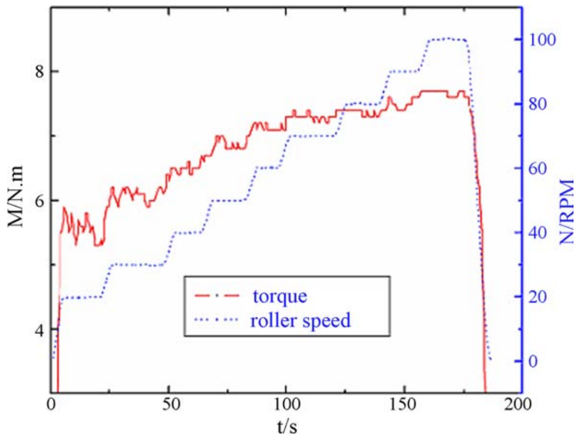

Fig. 1. Torque and shear rate data vs. time of paste 1.

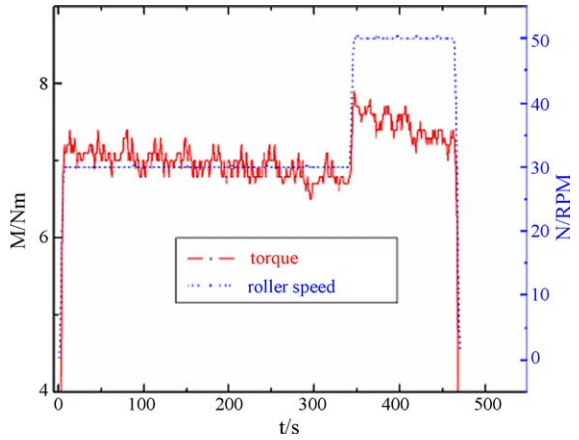

Fig. 3. Torque–shearing time dependence at 30 and 50 rpm for paste 1.

effectiveness of model (5) for γ-LiAlO$_2$ paste, the average torque values at each roller speed were taken to calculate logarithm of torque. The log (torque)–log (rate) dependence of paste 1 is plotted in Fig. 2.

As shown in Fig. 2, the log (torque) vs. log (rate) conforms to linear relation. The linear relation between log M and log N indicates that the model (5) fits well for the aqueous MC-plasticized γ-LiAlO$_2$ paste with high solid loading. The power law exponent n was determined by fitting a line to the data points and calculating the slope. The low value of n ($n = 0.198 < 1$) demonstrates the shear thinning behavior of the sample.

With the values of slope and intercept, the constants in models (2) and (5) can be calculated. With the constants, it is possible to predict the torque and power loading during screw extrusion of ceramics using the power law model (2) or (5).

3.2. *Influence of shearing time and shearing history*

The rheological behavior discussed above was assumed to be independent of shearing history and shearing time. However, for some materials the shear resistance may change with shearing time. The behavior that viscosity decreases with shearing time is called thixotropy, which is commonly observed for shear-thinning materials, while the behavior viscosity increases with shearing time is called rheopexy [7]. The effect of sheering time and sheer history on γ-LiAlO$_2$ pastes was studied.

Fig. 3 displays the effect of shearing time on torque value for paste 1. In Fig. 3, the torque value at 30 rpm decreases gradually with shearing time, and then tends to be stable. At 50 rpm the torque value reduces faster than that at 30 rpm. The drop of torque at a certain shear rate reflects the decrease of viscosity with shearing time, displaying the thixotropy behavior of γ-LiAlO$_2$ paste. This phenomenon may be attributed to the particle orientation [8] or the breakout of polymer–polymer and polymer–particle linkages.

After the above test, the paste was at rest for about 10 min, and then kept being sheared at 50 rpm. Fig. 4 presents the torque vs. shearing time dependence of paste 1 after 10 min rest.

In Fig. 3, the torque value at 50 rpm was finally stable around 7.3 N m. In Fig. 4, the torque value recovered to 8 N m at the beginning after the rest. This recover in torque value reflects the reconnection of polymer–particle and polymer–polymer. Therefore, the breakout of polymer–polymer and polymer–particle linkages was found to be the main cause of torque drop during shearing in our study.

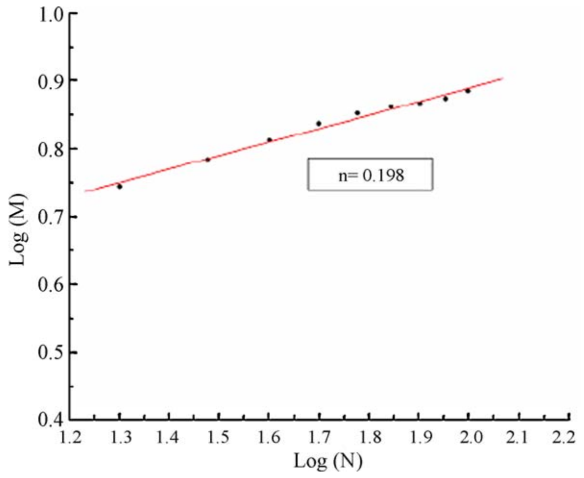

Fig. 2. log (torque)–log (rate) dependence of paste 1.

