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Processing of Al_2O_3 sheets by the gel–tape-casting process

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Abstract

Flat ceramic sheets have been produced by a novel method, i.e. the gel–tape-casting process, has been developed. The process makes use of a monomer solution to prepare the ceramic slurry. During casting, a network is formed by the polymerized organic monomers, and the ceramic particles are fixed within the network thus resulting in a green tape. The mechanism of polymerization of ceramic slurry is outlined and the influencing factors on solidification are discussed. Excellent green tapes can be produced by accurately controlling the concentration of the monomer solution, the pH of the slurry, the polymerizing temperature, and the amount of initiator and catalyst. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Tape casting; Gel; Ceramic substrate; Polymerizing mechanism; Dynamics

1. Introduction

With the rapid development of electronic and information technology industries, flat ceramic sheets, the backbone of two kinds of increasingly important electronic ceramic materials: multilayered capacitors and multilayered ceramic packages, are facing more and more market demands [1,2]. Tape-casting is studied and applied widely in the world as a prominent technique for producing flat ceramic sheets [3,4].

The main drawbacks of the typical tape casting process is that substantial amounts of organic components are used, which usually result in (i) skin formed at the surface of the green tape while solvents dry out, (ii) anisotropic drying shrinkage and residual tresses always generated in the green tape, (iii) formation of crack within the green tape during binders burn-out, (iv) inhomogeneous microstructure along the thickness of the tape due to solvents migration which can carry binders, plasticizers and fine particles to the tape surface [5–8].

To overcome these shortcomings, a novel process, the gel–tape-casting process which combines tape-casting and gel-casting technology together, has been developed by the authors for the production of flat ceramic sheets. In general, gel-casting is not suitable for flat ceramic sheets forming because of the anti-polymerizing effect of oxygen. In the gel–tape-casting process, an inert atmosphere is applied to protect the slurry from the air and the anti-polymerizing effect is thus avoided. The slurry can be solidified to a green tape successfully.

In the process, a monomer solution is used as substitute of organic solvents and binders, and a ceramic slurry containing over 50 vol.% solid is prepared with the monomer solution. So the amount of organic components used in the slurry is substantially lower compared to the slurry for a typical tape-casting process. During casting, the slurry is protected with an inert atmosphere and heated to about 40–80 °C. Then monomers are polymerized and a network is formed, with ceramic particles being fixed within the network, then the slurry is solidified to green tape. The tape can be dried within a few minutes. Since very small amounts of organic components are used, the green tape can be sintered without any special organic burn-out procedure.

In this paper, the mechanism of polymerization of the ceramic slurry is explained and influencing factors on solidification are discussed. It is found that the polymerizing rate largely affects the quality of the green tape. The polymerization rate can be adjusted by controlling the concentration of the monomer solution, the pH of the slurry, the polymerizing temperature, and the amount of initiator and catalyst.

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2. Experimental procedure

2.1. Starting materials

A commercial α-Al_2O_3 powder has been used (mean particle size, 2.9 μm; specific surface area, 0.434 m^2/g; supplied by Henan Xinyuan Aluminium Corporation, PR China). Chemical composition of the α-Al_2O_3 powder and its particle size distribution are given in Table 1 and Fig. 1, respectively.

Acrylamide has been used as organic monomer, whereas *N,N′*-methylene bis-acrylamide has been used as crosslinker. $(NH_4)_2S_2O_8$ solution and *N,N,N′,N′*-Tetramethyl ethylenediamine have been used as polymerizing initiator and catalyst respectively.

2.2. Gel–tape-casting

The precursor is prepared with acrylamide (monomer) and *N,N′*-methylene bis-acrylamide (crosslinker) according to the ratio 90:1. Monomer solutions with different concentrations are obtained by diluting the precursor with different amounts of distilled water and used as the solvent for slurry.

Alumina powder and dispersant are added in the solvent, and a slurry with more than 50 vol.% solids is prepared. The slurry is ball milled to break down agglomerates and achieve a good homogeneity, vacuum deaired, added with initiator and catalyst, poured into the reservoir, and tape cast, then the cast tape is heated and protected with an inert atmosphere (nitrogen) and made to solidify to a green tape. The flow chart of this process is shown in Fig. 2.

2.3. Characterization

S-450 scanning electron microscopy (Hitachi Corporation, Japan) has been used to characterize the microstructure of the green tape.

