

Mullite fibres prepared by sol–gel method using polyvinyl butyral

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Abstract

Mullite fibres with uniform diameter and smooth surface have been synthesized using commercial grade polyvinyl butyral (PVB) as binder. The sol with good spinnability was obtained at reaction temperature of 60 °C for 1 h. The results of X-ray diffraction indicated that the Al–Si spinel was obtained before complete mullitization, which implied the addition of PVB retarded the phase transformation of mullite. The fibres showed a rough surface and lateral cracks at 800 °C. Smooth and dense surface was observed when fibres were sintered at 1200 °C and completed transformation to mullite was achieved. This technique offered the possibility of synthesizing mullite fibres at considerably lower cost than at present. Crown Copyright © 2008 Published by Elsevier Ltd. All rights reserved.

Keywords: Mullite; Fibres; Sol–gel processes; Spinel; Polyvinyl butyral

1. Introduction

Compared to organic fibres and other inorganic fibres, mullite fibres exhibit various kinds of excellent properties which include high temperature strength, creep resistance, thermal and chemical stability, low thermal expansion coefficient and good dielectric properties.^{1–6} As high strength materials, they are mainly used as reinforcement of metals, ceramics and resins. The attractive properties of thermal stability and dielectric properties lead to the application of high temperature and electrical insulating materials.

Conventionally, drawing the melt method was adopted for the synthesis of low-melting point ceramic fibres through the orifice at high temperature.^{7,8} The raw materials are made into homogeneous melt with a certain viscosity at high temperature. However, it is difficult to draw the fibres from starting materials with high-melting points. In order to overcome the difficulties, the sol–gel technique is employed to synthesize the high-melting point ceramic fibres.^{9–13} The sol is hydrolyzed and then condensed or polymerized/co-polymerized until an appropriate viscosity for spinning is achieved for production of fibres. In comparison to high temperature melt technique, the sol–gel method not only makes the starting materials homogeneous, but

also lowers the sintering temperature because of their fine grains and homogeneous composition.

Many successful processes have been reported in the preparation of mullite fibres by the sol–gel method. Mullite fibres were prepared from the aluminum isopropoxide (AIP), aluminum nitrate and tetraethylorthosilicate (TEOS).¹⁴ Okada et al. also studied the effect of Al source on the mullite fibre.¹⁵ In most of starting materials, AIP was selected as Al source, because its polymerization was responsible for the appropriate spinning viscosity. However, since the AIP which is expensive was involved in the synthesis process of mullite fibres, the process is limited to its widespread applications, although mullite fibres with smooth surface and dense microstructure are obtained.

