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Calcium Phosphates as Fissure Sealant Materials Fused to Enamel by CO_2 Laser. II. Calcium Phosphate Cement that Forms DCPD

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Calcium phosphate cement that forms DCPD during setting was evaluated as a laser-fused sealant. CaF_2 was added to the β-TCP/MCPM cement in order to enhance the anticariogenic potential and to lower the melting temperature of the set cement. Without any additives, however, the cement set in a short time, allowing no practical working time. To control the setting time, β-$Ca_2P_2O_7$, which is one of the phases obtained from lased DCPD, was added to CaF_2/β-TCP/MCPM cement. The addition of β-$Ca_2P_2O_7$ at 50 wt% was found to greatly improve the handling characteristics of the cement. When 50 wt% β-$Ca_2P_2O_7$-added CaF_2/β-TCP/MCPM cement was applied to occlusal surfaces of the teeth, adequate properties were obtained. At 3 min after mixing, a CO_2 laser was applied to the setting cement on the occlusal tooth surface under appropriate conditions, and only surface regions of the lased cement were melted. Around the margins, the enamel and the cement were fused together.

Key words: CO_2 laser, Calcium phosphate, Fissure sealants, Calcium phosphate cement

INTRODUCTION

Pit and fissure areas of posterior teeth, particularly in children, are associated with a high risk of caries, as it is practically impossible to thoroughly clean the areas due to form complexity. In pedodontics, pit and fissure sealants consisting of resin systems and glass ionomer cement systems[1)] have been employed to prevent caries. For both resin and cement sealants, some studies[1～6)] have reported that the sealants must often be re-sealed due to removal of materials or fractures at material edges, thus suggesting that durability is insufficient.

In a trial preservation, enamel was exposed to dental lasers in order to enhance acid resistance and to prevent dental caries[6～10)]. The potential applications for various lasers, such as neodymium-doped YAG (Nd: YAG) lasers, erbium-doped YAG (Er: YAG) lasers and carbon dioxide (CO_2) lasers have been shown. Among these, Nd: YAG lasers have a high light permeability for enamel and dentin[11)]. Er:YAG lasers have a wav length of 2.94 µm[12)], and a high absorption efficiency by water, which can cut teeth[13, 14)] via microexplosions[15, 16)]. On the other hand, CO_2 lasers have a wavelength of 10.6 µm[17, 18)], which coincides closely with the absorption bands of apatite and can provide a heat source with very high intensity.

As high energy density can bring about the loss of phosphorus from the material during laser irradiation, calcium phosphates with calcium and phosphate molar ratios of near that of enamel are unfavorable. In a previous study monocalcium phosphate monohydrate (MCPM) and dicalcium phosphate dihydrate (DCPD) were evaluated as laser−fused sealants, as they both satisfy the above-mentioned requirements and are also melted at temperatures much lower than those required to melt HA and/or enamel. Detailed comparisons of MCPM and DCPD have suggested that the latter is better as a laser-fused sealant[19)]. Powdered DCPD, however, suffers from poor handling characteristics and it is practically impossible to place the powder evenly on the enamel surface.

In the present study, a calcium phosphate cement consisting of β-calcium pyrophosphate and MCPM developed by Mirtchi et al.[20, 21)] was thus evaluated as a laser-fused sealant after necessary modifications were introduced.

MATERIALS AND METHODS

β-TCP/MCPM cement

Calcium carbonate (KISHIDA Co. Ltd., Osaka, Japan), MCPM (SIGMA ALDRICH Co. Ltd., St. Louis, MO, USA) and CaF_2 (NAKARAI-TESC Co., Ltd., Kyoto, Japan.) were used as received.

β-tricalcium phosphate (β-$Ca_3(PO_4)_2$: β-TCP) was prepared by heating a mixture of 1 mol $CaCO_3$ and 2 mol MCPM at 1100℃ for 24h. β-TCP was then powdered in an alumina mortar and sieved through a 32-µm mesh. β-TCP was mixed with MPCM at an equimolar ratio to prepare β-TCP/MCPM cement[20, 21)].

