

The Effect of Titanium Tetrafluoride Treatment and the CO₂ Laser on Acid Resistance of Human Enamel



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Abstract

Introduction: Titanium tetrafluoride (TiF₄) is deemed more effective than the previous fluoride compounds. To enhance the effect of the fluoride compounds, researchers have suggested their association with lasers, although there are conflicting results in this area. We evaluated the acid resistance of enamel after treatment with the CO₂ laser and TiF₄.

Methods: Thirteen human premolar teeth were sectioned into 5 parts and each segment was assigned to a study group: co (control): without treatment, AF: enamel treatment with APF 1.23% for 4 minutes, TF: enamel treatment with TiF₄ 4% for 1 minute, TF-L: enamel treatment with TiF₄ 4% and then the CO₂ laser (Peak power: 1 W, pulse duration: 10 ms, interval time: 500 ms, Beam spot size: 0.2 mm, distance: 2 cm), L-TF: enamel treatment with the CO₂ laser and then TiF₄ 4%. Each sample was kept for 7 days in acidic solution of hydroxyethyl cellulose at pH=4.5, and the amount of the calcium ion released in the solution was measured by atomic absorption spectrometry. Data were analyzed by ANOVA and Bonferroni tests. The significance level was set at 0.05.

Results: The average concentration of the calcium ion released in acidic solution was 197.46, 153.30, 99.23, 61.23, 55.46 ppm in the groups respectively. There was a significant difference between the study groups ($P<0.0001$). Only the difference between TF-L and L-TF was not significant ($P>0.05$).

Conclusion: The loss of calcium from the enamel samples in the groups treated with a combination of the laser and TiF₄ was significantly lower than the groups treated with fluoride alone, or the control group. It did not make a significant difference whether the CO₂ laser was applied before or after TiF₄.

Keywords: Acidulated phosphate fluoride; Fluorides; Lasers; Titanium tetrafluoride; Tooth demineralization.



Introduction

Despite advances in oral health care techniques and preventive materials, dental caries is one of the most common infectious diseases all over the world. In the caries process, the tooth structure loses its mineral by the acid produced due to the metabolic activity of the cariogenic bacteria.¹ Current caries preventive methods including fluoride therapy do not completely prevent the caries incidence. Another drawback of fluoride therapy is its inefficiency in preventing caries on the occlusal surfaces.² Additionally, since the number of the elderly population is increasing all over the world, novel preventive methods for caries prevention seem necessary.

Topical fluorides in forms of gel, solution, and varnishes such as sodium fluoride (NaF), acidulated phosphate fluoride (APF), and titanium tetrafluoride (TiF₄) are of the

most current caries preventive methods. One of the major mechanisms of action for fluorides is preventing teeth from demineralization and inducing remineralization of teeth. The fluoride ion penetrates the hydroxyapatite crystals via the replacement by the hydroxyl ion and forms fluorapatite which is more resistant to caries.^{3,4} Among the fluoride compounds, TiF₄ is a strong inhibitor of tooth demineralization and has been reported more effective in preventing caries.⁵

For better effectiveness of the fluoride compounds, their application in combination with other preventive measures is suggested for caries prevention.⁶ One of these novel methods is the combination of fluoride and the laser. Lasers are reported effective in caries prevention; however, the additive effect of the laser and fluoride has indicated better results in this field.^{6,7} The carbon dioxide

(CO₂) laser has increased the effectiveness of different forms of fluoride in some studies. It has caused increased fluoride uptake and has simplified the modification of hydroxyapatite into fluorapatite in those studies.^{4,8} In some other studies, laser irradiation did not show better results than fluoride application alone.^{9,10} In addition to the controversy that exists concerning the effectiveness of laser irradiation in caries prevention, it is not known which treatment protocol of the laser and fluoride would lead to the best results.

Considering the importance of the novel preventive measures to prevent the need for extensive restorations in future, the aim of the present study was to evaluate the acid resistance of human enamel after treatment with TiF₄ and the CO₂ laser and the combination of the laser and TiF₄.

Methods

In this in vitro study, 13 intact human premolar teeth extracted for orthodontic purposes were selected (approved ethical code: 310121). The teeth were devoid of any cracks, caries, wear or other abnormalities in a visual examination. After disinfection in 0.1% thymol solution, each tooth was longitudinally sectioned into 5 blocks using a sectioning machine (MECATOME T 201 A PRESI, Germany). The tooth sections were covered with nail polish in all the surfaces, except a 2×4 mm window of enamel. One section from each tooth was allocated into a study group, but each group of teeth was randomly assigned to a study group as follows (N=13):

Group 1: The control group; the samples were kept without any treatment in artificial saliva (HYPOZALIX solution, Biocodex, French).

