

Preparation of glass fibres of the ZrO_2-SiO_2 and $Na_2O-ZrO_2-SiO_2$ systems from metal alkoxides and their resistance to alkaline solution

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Glass fibres of the ZrO_2-SiO_2 and $Na_2O-ZrO_2-SiO_2$ systems containing up to 33 wt % ZrO_2 were prepared by a non-melting technique using zirconium *n*-propoxide, sodium methoxide and silicon tetraethoxide as raw materials. The mixed alkoxide solutions were exposed to moist air for hydrolysis. The fibrous gels were drawn from these solutions in the course of hydrolysis, and converted to the corresponding oxide glass fibres by heating at 500 to 700° C. It was found that chemical durability of the fibres toward alkaline solution increased with ZrO_2 content. The weight loss due to the corrosion by 2 N NaOH solution at 96° C for 4 h was around 14 mg dm⁻² for the fibres containing 17 to 26 wt % ZrO_2 , which was comparable to the alkali-resistant glasses so far obtained by the conventional melting technique. The glass fibres containing 33 wt % ZrO_2 showed higher resistance.

1. Introduction

The preparation of oxide glasses [1, 2] through hydrolysis and gelling of metal alkoxides or metal alcoholates, $M(OR)_n$, where M is the metal atom and R is the alkyl group, has the advantage over the conventional melting technique of supplying glasses at lower temperatures, achieving higher homogeneity [3] and purity and producing glasses from compositions which would be phase-separated or crystallized in the conventional technique.

The formation of oxide glasses from the corresponding metal alkoxides has been investigated by the present authors [4, 5], Nogami and Moriya [6-8], Carturam *et al.* [9], Yoldas [10], Yamane and co-workers [11, 12] and Decottignies *et al.* [13]. The present authors have found that certain alkoxide solutions show a remarkable spinnability over the viscosity range of several poise to several hundred poise in the course of hydrolysis just before the solution gels into a solid mass [14, 15], giving fibrous gels on drawing and glass fibres on

heating. Glass fibres of the $Al_2O_3-SiO_2$ [12], TiO_2-SiO_2 [12, 16, 17] and SiO_2 systems [18] have been obtained by this technique.

The glasses containing ZrO_2 , known for their high resistance towards attack by alkaline solution [19-22], are employed to reinforce cement in place of asbestos [23, 24]. The glasses with a ZrO_2 content higher than 20 wt %, however, are difficult to obtain by the conventional melting technique because of high melting temperatures. The application of the "alkoxide method" to the production of the ZrO_2 -containing glass fibres is, therefore, attractive [25]. In the present work, details of the preparation of the ZrO_2 -containing glass fibres of the ZrO_2-SiO_2 and $Na_2O-ZrO_2-SiO_2$ systems and their alkali-resistance will be reported.

2. Experimental details

2.1. Preparation of glass fibres

The preparation of glass fibres from metal alkoxides consists of three steps as shown schematically in Fig. 1; mixing and hydrolysis of the

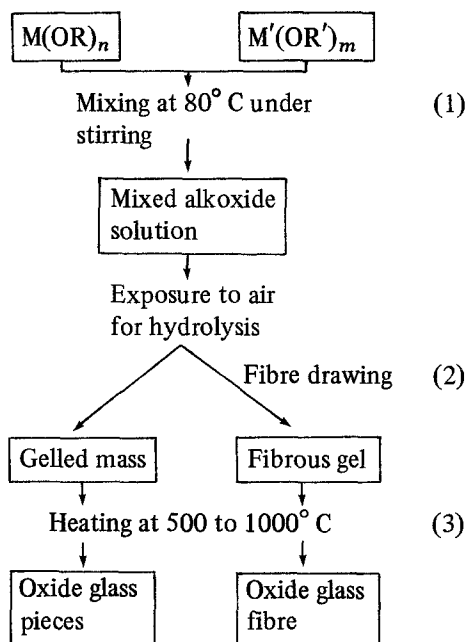


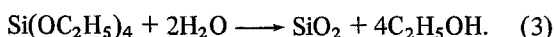
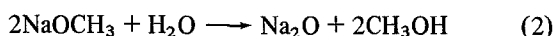
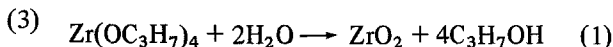
Figure 1 Schematic illustration of the preparation of glass fibres from metal alkoxides.

metal alkoxides, drawing fibres from the alkoxide solution in the course of hydrolysis, and conversion of the drawn fibres into oxide glass fibres by heating.

