

Original

Investigation of the Sol-Gel Process with Experimental Paste-Type Dental Phosphate-bonded Investments

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Abstract: Casting investments are used by mixing a powder and liquid, and there is a risk of fine powder inhalation causing respiratory disease. Previously, we investigated paste-paste type phosphate-bonded investment with oils. The objective of the present study was to produce paste-paste type phosphate-bonded investments with colloidal silica. Two pastes (PA and PB) were formed before the test. PA was an acidic mixture of cristobalite and magnesium dihydrogenphosphate solution, and PB was an alkaline mixture of MgO in colloidal silica solution. Five experimental investments (PB5, PB10, PB15, PB20, PB25) containing 5, 10, 15, 20, and 25 ml, respectively, of colloidal silica in PB were evaluated. Commercial phosphate-bonded investment was used as a control. PB5 took a long time to set (12 h or more), had no setting expansion, and its compressive strength was very small. Its thermal expansion and XRD analysis results were almost the same as those from the other experimental investments. The setting expansions of PB20 and PB25 were 0.40% and 0.62%, respectively, and they took approximately 16 min to set. These values were close to those of control. Full coverage cast crowns obtained from the experimental investments had a loose fit compared with the control. The gap with the crowns cast from PB20 was smaller than those of other experimental investments, and it showed no significant difference compared to that of the control. These results suggest that it is possible to produce paste-paste type investments using colloidal silica. This limited study suggests that the experimental investment with PB20 is suitable for clinical use.

Key words: phosphate-bonded investment, cast, paste-paste investment, colloidal silica.

Many dental materials require mixing of a powder with a liquid. This routine operation occurs often in dental laboratory work. Dental technicians are at risk of developing pneumoconiosis and other respiratory diseases because of inhalation of dust from grinding and polishing metals, resins, ceramics, plaster and abrasives.^{1–3)} Dental technicians also carry out model and mold making, and are exposed to dusts from these processes as well.

Gypsum and dental investments are the materials used most frequently in dental laboratory work. Recently, finer powders have been used because of the improvements these provide to strength and

reproducibility for fabrication of precision prostheses. These powders allow production of models without defects, and with excellent dimensional accuracy.

Because of the potential environmental and health issues with dental laboratory work, our group has been continuously researching the development of unique dental investments,^{4–10)} such as ammonia-free⁷⁾ and reusable^{8,9)} investments. Recently, we have investigated development of dust-free investments using two pastes with standard compositions of phosphate-bonded investment.^{11,12)} Initially, an acid paste and a basic paste were prepared. Because phosphate is a water-soluble acidic solution, the acid paste was easily prepared by

mixing with silicate oxide. However, it was not easy to make the basic paste because magnesium oxide is insoluble in water.¹¹⁾ Grease was then trialed for production of the basic paste, and this approach was successful. An aqueous paste and an oily paste were prepared. The fluidity and the hardening response of these pastes were similar to those of conventional investment material. However, the oily compound was difficult to use in typical manipulations like mixing or weighing because its high viscosity, and was not suitable as a dental investment product. Colloidal silica solutions were then examined for preparation of another water-soluble paste.¹²⁾ Production of this paste was based on the sol-gel process between magnesium oxide and colloidal silica solution. Therefore, it was suggested that the experimental investment could be handled in a similar manner to commercial silicone rubber impression material in a tube. However, MOD cast crowns obtained from the experimental investment had a loose fit in comparison to that from a control. Furthermore, long-term storage is questionable because gelation of colloidal silica is time dependency.

In this study, colloidal silica solution diluted with water was investigated to improve the above faults. Different paste investments were prepared and evaluated.

Materials and Methods

Preparation of two pastes

Two pastes (Table 1) were prepared according to our previous report before starting testing.^{11,12)} Because phosphate-bonded investments undergo a chemical reaction,¹³⁾ monomagnesium phosphate and magnesium oxide were completely separated.

Paste A (PA) was prepared by mixing 80 g of cristobalite powder (SiO₂, average particle size 9.1 μm, Tatsumori Ltd., Tokyo, Japan) with 30 ml of monomagnesium phosphate solution (Mg(H₂PO₄)₂, YCHEM Co., Ltd., Tokyo, Japan). Paste B (PB) was prepared by mixing 40 g of cristobalite and 10 g of magnesium oxide (MgO, RF-2, Tateho Chemical Industries Co., Ltd., Ako, Japan) with a diluted solution

Table 1 Experimental investments tested.

