Original

Evaluation of the Solubility, Calcium-Release Ability, and Apatite-Forming Ability of a Novel Chemically Curable Mineral Trioxide Aggregate Material

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Abstract: A novel chemically curable, resin-modified-type mineral trioxide aggregate (MTA) material polymerized by tri-n-butylborane (PCX-TBB), and light-curable, resin-modified-type MTA material (TheraCal LC) clinically useful were evaluated in terms of solubility, calcium-release ability, compressive strength and apatite-forming ability. The solubility of PCX-TBB conformed to ISO 6876, whereas that of TheraCal LC did not conform to the abovementioned standard. The calcium-release ability of PCX-TBB and TheraCal LC showed no difference after 1 day of immersion in purified water. However, after 30 days of immersion, the calcium concentration of PCX-TBB increased and became higher than that of TheraCal LC. The compressive strength of PCX-TBB was stable even if immersed in simulated body fluid (SBF) for 30 days. In contrast, the compressive strength of TheraCal LC showed a tendency to decrease slightly by immersion in SBF. Furthermore, the apatite-forming ability of PCX-TBB was determined to be superior to that of TheraCal LC. The results presented herein suggest that PCX-TBB has potential as a superior MTA material and may have improved hard tissue-induction ability compared to that of TheraCal LC.

Key words: Hard tissue-induction ability, Mineral trioxide aggregate, Tri-n-butylborane, Regeneration

Introdution

Mineral trioxide aggregate (MTA) is an endodontic material that was first developed at the University of Loma Linda in the early 1990s and has been used for root-canal filling, root-end filling, perforation repair, and direct pulp capping. Although the major component of MTA is Portland cement, it is also used in dental materials by modification with radiocontrast agents. MTA has been shown to exhibit excellent sealability and biocompatibility. Furthermore, it can induce regeneration of hard tissues with regular dentinal tubule structures. The hard-tissue-induction abilities of MTA are assumed to arise from the calcium hydroxide produced by the hydration reaction of MTA.

To date, many commercial products containing MTA have been developed, with a preceding ProRoot MTA (Dentsply Tulsa Dental, Tulsa, OK, USA). The curing mechanism of these products can be explained based on the hydration reaction of MTA by mixing water and MTA-containing powder. However, these materials need to be further improved in terms of operability and flow ability. Furthermore, they suffer from several problems such as variable curing time and physical properties due to differences in the mixing ratio of powder and water. Recently, a light-curable, resin-modified-type, pulp-capping material composed of Portland cement and resin monomer was on sale (TheraCal LC®, Bisco, Sahumburg, IL, USA). Compared to conventional MTA materials, TheraCal LC exhibits improved operability, greater physical strength, and reduced heavy metal content. Additionally, the calcium-release ability of TheraCal LC®, which is an important performance parameter for hard tissue-induction, is superior to that of ProRoot® MTA by incorporating a highly hydrophilic monomer. However, the cytotoxicity of TheraCal LC® caused by eluted unpolymerized monomer remains a concern.

The MMA/TBB resin is a poly(methyl methacrylate) prepared by polymerization of methyl methacrylate (MMA) with tri-n-butylborane (TBB) and has been recognized as a highly biocompatible resin that can achieve good clinical prognoses as a direct pulp capping material. The excellent biocompatibility of the MMA/TBB resin likely originates from the unique polymerization mechanism initiated by TBB. Based on the biocompatibility of MMA/TBB resin, materials prepared from combinations of MMA/TBB resin and MTA have been studied.

Therefore, this study was performed to evaluate the novel chemically curable, resin-modified-type MTA material polymerized by TBB (PCX-TBB) by comparison with a light-curable MTA material that is already used clinically (TheraCal LC®).

Materials and Methods

Materials

The materials used in this study, their manufacturer details, and compositions are listed in Table 1. PCX-TBB consists of Portland cement, zirconium dioxide, hydroxypropyl methacrylate, and partially oxidized tri-n-butylborane (TBOO) as a polymerization initiator. TheraCal LC® consists of Portland cement, polyethylene glycol dimethacrylate, bisphenol A glycidylmethacrylate (BisGMA) and barium zir-
Specimen preparation

The cured PCX-TBB specimen was prepared by mixing 0.1 g of paste with 1 drop of Catalyst V, which is a polymerization initiator containing TBBO. The cured TheraCal LC® specimen was laminated to be <1 mm thick and each layer was irradiated with an LED (LED.B Guilin Woodpecker Medical Instrument Co., Ltd.) for 20 s.