2.1.1. Raw materials and hydrolysis

Zirconium *n*-propoxide · *n*-propanol complex, $Zr(O \cdot n-C_3H_7)_4 \cdot 2C_3H_7OH$ of 95 wt % purity supplied by Alfa Chemicals Co, silicon tetraethoxide, $Si(OC_2H_5)_4$ and 12.5 wt % methanol solution of sodium methoxide, $NaOCH_3$ supplied by Wako Chemicals Co, were used as raw materials. For the

ZrO_2-SiO_2 system, 40 to 50 g alkoxide mixture was stirred and refluxed with 50 ml dried or absolute ethanol in a four-necked flask at 80°C for 3 h. For the $Na_2O-ZrO_2-SiO_2$ system, about 30 g alkoxide mixture was used. No further addition of solvent was made for this system because the methanol included in the raw material for Na_2O acted as solvent. The amounts of $Zr(OC_3H_7)_4$ deduced from $Zr(OC_3H_7)_4 \cdot 2C_3H_7OH$, $NaOCH_3$ and $Si(OC_2H_5)_4$, and oxide compositions calculated from the corresponding metal alkoxides, assuming that the metal atoms remain as their oxides, are shown in Table I. Hydrogen and carbon atoms were assumed to escape as alcohols formed according to the equations for hydrolysis:



The mixed alkoxide solutions were transferred to a 100 ml beaker and exposed to air at room temperature of 20 to 24°C and at regulated temperature of 30°C for hydrolysis.

2.1.2. Fibre drawing

The possibility of drawing fibres from the mixed alkoxide solution undergoing hydrolysis was checked by immersing a glass stick of about 6 mm diameter into the solution and pulling up by hand. This was repeated until the solution gelled into a jelly-like mass. Fibrous gels could be drawn when the solution became viscous and sticky, but not jelly-like.

TABLE I Amounts of raw materials and chemical compositions (wt %) of the samples used in the experiments

Sample	Amounts of raw materials				Chemical compositions (wt %)	
	$Na(OCH_3)$ (g)	$Zr(O \cdot n \cdot C_3H_7)_4$ (g)	$Si(OC_2H_5)_4$ (g)	C_2H_5OH (or CH_3OH^*) (ml)	Calculated	Analysed
1		3.9	46.1	50	$8ZrO_2 \cdot 92SiO_2$	$3ZrO_2 \cdot 97SiO_2$
2		8.1	42.0	50	$16ZrO_2 \cdot 84SiO_2$	$7ZrO_2 \cdot 93SiO_2$
3		12.4	37.6	50	$25ZrO_2 \cdot 75SiO_2$	$11ZrO_2 \cdot 89SiO_2$
4		16.9	33.1	50	$34ZrO_2 \cdot 66SiO_2$	$18ZrO_2 \cdot 82SiO_2$
5		21.7	28.3	50	$43ZrO_2 \cdot 57SiO_2$	$26ZrO_2 \cdot 74SiO_2$
6		18.7	24.5	50	$50ZrO_2 \cdot 50SiO_2$	$33ZrO_2 \cdot 67SiO_2$
7		22.1	19.4	50	$60ZrO_2 \cdot 40SiO_2$	$48ZrO_2 \cdot 52SiO_2$
8		26.3	15.1	50	$70ZrO_2 \cdot 30SiO_2$	$60ZrO_2 \cdot 40SiO_2$
9	1.0	9.6	24.1	9.0*	$6Na_2O \cdot 32ZrO_2 \cdot 62SiO_2$	$7Na_2O \cdot 17ZrO_2 \cdot 76SiO_2$
10	1.0	12.1	20.6	9.0*	$5Na_2O \cdot 41ZrO_2 \cdot 54SiO_2$	$7Na_2O \cdot 25ZrO_2 \cdot 68SiO_2$
11	1.0	15.0	16.1	9.0*	$5Na_2O \cdot 52ZrO_2 \cdot 43SiO_2$	$7Na_2O \cdot 33ZrO_2 \cdot 60SiO_2$

* CH_3OH comes from the raw materials.