Paste A	
Monomagnesium phosphohate solution	30 ml
Cristobalite	80 g
Paste B	
Magnesium oxide	10 g
Cristobalite	40 g
Colloidal silica solution + distilled water	50 ml
Experimental investment code:	
• PB 5: PA + PB (Solution 5 ml, Water 45 ml)	
• PB10: PA + PB (Solution 10 ml, Water 40 ml)	
• PB15: PA + PB (Solution 15 ml, Water 35 ml)	
• PB20: PA + PB (Solution 20 ml, Water 30 ml)	
• PB25: PA + PB (Solution 25 ml, Water 25 ml)	

of colloidal silica (Univest Nonprecious, Shofu Inc., Kyoto, Japan). Five paste investments (PB5, PB10, PB15, PB20, PB25) were prepared for the experiments (Table 1).

All of pastes were placed in plastic bags and stored for 1 week in the refrigerator. When required, each PB paste was squeezed out of the bag and mixed for 30 s by hand and then automatically for 30 s under vacuum using a mixing machine. Commercial phosphate-bonded investment (Univest Nonprecious, Shofu Inc., Kyoto, Japan) was examined as a control.

Setting time

To measure the hardening time, penetration testing using a vicat needle was performed for each investment mixture once poured into a paraffin wax ring (ø80 mm, height 20 mm). The total mass of the device with rod and needle (ø2 mm) was 300 g. The analysis was repeated three times for each investment.

Setting expansion

A stainless ring (ø32 mm, height 35 mm) with a casting liner that curved inward was used for analysis of setting expansion. The vertical displacement was measured using an electronic gauge meter (MINICOM, Tokyo Seimitsu, Tokyo, Japan). The investments to be tested were poured into the casting ring, and a thin cover glass was placed on top. Testing was continued until 2 h after mixing, and each value was calculated as a percentage of the original height. The examination was repeated three times.

Compressive strength

The green and fired compressive strengths of the specimens ($\phi 10$ mm, height 20 mm) 24 h after mixing were measured using a universal testing machine (Instron MD-1125, Instron Japan, Kawasaki, Japan) with a crosshead speed of 1.0 mm/min. Specimens for measuring the fired strengths were heated to 850°C at a rate of 10°C/min, held for 1 h, and then cooled to room temperature before testing. Five specimens for each investment both before and after heating were tested.

Thermal expansion

Thermal expansion was evaluated by thermo-mechanical analysis (TMA) (Thermo plus TMA 8310, Rigaku Corp., Tokyo, Japan). Specimens ($\phi 6$ mm, height 12 mm) were heated to 850°C at a rate of 10°C/min. Thermal analysis was performed five times for each investment and the average values at each casting temperature were calculated.

XRD analysis

The composition of the mold before and after heating was evaluated using X-ray diffraction analysis (XRD 6100, Shimadzu Corp., Kyoto, Japan) with $\text{Cu-K}\alpha$ radiation. XRD was run at 40 kV and 30 mA with a scanning speed of 5°/min and a scanning range of 15–85°. The reaction on hardening and heating was investigated.

Clinical application

A steel die representing a full coverage crown preparation was designed (Fig. 1). Commercial polyvinyl siloxane impressions (Duplicone, Shofu Inc., Kyoto, Japan) were used to duplicate this die and thirty duplications were prepared using dental plaster (Millenium, Shimomura Sekko Co., Ltd., Asaka, Japan) at a water/powder ratio of 0.25. All wax patterns of the crowns were fabricated using CAD/CAM (Decsy, Nissan Digital Process Co., Ltd., Atsugi, Japan) because dental wax has large thermal expansion coefficient. A cement layer of 100 μm at the occlusal side was estimated in advance. The wax sprue (Ready casting wax R25, GC Corp., Tokyo, Japan) was placed on the crown pattern. A casting liner (New Casting Liner, GC

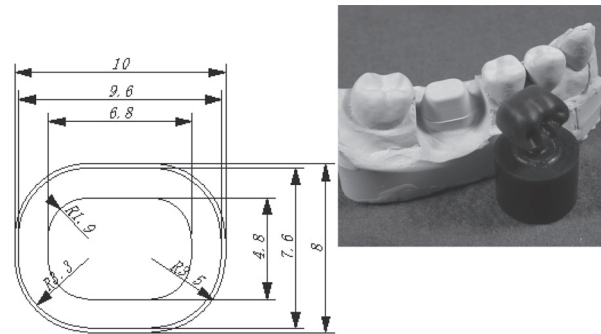


Fig. 1 Die for fitting test and wax pattern fabricated by CAD/CAM.