CaF_2 was added to β-TCP/MCPM cement at 10 wt% and distillated water was used as the liquid. To control the setting time, β-calcium pyrophosphate (β-$Ca_2P_2O_7$) was added to the CaF_2-β-TCP/MCPM cement.

Adjustment of setting time

β-$Ca_2P_2O_7$ was added to the CaF_2/β-TCP/MCPM cement at 10, 20, 30, 40 and 50 wt%. Setting time was measured according to JIS standard T6602-1993 (dental zinc phosphate cement). For each measurement, 0.6 g of cement powder was mixed with 0.4 m*l* of distillated water at a powder to liquid ratio of 1.5. Mixed cement was placed in a plastic cylinder (10 mm in diameter and

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5 mm in height) at 30 s after mixing. The Vicat needle (cross sectional area: 1 mm^2; weight: 300 g) was carefully lowered onto the surface of cement and was allowed to remain there for 5 s. A trial run was carried out in order to measure the initial setting time and final setting time, repeating the indentations at 30-s intervals. The time elapsed between the end of mixing to until the time when the needle started to make a complete circular indentation in the cement was defined as the initial setting time, and the time elapsed until the needle failed to make a complete circular indentation in the cement was defined as the final setting time. Five tests were repeated to measure both the initial and final setting time.

Crystalline phases by X-ray diffraction

Mixed cement samples at 5 and 30 min after mixing were frozen with liquid nitrogen temperature, and were then freeze-dried. Dried cement was powdered and examined by X-ray diffraction (RINT2000, RIGAKU Electronics Co., Ltd. Tokyo, Japan) at a scanning speed of 2.0 °θ/min, and at 56 kV and 200 mA. Cement powder before mixing was also examined.

Effective laser irradiation conditions

Cement specimens mixed at the same powder and liquid ratios as for setting time measurement in plastic cylinders (10 mm in diameter and 5 mm in height) were CO_2-lased at 3 min after mixing. Irradiation power varied from 5.0 to 8.0 W, and distance between the specimen and hand piece also varied between −20 mm from the focus and +20 mm from the focus. Diameter of lased spots was measured by light microscopy (VHX Digital Microscope, Keyence CO., Ltd. Tokyo, Japan).

Evaluation of cement as pit and fissure sealant material

Human premolars stored in 5 % formalin were used. Teeth were first cleaned ultrasonically in 50% NaOCl for 10 min, and were rinsed thoroughly with distilled water. Before laser irradiation, teeth were dried. 50 wt% β-$Ca_2P_2O_7$-added cement was mixed at a powder/liquid ratio of 1.5, and was applied to the pits and fissures of the dried teeth. At 3 min after mixing, CO_2 laser was applied at a power of 7.5 W. The distance from the focus of laser was +10 mm and irradiation time was 1.0 s. Lased teeth were then mounted in plastic (B.P.S. set Q Kyoto Chemical Co., Ltd., Kyoto, Japan) and cut into sections with a low speed diamond saw (ISOMET, Buehler Co., Ltd, Lake Bluff, IL, USA) cooled with water. Cut planes of the lased area were observed using a digital light microscope.

RESULTS

Figure 1 shows the effects of β-$Ca_2P_2O_7$ addition on the setting time of CaF_2-β-TCP/MCPM cement. Both the initial and final setting times were prolonged as β-$Ca_2P_2O_7$ increased, with the latter being prolonged more markedly. Although not shown, addition of β-$Ca_2P_2O_7$ beyond 50 wt% prolonged the initial setting time to more than 10 min and the final setting to more than 30 min.

Figure 2 shows X-diffraction patterns of setting 50 wt% β-$Ca_2P_2O_7$-added cement specimens. Although a specimen at 5 min after mixing was essentially the same as that before mixing, in the specimen at 30 min after mixing, diffraction peaks due to DCPD, which were not found in the starting cement, were clearly identified.