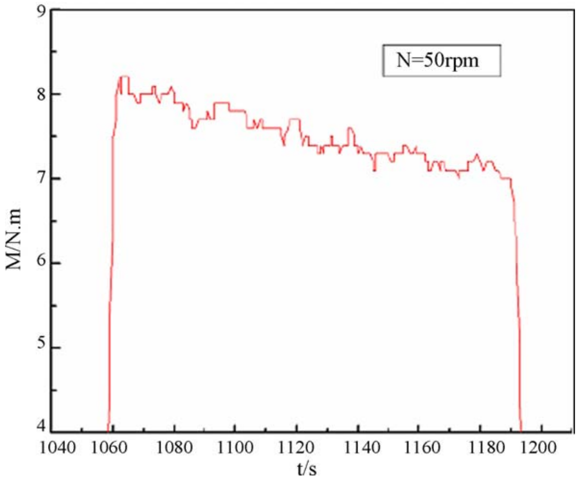

Fig. 4. Torque reading at 50 rpm after 10 min rest for paste 1.

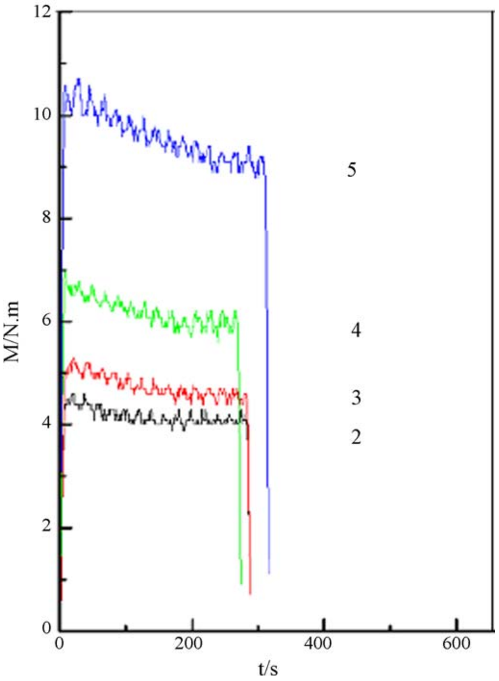

Fig. 5. Torque vs. time curves of pastes 2, 3, 4, and 5 at 50 rpm.

The torque drop during paste shearing suggests that the influence of shearing time on viscosity, shear stress and torque cannot be ignored in rheological tests of ceramic pastes. The rheological parameters of ceramic pastes recorded at the beginning of shearing may lead to deviations from their stable value.

3.3. *Influence of components content*

Solid loading and content of additives are two of the most important parameters relating to the flow of pastes. In the γ-$LiAlO_2$ pastes, deionized water was added to fill the larger intraparticle pores and interparticle voids to provide a lubricating layer around the ceramic particles. The polymers, i.e. MC, were added to improve plastic behavior and enhance green strength of extrudate. Solid loading and content of additives were found to have great influence in thixotropy behavior and plastic deformation of the paste.

As displayed in Fig. 5, there are large differences in torques of each paste at 50 rpm, which indicate the influence of solid loading and water content in the thixotropy property. Before getting stable, the torque value decreases at different slope. With the rise of solid loading and decline of water content, the extent and rate of torque descent become larger, so does the stable torque value. This means the thixotropy phenomena of paste with higher solid loading is more obvious than that of paste with less solid loading. When solid loading increases and lubricants decrease, the bonding of molecules or particles changes at higher rate during shear flow.

The plastic behavior of ceramic pastes is generally described by stress–deformation curves. From the stress–strain curve, the yield stress and plastic deformation region can be easily found. Fig. 6 shows the influence of solid loading and additives content on the stress–strain dependence. With the increase of solid loading, the paste appeared to have greater yield stress. At the same time, plastic deformation scope was influenced by the components content. At less solid loading (pastes 3 and 6), the paste showed extensive plastic deformation. When the solid loading increased up to 76 wt% (paste 5), the paste exhibited elastic transformation under stress. During plastic deformation, liquid film and polymers act as lubricant and plasticizer. Therefore, with the increase of ceramic loading and drop of additives content, γ-$LiAlO_2$ pastes became hard to be deformed, enhancing green strength of extrudate but imposing difficulty on extrusion process. According to the result shown in Fig. 6, the solid loading should not exceed 76 wt% for the aqueous methylcellulose (MC) plasticized γ-$LiAlO_2$ pastes.