2.1.3. Heating of the drawn fibres and gelled masses

Drawn fibres were changed into glass fibres by heating to temperatures from 500 to 700°C at a heating rate of 100°C h⁻¹.

The solution which remained in the glass beaker after drawing fibres gelled into a jelly-like mass which was broken into numerous small particles by further exposure to air. These particles were heated to various temperatures ranging from 100 to 1100°C at a rate of 100°C h⁻¹ and held there for 1 h and were subjected to chemical analysis, X-ray diffraction and density measurements.

2.2. Chemical analysis

The gels before and after being heated to various temperatures up to 700°C were chemically analysed by X-ray emission spectroscopy using a Rigaku Denki X-ray fluorescence spectrometer. The finely powdered specimen of 4 g was pressed into a disc of 4 cm diameter and 2 mm thick by adding cellulose powder as binder. The ZrO₂ content in the ZrO₂-SiO₂ specimen was determined from the intensity ratio of ZrL α to SiK α line. The calibration curve which related the intensity ratio to the ZrO₂ content was made beforehand for the mixtures of ZrO₂ and SiO₂. The SiO₂ content was determined by the difference. For determining the content of ZrO₂ in the Na₂O-ZrO₂-SiO₂ system, 20 wt % α -Al₂O₃ was added to the specimen. The intensity ratio of ZrL α to AlK α line was measured. The Na₂O and SiO₂ contents were determined by the difference, assuming that the ratio of Na to Si remained unchanged during hydrolysis and subsequent heating. The analytical compositions of the gels heated to 700°C are shown in the last column of Table I.

2.3. X-ray diffraction and density measurements of the heated gels

X-ray diffraction profiles of the heated gels were measured for diffraction angles between 5 and 40° in 2 θ using Ni-filtered CuK α radiation.

Densities of the gels heated to various temperatures were measured with a picnometer at 27°C. Water was used as the replacing liquid. Air included in the replacing water and attached to gel particles was carefully removed by evacuating the picnometer which contained water and specimen, to some reduced pressure.

2.4. Measurement of alkali-resistance of fibres

Several heated fibres of a composition about 1 cm long were mounted with polyester adhesive on a frame made of polypropylene, and immersed in the 100 ml 2 N NaOH solution which was contained in the 300 ml Pyrex glass flask equipped with a condenser. The testing temperature was 96°C. The attacking solution of 2 N NaOH was renewed after several hours to maintain its alkalinity. Fibres immersed in alkaline solution for some duration were taken out and washed with distilled water, and their diameters were measured on the photographs taken under an optical microscope and magnified by 200 to 400. Several tens of measurements of the diameter were made at different places in different fibres. The average reduction in diameter by alkaline attack was used as a measure of alkali-resistance of the fibre.

3. Results

3.1. Spinnability of the alkoxide solution

The mixed alkoxide solution became viscous and sticky with increasing exposure time as a result of polymerization of alkoxide through hydrolysis. The solutions showed spinnability just before gelling into solid masses. The times required for gelation and development of spinnability are shown in Table II. No influence of temperature of hydrolysis on the spinnability was noticeable. The spinnability depended markedly on the composition. Solution 1 showed the most remarkable spinnability, and long fibres of several tens of micron diameter were easily drawn from that solution. A photograph of the as-drawn fibres is shown in Fig. 2. The ease of drawing of fibres was

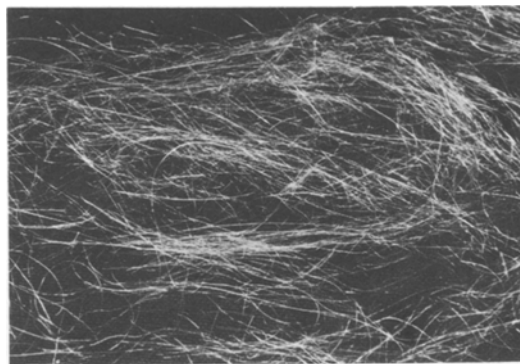


Figure 2 Fibrous gels obtained from solution 2.