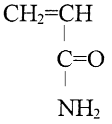
3. Results and discussion

3.1. Mechanism of the gel–tape-casting process

Table 1
Chemical composition of the α-Al_2O_3 powder

Al_2O_3 (wt.%)	Content of impurity (< wt. %)					Density (g/cm^3)	α-Al_2O_3 (wt%)
	SiO_2	Fe_2O_3	Na_2O	B_2O	Burn loss		
> 99.7	0.05	0.03	0.05	0.04	0.1	> 3.96	> 95

In the gel–tape-casting process, an AM monomer solution is used as the solvent, and the slurry is prepared by adding ceramic powders and additives in the solvent. During casting, initiator and catalyst are added in the slurry and polymerization proceeds. The slurry solidifies and a green tape is obtained. The structural formula of AM is

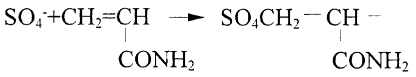


$$\begin{array}{l} CH_2{=}CH \\ \quad\;\; | \\ \quad\;\; C{=}O \\ \quad\;\; | \\ \quad\;\; NH_2 \end{array} \qquad (1)$$

Polymerization of AM may occur as follows. Firstly, the initiator is decompounded into primary free radicals,

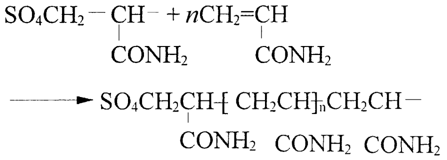
$$(NH_4)_2S_2O_8 \rightarrow 2NH_4^{+}+2SO_4^{-} \qquad (2)$$

Primary free radicals can be combined with the monomer molecule, which produces monomer free radicals,



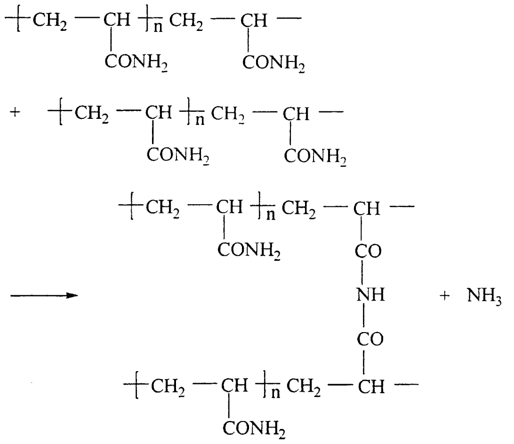
$$SO_4^{-}+CH_2{=}\underset{\substack{|\\ CONH_2}}{CH} \rightarrow SO_4CH_2-\underset{\substack{|\\ CONH_2}}{CH}- \qquad (3)$$

which can combine with monomers and result into chain free radicals,



$$\begin{array}{l} SO_4CH_2-\underset{\substack{|\\ CONH_2}}{CH}- + nCH_2{=}\underset{\substack{|\\ CONH_2}}{CH} \\ \longrightarrow SO_4CH_2\underset{\substack{|\\ CONH_2}}{CH}\!\left[CH_2\underset{\substack{\\ CONH_2}}{CH}\right]_n\!CH_2\underset{\substack{\\ CONH_2}}{CH}- \end{array} \qquad (4)$$

This reaction proceeds continuously and AM molecules polymerize into polymer chains. A network is formed by polymer chains by two ways, crosslinking (5) of polymer chains and bridging (7) between polymer chains by crosslinker molecules.



$$\begin{array}{l} \left[CH_2-\underset{\substack{|\\ CONH_2}}{CH}\right]_n CH_2-\underset{\substack{|\\ CONH_2}}{CH}- \\ +\;\left[CH_2-\underset{\substack{|\\ CONH_2}}{CH}\right]_n CH_2-\underset{\substack{|\\ CONH_2}}{CH}- \\ \longrightarrow \begin{array}{l} \left[CH_2-\underset{\substack{|\\ CONH_2}}{CH}\right]_n CH_2-\underset{\substack{|\\ CO\\ |\\ NH\\ |\\ CO\\ |}}{CH}- \qquad + NH_3 \\ \left[CH_2-\underset{\substack{|\\ CONH_2}}{CH}\right]_n CH_2-CH- \end{array} \end{array} \qquad (5)$$

In order to make monomers polymerize completely, MABM [molecular formula is shown as (6)] is added into the monomer solution as crosslinker.