Solubility

The solubility test was conducted according to the International Organization by standardization guidelines (ISO 6876:2012; dental root canal sealing materials). Four cured specimens with dimensions of 20 mm I.D.×1.5 mm were prepared and stored at 37°C and 95% relative humidity (RH) for 36 h, and then weighed twice using a digital scale with 0.1 mg accuracy (OHAUS, Morristown, NJ, USA). The samples were randomly divided into two groups of two samples and placed into a dish (A) to which 50 ml purified water was added. The dish was subsequently incubated at 37°C for 24 h. A funnel with a filter paper was placed 20 mm above the bottom of dish (B). Purified water was poured into the specimens and placed on the filter paper and then washed into the previously used dish (A) three times with 5 ml of purified water. Dish (B) and the collected water were placed in an oven at 110°C, and the water was evaporated until a constant mass was reached. The solubility rate was calculated according to the following formula and the test was repeated four times.

Solubility rate=[(Final mass of dish (B)-Original mass of dish (B))/Original combined mass of the two specimens]×100 (%)

Calcium-release ability

Five cured specimens with dimensions of 10 mm I.D.×2.0 mm were prepared and stored at 37°C and 95% RH for 24 h. The specimens were subsequently immersed in purified water and stored at 37°C. The specimens were then transferred to fresh purified water after 1, 3, 7, 14, and 30 days. The volume of purified water was adjusted to be 100 mm$^3$ with respect to the surface area of specimen of 1 mm$^2$. The calcium concentration in the purified water was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES; ICPE-9000, Shimadzu Corporation, Kyoto, Japan). The concentration results were calculated using a standard curve, established based on solutions with predefined calcium concentrations.

Compressive strength

Six cured specimens with dimensions of 4.0 mm I.D.×3.0 mm were prepared. Three cured specimens stored at 37°C and 95% RH for 30 days. Other cured specimens were immersed in SBF and soaked at 37°C for 30 days. Each specimen was places in an autograph (AG-X plus, Shimadzu Corporation, Kyoto, Japan) and the compressive strength test was conducted at a crosshead speed of 2.0 mm/min.

Apatite-forming ability

Evaluation of apatite-forming ability was performed with reference to the International Organization of standardization guidelines (ISO 23317:2014; evaluating the apatite-forming ability of implant materials). Five cured bodies with dimensions of 10 mm I.D.×2.0 mm were prepared and stored at 37°C and 95% RH for 24 h. The specimens were subsequently immersed in simulated body fluid (SBF) and soaked at 37°C for 1, 3, 7, 14, and 30 days. The volume of SBF was adjusted to be 100 mm$^3$ with respect to the surface area of specimen of 1 mm$^2$. The resulting ion concentrations in the SBF are shown in Table 2.

Fourier-transform infrared absorption (FT-IR) spectroscopic analysis

The surface of specimens before and after immersed in SBF for 7 days were analyzed by FT-IR spectroscopy (Spectrum 100, Perkin Elmer, Waltham, MA, USA). The spectra of specimens were compared to the spectrum of hydroxyapatite standard. All spectra were recorded at a resolution of 4 cm$^{-1}$ throughout the spectral range 4,000–650 cm$^{-1}$.

Results

Solubility

The ISO 6876:2012 standard recommends a test to evaluate the ma-

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Table 1. Materials used in this study, composition and manufacturer information

| Material          | Manufacture                                  | Component                           | Composition (Compounding ratio %) |
|-------------------|----------------------------------------------|-------------------------------------|-----------------------------------|
| PCX-TBB           | Sun Medical Co., Ltd. Moriyama, Japan         | Chemically-curable paste            | Portland cement (30–40)          |
|                   |                                               | Catalyst V                          | Zirconium dioxide (30–40)         |
|                   |                                               |                                     | Hydroxypropyl methacrylate (20–30) |
|                   |                                               |                                      | TBBO                             |
|                   |                                               |                                      | n-Hexane                         |
|                   |                                               |                                      | Ethanol                          |
| TheraCal LC®      | BISCO Dental Products, Schaumburg, IL, USA    | Light-curable paste                 | Portland cement (30–50)          |
|                   |                                               |                                     | Polyethylene glycol dimethacrylate (10–30) |
|                   |                                               |                                      | BisGMA (5–10)                    |
|                   |                                               |                                      | Barium zirconate (1–10)          |

