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# Rheology and chemorheology of aqueous γ-$LiAlO_2$ slurries for gel-casting

Xiaogang Xu, Zhaoyin Wen [*], Xiangwei Wu, Jiu Lin, Xiuyan Wang

*Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 DingXi Road, Shanghai 200050, PR China*

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## Abstract

The rheological and chemorheological properties of aqueous γ-$LiAlO_2$ slurries for gel-casting as well as their precursor solutions of methacrylamide and N,N′-methylenebisacrylamide (MAM/MBAM) were studied in the present work. The influences of mean particle size of γ-$LiAlO_2$ powder, the dispersant content and solid loading, mechanical stirring time on the rheology of γ-$LiAlO_2$ slurries were investigated systematically. It was demonstrated that the slurries exhibited shear-thinning behaviors with relatively low viscosity which could satisfy the gel-casting process. A rotary rheometer was used to study the chemorheology of the copolymerization of MAM/MBAM solution and the gelation process of γ-$LiAlO_2$ slurries. The activation energy calculated from the idle time for MAM/MBAM solutions and γ-$LiAlO_2$ slurries were $27.5 \pm 0.4$ kJ/mol and $25.3 \pm 0.4$ kJ/mol, respectively, which revealed the catalytic effect of the γ-$LiAlO_2$ particles on the copolymerization process.

*Keywords:* γ-$LiAlO_2$; Gel-casting; Rheology; Chemorheology

## 1. Introduction

Gel-casting process which combines polymer chemistry, colloidal chemistry and ceramic technology has been receiving an increasing attention in the past decade [1–4]. During the process, a high solid loading slurry with low viscosity should first be prepared by dispersing the ceramic powders in a premixed solution of the monomer and the crosslinker. After the addition of an initiator and a catalyst, the slurry is poured into a mold. The monomer and crosslinker then copolymerize in situ to create a macromolecular network, holding ceramic particles very close to each other. Homogeneous ceramic green bodies with uniform chemistry and excellent mechanical property are therefore obtained.

As is well known, the performance of the precursor slurry is the basis of the gel-casting technique. The solid loading of the slurry to great extent determines the density of the green body, and a high solid loading could alleviate the shrinkage during the drying and sintering steps. It is important to make a slurry with solid loading as high as possible while maintaining its proper fluidity. Studies have been conducted on the rheological properties of various ceramic slurries, such as $Al_2O_3$ slurry [5–6], SiC slurry [7], hydroxyapatite slurry [8], etc. It is the kernel of the gel-casting process for the copolymerization of monomer and crosslinker to form a strong, three-dimensional copolymer network. However, up to now, only a few researches have been conducted on the chemorheology of the gelation process. Babaluo et al. studied the chemororheological properties of gelation of aqueous-based alumina-organic monomers slurries [9], Omatete and Janney evaluated the active energy of slurry gelation by measuring the idle time of the monomer and crosslinker copolymerization [1], Potoczek investigated the catalytic effect of alumina grains onto polymerization rate of the monomer systems used in gel-casting [10], and so on.

γ-$LiAlO_2$ has been recognized as a potential candidate for tritium-breeding materials in nuclear fusion reactors because of its good thermophysical and mechanical stability as well as favorable irradiation behavior [11–13]. For such an application, various shapes of the breeding ceramics would be adopted which should be prepared by different ceramic forming processes, among which dry pressing has been generally used so far. However, density gradient occurred in its green bodies and the sintered ceramics. The gel-casting process for the forming of the γ-$LiAlO_2$ green bodies was reported in our previous paper, it has been certified as a favorable route for such a ceramic system [14]. Furthermore, in this work, the rheological and chemorheological

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[*] Corresponding author. Tel.: +86 21 52411704; fax: +86 21 52413903.
*E-mail address:* zywen@mail.sic.ac.cn (Z. Wen).

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properties of the precursor MAM/MBAM solutions and the aqueous gel-casting γ-$LiAlO_2$ slurries were studied systematically.