TABLE II Temperature of hydrolysis, time required for gelation, spinnability and length of fibre obtained

Sample	Temperature of hydrolysis ($^{\circ}$ C)	Time required for gelation (day)	Spinnability	Length of fibre (cm)
1	20 \pm 1	12	yes	> 100
2	30	2	yes	30
3	20 \pm 1	11	yes	> 100
	30	3	yes	> 100
4	20 \pm 1	9	yes	> 100
	30	2	yes	30
5	30	2	yes	60
6	23 \pm 1	2	yes	40
7	24 \pm 1	2	yes	40
8	30	1	yes, but drawing fibres is difficult	
	22 \pm 2	2	yes	4
9	20 \pm 2	5	yes	> 100
10	20 \pm 2	4	yes	> 100
11	20 \pm 2	3	yes	> 100

lowered by increasing the amount of zirconium alkoxide. Only short fibres several centimeters long were obtained from solution 8 corresponding to the composition of $48\text{ZrO}_2 \cdot 52\text{SiO}_2$ in weight. Solutions for the compositions with higher ZrO_2 contents produced white flocculent precipitates as the hydrolysis progressed, which was probably caused by the differential hydrolysis of zirconium alkoxide. These solutions gelled into milky solids without exhibiting any spinnability. All three solutions for the $\text{Na}_2\text{O}-\text{ZrO}_2-\text{SiO}_2$ system showed remarkable spinnability which made it possible to draw long fibres.

The viscosity of the solutions for the $\text{ZrO}_2-\text{SiO}_2$ system continued to increase until the whole of the remaining solution gelled. However, the solution was spinnable for a few hours. In the solutions for the $\text{Na}_2\text{O}-\text{ZrO}_2-\text{SiO}_2$ system, a thin gel film developed over the solution within several hours after the solution became spinnable, which inhibited further hydrolysis of the bulk solution and made it possible to draw fibres even after 1 day.

The fibres drawn from the solution were readily solidified in air because of the quick progress of hydrolysis and gelling due to their large surface area.

3.2. Chemical compositions

Appreciable difference between calculated and analysed compositions due to a partial loss of zirconium is seen in Table I. In order to determine in which step the loss of zirconium occurs, the chemical compositions of the alkoxide solution and the gels before and after heating to 500°C

were determined for solution 6. The content of zirconium as ZrO_2 was 50, 35 and 33 wt%, respectively, indicating that the loss of zirconium occurs in the liquid state due to the vaporization of zirconium alkoxide in the course of hydrolysis.

3.3. Transformation of the gel to oxide glass

Fig. 3 shows the results of X-ray diffraction on the gels of the $\text{ZrO}_2-\text{SiO}_2$ system heated to various temperatures. It is seen that the gel containing 3 wt% ZrO_2 (no. 1) remains non-crystalline up to 1000°C . The crystallization temperature of the gel is lowered with the content of ZrO_2 , and the gel containing 48 wt% ZrO_2 (no. 7) is already partially crystallized at 500°C . The crystalline species precipitated was tetragonal zirconia, irrespective of the composition and heating temperatures.

The density changes of the gels 1, 3 and 5 with

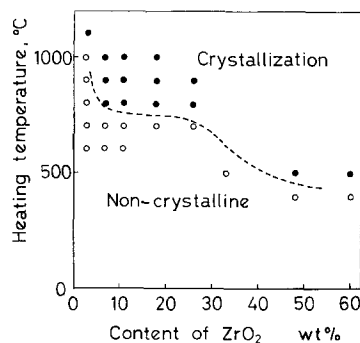


Figure 3 Crystallization of the gels of the $\text{ZrO}_2-\text{SiO}_2$ system determined by X-ray diffraction. ● Sharp crystalline peaks (precipitation of crystals), ○ amorphous halo (non-crystalline).

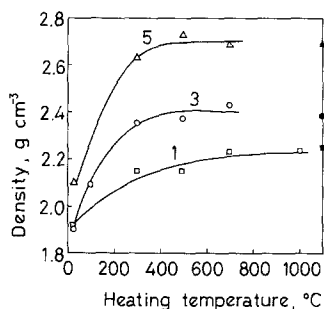


Figure 4 Changes of density of gels 1, 3 and 5 with heating temperature. Solid marks represent the calculated densities of the glasses of the corresponding compositions.

heating temperatures are given in Fig. 4. It can be seen that the density of the gel increases with heating temperature until it levels off at 2.24, 2.40 and 2.70 g cm⁻³ around 700, 500 and 500°C, respectively. The hypothetical densities of the glasses of the compositions equivalent to 1, 3 and 5 were calculated as 2.25, 2.39 and 2.69 g cm⁻³, using the Huggins' equation, [26],

$$D = 1/\sum f_m \cdot v_m \quad (4)$$

in which D is the density in g cm⁻³, f_m is the weight fraction of the constituent and v_m is the specific volume at any weight fraction. The saturated densities agreed with calculated densities as shown in Fig. 4.