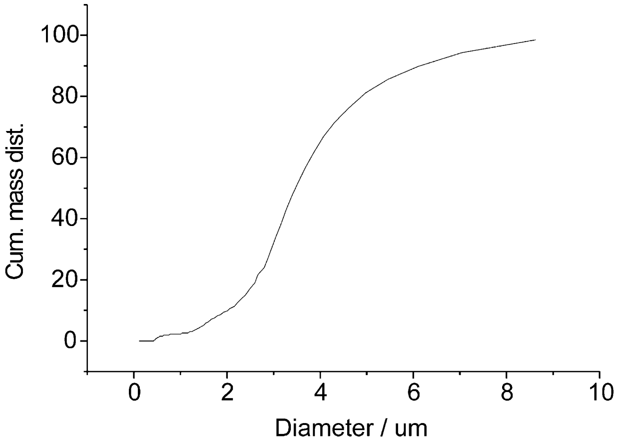
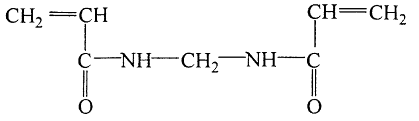
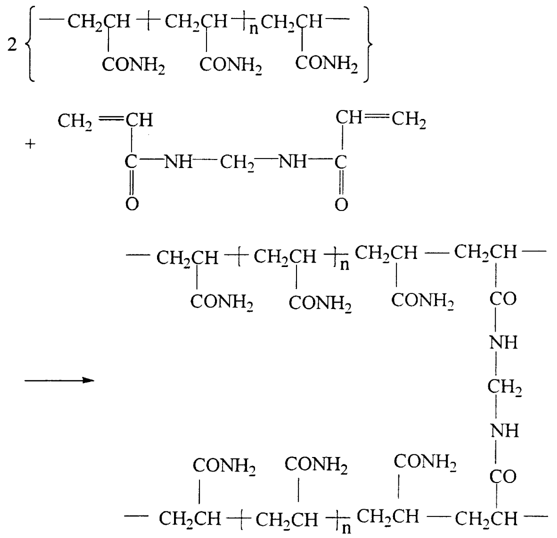


Fig. 1. Distribution of the particle size of the Al_2O_3 powder.



$$CH_2{=}CH{-}C({=}O){-}NH{-}CH_2{-}NH{-}C({=}O){-}CH{=}CH_2 \qquad (6)$$

MABM has two C = C double bond and can be connected between two polymer chains by a bridge effect, which is beneficial for network formation (7).



(7)

The ceramic slurry solidifies by polymerization of AM, so a ceramic green tape is obtained. The network of PAM acts as a frame, which fixes ceramic powders by adsorption. The details of combination between ceramic powder and PAM can be viewed in Fig. 3.

It should be mentioned that the slurry exposed to air could not be solidified to a green tape because of the anti-polymerizing effect of oxygen, therefore, during the casting process the slurry should be protected by an inert atmosphere of nitrogen or argon.