## 2. Experimental

### 2.1. Raw materials

The γ-$LiAlO_2$ powders were prepared with stoichiometric amounts of lithium hydroxide ($LiOH \cdot H_2O$) and γ-alumina (γ-$Al_2O_3$) via solid state reaction at 900 °C for 2 h. For the γ-$LiAlO_2$ slurry and gelation process, monofunctional methacrylamide (MAM), $CH_2{=}C(CH_3)CONH_2$ was used as a monomer. Difunctional N,N′-methylenebisacrylamide (MBAM), $(CH_2{=}CHCONH)_2CH_2$ was used as a cross-linker, ammonium persulfate (APS), $(NH_4)_2S_2O_8$ as an initiator, N,N,N′,N′-tetramethylethylenediamine (TEMED), $(CH_3)_2NCH_2CH_2N(CH_3)_2$ as a accelerator, the polyelectrolyte, ammonium polyacrylate (PAA, 40 wt.% solution) as a dispersant. All the reagents used were chemically pure.

### 2.2. Slurry preparation and rheological properties

A certain amount of MAM and MBAM was first completely dissolved in deionized water to prepare a 10 wt% solution, the weight ratio of MAM to MBAM was 5:1. γ-$LiAlO_2$ powders with different mean particle sizes were slowly added to the precursor monomer solution, and the concentration of the dispersant was controlled in the range of 0.3–1 wt%. The slurries, with solid loadings between 45 vol% and 55 vol% were obtained after mechanical stirring for 1–12 h. The temperature was kept at 0 °C by an ice water bath during the whole process. The rheological properties of the γ-$LiAlO_2$ slurries were evaluated by a rotary rheometer (Brookfield RVDVIII+, USA).

### 2.3. Chemorheological characterization

The weight ratio of monomer to cross-linker in the premixed solutions was ranged from 9:1 to 3:2, and the solid loading content of the γ-$LiAlO_2$ slurries was kept at 25 vol%. Before the addition of initiator and accelerator, the MAM/MBAM solution and γ-$LiAlO_2$ slurry were degassed to avoid the inhibition effects caused by $O_2$. The copolymerization process of MAM and MBAM was initiated by APS and accelerated by TEMED. The amount of APS was varied from 0.3 wt% to 1 wt%, and the quantity of TEMED was equal to the APS. The apparent viscosity versus time for the precursor solutions and γ-$LiAlO_2$ slurries was evaluated to characterize the copolymerization of MAM and MBAM.

## 3. Results and discussion

### 3.1. Rheological properties of γ-$LiAlO_2$ slurry

Fig. 1 shows the apparent viscosity versus shear rate of the slurries with 50 vol% γ-$LiAlO_2$ after mechanical stirring for different time. It can be seen that the slurry stirred for 2 h displays a relatively high viscosity over the range of shear rates evaluated. With the increase of stirring time, the viscosity decrease over the whole measuring shear rate range. While the stirring time is over 8 h, the apparent viscosity of the slurry nearly keeps constant, indicating homogeneity and stability of the γ-$LiAlO_2$ slurry after the mechanical stirring. It can also be observed that all the γ-$LiAlO_2$ slurries exhibit a shear-thin behavior, which is beneficial for the slurry casting and gelation.

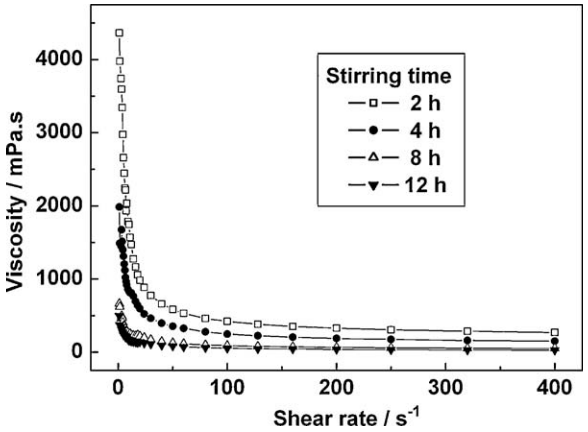

Fig. 1. Effect of mechanical stirring time on the viscosity of γ-$LiAlO_2$ slurries.