Both the X-ray diffraction and density measurements indicate that the transformation of the gel to oxide glass is completed by heating to 700°C for solution 1 and to 500°C for other solutions except no. 8. Fibres from solution 8 showed partial crystallization when heated at 500°C. However, other fibres could be converted to glass fibres, maintaining their shapes. The fibres blackened on heating due to the carbonization of residual organic matters. The fibres for the Na₂O-ZrO₂-SiO₂ system were also converted to corresponding glass fibres by heating to 500°C.

3.4. Alkali-resistance of glass fibres

The average decrease in diameter of fibres as a function of the time of immersion in the 2 N NaOH solution at 96°C is shown in Fig. 5a for the ZrO₂-SiO₂ system and in Fig. 5b for the Na₂O-ZrO₂-SiO₂ system. The scattering of the measured values of the decrease in diameter at any time of immersion was ± 1 μm at most. Measurements on the Pyrex- and E-glass fibres are also shown in Fig. 5a. The decrease in diameter with time appears

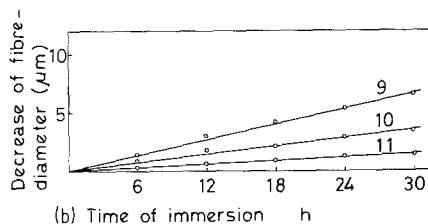
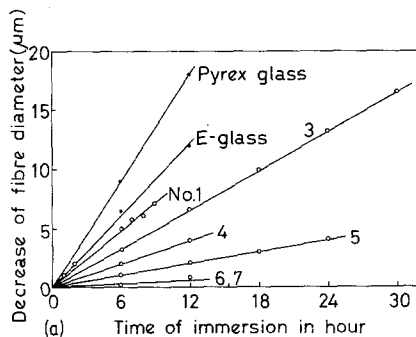


Figure 5 Changes of decrease in fibre diameter with time of immersion in 2 N NaOH solution at 96°C. Attached are the sample numbers given in Table I. (a) ZrO₂-SiO₂ system, (b) NaO-ZrO₂-SiO₂ system.

linear. It is seen that the ZrO₂-containing glass fibres show higher alkali resistance than the Pyrex- and E-glass fibres. The alkali resistance increases as the ZrO₂ content increases in both the ZrO₂-SiO₂ and Na₂O-ZrO₂-SiO₂ systems.

The reductions in diameter at 4 h immersion in alkaline solution were changed to weight losses in mg dm⁻² and are plotted in Fig. 6 as a function of the ZrO₂ content. It is seen that the alkali resistance of the Na₂O-ZrO₂-SiO₂ glass fibre is almost the same as the ZrO₂-SiO₂ glass at the same ZrO₂ content. The weight loss data of the 15Na₂O · 12CaO · xZrO₂ · (73-x)SiO₂ (in weight) glasses reported by Ohta and Suzuki [22] are shown in

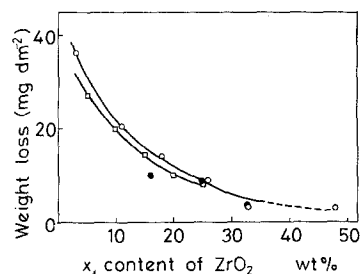
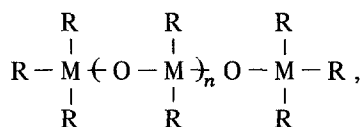


Figure 6 Weight loss in 2 N NaOH solution at 96°C for 4 h, plotted against the ZrO₂ content. Weight loss data are calculated based on the decrease in fibre diameter given in Fig. 5a and b. ○ fibres of the ZrO₂-SiO₂ system, ● fibres of the Na₂O-ZrO₂-SiO₂ system, □ 15Na₂O · 12CaO · xZrO₂ · (73-x)SiO₂ glass, reproduced from [22].

