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Preparation of SiO_2–Al_2O_3 glass powders by the sol–gel process for dental applications

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SiO_2–Al_2O_3 binary glass powders with Al_2O_3 contents up to 50 wt% have been synthesized by the sol–gel process. The starting solution (sol) consisted of 1 mole of tetraethoxysilane, 50 moles of water containing aluminum nitrate, 10 moles of ethyl alcohol and 0.02 moles of HCl catalyst. The sol was converted into gel by heating at 85 °C and suction by running water. The sintering process was analysed by DTG thermal analysis. The fired powders were examined by XRD. It was confirmed that the gels were converted into the glass structure without crystallization. The measurements of refractive index and powder size of fired powders revealed that these powders could be used as refractive-index-adjustable fillers for dental composite resins. The other potential usage of the SiO_2–Al_2O_3 powders obtained might be in the production of powders for dental cements.

1. Introduction

Although the sol–gel process has the potential to yield new glasses for dental applications such as the filler for dental composite resins [1, 2], it has not yet been extensively studied in the dental materials field. The advantageous features of this technique are the homogeneity and purity of the glass and the low sintering temperature, important in manufacturing new glasses which cannot be otherwise prepared by the conventional melting method [3]. In the sol–gel process, the liquid silicon–organic compound (i.e. silicon alkoxide) is transformed into the solid of the silicon–oxygen network through the sol–gel reaction (i.e. hydrolysis and polycondensation) and subsequent densification (i.e. drying and sintering).

The addition of other cations into SiO_2 glass can produce new functional SiO_2-based glass and glass–ceramic [4]. The SiO_2–Al_2O_3 system, which can be called the "mother glass", can accommodate other additive cations (e.g. Ba^{2+}) while maintaining the well-established SiO_2-based glass structure. This is because the Al^{3+} ion can act as both the network-former and modifier (i.e. intermediate cation) against the basic glass network-former, SiO_4^{2-} [4]. SiO_2–Al_2O_3 glass is, however, difficult to produce by the conventional melting method due to its high melting point and phase separation at elevated temperatures [5]. SiO_2–Al_2O_3 glass has therefore been synthesized by the sol–gel process in industry [6–8]. Its manufacturing process has, however, not been well clarified.

The purpose of this investigation was to self-formulate SiO_2–Al_2O_3 powder by the sol–gel process in a dental materials laboratory, and evaluate its usefulness for dental applications.

2. Materials and methods

2.1. Sol–gel synthesis of SiO_2–Al_2O_3 glass powders

The raw materials used for the sol–gel synthesis were commercially pure tetraethoxysilane, $Si(OC_2H_5)_4$ (LS-2430, Shinetsu Chemical Co., Tokyo, Japan) (TEOS) and aluminum nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$ (Wako Junyaku Co., Osaka, Japan) (Al-nitrate). Table I shows the molar mixing ratios of the starting materials and target oxide batches, namely 100 wt% SiO_2, 90 wt% SiO_2–10 wt% Al_2O_3, 70 wt% SiO_2–30 wt% Al_2O_3 and 50 wt% SiO_2–50 wt% Al_2O_3. For the starting solution (sol), molar mixing ratios of TEOS, ethyl alcohol (C_2H_5OH), distilled water (H_2O) and hydrochloric acid (HCl) as a catalyst were maintained at 1:10:50:0.02. One mole of TEOS was first mixed with 5 moles of C_2H_5OH and stirred at room temperature for at least 1 h with a magnetic stirrer (the A liquid). The B liquid consisting of 5 moles of C_2H_5OH, 50 moles of H_2O and 0.02 moles of HCl mixed with Al-nitrate powder was added dropwise to the A liquid, using a pipette, and the fully mixed solution was stirred at room temperature for one additional hour. To facilitate hydrolysis and condensation reactions, the prepared sol was transferred to a hot plate equipped with a magnetic stirrer (Nuova 7, Sybron Co., MI, USA) and vigorously stirred at 85 °C under the partial vacuum generated by a water-powered Venturi pump for a few hours until a wet gel was obtained. The wet gel was then placed in a drying bath (Model DN-41, Yamato Co., Tokyo, Japan) at 85 °C for 3 h, then ground in a milling machine (MS No. 36090, Retsch Co., Germany). After the pulverized dry gel was passed through a 325-mesh sieve, it was age-dried at