As is well known, the particle size distribution and specific surface area of ceramic powders have great influences on the rheological performances of a slurry. Fig. 2 gives the plots of apparent viscosity versus applied shear rate of the stable slurries prepared with the γ-$LiAlO_2$ powders having different mean particle sizes. As shown in Fig. 2, the slurry prepared from the γ-$LiAlO_2$ powders of 1.1 μm mean particle size has a relatively high viscosity, even with the solid loading as low as 30 vol%. Compared to the former one, the powder with mean particle size of 3.4 μm is more suitable to prepare the slurry with a solid loading as high as 50 vol% and with better fluidity. However, we found it difficult to make stable slurry with the γ-$LiAlO_2$ powders having a mean particle size bigger than 8.8 μm, which sedimentate rapidly after a short time standing.

The effects of dispersant content on the rheology of slurries are shown in Fig. 3. It is observed that the viscosity

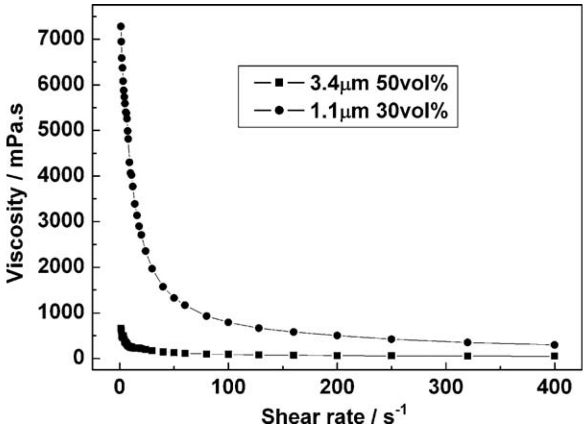

Fig. 2. Effect of mean particle size of powder on the viscosity of γ-$LiAlO_2$ slurries.

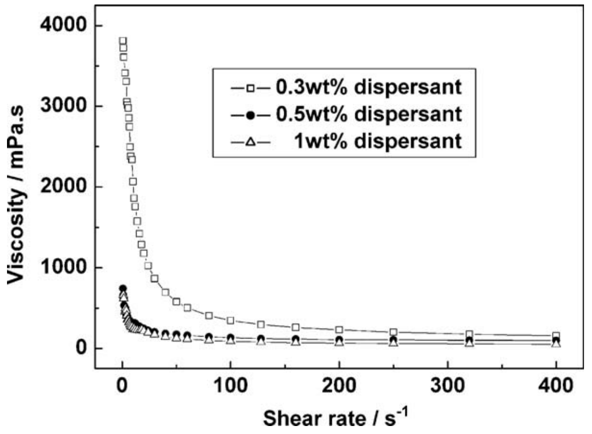

Fig. 3. Effect of dispersant concentration on the viscosity of γ-$LiAlO_2$ slurries.

of the slurry displays a tendency to decrease with the increase of dispersant amount especially at the dispersant amount lower than 0.5 wt%. While the dispersant quantity varies higher than 0.5 wt%, the change in viscosity is very weak. Therefore, 0.5 wt% is taken as an appropriate dispersant concentration for the aqueous γ-$LiAlO_2$ slurries in this work.

The viscosity versus shear rate curves of the γ-$LiAlO_2$ slurries with different solid loadings are given in Fig. 4. It is found that, like the former several cases, all the slurries exhibit shear-thinning behaviors, which could be attributed to the perturbation of the slurry structure by the shear. As suggested [15], at lower shear rates, the slurry structure is close to equilibrium state owing to the dominant effect of the thermal motion over the viscous force. While the shear rate increases, the viscous force affects the slurry structure and leads to the shear-thinning behavior. At a very high shear rates, the viscous force even dominates and the viscosity plateau measured the resistance to flow of a slurry with a completely hydrodynamically controlled structure. As shown simultaneously in Fig. 4, the higher the solid loadings, the higher viscosity the slurry exhibits. The slurry containing 55 vol% of γ-$LiAlO_2$ possesses a viscosity of 615 mPa s at the shear rate of 100 $s^{-1}$, which can still meet the requirements of the casting process.