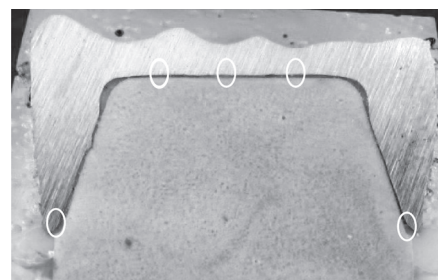


Fig. 2 Measuring points for a fit test.

Corp., Tokyo, Japan) was placed inside the stainless ring ($\phi 38$ mm, height 45 mm) and each investment was poured into the ring. Twenty-four hours later, the molds were heated to 850°C in an electric furnace (KDF-900, Yoshida Co., Ltd., Tokyo, Japan) at 10°C/min. After holding the maximum temperature for 60 min, Cu-Zn alloy (K-metal, GC Corp., Tokyo, Japan) was cast using a commercial spring-type centrifugal casting apparatus (Centrifico Casting Machine, SDS Kerr Japan, Tokyo, Japan). The spring was wound twice before casting, and after casting the cast crown was removed. The crowns were ultrasonically cleaned and carefully checked for any external defects. Each of the crowns was individually cemented using resin-modified glass ionomer cement (3M™ ESPE™ Vitremer™ Core-buildup Restorative, 3M, St. Paul, MN, USA) to one of the dental plaster duplications with a load of 2 kg, and then embedded in an acrylic tube ($\phi 30$ mm, thickness 1 mm) by a commercial acrylic resin (Unifast, GC Corp., Tokyo, Japan). After cutting in the mesial-distal direction using a cutting saw (Isomet, Buehler, Lake Bluff, IL, USA), gaps between the die and crown

at both the occlusal side and marginal sides were measured at the points shown in Fig. 2. Five crowns were fabricated from each investment and an average value was calculated for the gap at each point.

Statistics

The results were statistically evaluated and analyzed by one-way ANOVA with Scheffe's method at a significance level of $\alpha=0.05$.

Results

The setting time results are shown in Table 2. Decrease content of colloidal silica resulted in a longer setting time for the molds. Particularly, PB5 did not harden even 12 h after mixing. There was no significant difference between PB20 and PB25, and the setting time was approximately 16 min. PB10 had an initial setting time of around 1 h, but required further time to complete hardening.

Table 3 shows the setting expansion results for each investment. The expansion was obviously influenced by the content of colloidal silica. PB5 and PB10 did not expand or only expanded a little when setting. Expansion of the control was and significantly higher ($p<0.05$) than that with the experimental investments.

Table 2 Setting time of experimental investments.

Exp. investment	Setting time (min)
Cont.	6.8 (1.7) ^a
PB5	not set
PB10	63.3 (20.2) ^b
PB15	29.3 (7.4) ^c
PB20	16.7 (7.6) ^d
PB25	16.3 (8.5) ^d

(): standard deviation

Identical alphabetical letters indicate that the values were not statistically different.

Table 3 Setting expansion of experimental investments.

Exp. investment	Setting expansion (%)
Cont.	0.90 (0.08) ^a
PB5	undetected
PB10	0.03 (0.02) ^b
PB15	0.12 (0.06) ^b
PB20	0.40 (0.06) ^c
PB25	0.62 (0.17) ^d

(): standard deviation

Table 4 Compressive strength of experimental investments.

Exp. investment	Comp. strength (MPa)	
	green	fired
Cont.	7.38 (1.08) ^a	6.65 (0.69) ^a
PB5	0.42 (0.03) ^b	0.13 (0.05) ^b
PB10	0.91 (0.22) ^{b,c,d}	0.16 (0.04) ^b
PB15	0.83 (0.13) ^{b,c}	0.33 (0.09) ^{b,c}
PB20	1.06 (0.23) ^{c,d}	0.32 (0.06) ^{b,c}
PB25	1.34 (0.29) ^d	0.39 (0.04) ^c

(): standard deviation

Table 5 Thermal expansion of each investment.

Exp. investment	Thermal expansion (%)
Cont.	0.64 (0.05) ^a
PB5	0.81 (0.13) ^b
PB10	1.15 (0.07) ^c
PB15	1.22 (0.10) ^c
PB20	1.27 (0.04) ^c
PB25	1.22 (0.02) ^c

(): standard deviation

Both the green and fired mold strengths gradually reduced with the decrease of colloidal silica content (Table 4). However, the fired strengths of PB5 and PB10 were approximately 0.15 MPa, and significantly ($p<0.05$) smaller than those of the other investments. PB5 and PB25 showed the smallest and largest compressive strengths, respectively, and there was no difference among the other investments tested. The green and fired values for the control were 7.38 ± 1.08 and 6.65 ± 0.69 MPa, respectively, and significantly ($p<0.05$) higher than the compressive strengths of the experimental investments.