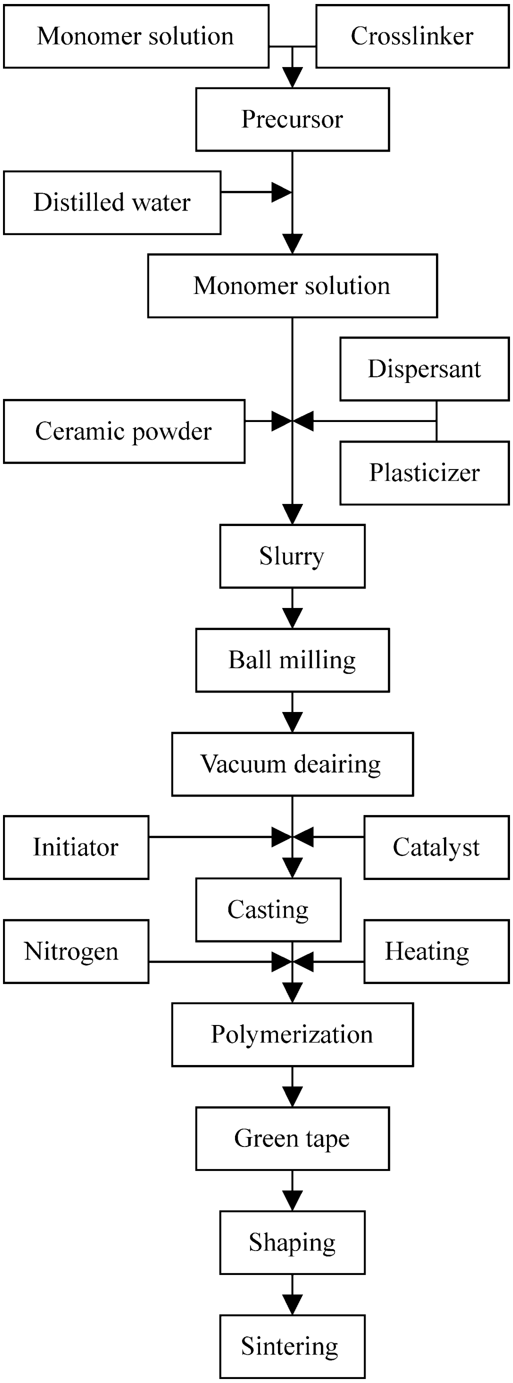
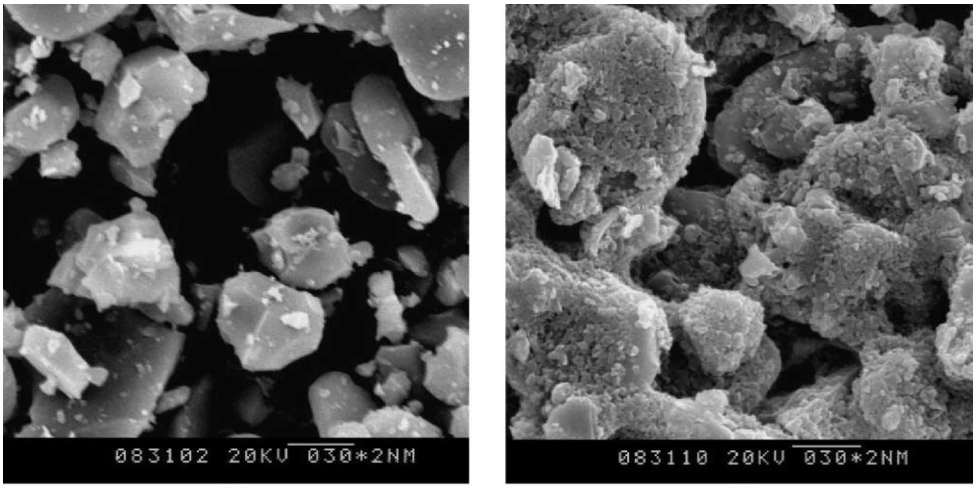


Fig. 2. Flow chart of the gel–tape-casting process.

3.2. Dynamics study of polymerization

The polymerization rate of a ceramic slurry depends on the properties of slurry, such as the concentration and pH value of the monomer solution, and the reaction conditions, such as polymerization temperature and amount of initiator and catalyst. To obtain a green tape with high strength and suitable flexibility, slurry preparation and polymerization condition should be controlled precisely.



(a) (b)

Fig. 3. SEM of ceramic particles before and after polymerization; (a) pre-polymerization, (b) after polymerization.

Experimental results show that pores are always present in the green tape if the slurry solidifies too fast because the gas released during polymerization cannot be eliminated from the green tape completely. Pores in the green tape would decrease the strength of the green tape and of the sintered sample. Therefore, it is necessary to keep the polymerization rate within a suitable range. In other words, the slurry would be better polymerized within a few minutes than a few seconds.

3.2.1. *Concentration of the monomer solution*

The relationship between polymerization rate and concentration of the monomer solutions is shown in Fig. 4. The higher the concentration, the shorter the polymerization time, i.e. the higher the polymerization rate.

The polymerization time decreases sharply with the increase of the monomer solution concentration up to 40 wt.% after which it remains practically constant. Thus, the polymerization rate can be adjusted by controlling the monomer solution concentration more easily if the concentration is less than 40 wt.%. For the Al_2O_3 slurry, in order to obtain a suitable polymerization rate in the gel–tape-casting, the concentration of monomer solution should be kept within the range of 30–40 wt.%.