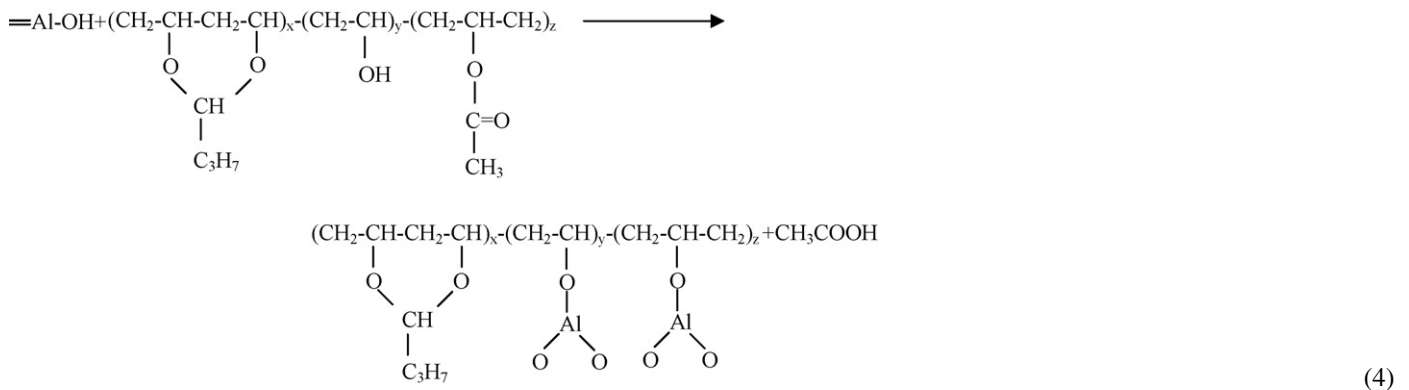
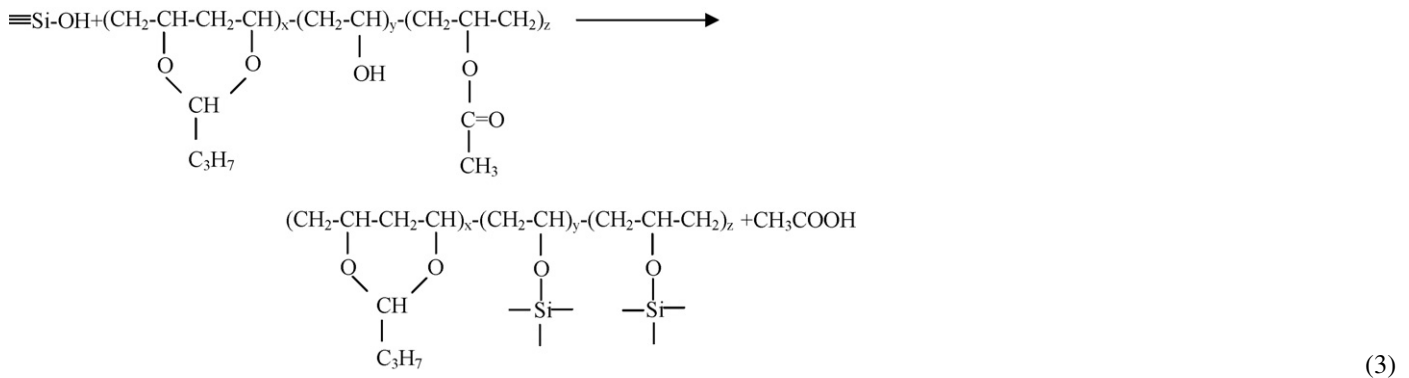
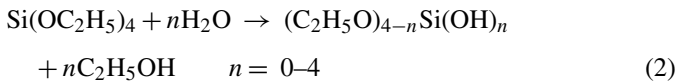
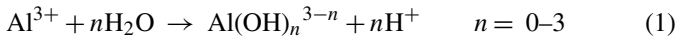
In this work, we fabricated mullite fibres with smooth surface and no cracks using aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, AN), TEOS with commercial grade PVB as binder. In addition, the process of long mullite fibres including sol flow behavior, viscosity, diameter change, crystallization phase and surface morphology at different temperature is also investigated in detail.

2. Reactions in the sol

When AN with crystallization water and TEOS are dissolved into ethanol (EtOH), Al^{3+} and TEOS reacts with crystallization water, and hydrolytic process takes place. Commercial grade PVB typically contains 18–22% hydroxyl groups among

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three segments.¹⁶ Dissolved in ethanol, the hydroxyl groups and ester groups react with the aluminosilicate sol and an organic–inorganic hybrid structure was formed.¹⁷ These overall reactions can be written as:



Although the hydrolytic reaction (Eq. (2)) of TEOS is prevented in the solution due to the presence of H^+ , it can be promoted by the actual reaction temperature. Another fact that should be considered is that some complex network structures are formed as a result of the further reaction of Eqs. (3) and (4). However, linear structures in the sol are good for the spinning of fibres.^{18–20} Accordingly, in order to inhibiting the formation of non-linear polymers or network structures during the synthesis of aluminosilicate sols with spinnability, the reactions time should also be adopted. For the formation of hybrid organic–inorganic sol which contains large amount of linear structures, the process parameters (reaction temperature and time), the compositions of the starting powders (PVB which contains hydroxyl groups) used as binder are most important.

There is a relationship between intrinsic viscosity $[\eta]$ and molecular weight M , which is given by the Mark–Houwink equation.^{21–23}

$$[\eta] = KM^a \quad (5)$$

where K and a are constants for a given polymer–solvent–temperature system.

So the change of molecular weight could be implied by viscosity of solution in the studies.

3. Experimental

Starting materials used were AN (Chemically grade, Xi'an reagent factory, Xi'an, China), TEOS (Chemically grade, Xi'an reagent factory, Xi'an, China), PVB (SD-1, Tianjin Huida

Chemical Industry Co., Ltd., Tianjin, China) and ethanol (Chemically grade, Xi'an reagent factory, Xi'an, China).