Table 5 shows the thermal expansion results for the experimental investments at 850°C. The differences among the experimental investments tested were not significant, except for PB5. These thermal expansion values of PB10-PB25 were approximately 1.2% and larger than that of the control ($0.64\pm 0.05\%$). The expansion curves on heating are presented in Fig. 3. Initial contraction with dehydration and then expansion after 200°C with phase change of the cristobalite were clearly observed.

Figures 4 and 5 present the results of XRD analyses for PB5, PB15 and PB25. All of the experimental investments were in the same class. A sharp peak for

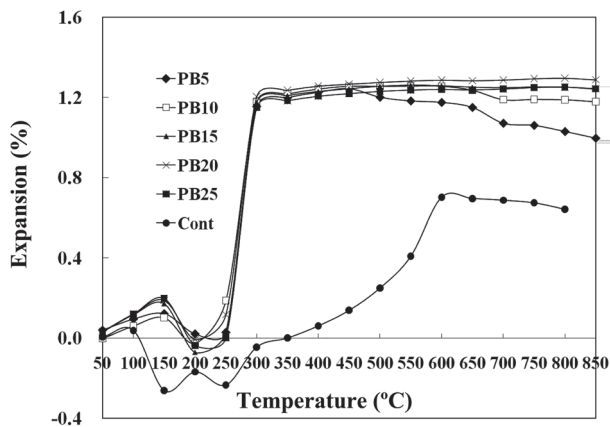


Fig. 3 Thermal expansion curves of investments tested.

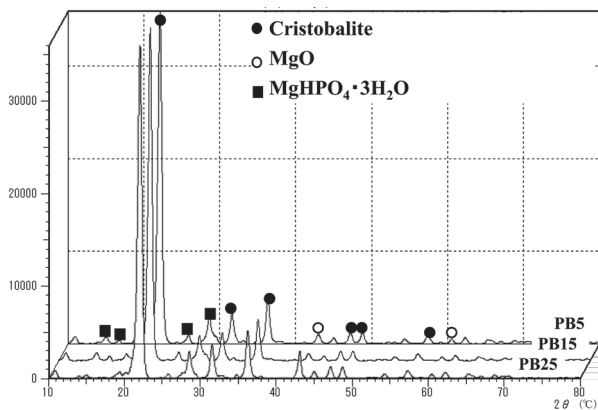


Fig. 4 Composition of experimental investments at setting.

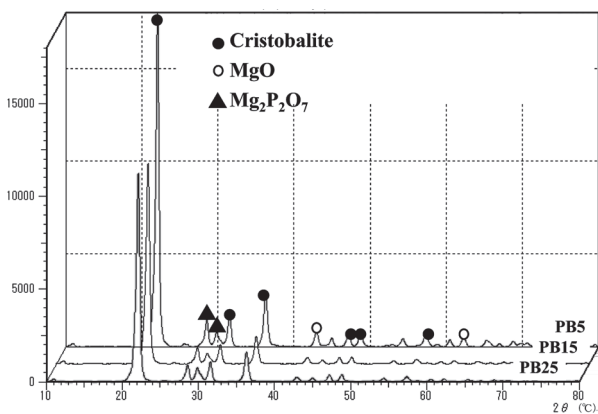


Fig. 5 Composition of experimental investments after firing.

cristobalite was detected. Dimagnesium phosphate was detected as a new compound formed by chemical reaction during setting. This decomposed during heating, and pyromagnesium phosphate formed.

The gap results calculated from the cement layer

Table 6 Thickness of cement layer of cast crowns.

Exp. investment	Cement layer (μm)	
	occlusal	margin
Cont.	163.7 (89.2) ^a	105.2 (111.8) ^a
PB15	417.5 (112.1) ^b	295.5 (141.3) ^b
PB20	254.3 (69.2) ^c	240.4 (130.3) ^{a,b}
PB25	385.5 (64.8) ^b	296.6 (163.3) ^b

() : standard deviation

on the cast crowns are presented in Table 6. Although the control had a significantly smaller gap than the experimental investments, the difference between the control and PB20 at the marginal side was not significant. Crowns from PB20 had the thinnest cement layer in the experimental investments. There were no differences between PB15 and PB25. Cast crowns produced from PB5 and PB10 were incomplete with many external defects on the casting surfaces, and were excluded from this evaluation.