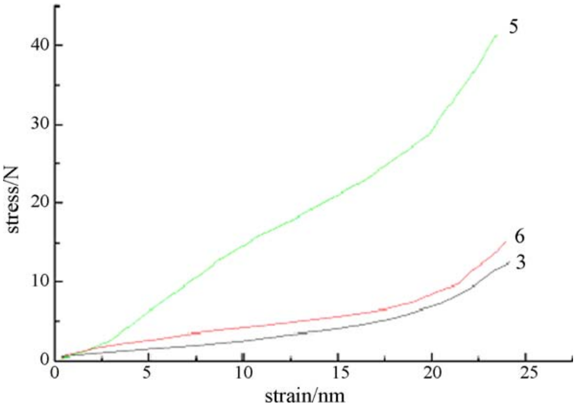

Fig. 6. Stress–strain dependence of pastes 3, 5 and 6.

3.4. *Influence of temperature*

Fig. 7 displays the effect of temperature on the rheological properties of paste 6 at 30 rpm. The torque value of paste 6 was around 6 N m below 43 °C. When the temperature was up to 43 °C, the torque climbed with the rise of temperature, and finally got stable around 8 N m though the temperature kept increasing. The rise of torque value is mainly due to the gelation of MC in this aqueous system. The explanation of sol–gel transformation for MC was provided by Rosiak and Yoshii [14].

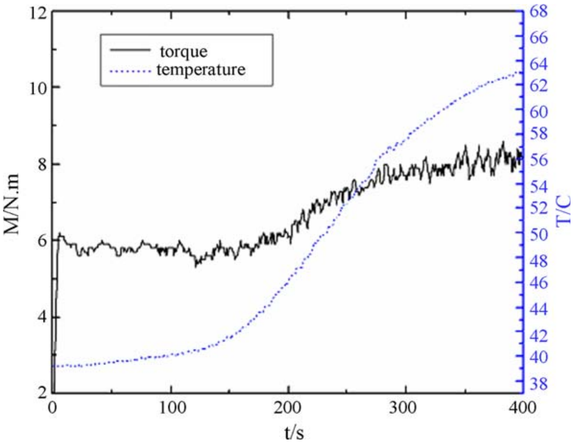

Fig. 7. Torque reading of paste 7 on heating.

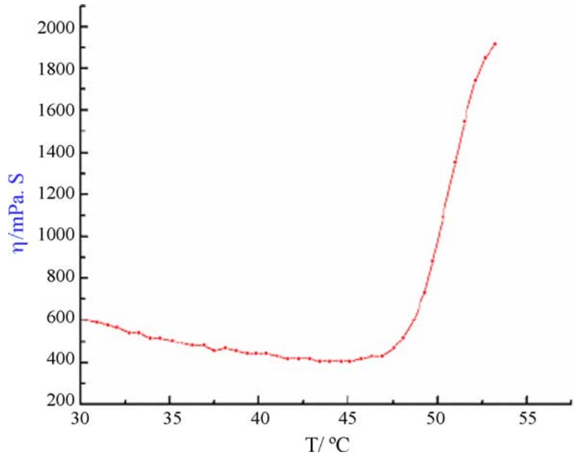

Fig. 8. Viscosity–temperature dependence of MC solution (2.43 wt%).

It is suggested that below gelation temperature, MC is soluble due to the water molecules cages formed around their hydrophobic methoxyl groups. At high temperature, the water cages break and the hydrophobic groups of MC associate, inducing gelation. Fig. 8 shows the effect of MC gelation on rheological property of its aqueous solution. The viscosity of MC solution turned to increase when it is heated up to 46 °C. Therefore, the gelation temperature of around 46 °C is obtained for MC. The gelation temperature of MC in γ-$LiAlO_2$ paste is a bit lower than that in the previous aqueous solution. This is mainly because the higher concentration of MC decreases the thermal gelation temperature [12].

4. Conclusions

The rheological behavior of aqueous methylcellulose plasticized γ-$LiAlO_2$ pastes with solid loading around 70 wt% was investigated. The power law model fits well the torque-revolution data obtained during shearing. There was significant influence of shearing time and shearing history on rheological parameters of the ceramic pastes.γ-$LiAlO_2$ pastes exhibited thixotropy behavior. The drop of torque during shearing could be attributed to the breakage of interaction between polymers and ceramic particles. The thixotropy of paste with higher solid loading is more obvious than that of paste with less solid loading. The shear resistance increased with temperature rise in aqueous methylcellulose (MC) plasticized γ-$LiAlO_2$ paste because of sol–gel transformation of MC in that system.

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