The solutions with different compositions were prepared according to Table 1 for a comparison of viscosity. The processing steps are shown in Fig. 1. 11.1 wt% PVB was added into EtOH with magnetic stirring until PVB was dissolved into EtOH completely. It was named as solution (1). Solution (2) was prepared as following: AN was dissolved into EtOH at room temperature (20 °C) with vigorously stirring until an aqueous solution with a molar concentration of 1.6 M was obtained,

Table 1
Solution with different compositions used for a comparison of viscosity

Solution	Weight ratio (wt%)				Spinnability after laying at 20 °C for 20d
	EtOH	AN	TEOS	PVB	
1	88.9			11.1	No
2	57.4	35.9	6.7		No
3	53.6	33.5	6.2	6.7	Good

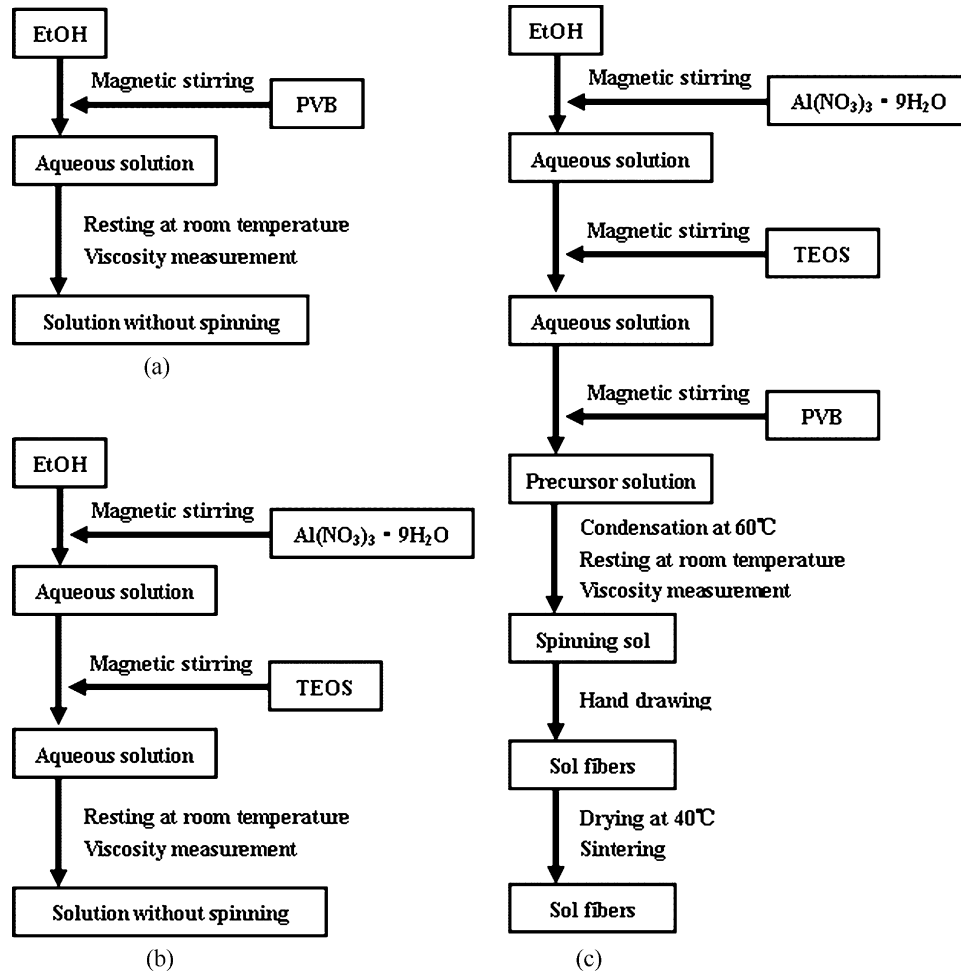


Fig. 1. Schematic view of the mullite fibres production route for (a): solution (1), (b): solution (2) and (c): solution (3).

then TEOS was added into the solution with further stirring for 1 h.

Aluminosilicate sols with the stoichiometric mullite composition ($\text{Al}:\text{Si} = 3:1$) using PVB as binder (solution (3)) was prepared on the basis of solution (2). Commercial grade PVB was added slowly into a solution with the same composition of solution (2). It was stirred vigorously at room temperature until PVB was dissolved into the solution completely. The weight ratio $[\text{AN}]/[\text{PVB}]$ in the mixture solution was 5, which corresponds to a weight ratio $[3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2]/[\text{PVB}]$ of 1.13. The solution (3) with a viscosity of about 300 mPa s was obtained. One part of solution (3) was condensed at 60°C using a water bath, and another part was laid at room temperature for a viscosity measurement. After appropriate condensation, the solution with a viscosity of 1200 mPa s was suitable for spinning. Subsequently, gel fibres were drawn at room temperature by a hand drawing method. The gel fibres were then dried around 10 min at 40°C using an evaporator. The dried gel fibres were then calcined at various temperatures at heating rate of $5^\circ\text{C}/\text{min}$. The holding time was 1 h.