Discussion

The setting mechanism of phosphate-bonded investment can be controlled by an acid-base reaction between phosphate and metal oxide, and by phase change because of the sol-gel process that occurs when using colloidal silica solution. Because of this chemical reaction, monoammonium phosphate and magnesium oxide are generally selected for use in investments. Magnesium oxide participates in both of the above reactions to control setting.

Zhang et al.¹¹⁾ reported that monomagnesium phosphate could be acceptable as dental phosphate-bonded investments without ammonia. In this study, the following two pastes were prepared: PA was an acidic mixture of cristobalite and magnesium dihydrogenphosphate solution, and PB was an alkaline mixture of MgO in colloidal silica solution. Setting occurs by the following chemical equation:



Dimagnesium phosphate is formed when magnesium oxide contacts monomagnesium phosphate, and then the mixture starts to harden. In our recent study,^{11,12)} a paste type phosphate-bonded investment based on

these ammonia-free compositions was investigated in order to minimize the risk to dental technician health from inhalation of dust. Paste type investment was successfully produced, but the storage and usable time of the paste were not examined. In addition, the accuracy of fit obtained from the experimental investment seemed to be insufficient. These experimental pastes were modified, and reevaluated in a similar experiment in the present study.

In the earlier study,¹²⁾ PB was used without diluting the colloidal silica solution with water. In the present experiment, five different PB pastes were prepared with different volumes of water to dilute the colloidal silica. Cristobalite was also added into PB as it was thought it would produce larger thermal expansion, as shown in Table 1. However, the expected expansion was not achieved. One of reasons for this could be the large quantity of water that would be required to retain a paste-like consistency with cristobalite. To avoid condensation of colloidal silica with dehydration when drying, all of the pastes were stored in refrigerator. The pastes could be stored long-term in this manner, and experimental pastes were successfully stored for at least 1 week in this study. Based on these trial results, the volume of a liquid required for PB was determined. PA paste was not altered in this study.

There were definite differences in the fundamental properties among the investments tested. As the colloidal silica was diluted, the hardening time lengthened, the strength decreased, and the setting expansion decreased. However, the thermal expansion did not change. XRD data proved that the expected hardening reaction occurred for all of the investments. The structural changes with heating were equivalent for all the investments tested. Therefore, the ratio of water to PB liquid was thought to produce the differences in the properties among the investments.

In the original pastes, a large volume of water was required to produce the paste type investment with suitable fluidity. In the present study, volume of colloidal silica used with PB was up to 50 ml.

The colloidal silica in the solution combines with magnesium oxide, and forms a gel. This increases the viscosity of PB and produces setting. Therefore, storage stability depends on the volume of colloidal silica and its condensation. PB5 and PB10 enabled long-storage term, but some of their properties were not suitable for use as a dental investment material because of excess water. Particularly, PB5 required approximately 12 h for initial setting. Moreover, the crowns cast using these pastes had defects on the surface because of insufficient fired compressive strength. Accordingly, these paste type investments would not be suitable for casting molds.

Fit of each casting was evaluated using the gap length at the occlusal position. Generally, phosphate-bonded investment should be developed for non-precious alloy. However, these alloys are easy to react to the mold components. As results, the castings obtained from them have rough surfaces. Therefore, the alloy with lower melting point than dental non-precious alloys was convenient to evaluate the properties of experimental investments. Wax pattern of a single crown with clinical design was shaped by CAD/CAM to prevent thermal deformation. Then the gap for cementing at the occlusal side was set to 100 μm as the default, and this was specified from the cemented gap of the wax pattern. Dimensional accuracy of the crowns obtained from PB15 and PB25 was obviously inferior to that from the control. PB15 had the gap of the investments tested. It also had approximately twice the thermal expansion of the control, but setting expansion of nearly 0.1% occurred with exothermic reaction. These findings suggest that cast crowns from PB15 might be undersized. By contrast, PB25 was expected to fabricate oversized crowns because it had the largest total expansion. However, the gap with PB25 was the same as that with PB15. This was because the quantity of colloidal silica included in PB influences the fluidity as it promotes gel formation. Cast crowns from PB20 had a smaller gap than those from PB15 and PB25. In addition, the PB20 crowns

had a similar gap at marginal side compared to the control. Therefore, PB20 seems to be acceptable as dental casting investment within the limitations of this study, and could reduce the risk of developing pneumoconiosis and other respiratory diseases.

According to fundamental properties described above and casting examination, we concluded that the experimental paste type investment with PB20 could be applied clinically. Because the Co-Cr alloy that is usually cast using phosphate-bonded investment has a higher melting temperature and larger casting shrinkage than the alloy tested in this study, further investigations are required to evaluate the clinical performance.

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