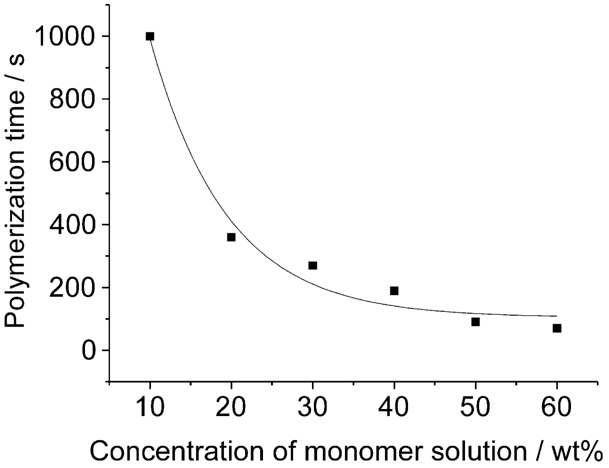


Fig. 4. Relationship between concentration of monomer solution and polymerization time.

3.2.2. *pH value*

The pH value of the slurry affects the polymerization rate significantly because the initiator $(NH_4)_2S_2O_8$ decomposes more quickly in an acidic condition than in an alkaline condition. As a result, the polymerization rate decreases with the increase of the pH value and the polymerization time increases almost linearly with pH increase (Fig. 5). Besides influencing the polymerization

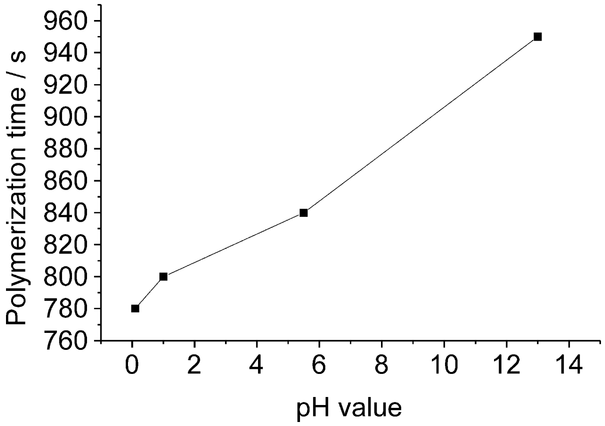
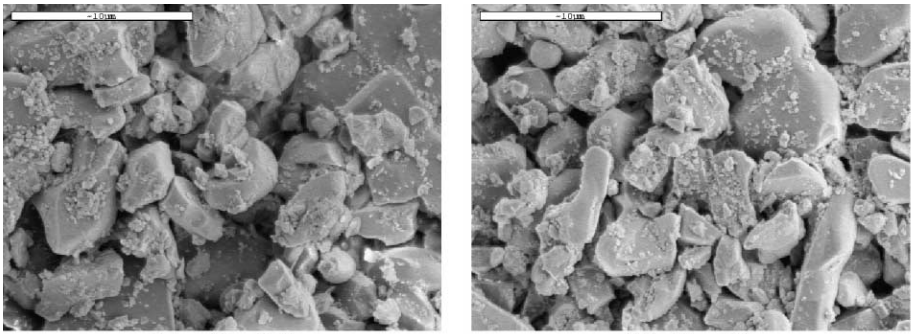


Fig. 5. Relationship between the pH of the ceramic slurry and polymerization time.



(a) pH = 3.5 (b) pH = 8.5

Fig. 6. SEM of the broken section of green tape made from slurries with different pH value.

rate, the pH value also influences the microstructure of the green tape. At low pH, polymerization of AM tends to release NH_3 which forms pores in the green tape leading to an inhomogeneous microstructure [Fig. 6(a)]. Experimental results show that a suitable pH value of Al_2O_3 slurry lies in the range 7–9, a condition beneficial for both inhibiting pore formation in the green tape and improving the dispersibility of the ceramic powder in the slurry. As a result a green tape can be obtained with a homogeneous microstructure [Fig. 6(b)].

3.2.3. *Polymerization temperature*

Temperature is one of the most important factors influencing polymerization rate. Although a high temperature is beneficial for improving polymerization rate, a too high temperature will make the water in the slurry gasify so quickly that pores will be formed in the green tape.

Fig. 7 shows the relationship between temperature and polymerization time. With the increase of temperature, polymerization time is reduced dramatically. A suitable temperature for polymerization of the system lies in the 40∼80 °C range.

During the forming process, it is expected that the slurry can be kept stable for a long time before casting, and to polymerize very quickly after casting. According to the sensitivity of the polymerization rate on temperature, the starting time of polymerization can be controlled accurately by keeping the ceramic slurry at low temperature (such as 25 °C) before casting, and heating it to 40–80 °C to complete polymerization after casting.