Viscosity measurement of solution (1)–(3) treating for different time was carried out at room temperature by using a NDJ-1 viscometer (Shanghai Balance Tech. Co., Ltd., Shanghai, China) at different shear rate (6, 12, 30 and $60 \text{ r}/\text{min}$). The aver-

age values of viscosity at different shear rate were calculated. The prepared fibres were characterized by thermo-gravimetric analysis/differential scanning calorimetry (TG/DSC), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The TG/DSC was measured on SDT Q600 with a heating rate $10^\circ\text{C}/\text{min}$ and sample weight was about 15 mg. The FTIR spectroscopes were detected on Prestige-21 (Shimadzu, Tokyo, Japan). The microscopy was used to measure the diameter of fibres. The XRD patterns were obtained on D/max - 3C diffractometer (Rigaku Co., Ltd., Tokyo, Japan.) at 40 kV and 100 mA using $\text{Cu K}\alpha$ radiation, a step width of 0.02° and a counting time of 0.3 s. The SEM observation was done on JSM-35C instrument (JEOL, Tokyo, Japan).

4. Results and discussion

In the mullite sol, the shape of polymers added into the sols is an important factor for the spinnability of the sols. Fig. 2(a) shows the dependence of the viscosity on the aging time at room temperature for solution (1), (2) and (3) in Table 1, respectively. No change in the viscosity by the time can be seen for solution (1) with 11.1 wt% PVB and solution (2), which contains TEOS and AN without PVB. The solution (1) and (2) showed no

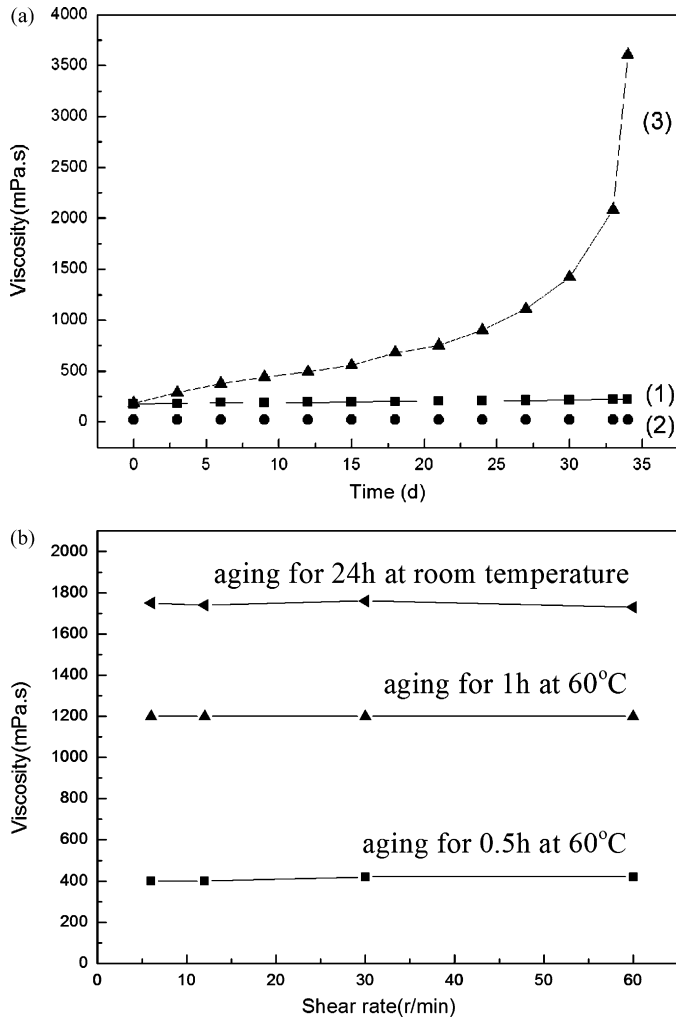


Fig. 2. (a) Variation of viscosity of solution (1)–(3) as a function of aging time at room temperature, and (b) rheological properties of solution (3) aged for different time at 60 °C.

spinnability, which indicated that no linear shapes were formed in these two solutions. The change of viscosity by the time is clearly seen for the solution (3) in Fig. 2(a). The change of molecular weight could be presented by the variation of viscosity, according to Eq. (5). The increase of viscosity with time at room temperature implied the occurrence of chemical reactions of Eqs. (3) and (4) and increase of molecular weight in the hybrid organic–inorganic sol.