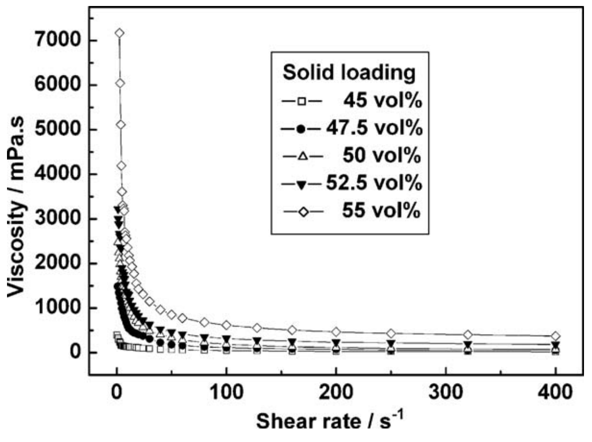

Fig. 4. Effect of solid loading on the viscosity of γ-$LiAlO_2$ slurries.

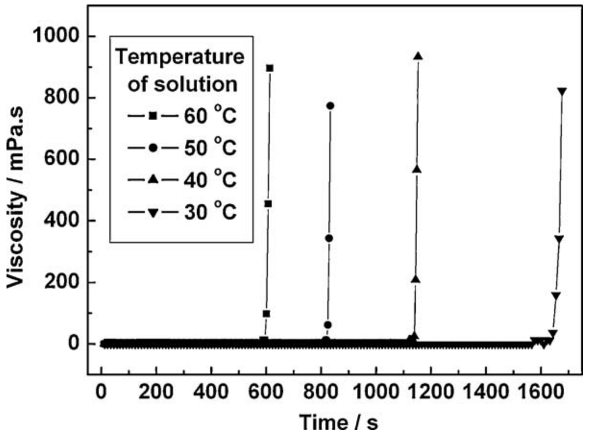

Fig. 5. The apparent viscosity as a function of time for MAM/MBAM solution at different temperatures.

### 3.2. Chemorheological properties of the MAM/MBAM solutions

Fig. 5 illustrates the apparent viscosity as a function of time for the 10 wt% MAM/MBAM solution. It is found that, after the addition of initiator and accelerator, there is a short period with constant viscosity, then the viscosity increases rapidly towards infinity. The inactive period is known as idle time or induction time in the free radical polymerization process, and it affords the time available to cast the slurry into the mold for the gel-casting technique. As shown in Fig. 5, the idle time of the MAM/MBAM solution is reduced from more than 25 min to less than 10 min while the temperature rose from 30 °C to 60 °C.

In the free radical polymerization process, the activation energy is often used to characterize the kinetics of the initiation step and it can be directly calculated from the idle time. The idle time is inversely proportional to the rate of production of free radicals, which is related to the solution temperature. This relationship may be expressed by an Arrhenius-type equation [9]:

$$t_{\mathrm{idle}} \propto \frac{1}{r} = A\,\mathrm{e}^{E_{\mathrm{a}}/RT}$$

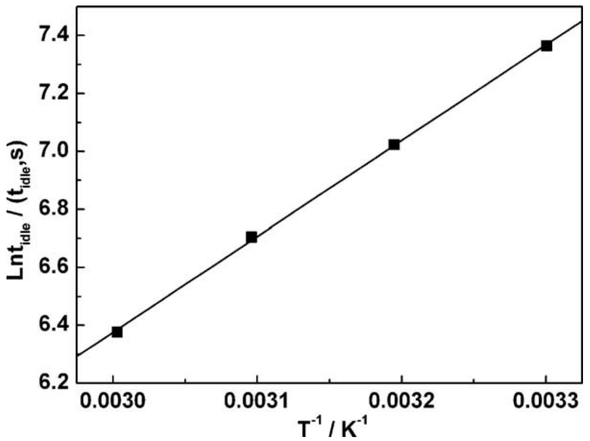

Fig. 6. Semi-log plot of idle time vs. inverse of temperature for MAM/MBAM solution.