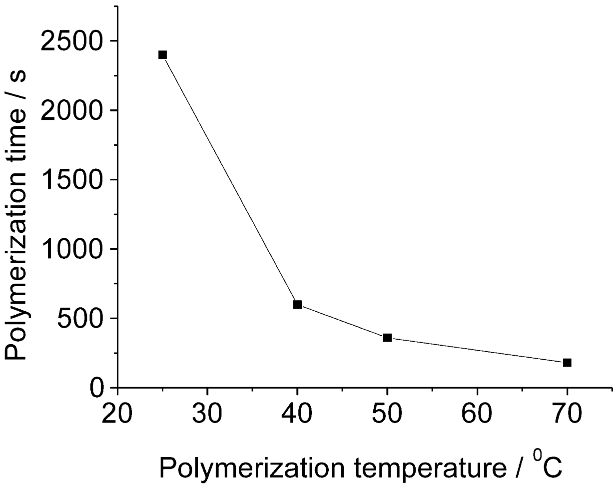


Fig. 7. Relationship between temperature and polymerization time.

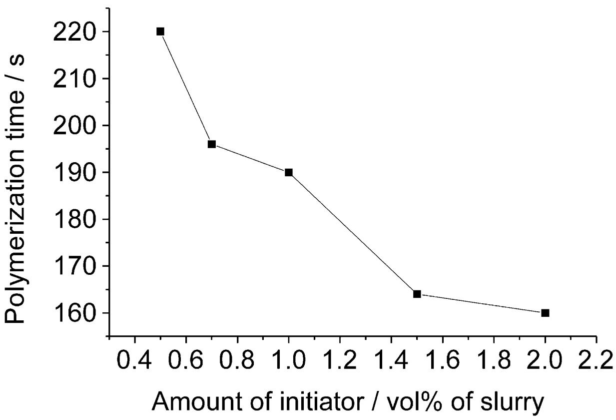


Fig. 8. Relationship between amount of initiator and polymerization time.

3.2.4. *Initiator and catalyst*

It is proved that the higher the polymerization rate, the more difficult to control the casting process. If the polymerization proceeds too quickly, the slurry may polymerize in the reservoir before passing the blade.

The role of the initiator is creating primary free radicals to start the polymerization of the monomers. A large amount of initiator will increase the initiating rate and lead to a very fast polymerization. Fig. 8 shows the relationship between the amount of initiator and the polymerization time of the Al_2O_3 slurry. A suitable amount of initiator lies in the range 0.5–1 vol.% of slurry.

The catalyst can significantly depress the activation energy of the reaction and improve the polymerization rate. Experimental results show that the slurry can not

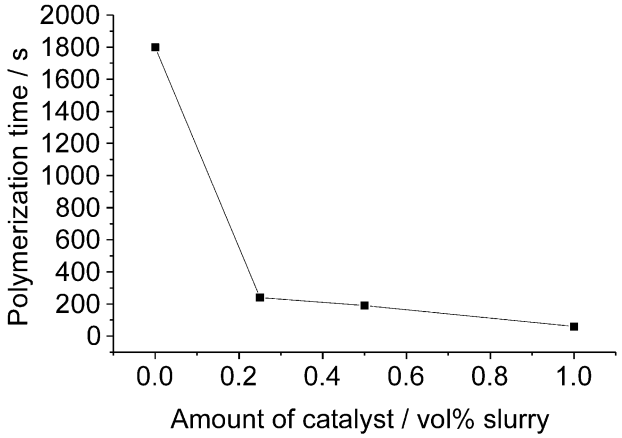


Fig. 9. Relationship between amount of catalyst and polymerization time.

polymerize without a catalyst even if a certain amount of initiator is added. Nevertheless, a too large amount of catalyst makes the polymerization rate uncomfortable. For the studied Al_2O_3 slurry, one appropriate amount of catalyst is about 0.5 vol.% of the slurry. The relationship between polymerization time and amount of catalyst is shown in Fig. 9.

4. Conclusions

The solidification mechanism of the gel–tape-casting is analysed. The polymerization rate of AM depends on the properties of the slurry and on reaction conditions. The concentration of the monomer solution should be kept within 30–40 wt.% to obtain a suitable polymerization rate. A suitable range of pH values of the Al_2O_3 slurry and temperature are 7–9 and 40–80 °C, respectively. The AM sensitivity to temperature can be used to control the starting time of polymerization accurately. For the studied Al_2O_3 slurry, the suitable amount of initiator and of catalyst are 0.5–1 vol.% and $\sim$0.5 vol.% of the Al_2O_3 slurry, respectively.

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