Fig. 2(b) shows the viscosity and rheological behavior of the solution (3) aged for different time at 60 °C. The viscosity of as-prepared solution (3) was about 300 mPa s before condensation. After aging for 1 h in a 60 °C water bath, the viscosity was up to higher (about 1200 mPa s), and the sol (3) showed spinnability, which was attributed to the formation of linear shape due to the reactions. No change in the viscosity as a function of the shear rate can be seen. Newtonian behavior which has been known to be a prerequisite for fibre spinning sols was presented. However, the viscosity increased still from 1200 to 1700 mPa s, when sol (3) was aging for 24 h at room temperature and the Newtonian behavior was also shown. It was attributed to the further reaction of Eqs. (3) and (4).

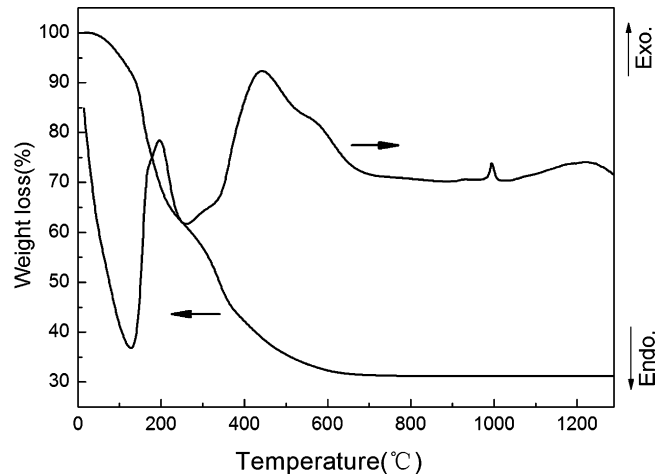


Fig. 3. TG/DSC curve of as-prepared fibres prepared from solution (3).

For the preparation of the sol (3) with PVB as binder which performs good spinnability, relative high temperature (60 °C) and long aging time (1 h) should be beneficial, according to the reaction analysis.

The TG/DSC curves of the sol (3) with PVB as binder are shown in Fig. 3. From room temperature to ~1300 °C, there was a weight loss of ~70%, which was chiefly attributed to the evaporating of ethanol/H₂O, decomposition of organic materials and nitrates. The two sharp endothermic peaks at ~130 and ~240 °C corresponded to the loss of ethanol/H₂O and combustion of organic materials, respectively. There was an exothermic peak at around 450 °C, implying that the decomposition of nitrates took place. So the weight decreased quickly before 400 °C and did slowly between 400 and 600 °C. The mass of sol became almost constant above 600 °C. The sample also showed a small exothermic peak at about 1000 °C, which was assigned to crystallization of mullite.

The solution (3), sol fibres and fibres calcined at 800 and 1000 °C were also studied through FTIR analysis in the wavenumber region of 4000–400 cm⁻¹. Fig. 4 shows the infrared spectra of solution (3), sol fibres from solution (3) and

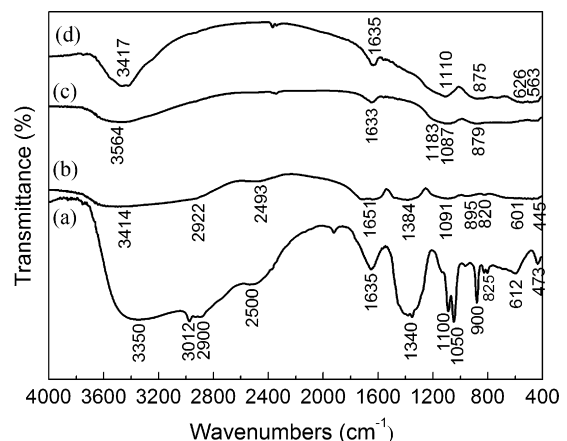


Fig. 4. FTIR spectra of (a) as-prepared sols, (b) sol fibres and fibres calcined at (c) 800 °C, (d) 1000 °C.