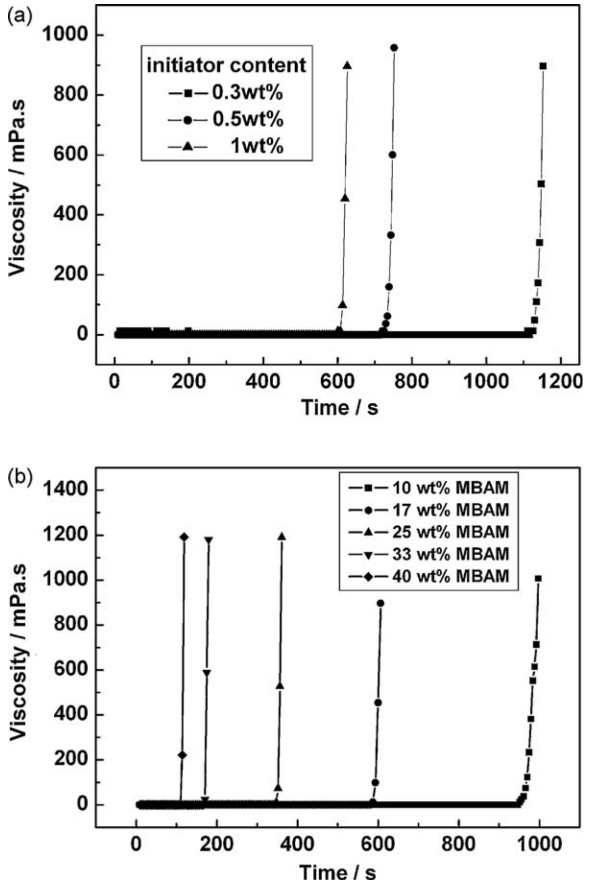

Fig. 7. The apparent viscosity as a function of time for the slurries with (a) various initiator concentrations and (b) different crosslinker weight ratios.

where $r$ is the reaction rate, $R$ the gas constant and $E_a$ is the activation energy of the free radical polymerization process. Fig. 6 gives the Arrhenius plot of the idle time for the 10 wt% MAM/MBAM solution. The calculated value of activation energy is $27.5 \pm 0.4$ kJ/mol.

Fig. 7a shows the apparent viscosity as a function of time for the solution with different initiator concentrations and Fig. 7b gives the apparent viscosity as a function of time for different crosslinker weight ratios. It can be seen from the figures that the increase of both the initiator concentrations and the crosslinker weight ratios result in the decrease in the idle time of the MAM/MBAM solutions. The idle time is related to the chain initiation stage, which can be divided into two steps. The first is the formation of the primary free radicals by the decomposition of initiators, and the second is the addition reaction between the primary free radicals and the monomers. Consequently, the increases of the reactant concentrations lead to the decrease of the idle time during the initiation period.

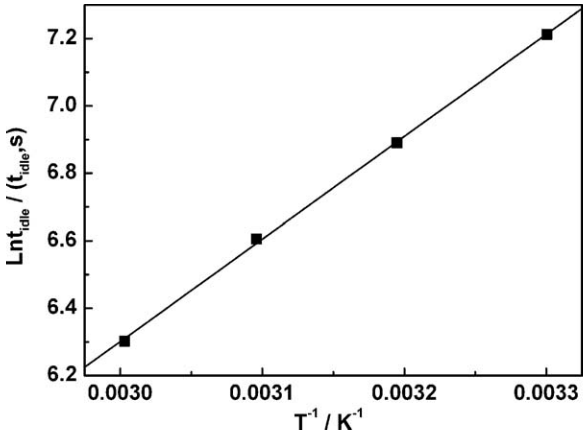

Fig. 9. Semi-log plot of idle time vs. inverse of temperature for the γ-$LiAlO_2$ slurries.

### 3.3. Chemorheological properties of the γ-$LiAlO_2$ slurries

Fig. 8 shows the effects of temperature on the apparent viscosity as a function of time for the slurries with 25 vol% γ-$LiAlO_2$. The idle time of the gelation process for the γ-$LiAlO_2$ slurries displays a tendency to decrease with the increasing temperature, which is similar to that for the copolymerization of the MAM/MBAM solution. At the same temperature, the idle time of the slurry gelation is shorter than that of the MAM/MBAM solution, indicating the accelerating effects of the γ-$LiAlO_2$ powder. Before the initial reaction occurs, the apparent viscosity of the γ-$LiAlO_2$ slurries do not keep constant as the precursor monomer solutions do, but increases slowly due to the evaporation of the water from the slurry.