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TABLE I Mixing ratio of the starting materials for sol-gel synthesis of SiO_2–Al_2O_3 powders, along with target oxide batches

Starting materials TEOS	Al-nitrate	H_2O	C_2H_5OH	HCl	Target oxide batch
1	0	50	10	0.02	100 wt % SiO_2
1	0.131	50	10	0.02	90 wt % SiO_2–10 wt % Al_2O_3
1	0.504	50	10	0.02	70 wt % SiO_2–30 wt % Al_2O_3
1	1.177	50	10	0.02	50 wt % SiO_2–50 wt % Al_2O_3

150 °C for 3 h and then slowly fired at 200 °C, 400 °C, 600 °C and 800 °C for 2 h each, successively, and finally at 1000 °C for 1 h in a ceramic crucible in an air atmosphere in an electrically heated furnace (Accutherm II 100, Jelenko Co., NY, USA).

2.2. DTG thermal analysis

To evaluate the sintering process, the ground and sieved sample was taken out of the bath at 85 °C, and differential thermogravimetric thermal analysis (DTG) was carried out with a thermal analyser (DT-30, Shimadzu Co., Kyoto, Japan), using the following experimental conditions: sample weight, 20 mg; reference, α-alumina; DTA sensitivity, 100 μv; TG sensitivity, 20 mg; heating rate, 5 °C/min; temperature range, room temperature to 1000 °C; atmosphere, air under a flow of 30 ml/min N_2.

2.3. XRD analysis

The crystallographic states of the fired powders were examined using X-ray diffraction analysis (XRD), using the following experimental conditions: X-ray, CuK_α radiation; accelerating voltage, 30 kV; current, 10 mA; scan rate (2θ/min), 2 degrees/min; scan range (2θ), 10 to 50 degrees.

2.4. Particle size analysis

The particle size distribution of the fired powder was checked by Laser-beam diffraction counter (SALD-1100, Shimadzu Co., Kyoto, Japan). The control powder specimen examined was the filler extracted from a commercial dental composite resin (Occlusin, I.C.I. Dental Co., England, Lot No., LH06) by heating from room temperature to 800 °C.

2.5. Measurements of refractive index

The refractive index, n_D^{20} of each fired powder was determined by the immersion method. The powder was filled in the specimen chamber (10 × 10 × 1 mm) of the quartz cell and mixtures of isobutyl alcohol (n_D^{20} = 1.39) and trichlorobenzene (n_D^{20} = 1.59) with varying concentrations and known refractive index [2] were poured into the cell. The light transmittance through the cell was then examined with an ultraviolet-visible light double beam spectrophotometer (UVIDEC-6100, Japan Spectroscopic Co., Tokyo, Japan). The light transmittance became maximum when the refractive index of the powder coincided with that of the mixture of the two liquids [2].

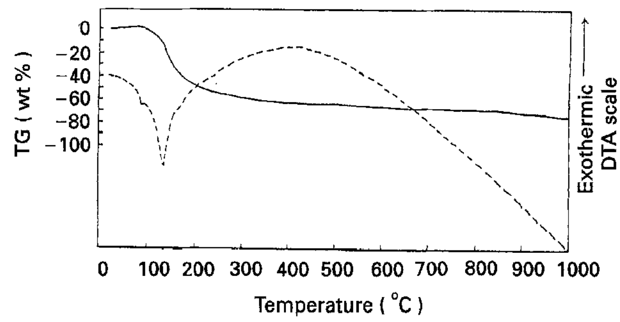

Figure 1 DTG (DTA/TG) profile of 70 wt % SiO_2–30 wt % Al_2O_3 gel dried at 85 °C, ground, and heated to 1000 °C (—— TG; ---- DTA).