Table 2
FTIR frequency assignments of as-prepared solution (3), sol fibres and fibres calcined at 800 and 1000 °C

As-prepared solution (3)	Sol fibres	800 °C	1000 °C	Assignments*
473 m	445 w		563 vw	ν (AlO ₆)
612 m	601 w		626 vw	ν (AlO ₆)
804 m	820 w			
825 m				
900 s	895 w	879 w	875 vw	ν (AlO ₄)
1050 s	1091 m & br	1087 m	1110 m	ν (Si–O–Si of SiO ₄)
1100 s		1183 sh		ν (Si–O–Al)
1340 s	1384 m & br			
1635 s	1651 m & br	1633 m	1635 m	OH of H ₂ O
2500 sh	2493 sh			
2900 m	2922 w			
3012 m				
3350 s & br	3414 m & br	3564 m & br	3417 m	OH of H ₂ O

s, strong; w, weak; vw, very weak; m, medium; sh, shoulder; br, broad.

* Assignments are based on temperatures at 1000 °C.

fibres calcined at different temperature. The observed frequencies are listed in Table 2.

As shown in Fig. 4(a), the broad peak at 3350 cm⁻¹ and the one at 1635 cm⁻¹ are assigned, respectively, to the OH stretching and bending modes of alcohol and PVB. The band at 3012 cm⁻¹ along with the shoulder around 2900 cm⁻¹ is assigned to the asymmetric and symmetric stretching vibrations of CH₂ and CH₃ groups, respectively. The absorption peak at 2500 cm⁻¹ was attributed to the OH stretching vibration of COOH group in CH₃COOH as a result of Eqs. (3) and (4). The absorption band observed at 1340 cm⁻¹ is corresponded to N=O symmetric stretching vibration. Under basic conditions, hydrolytic-polymeric reaction can take place resulting in forming of Si–OH, Al–OH, Si–O–Si and Al–O–Al. The two bands at 1050 and 1100 cm⁻¹ were due to Si–O–Si stretching vibration. In addition to that a band was observed at 900 cm⁻¹, which corresponded to Al–O vibration band. The two peaks at 825 and 804 cm⁻¹ are assigned to Si–OH stretching mode. The stretching modes of Al–O–Al linkages are observed at 612 and 473 cm⁻¹.

The structural evolution took place within the sol during condensation at 60 °C. The spectra of the spinning sol fibres is shown in Fig. 4(b). The two peaks at 3414 and 1651 cm⁻¹ corresponded to the OH group in EtOH and PVB is also presented. The CH₂ and CH₃ bands around 2900 cm⁻¹ in Fig. 4(a) develops into a shoulder observed at 2922 cm⁻¹. The absorption peak at 2493 cm⁻¹ due to OH vibration in COOH group is also present in Fig. 4(b). The N=O stretching vibration mode at 1384 cm⁻¹ showed the presence of NO₃⁻. During condensation at 60 °C, some reactions took place resulting in organic–inorganic hybrid structure and some broad and weak bands in the 400–1200 cm⁻¹ region were observed. The broad band at around 1091 cm⁻¹ was attributed to the Si–O–Si group. The peaks at 900, 612 and 473 cm⁻¹ corresponded to the Al–O bonds and at 804 cm⁻¹ due to the Si–OH in Fig. 4(a) became weak after condensation at 60 °C.

Fig. 4(c) and (d) shows the FTIR spectra of fibres calcined at 800 and 1000 °C in the wavenumber region 400–4000 cm⁻¹. During heat-treating removal of the hydroxyl groups and of

the organic materials in the gel structure is expected. This is confirmed by the disappearance of the bands. The OH vibration modes at about 3500 and 1633 cm⁻¹ in Fig. 4(c) and (d) were due to the absorption water. The bands appeared at 1087 and 879 cm⁻¹ in the 800 °C spectrum develops into a well-defined band with components at 1110 and 1000 cm⁻¹, which is attributed to the Si–O–Si vibration of SiO₄. The shoulder peak was appeared at 1183 cm⁻¹ in the 800 °C spectrum. These bands are assigned, respectively, to the Si–O–Si and Si–O–Al networks. In the 1000 °C spectrum, several weak peaks also are observed. The bands at 563, 626 and 875 cm⁻¹ were assigned to the vibration of tetrahedrally and octahedral coordination Al–O bonds. It may be note that an Al–O band in [AlO₆] gives Al–O stretching modes in the region of 760–900 cm⁻¹.^{24–26} The presence of both tetrahedrally and octahedrally coordinated Al–O bonds and Si–O bonds indicated the starting of a transformation. This is further supported by the exothermic peak at 980 °C in the DTA pattern and the XRD data.