Group 2: The APF group; the samples were treated with 1.23% APF gel (POLIMO, Imicryl, Turkey) for 4 minutes (according to the instructions of the manufacturer). Then, they were washed with water and air-dried for 5 seconds (APF was studied in a separate group as a kind of control for the acidic compound of TiF₄).

Group 3: The TiF₄ group: the specimens were treated with 4% TiF₄ gel for 1 minute and then washed and air-dried like in group 2. TiF₄ gel was freshly prepared immediately before its use.

Group 4: The TiF₄-Laser group: after treatment of the samples by the same way as in group 3, they were irradiated by 10.6 µm CO₂ laser (DSE, South Korea) for 15 seconds. The laser parameters were as follows: Peak power: 1 W, pulse duration: 10 ms, interval time: 500 ms, Beam spot size: 0.2 mm, distance: 2 cm.

Group 5: The laser-TiF₄ group: the specimens were irradiated by the CO₂ laser the same way as in group 4, and then they were treated by 4% TiF₄ gel the same way as in group 3. All of the treatment steps were performed by a trained and calibrated technician.

The TiF₄ gel with pH=1.2 was prepared by the dissolution of 4 g of TiF₄ powder (Aldrich Chemical Company,

Milwaukee, WI, USA) in 100 ml deionized water and the addition of carboxymethyl cellulose immediately before the application.

In the next step, each sample was separately immersed in 5mL of a demineralizing solution (NaCl 2.9 g, CaCl₂ 0.12 g, NaH₂PO₄ 0.13 g, NaF 5 cc, NaN₃ 5 cc, acetic acid 1.5 cc) with pH=4.5 for 7 days.

Finally, in order to determine the enamel acid resistance of each study group, the samples were analyzed by atomic absorption spectrometry to measure the amount of the calcium ion released in the acidic solution by ppm or µg/mL. The technician who read the values of the spectrometry was blind to the study groups. Data were analyzed by a repeated measures ANOVA and Bonferroni tests. The significance level was set at 0.05.

Results

Evaluation of the calcium ion released into the acidic solution indicated that the TiF₄-laser and laser-TiF₄ groups caused the least tooth demineralization. About 70% reduction in demineralization was observed in these groups compared to the control group. The amount of the calcium ion released in the study groups is mentioned in Table 1.

A normal distribution of data was observed in the amount of the calcium ion released among the study groups. The results from conducting a repeated-measures ANOVA revealed significant differences among the study groups ($P<0.0001$). Table 2 indicates the pairwise comparison of the study groups by the Bonferroni test. Significant differences were observed between all of the study groups, except the difference between the TiF₄-Laser and Laser-TiF₄ groups ($P>0.05$).

Discussion

TiF₄ was used in the form of gel in this study to be similar in form to the commercially available APF gel. The gel form had the suitable consistency to have ion exchange with the enamel hydroxyapatite crystals. In addition, the protective effect of the material was not related to any other components such as the resin that exists in the form of varnish. Since the low pH (pH=1.2) of TiF₄ might cause damage to the oral soft tissues, it seems that the gel form is preferred to the solution because it is better controlled in clinical application.

Fekrazad et al reported that enamel remineralization potential could increase by treatment with TiF₄ applied before CO₂ laser treatment. However, CO₂ laser treatment

Table 1. The Amount of Ca Ion Release in Acidic Solution (ppm)

Group	Average Ca Release	Standard Deviation	Number
Control	197.1615	29.06999	13
APF	153.3077	10.83629	13
TiF ₄	99.2308	11.36520	13
TiF ₄ -Laser	61.2308	6.72252	13
Laser-TiF ₄	55.1615	2.96129	13

Table 2. Pairwise Comparison of the Groups by the Bonferroni Test

Group	Group	P Value
Control	APF	0.002
	TiF ₄	0.000
	TiF ₄ -Laser	0.000
	Laser-TiF ₄	0.000
APF	TiF ₄	0.001
	TiF ₄ -Laser	0.000
	Laser-TiF ₄	0.000
TiF ₄	TiF ₄ -Laser	0.000
	Laser-TiF ₄	0.000
TiF ₄ -Laser	Laser-TiF ₄	0.234

of enamel before TiF₄ application could not remineralize white spot lesions.¹¹ The acid resistance of enamel was not previously evaluated by the combination of the CO₂ laser with TiF₄. This study evaluated the combination therapy in two ways. Laser irradiation was performed both before and after the tooth treatment with TiF₄ in order to compare the probable differences in the effect of the CO₂ laser on the enamel structure.