Figure 3 shows the dependence of distance from the focus on the size of lased spots at various irradiation intensities by plotting the diameter of lased spots. Generally, as the power increased, the lased spots became lager. When irradiated at distances over ±20 mm from the focus, lased spots became markedly smaller.

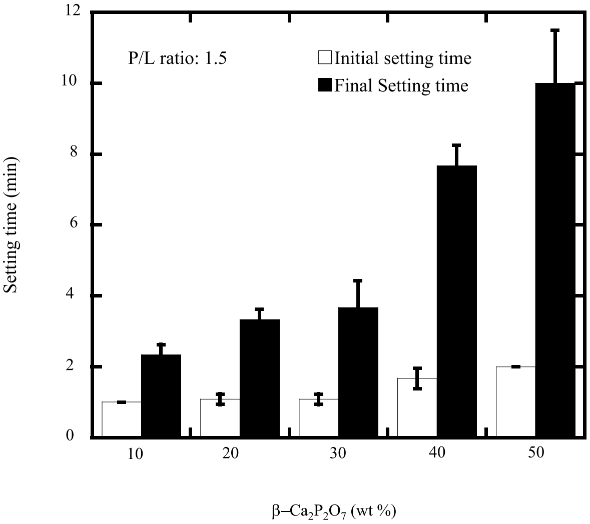

Fig. 1 Influence of β-$Ca_2P_2O_7$ on setting times of CaF_2/β-TCP/MCPM cement.

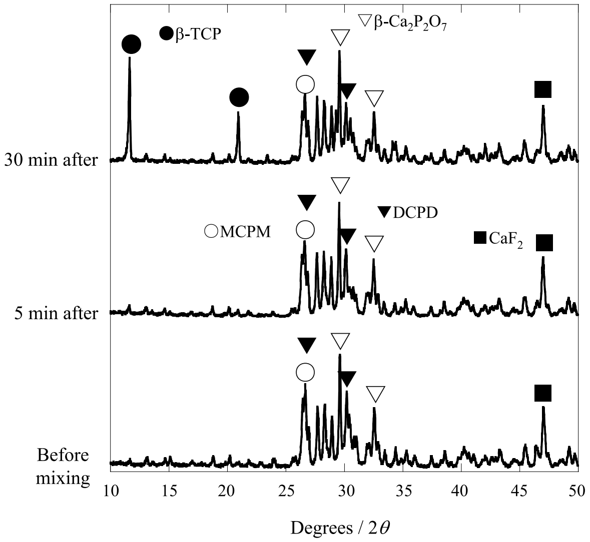

Fig. 2 X-ray diffraction patterns of 50wt% β-$Ca_2P_2O_7$-added cement before and after mixing

Figure 4 shows optical microscope images of pits and fissures before and after cement application. As Fig.4B shows, the applied cement filled pits and fissures quite efficiently and was retained after setting. The cross-sectional view shown in Fig.5 indicates that surface regions of the lased cement consist of fused layers. The enamel and the cement fused together around the margins, where the cement thickness was small. In lesions where cement thickness exceeded 1 mm, no damage on the enamel surface was observed.

DISCUSSION

In order to protect against caries in susceptible regions, particularly pit and fissure areas of posterior teeth in children, various materials have been employed as sealants, including resin systems[22] and glass ionomer cement systems[23]. Durability, however, is poor, due to the lack of direct chemical bonds between sealant and enamel, as well as the difference in thermal expansion coefficients between them. Sealant materials that have the chemical compositions similar to that of enamel and that can form chemical bonds to enamel would be ideal in this regard.