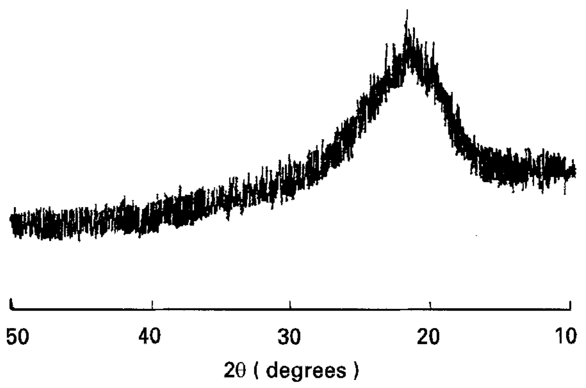

Figure 2 XRD profile of 70 wt % SiO_2–30 wt % Al_2O_3 powder fired to 1000 °C.

3. Results

Fig. 1 shows the DTG (DTA/TG) profile of 70 wt % SiO_2–30 wt % Al_2O_3 gel dried at 85 °C, ground, and heated to 1000 °C. The small DTA endothermic peak at around 90 °C was related to the evaporation of H_2O and C_2H_5OH. The large DTA endothermic peak at around 130 °C was due to the thermal decomposition of $Al(NO_3)_3 \cdot 9H_2O$. No DTA exothermic peak associated with crystallization was observed during heating to 1000 °C. The gel lost weight continuously from about 90 °C to 1000 °C, with the rate of the weight loss being very extensive from 90 °C to about 240 °C, and then sluggish up to 1000 °C. Similar observations were made on all gels prepared.

Fig. 2 indicates the XRD profile of 70 wt % SiO_2–30 wt % Al_2O_3 powder fired to 1000 °C. It was confirmed that all products obtained were X-ray amorphous.

Fig. 3a and b show the particle size distributions of 70 wt % SiO_2–30 wt % Al_2O_3 powder fired to 1000 °C and the filler extracted from a commercial composite resin, Occlusin, respectively. It was clear that the

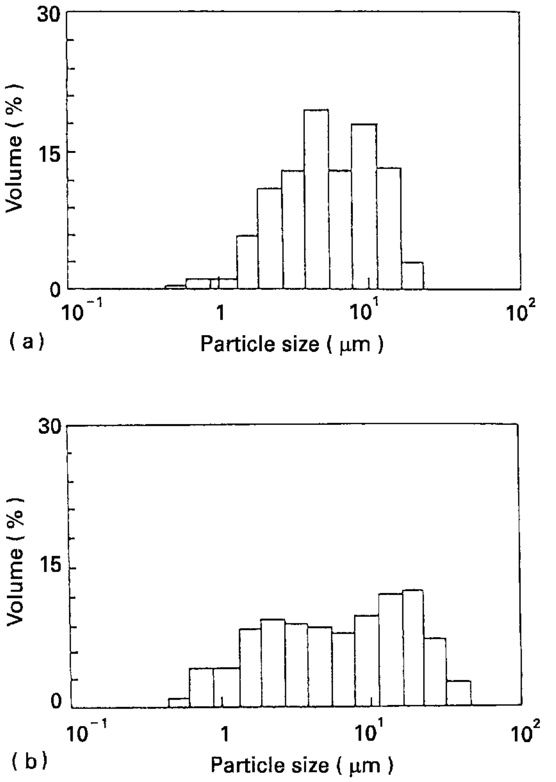

Figure 3 Particle size distributions of (a) 70 wt % SiO_2–30 wt % Al_2O_3 powder fired to 1000 °C and (b) the filler extracted from a commercial composite resin, Occlusin.