Table 2. Ion concentrations contained in SBF (pH 7.4)

| Ion          | Concentration (mM) |
|--------------|--------------------|
| Na$^+$       | 142.0              |
| K$^+$        | 5.0                |
| Mg$^{2+}$    | 1.5                |
| Ca$^{2+}$    | 2.5                |
| Cl$^-$       | 147.8              |
| HCO$_3^-$    | 4.2                |
| HPO$_4^{2-}$ | 1.0                |
| SO$_4^{2-}$  | 0.5                |
terial solubility. To meet this standard, the solubility of the material is stipulated to be ≤3.0%\(^\text{26}\). The solubility (wt%) of the PCX-TBB and TheraCal LC\(^\text{®}\) samples is shown in Table 3. The solubility of PCX-TBB (2.4 wt%) conformed to the ISO 6876:2012 standard. In contrast, the solubility of TheraCal LC\(^\text{®}\) (4.0 wt%) exceeded that of the standard value (3.0 wt%).

**Calcium-release ability**

The sustained release of calcium was monitored and the results are shown in Table 4. The calcium concentrations after 1 day, 3 days, 7 days, 14 days and 30 days were 49.1 mg/l, 44.1 mg/l, 45.4 mg/l, 41.3 mg/l and 81.3 mg/l, respectively for PCX-TBB, and 51.2 mg/l, 25.3 mg/l, 27.6 mg/l, 18.1 mg/l and 37.5 mg/l, respectively, for TheraCal LC\(^\text{®}\). Almost no difference in the calcium concentration was observed between the PCX-TBB and TheraCal LC\(^\text{®}\) after 1 day of immersion. However, after 3 days of immersion, the calcium concentration of PCX-TBB was higher than that of TheraCal LC\(^\text{®}\), and more than doubled at 14 days and 30 days of immersion.

**Compressive strength**

The compressive strength of PCX-TBB and TheraCal LC\(^\text{®}\) are shown in Fig. 1. The compressive strength of PCX-TBB was 82.5 MPa without immersion in SBF and 86.2 MPa with SBF immersion. The compressive strength of TheraCal LC\(^\text{®}\) was 124.6 MPa without immersion in SBF and 99.8 MPa with SBF immersion. Although TheraCal LC\(^\text{®}\) has higher physical property compared to PCX-TBB, the property was affected by SBF immersion.

**Apatite-forming ability**

The SEM image showed that small granular crystals formed in the PCX-TBB and TheraCal LC\(^\text{®}\) specimens immersed in SBF for one day (Fig. 2A and F). The SEM images obtained of the specimens immersed in SBF for 3 days showed that the number of crystals increased in both materials (Fig. 2B and G). At 7, 14, and 30 days of SBF-immersion, the crystals in the PCX-TBB specimen grew continuously and nano-cluster crystals overlapped with each other (Fig. 2 C–E). In contrast, the TheraCal LC\(^\text{®}\) specimens showed crystals that were sparsely formed on the surface (Fig. 2 H–J).

**Fourier-transform infrared absorption (FT-IR) spectroscopic analysis**

Fig. 3 shows FT-IR spectra of PCX-TBB and TheraCal LC\(^\text{®}\) (without immersion in SBF or immersed in SBF for 7 days), and hydroxyapatite standard. Hydroxyapatite shows a characteristic peak around 1,020 cm\(^{-1}\). Although there is no matched peak in both PCX-TBB and TheraCal LC\(^\text{®}\) to hydroxyapatite without immersion in SBF, a peak corresponding to specific to Hydroxyapatite in each sample immersed in SBF.

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### Table 3. Solubility of each material

| Material       | PCX-TBB          | TheraCal LC\(^\text{®}\) |
|----------------|------------------|-------------------------|
| Solubility (wt%, Ave±SD) | 2.4±0.2          | 4.0±0.2                 |

Ave, Average value; SD, Standard Deviation.