The results of the present study indicated about 70% increase in the acid resistance of the samples which were treated by the combination of the CO₂ laser and TiF₄. TiF₄ was more effective than APF in this study. This is in accordance with the results of the previous studies that have reported better effectiveness of TiF₄ in caries prevention compared to other fluoride compounds.^{5,12,13} Exterkate et al reported a 80% reduction in demineralization after the application of TiF₄.⁵ Buyukyilmaz et al observed a 15% reduction in the formation of white spot lesions after the application of TiF₄ once.¹³ Magalhaes et al also reported the effect of TiF₄ on reduced demineralization and an increase in remineralization of carious teeth.¹² There are different theories for the protective mechanism of TiF₄. Some of the protective effects are related to the fluoride ion which acts the same way as the other fluoride compounds. The fluoride ion attaches to the calcium ion on the tooth surface and creates CaF₂ globules. When the hydroxyl ion releases from the enamel structure as the result of the acidic attack, fluoride replaces the hydroxyl ion and forms fluorapatite crystals.^{14,15} The higher effectiveness of TiF₄ can be related to the titanium ion and its great affinity to oxidation. In the aqueous environment of the oral cavity, TiF₄ oxidizes and decomposes into TiO₂ and HF. The acidic pH of HF helps demineralization of the tooth surface, and hence deeper penetration of fluoride. TiO₂ forms an adherent glaze-like layer on the tooth surface, which acts as a barrier to the effect of acids and bacterial toxins.^{3,12}

In the present study, the CO₂ laser in combination with TiF₄ resulted in higher acid resistance compared to TiF₄ alone. The effect of the CO₂ laser on caries resistance of enamel is related to the fusion of the surface crystals,

the formation of a physical seal, and some melting of the surface crystals and recrystallization. There are also some important chemical changes such as the elimination of water and organic material from the enamel structure, and the removal of the carbonate ion from the hydroxyapatite crystals. Another important theory, especially in cases which receive CO₂ laser irradiation prior to fluoride therapy, is the formation of some micro-spaces within the enamel surface that acts as reservoirs for the released ions during demineralization. These ions stay available for the future remineralization process.¹⁶⁻²¹

The increase in temperature during laser irradiation helps the removal of the organic material from the tooth structure and an increase in the mineral content of enamel.^{19,20} The changes in enamel should be limited to the surface crystals. The temperature increase due to laser irradiation causes some morphologic changes in enamel, like melting, and some cracks and surface desiccation. If the laser energy increases more than the protective parameters, it can cause some carbonization and cracks which jeopardize the benefits of the laser on caries prevention.²⁰ The CO₂ laser wavelength has high absorption in enamel and can melt the enamel surface even in low energy levels; therefore, this laser has the potential to damage the tooth surface. The CO₂ laser parameters are very important regarding its effects on tooth structure.²²

The synergic effect of the laser and fluoride in caries prevention is reported in the literature. In the present study, the sequence of the treatments in the combination groups did not make any difference in the results. Moslemi et al reported the same results.²³ One theory for the better effectiveness of combination therapy is the accumulation of CaF₂ globules in the micro-spaces that were created on enamel surface after laser irradiation as well as the firm attachment of these globules to a tooth by the temperature created by laser irradiation. The other theory for fluoride therapy before laser irradiation is the incorporation of the fluoride ion into the hydroxyapatite structure due to the increase in temperature and partial melting of the hydroxyapatite crystals during laser irradiation and the formation of the fluorohydroxyapatite crystals during recrystallization.^{4,20,21} Studies that have reported the effectiveness of the CO₂ laser on acid resistance before fluoride application assign this effect to the removal of the carbonate ion from the hydroxyapatite molecules and an increase in the mineral percentage of enamel.²¹ A laboratory study reported a significant decrease in the critical pH of enamel from 5.5 to 4.8, which increased the acid resistance of enamel even in the presence of a little amount of fluoride.²⁴

For future studies, the authors suggest the evaluation of the long-term effect of the laser-fluoride combination therapy on caries resistance of enamel. Studies on the microstructure of enamel after laser irradiation, especially in accordance with adhesion properties of enamel and

surface irregularities which would increase plaque accumulation and discoloration of the teeth, would be helpful in reaching a comprehensive approach to suggest more effective methods of caries prevention.

Within the limitations of the present study, it was concluded that APF, TiF_4 and combination treatments increased the acid resistance of enamel. TiF_4 was more effective than APF. The best results were observed in the combination therapy groups, without a significant difference between the TiF_4 - CO_2 laser and CO_2 laser- TiF_4 groups.

Ethical Considerations

Considering the in-vitro situation of the study, there were not any ethical concerns in this research

Conflict of Interests

The authors declare no conflict of interest.

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