In an attempt to produce a chemical bond between enamel and sealant, a CO_2 laser was employed by Stewart et al.[24], as the CO_2 laser can provide a source of heat of very high intensity in the oral environment. Energy density that exceeds a certain threshold, however, causes cracking of enamel[25]. To fuse a sealant consisting of hydroxyapatite (HA) to enamel successfully, while avoiding cracking of enamel, there would need to be a eutectic fluoride compound to lower the temperature for HA sintering. The melting point of HA[26], however, is generally about 200°C higher than the sintering temperature, which ranges between 1200-1300°C. Levy and Koubi[27] used traicalium phosphate (TCP) to fuse cracked teeth with a Nd-YAG laser. They found melted TCP particles filled the cracked root after laser irradiation, but no calcium phosphate was apparently attached to the dentin.

In a previous study[19], calcium phosphates that melt at temperatures lower than the melting point of HA were investigated as laser fused sealants. As compared with MCPM, DCPD melted at a slightly higher temperature (971°C for MCPM and 1348°C for DCPD). Nevertheless, phases decomposed from DCPD after heating were less soluble than those decomposed from MCPM, indicating that DCPD would be superior to MCPM as a laser-fused sealant. For practical application, however, powdered DCPD must be suspended in appropriate solutions, such as alcohol, before placement on the surface of enamel. After the solvent evaporates, DCPD is expected to fill in pits and fissures to achieve better retention before laser irradiation. After irradiation with the CO_2 laser, however, some DCPD particles left the enamel surface, probably due to blasts from sudden vaporization, while retained DCPD particles fused to the surface, resulting in the lased surface appearing porous. Many particle crevices were also noted, indicating that no strong retention or condensation was achieved with this method.

A calcium phosphate cement that forms DCPD during setting

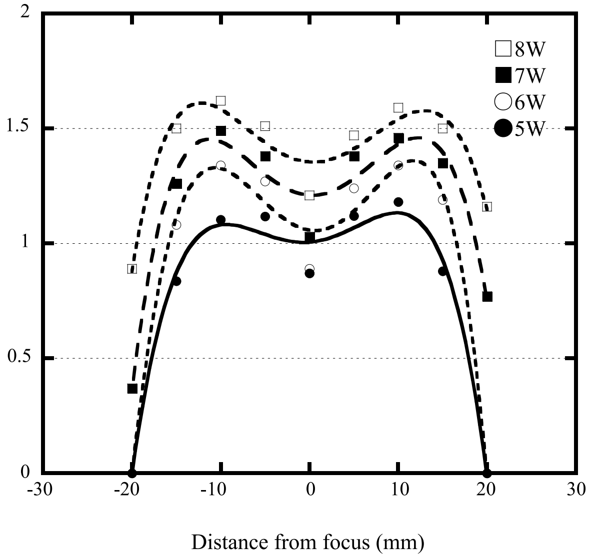

Fig. 3 Diameters of irradiated spots as a function distance from the focus at different powers

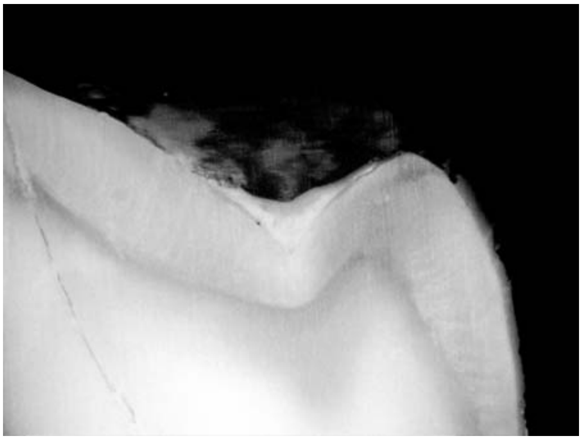

Fig. 5 Cross-sectional view of a lased specimen.
The specimen was exposed to a CO_2 laser at 7.5W for 1 s. The distance from the focus was +10mm.