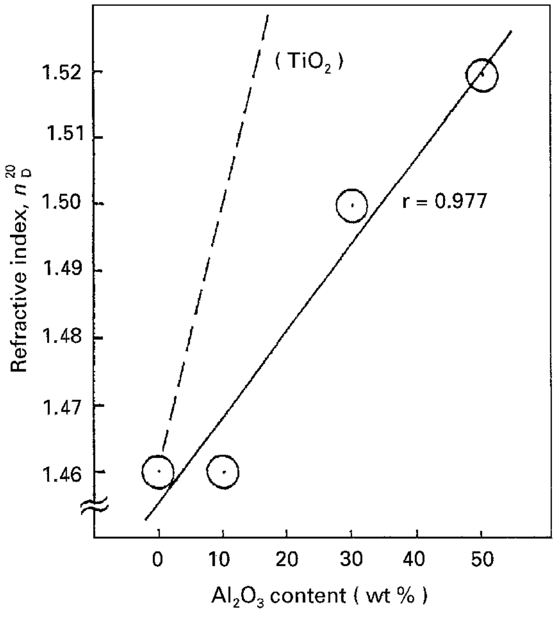

Figure 4 Effects of Al_2O_3 content (wt %) in SiO_2–Al_2O_3 powders on the refractive index, n_D^{20} of the said powders.

former particles were smaller than the latter particles. The median and mode diameters of the former particles were 5.08 and 4.44 μm, while those of the latter particles were 6.30 and 16.17 μm

Fig. 4 indicates the effect of Al_2O_3 content (wt %) in SiO_2–Al_2O_3 powder on the refractive index, n_D^{20} of the said powders. It was found that with increasing Al_2O_3 up to 50 wt %, the refractive index, n_D^{20} of the SiO_2–Al_2O_3 powders increased linearly from approximately 1.46 to 1.52.

4. Discussion

SiO_2–Al_2O_3 glasses are high-temperature materials with excellent strength and alkali resistance [5–8]. As stated, these glasses are difficult to manufacture by the conventional melting method due to phase separation and crystallization at elevated temperatures [5]. Many reports have discussed the production of SiO_2–Al_2O_3 glass by the sol–gel process, including the basic science dealing with the sol to gel conversion [9] and the application, for example, of sintering the gel into mullite ($3SiO_2 \cdot 2Al_2O_3$) [10]. Each area is, however, very specialized and for providing new glasses for dental applications, it was considered necessary to investigate the sol–gel process from the beginning. This is because the sol–gel (hydrolysis and polycondensation) reaction is very complicated, producing many reaction intermediates (oligomers containing organic side-chains) and the subsequent sintering process is also complex, both being strongly affected by such factors as the nature of the catalyst (acid or base), selection of the starting materials and their mixing ratios, and heating conditions [3, 4].

In the material design of SiO_2-based glass, Pauling's law [11] has often been used. It states that SiO_2-based glass requires that electrical neutrality is maintained between cations (metal ion) and anions (O^{2-}), and both cations and anions are densely packed (i.e. the coordination-polyhydron is densely packed). The coordination number (i.e. the preferred number of oxygen anions surrounding a specific metal cation) and valance number of Si, Al and Sr are 4 and 4 +, 6(4) and 3 +, 8 and 2 +, respectively. If a Si ion is replaced by an Al ion, one valance (+ 1) and some space is left in the glass structure. Other cations can be added to this binary system. One recommended stoichiometric stable oxide batch in the SiO_2–Al_2O_3–SrO system, which maintains electrical neutrality and is potentially useful as a radiopaque filler for dental composite resins [12], is 60 wt % SiO_2–20 wt % Al_2O_3–20 wt % SrO (1.0 mol % SiO_2–0.196 mol % Al_2O_3–0.193 mol % SrO). For this reason, SiO_2–Al_2O_3 glass can be termed the mother glass, and was studied here first.