The diameters of fibres, which were calcined at 150, 240, 450 and 1200 °C, were measured on microcopy in Fig. 5. The

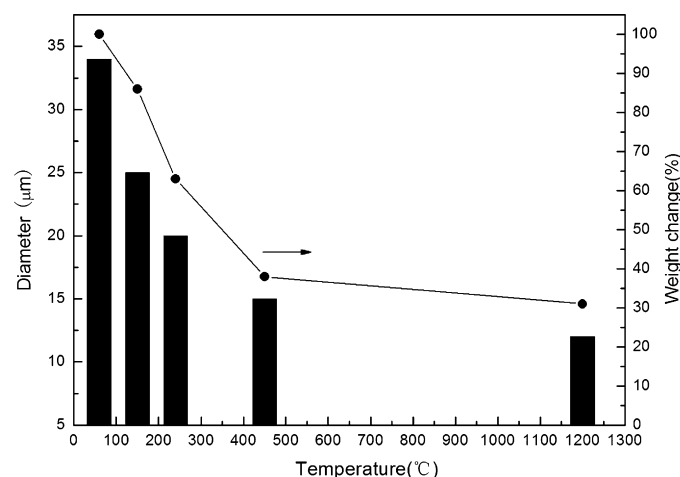


Fig. 5. Shrinkage in diameter and weight change percent of fibres from sol (3) containing 11.1 wt% PVB.

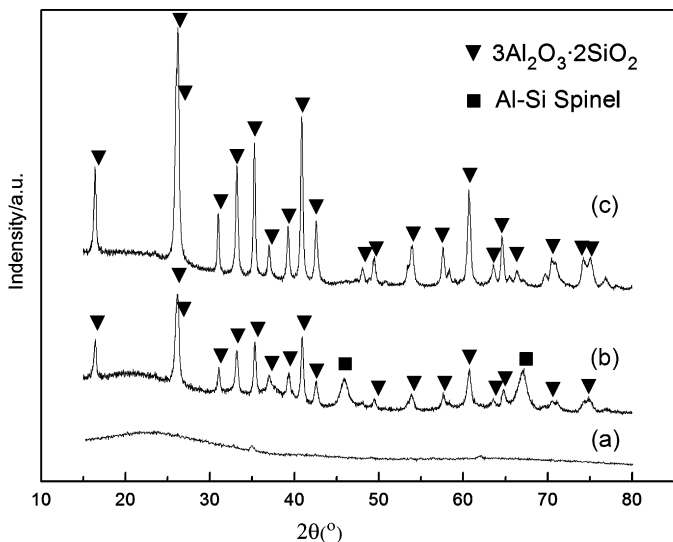


Fig. 6. X-ray diffraction analysis of sintered mullite fibre at (a) 800 °C, (b) 1000 °C and (c) 1200 °C.

change of diameters is compared with the weight change at different temperature from data of TG measurement in Fig. 3. The diameter values give the good agreement with the weight change. It was found that the fibre diameter decreased with temperature increasing. After sintering at 1200 °C, the fibres diameter was changed from original 34 to 12 μm. The decrease of diameter was attributed to the evaporation of solvent EtOH and decomposition of NO₃⁻, organic materials and the transformation from amorphous phase to mullite.

The X-ray diffraction patterns of mullite fibres calcined at 800, 1000 and 1200 °C are shown in Fig. 6. The amorphous phase was shown when fibres were calcined at 800 °C. The main phase in the samples sintered at 1000 °C was mullite phase, although some Al-Si spinel remained. It was implied that the mullite and Al-Si spinel phase formed simultaneously as a result of the reaction of amorphous SiO₂ and Al₂O₃, according to the TG/DSC curve in Fig. 3. The quantification of Al-Si spinel content was about 48.3 wt%. Complete transformation to mullite was observed at 1200 °C.

Usually, the formation of mullite by sol-gel methods starts at 1000 °C and there is no other phase in the samples.^{14,15} However, when organic materials are used as binder, retardation in the phase transformation of mullite is observed. This could possibly be due to the formation of hybrid organic-inorganic sol. The structure and the homogeneity of the sol affect the material properties such as crystallization behavior and sinterability.^{27,28} Al-Si spinel peaks were observed in fibres containing PVB, which suggested the PVB binder plays an important role on the mullitization. The formation of hybrid organic-inorganic sol retarded the phase transformation of the fibres containing PVB.