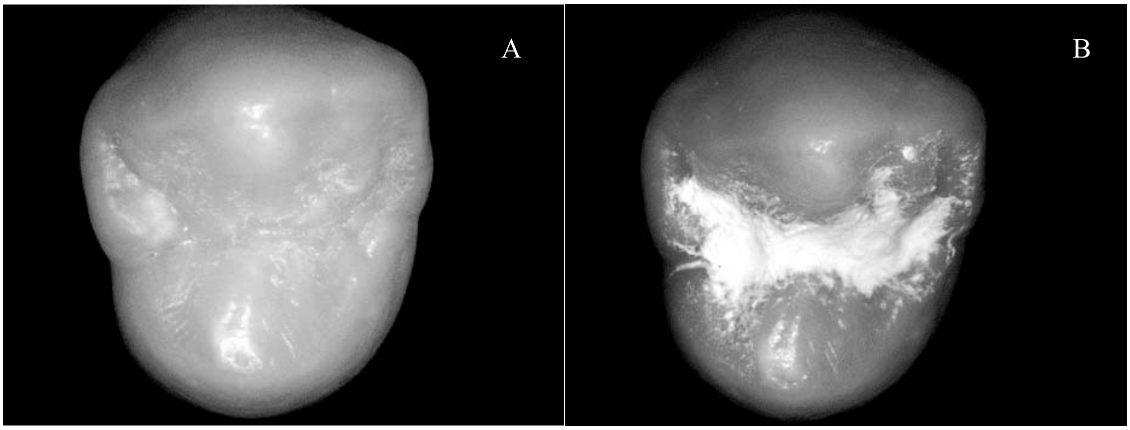

Fig. 4 Occlusal views of a tooth before (A) and after (B) condensation of 50wt% β-$Ca_2P_2O_7$-added CaF_2/β-TCP/MCPM cement

A : Before condensation
B : After condensation

would overcome this problem. Mirtchi et al.[20, 21] developed a self-curing calcium phosphate cement that precipitates DCPD during setting. This cement consists of β-TCP and MCPM, and is mixed with water. The problem with thus cement is that the setting time is too short for use as a lased sealant. In the present study, CaF_2 was added to increase the anticariogenic potential[28] and to lower the melting temperature, while β-$Ca_2P_2O_7$ was added to control the setting time. As Fig.1 shows, the addition of β-$Ca_2P_2O_7$ markedly decreased the final setting time with the initial setting time being almost unchanged. As the time elapsed between the initial and setting time is the working time, the addition of β-$Ca_2P_2O_7$ was found to greatly improve the handling characteristics of the laser-fused sealant.

When 50 wt% β-$Ca_2P_2O_7$-added cement was mixed with water, DCPD precipitated in about 5 min after mixing (Fig.2). As demonstrated in a previous paper[19], DCPD is decomposed into α, β and γ-$Ca_2P_2O_7$ at high temperatures, and the addition of β-$Ca_2P_2O_7$ to control the setting time had little effect on the general properties of the cement as a laser-fused sealant in the present study. As Fig.4b shows, the set cement appears to fill the pits and fissures quite well. No detachment of cement was observed, even when specimens were subjected to mechanical force with a small hummer. On extracted human bicuspid pits and fissures, the maximum cement thickness was approximately 1.3 mm (n=5). This evidence, together with the findings shown in Fig.3, suggest that the laser should be applied from a distance of 10 mm from the focus, in order to prevent damages to the enamel surface beneath the set cement.

In many reports[15~19], in order to determine the energy density of laser radiation, criterion such as enamel cracking[15] or fusion of the selected the material[16~19] have been employed. As shown in Fig.4, when irradiated at a distance of +10 mm from the focus, an output power of 7.5 W and an exposure time of 1s, almost all areas of the set cement were covered with a single pulse, and no damage to the enamel surface was seen. Although the energy density employed in the present study appeared to be greater than those used in other reports[15~19], no obvious damage was evident on the enamel surface beneath the lased cement. Close examination of sectioned specimens by optical microscopy (Fig.4c) demonstrated that only surface regions of the lased cement were melted. More importantly, however, around the margins, where the cement thickness was smaller, the enamel and cement were fused together.