### Table 4. Calcium concentration in purified water (mg/l: Ave±SD)

| Material       | Soaked days |
|----------------|-------------|
|                | 1           | 3           | 7           | 14          | 30          |
| PCX-TBB        | 49.1±17.5   | 44.1±12.2   | 45.4±12.3   | 41.3±9.0    | 81.3±23.9   |
| TheraCal LC\(^\text{®}\) | 51.2±22.9   | 25.3±9.1    | 27.6±7.5    | 18.1±8.2    | 37.5±10.9   |

Ave, Average value; SD, Standard Deviation.

### Table 5. at % of the element and Ca/P ratio in the crystal of SBF-immersed specimens

| Material       | Days of immersion in SBF |
|----------------|--------------------------|
|                | 1           | 3           | 7           | 14          | 30          |
|                | Ca at%      | P at%       | Ca/P ratio  | Ca at%      | P at%       | Ca/P ratio  |
| PCX-TBB        | 63.05       | 36.95       | 1.71        | 75.05       | 24.95       | 3.01        |
|                | 65.94       | 34.06       | 1.94        | 69.93       | 30.07       | 2.33        |
|                | 67.46       | 32.54       | 2.07        | 70.15       | 29.85       | 2.35        |
|                | 66.49       | 33.51       | 1.98        | 71.36       | 28.64       | 2.49        |
|                | 74.60       | 25.40       | 2.94        | 72.60       | 27.40       | 2.65        |

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Figure 1. The compressive strength of PCX-TBB and TheraCal LC\(^\text{®}\). The compressive strength test of each material was carried out after 30 days storage at 37°C, RH 95% or after 30 days immersion in SBF. The compressive strength of PCX-TBB was stable, whereas that of TheraCal LC\(^\text{®}\) showed a tendency to decrease slightly by immersion in SBF.
Figure 2. Scanning electron micrographs showed the surface morphology of PCX-TBB and TheraCal LC® after immersion in SBF: PCX-TBB after: 1 day (A), 3 days (B), 7 days (C), 14 days (D) and 30 days (E); TheraCal LC® after: 1 day (F), 3 days (G), 7 days (H), 14 days (I) and 30 days (J).
Discussion

This study comparatively evaluated a novel chemically curable MTA material polymerized by TBB (PCX-TBB) and a light-curable MTA material (TheraCal LC®) used clinically in terms of solubility, calcium-release ability, and apatite-forming ability.

Calcium hydroxide has been used in a number of treatment modalities for pulp-capping. However, its high solubility is controversial, since the dissolution of calcium hydroxide can result in the majority of dentine bridges under the materials producing tunnel-like defects within 1–2 years. Therefore, approximately 50% of the pulps may become infected or become necrotic owing to microleakage\(^2\),\(^2\). Similarly, in root-end filling cement, the volume loss of the material is undesirable because it reduces sealing ability, creating ideal conditions for bacteria to enter the treatment site\(^3\),\(^4\). Hence, the ISO 6876:2012 standard recommends a test to evaluate the material solubility. There has been some discussion regarding the abovementioned evaluation method in the context of sustained release materials such as MTA\(^5\) because these materials are required to release active ingredients such as calcium. Therefore, in this study, the sustained release of the active ingredient calcium from MTA and its solubility were evaluated simultaneously. The results showed that the solubility of PCX-TBB (2.4 wt%) was lower than that of TheraCal LC® (4.0 wt%) and its calcium-release ability was higher than that of TheraCal LC® (Table 4).

TBB as the initiator can promote the polymerization of the monomer in a high conversion ratio compared to conventional photo-polymerization initiators such as camphorquinone\(^6\). In addition, the polymerization activity of TBB was improved in an environment containing a certain amount of oxygen and water\(^7\). On the other hand, the polymerization of TheraCal LC® was inhibited by oxygen\(^8\). Therefore, it is likely that differences between the solubility of PCX-TBB and that of TheraCal LC® can be ascribed to the elution of insufficiently cured components such as monomer and oligomer. In clinical condition, there are polymerization inhibitors such as water and oxygen. Under such condition, PCX-TBB may be more effective materials compared to TheraCal LC®. Gandolﬁ MG et al. report that the solubility of TheraCal LC® (1.58 wt%) was lower than that of ProRoot MTA (18.34 wt%)\(^9\). Compared with the solubility results of the previous study, there is a slight difference in the elution volume of TheraCal LC® (4.0 wt%) in this study (Table 3). However, there are some differences in sample preparation and immersion methods between the previous and present study. In particular, the sample adjusted based on ISO 6876:2012 in this study, and the surface area is larger than the previous report. Moreover, since the amount of water to be immersed is larger in this study, solubility in water may be increased. There is a possibility that these factors influence the difference in these results.