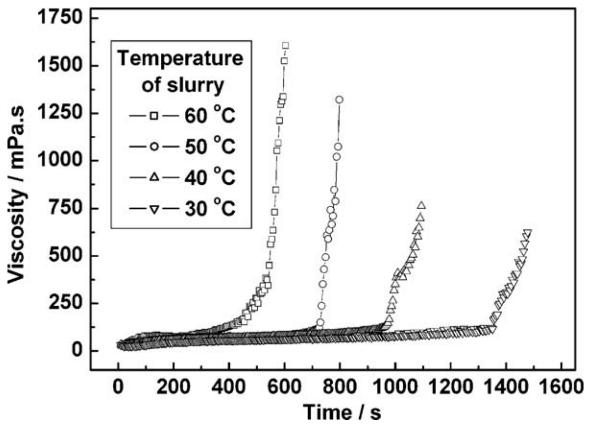

Fig. 8. The apparent viscosity as a function of time for the γ-$LiAlO_2$ slurries.

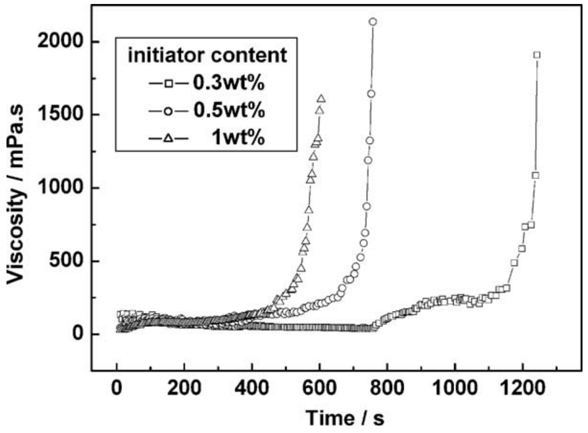

Fig. 10. The apparent viscosity as a function of time for the slurries with different initiator concentrations.

The Arrhenius plot of idle time versus inverse of temperature for the γ-$LiAlO_2$ slurry with 25 vol% solid loading is given in Fig. 9. The activation energy calculated from the slope of the fitting line is $25.3 \pm 0.4$ kJ/mol, which is less than that of the copolymerization of the premixed MAM/MBAM solution.

Fig. 10 shows the apparent viscosity as a function of time of the slurry with 25 vol% γ-$LiAlO_2$ and different initiator concentrations. The decrease trend of the idle time with the increasing initiator concentration for slurries is similar to that of the MAM/MBAM solution. Moreover, the catalytic effect of the γ-$LiAlO_2$ powder can also be observed from the comparison of the idle time. When the γ-$LiAlO_2$ powder is dispersed into the monomer solutions, the MAM and MBAM molecules can be absorbed by the γ-$LiAlO_2$ particles through hydrogen bonds. The concentration of the monomer and crosslinker in the region around the γ-$LiAlO_2$ particles becomes higher than that of the solution. After the addition of the initiator and accelerator, the γ-$LiAlO_2$ particles absorb APS and TEMED in the similar way. As a result, it becomes easier for the MAM and MBAM in the slurry to copolymerize.

## 4. Conclusions

γ-$LiAlO_2$ slurries exhibited a shear-thinning behavior, which is beneficial for the casting and gelation process. With the dispersant concentration of 0.5 wt%, the solid loading of the slurry reaches as high as 55 vol%. Temperature, initiator and accelerator concentration, and the amount of crosslinker all had significant effects on the idle time of the slurries of γ-$LiAlO_2$. The calculated values of activation energy for the copolymerization of MAM/MBAM solution and the gelation of the slurry are $27.5 \pm 0.4$ kJ/mol and $25.3 \pm 0.4$ kJ/mol, respectively. The decrease of activation energy of the slurry indicates the accelerating effect of the γ-$LiAlO_2$ particles for the copolymerization of MAM/MBAM.

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