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CONCLUSIONS

Addition of β-$Ca_2P_2O_7$ to the CaF_2/β-TCP/MCPM cement was found to be effective in controlling the setting time. The β-$Ca_2P_2O_7$-added CaF_2/β-TCP/MCPM cement developed in the present study may thus be useful as a laser-fused sealant. When irradiated with a CO_2 laser under appropriate conditions, the sealant material and enamel at the margins were fused together, without accompanying any damage in other regions.

REFERENCES

1) Simonsen RJ. Pits and fissure sealant: review of the literature. *Pediatr Dent.* 2002; 24: 393-414.

2) Houpt M, Fuks A and Eidelman E. The Preventive resin (composite resin/sealant) restration: nine-year results. *Quintessence Int.* 1994; 25: 155-159.

3) Ismail AI and Gagnon P. A longgitudinal evalution of fissure sealants applied in dental practices. *J Dent Res.* 1995; 74: 1583-1590.

4) Kilpatric NM, Murray JJ and Mccabe JF. A clinical comparison of a light cured glass ionomer sealant restration with a composite sealant restration. *J Dent Res.* 1996; 24: 399-405.

5) King NM, Yung KL and Holmgren CJ. Clinical performance of preventive resin restrations placed in a hospital enviroment. *Quintessence Int.* 1996; 27: 627-631.

6) Featherstone JDS and Nelson DGA. Laser effects on dental hard tissue. *Adv Dent Res.* 1987; 1: 21-26.

7) Wigdor HA, Walsh JT, Featherstone JDS, Visuri SR, Fried D and Waldvogel JL. Laser in Dentistry. *Laser in Surg and Med.* 1995; 16: 103-133.

8) Yamada K. Laser Application in Pediatric Dentistry. *J Jpn Soc Laser Med.* 1999; 20: 47-53.

9) Sognnaes RF and Stern RH. Laser effect on resistance of human dental enamel to demineralization in vitro. *J Calif Dent assoc.* 1965; 33: 328.

10) Stern RH, Vahl J and Sognnaes RF. Lased enamel: Ultrastructual observations of pulsed carbon dioxide laser effects. *J Dent Res.* 1972; 51: 455-460.

11) Kitamura S, Nakashima M, Hirata K and Sekine I. A Study on Removal of Pit and Fissure Caries Lesion by Nd: YAG Laser Irradiation: Part 1. Effect of Color Mediators on Enamel and Dentin Ablation. *Japan J Conserv Dent.* 2004; 47: 723-732.

12) Takizawa M, Amagai T, Haruyama C, Kameyama A, Takase Y, Hirai Y and Kumazaki M. Effect of water Spray Amounts on Dentin Cutting with Er: YAG Laser Irradiation. *J Jpn Soc Laser Dent.* 2001; 12: 84-91.

13) Kumazaki M, Fujiwara H, Matsuda T, Zennyu K, Kumazaki M, Toyoda K and Fujii B. Excision of dental caries. *J Jpn Soc Laser Dent.* 1992; 3: 23-27.

14) Takizawa M. A Study on Er: YAG. Laser Ablation for Dental Hard Substances. *Japan J Conserv Dent.* 1996; 39: 1089-1128.

15) Nelson JC, Yow L, Liaw LH, Macleay L, Zavar RB, Orenstein A, Wright WH, Andrews JJ and Berns MW. Ablation of bone and methacrylate by a prototype mid-infrared erbium: YAG laser. *Lasers Surg Med.* 1988; 8: 494-500

16) Keller U and Hibst R. Experimental studies of the application of the ER: YAG laser on dental hard substances: II Light microscopic and SEM investigations. *Lasers Surg Med.* 1989; 9: 345-351.