The compressive strength of PCX-TBB and TheraCal LC® were examined in order to evaluate the influence of calcium-release on physical properties. The compressive strength of PCX-TBB was not affected by immersion in SBF, whereas that of TheraCal LC® showed a tendency to decrease slightly (Fig. 1). It is reported that MTA releases calcium ion due to reaction of MTA and water\(^10\), and the compressive strength of MTA is improved by the hydration reaction\(^11\). Thus, it was presumed that the reduction of the compressive strength of TheraCal LC® which has higher solubility than PCX-TBB may be caused by outflow of the monomer, oligomer and the inorganic material from the cured specimen. In particular, the outflow of the inorganic component derived from MTA

![Figure 3 FT-IR spectra of PCX-TBB and TheraCal LC® (without immersion in SBF, immersed in SBF for 7 days), and hydroxyapatite standard.](image-url)
may be preventing the progression of hydration reaction in SBF. Apatite phase formation and regeneration of hard tissues are important for the clinical success of MTA. Kokubo et al. concluded that the examination of apatite formation on a material in simulated body fluid (SBF) is useful for predicting in vivo bone bioactivity. Therefore, we evaluated the apatite-forming ability according to the ISO 23317:2014 standard. From the SEM observations, it was apparent that PCX-TBB was able to form an increased number of calcium phosphate crystals compared to TheraCal LC (Fig. 2). In the PCX-TBB specimen, nano-cluster crystals were densely formed on the surface and were similar to apatite crystals. In addition, the results of FT-IR supports that the crystals formed on the surface of PCX-TBB and TheraCal LC are calcium phosphate.

The generated crystal morphology significantly influences the bioactivity of the material. Smaller crystal particles absorb more protein, leading to further absorption of cells that can induce hard tissue regeneration. As shown in Fig. 2, in the PCX-TBB samples, many small crystals were densely formed, suggesting that PCX-TBB can induce greater cell proliferation and improved hard tissue regeneration. The ratio of calcium to phosphorus (Ca/P ratio) significantly affects the degree of bioactivity of the material. Previous reports have shown that the Ca/P ratios of MTA immersed in SBF for 1, 7, and 14 days were 3.84, 8.33, and 2.74, respectively. These Ca/P ratios in MTA were higher than the stoichiometric Ca/P ratio for hydroxyapatite (Ca/P = 1.67). Higher Ca/P ratios indicate calcium precipitation on the surface, which can lead to the desired bioactivity, biocompatibility, and hard tissue-induction abilities. The Ca/P ratios obtained in this study are shown in Table 5 and ranged from 1.71 to 2.94 for PCX-TBB and from 2.33 to 3.01 for TheraCal LC. The Ca/P ratios of PCX-TBB and TheraCal LC were higher than that of the stoichiometric ratio of hydroxyapatite; therefore, it is likely that these materials would possess the abovementioned properties.

According to the SEM observations, EDS and FT-IR analyses, both PCX-TBB and TheraCal LC exhibited apatite-forming ability. The number of crystal formed on PCX-TBB was much higher than that of TheraCal LC at all time points (Fig. 2). Thus, PCX-TBB may have improved hard tissue-induction ability compared to that of TheraCal LC.

In conclusion, the novel chemically curable MTA material (PCX-TBB) exhibited low solubility, high calcium-release ability and stable compressive strength. The relevant properties of PCX-TBB were superior to those of the light-curable MTA material (TheraCal LC). Both PCX-TBB and TheraCal LC showed ability to form calcium phosphate crystals (apatite derivatives) with high Ca/P ratios. From the SEM observations, it was apparent that PCX-TBB was able to form an increased number of calcium phosphate crystals compared to TheraCal LC.

**Conflicts of Interest**

The materials costs relevant to this study were borne by Sun Medical Co., Ltd. Author Chidzuru Inami is an employee of Sun Medical Co., Ltd. Author Chidzuru Inami applied for a patent related to this research, but has not received any patent royalty. There are no other conflicts of interest to disclose.

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