The photograph of the calcined fibre prepared from sol (3) was shown in Fig. 7. It can be seen from Fig. 7 that the mullite fibre with uniform diameter showed flexibility. The fibres length was about 40 cm. The fibres length was influenced by viscosity and surface tension of spinning sol, speed of hand drawing and so on. The further research about these factors is carrying on.

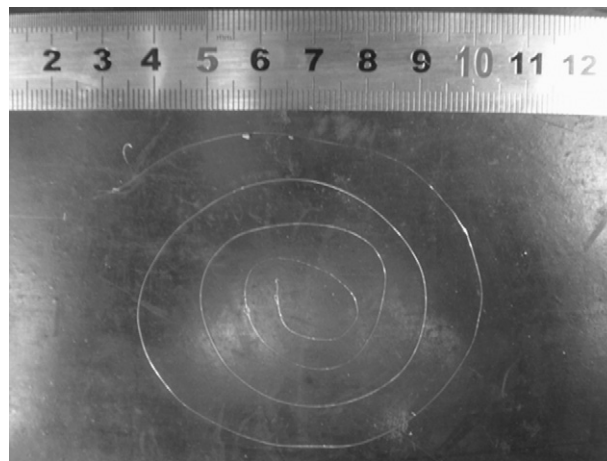


Fig. 7. Photograph of the calcined fibres prepared from sol (3).

The surface morphology of mullite fibre sintered at 800 and 1200 °C is shown in Fig. 8. The average diameter of fibres sintered at 800 and 1200 °C was found to be ~15 and ~12 μm, respectively. The fibres sintered at 800 °C showed a rough surface as a result of the combustion of organic and decomposition of nitrates. When fibres were sintered at 800 °C, there were large amount of lateral cracks running to the elongated direction of the fibres. Completed transformation to mullite was achieved at 1200 °C, and dense surface formed. The fibres showed uniform diameter. No defects were found on the surface of the fibres.

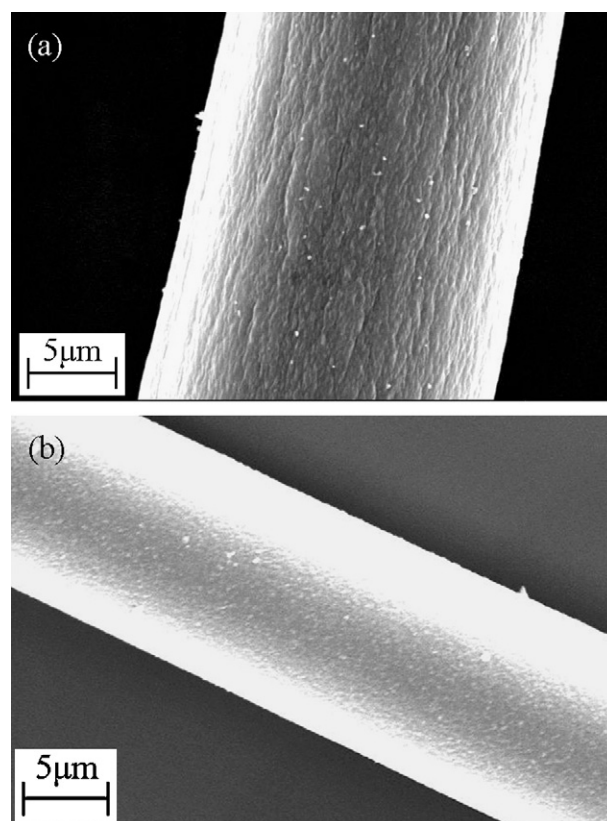


Fig. 8. SEM photograph of sintered fibres at (a) 800 °C and (b) 1200 °C.

5. Conclusions

A spinnable hybrid organic–inorganic aluminosilicate sol was prepared using commercial grade PVB and mullite fibres were synthesized. The viscosity of solution with different compositions showed that PVB played an important role in the formation of spinnable sol with linear polymers. Sol with good spinnability was obtained using water bath at 60 °C for 1 h. The presence of organic materials had a pronounced effect in phase transformation to mullite. The result of X-ray diffraction indicated that the formation of Al–Si spinel phase took place before complete mullitization, which implied that the hybrid organic–inorganic sol retarded the mullitization. The fibres showed a rough surface at 800 °C and smooth surface at 1200 °C, which is implied that the densification of fibres occurred after phase transformation.

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