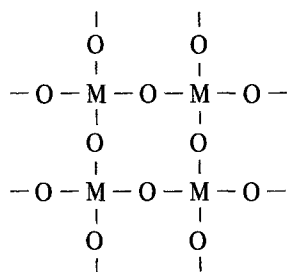
the same figure for comparison. The change of alkali resistance with ZrO_2 content of the present glass fibres is similar to that by Ohta and Suzuki. The weight losses of $18ZrO_2 \cdot 82SiO_2$ and $26ZrO_2 \cdot 74SiO_2$ glass fibres were 15 and 13 mg dm^{-2} , being comparable to that of the $1.0Li_2O \cdot 11.5Na_2O \cdot 16.5ZrO_2 \cdot 71.0SiO_2$ glass (G 20 glass) [20], which is an alkali-resistant glass obtained by the conventional melting technique. The $33ZrO_2 \cdot 67SiO_2$ glass fibre showed a higher alkali resistance. The partially crystallized glass fibre of the composition of $48ZrO_2 \cdot 52SiO_2$ had an alkali resistance as high as the $33ZrO_2 \cdot 67SiO_2$ glass fibre.

4. Discussion

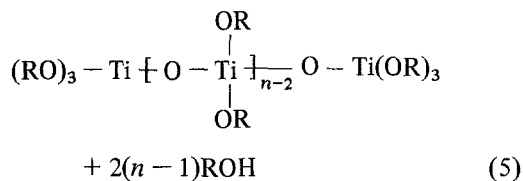
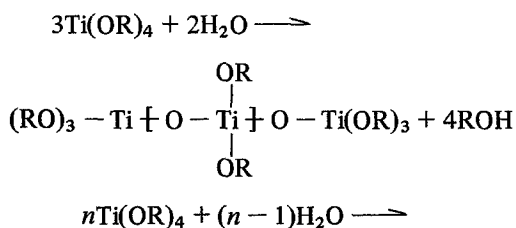
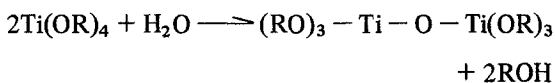
The metal alkoxides, $M(OR)_n$ are hydrolysed to produced metaloxane chains,



or two- or three-dimensional network polymers:



and finally the corresponding metal oxides. Among the polymerized products, linear polymers should be preferable for drawing the fibres. It is known that the linear polymers are obtained from titanium alkoxide through hydrolysis as in Equation 5, when the water content added for hydrolysis is less than unity in molar ratio of water to alkoxides [27].



Addition of more water produces cross-linked polymers. This is assumed to be applicable to the hydrolysis of other metal alkoxides. Actually, fibrous gels as the precursor of SiO_2 glass fibres could be drawn from silicon tetraethoxide solution when the added water was less than 2 in the molar ratio of water to alkoxide [18]. A jelly-like gel which did not exhibit spinnability resulted when more water was added. Instead, such a gel prepared from the solution with a higher amount of water, was converted to silica glass masses without heavy breaking when it was subjected to carefully designed heating [18].

The addition of water to metal alkoxide should be done very slowly, in order to form linear or chain polymers, if an alkoxide of high reactivity toward hydrolysis is used. One of the simple and successful ways to satisfy this requirement is to keep the alkoxide open in air and to hydrolyse it by the moisture, as in the present case. The time required for the solution to reach the viscosity suitable for drawing fibres depends on the ambient temperature, relative humidity, liquid surface area in contact with air and volume of the solution.

The alkoxide solution remained spinnable for a few hours when the solution was exposed to air. However, it was possible to maintain the solution in a spinnable state for a longer time if the progress of hydrolysis was stopped by closing the container of the solution or transferring it to a dry atmosphere. A thin film of gel developed at the liquid surface in the $Na_2O-ZrO_2-SiO_2$ system which also inhibited further hydrolysis of the alkoxide solution. This fact would be very useful when the present method of preparing glass fibres is brought into practical use.

The alkali resistance of the glass fibres prepared from metal alkoxides depended on the content of ZrO_2 as reported for the glasses obtained by the melting technique. The addition of Na_2O had no influence on the alkali resistance of the fibres. However, the spinnability of the solution for the $Na_2O-ZrO_2-SiO_2$ system was higher than the solution for the ZrO_2-SiO_2 system, which is an advantage of using Na_2O .

The blackening of the fibres on heating [28]

due to the carbonization of residual organic matters, which is one of the problems to be solved in the future investigation, does not seem to have any detrimental effect when they are used as a filler material for reinforcing cement.

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