TEOS was selected as the most common and inexpensive starting material (silicon alkoxide) to produce SiO_2 glass. Al-nitrate was considered easy to handle. It was instantaneously possible to mix TEOS, C_2H_5OH and H_2O containing Al-nitrate. The necessary mixing ratios of TEOS, C_2H_5OH and H_2O containing Al-nitrate was determined in preliminary experiments. Abundant H_2O was needed to completely dissolve Al-nitrate. Once mixed, the sol quickly lost the H_2O content by heating at 85 °C and suction by running water. DTG thermal analysis revealed that the gel obtained at 85 °C was basically composed of TEOS-derived oligomer containing Al-nitrate intact, and upon heating to more than 130 °C, Al^{3+} were released into the TEOS-derived oligomer system. It has been reported that a –O–Si–O– glass structure containing Al ions could be established at temperatures of more than 400 °C, followed by densification upon heating to more than 400 °C [9]. It appeared that the sintering process of the SiO_2–Al_2O_3 glass system occurred over the broad temperature range between 200 and 1000 °C [9]. Slow heating was needed so that volatile material could escape from the gel, and free carbon could be oxidized [1]. XRD analysis confirmed that the sintered product heated to 1000 °C was X-ray amorphous. However, it has been reported that when heated to more than 1300 °C, crystallization of mullite occurred in the glass matrix [13]. Such glass–ceramic is not useful as the filler in dental composite resins because it significantly scatters the light, rendering the restorative material opaque to visible light, leading to a limited depth of cure [14]. A wholly-glass structure was regarded as better for filler use. It was also confirmed that the sintered powder had a particle size distribution comparable to that of the filler of a commercial dental composite resin. It was also observed that the refractive index of SiO_2–Al_2O_3 glass powder increased linearly with increasing Al_2O_3 content up to 50 wt %. The range of refractive index of these glasses ($n_D^{20} = 1.46$–1.52) covered those of the monomer mixtures currently most widely utilized; e.g. n_D^{20} of 60 wt % Bis–GMA + 40 wt % TEGDMA is about 1.52 (Bis–GMA = Bis-phenol A glycidyl dimethacrylate; TEGDMA = Triethyleneglycol dimethacrylate) [2]. It can therefore be said that the SiO_2–Al_2O_3 glass powders obtained are refractive-index-adjustable fillers for dental composite resins containing (Bis–GMA + TEGDMA) monomer mixture.

Other potential uses of SiO_2–Al_2O_3 glass prepared by the sol–gel process might be in the production of the powder for dental cement such as that for glass ionomer cement [15]. The powder of this cement releases Ca^{2+} ions and Al^{3+} ions when reacting with polyacrylic acid. If the sintering temperature were intentionally lowered, the glass structure of the SiO_2–Al_2O_3 system would not be firmly constructed, which might easily release Al^{3+} ions by acid attack. The kinetics of metal release might be controlled by adjusting the mixing ratios of the starting materials and by the sintering temperature. New SiO_2-based investment materials to cast dental alloys might be created by the application of the sol–gel process. Bioactive apatite-based granular implant materials have also been experimentally synthesized by the sol–gel process [16].

5. Conclusions

The sol–gel synthesis of SiO_2–Al_2O_3 powders with Al_2O_3 content up to 50 wt % was examined by DTG thermal analysis and XRD. It became evident that Al-nitrate was thermally decomposed when heated to more than 130 °C, releasing Al^{3+} ions into the TEOS-derived oligomer system. The sintering process took place over the broad temperature range up to 1000 °C. The final sintered product fired to 1000 °C was X-ray amorphous.

Measurements of particle size distribution and refractive index of the fired powders revealed that SiO_2–Al_2O_3 glass powders could be used as refractive-index-adjustable fillers for visible-light-cured dental composite resins containing (Bis–GMA + TEGDMA) monomer mixture.

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