17) Murakami S, Koide N, Koike S, Matuzaka K and Inoue T. An Experimental Study on Wound Healing after CO_2 Laser Irradiation to Palate Mucosa of Beagle Dog. *Japan J Conserv Dent.* 2003; 46: 343-348.

18) Kato J, Morita K and Hashimoto Y. Prevention of Dental Caries of Permanent Molar Tooth with a Covering Operculum by Using CO_2 Laser. *J Jpn Soc Laser Dent.* 2002;13: 13-16.

19) Goto H, Tagaya H, Wakamatsu N, Kamemizu H, Tsukahara T, Aoki S, Doi Y and Tamura Y. Calcium phosphates as fissure sealant materials fused to enamel by CO_2 laser. I. Monocalcium phosphate monohydrate and dicalcium phosphate dihydrate as fissure sealant materials. *J Gifu Dent Soc.* 2008; 35: 48-54.

20) Mirtchi AA, Lemaitre J and Terao N. Calcium phosphate cements: study of the β-tricalcium phosphate-monocalcium phosphate system. *Biomaterials.* 1989; 10: 475-480.

21) Mirtchi AA, Lemaitre J and E Munting. Calcium phosphate cements: effect of fluorides on the setting and hardening of β-tricalcium phosphate-dicalcium phosphate-calcite cements. *Biomaterials.* 1991; 12: 505-510.

22) Simonsen RJ. Retention and effectiveness of dental sealant after

15 years. *J Am Dent Assoc.* 1991; 122: 34-42.

23) Sipahier M and Ulusu T. Glass-ionomer-cermet cements applied as fissure sealants-II. Clinical evaluation. *Quintessence Int.* 1995; 26: 43-47.

24) Stewart L, Powell GL and Wright S. Hydroxyapatite attached by laser: A potential sealant for pits and fissures. *Operative Dentistry.* 1985; 10: 2-5.

25) Boehem R, Rich J, Webster J and Janke S. Thermal stress effects and surface cracking associated with laser use on human teeth. *J Biomech Eng.* 1977; 99: 189-194.

26) Fowler BO and Kuroda S. Changes in heated and in laser-irradiated tooth enamel and their probable effects on solubility. *Calcif Tissue Int.* 1986; 38: 197-208.

27) Lecy GC and Koubi GF. An experimental technique to repair cracked teeth using calcium phoshate, melted by a laser beam: an in vitro evaluation. *Compend Contin Educ Dent.* 1993; 11: 1444-1452.

28) Anusavice KJ, Zhang N-Z and Shen C. Effect of CaF_2 content on rate of fluoride. *J Dent Res.* 2005; 84: 440-444.

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CO_2レーザー融着による小窩裂溝予防填塞としてのリン酸カルシウム
2. DCPD 析出リン酸カルシウムセメントによるシーラント材

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硬化時に DCPD を析出するリン酸カルシウムセメントのレーザー融着シーラント材としての可能性を検討した．フッ素徐放性を期待し，また，セメントの融点を下げるためにフッ化カルシウムを添加したβ-TCP/MCPM セメントを開発した．このセメントは有効な作業時間が確保できないほど短時間で硬化するため，硬化時間調整材として DCPD の加熱生成物の１種であるβ-ピロリン酸カルシウムの有効性を検討した．その結果，β-ピロリン酸カルシウムの添加が50%になると，セメントの操作性は著しく向上し，小窩裂溝に填塞すると，適切な填塞が得られた．小窩裂溝に填塞し硬化後，CO_2レーザー照射すると，レーザー照射されたセメントの表面層のみが融解し，セメント下部のエナメル質は何らの影響を受けなかった．しかしながら，境界部では，エナメル質とセメントは融着し，本研究で開発した50%β-$Ca_2P_2O_7$添加 CaF_2/β-TCP/MCPM セメントは小窩裂溝填塞のレーザー融着材として有効であることが示唆できた．

キーワード：炭酸ガスレーザー，リン酸カルシウム，フィッシャーシーラント，リン酸カルシウムセメント

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