1. Introduction

The implant and crowns are luted together to ensure a good retention between the abutment and crown and also in order to seal the margin from infiltration of saliva and intraoral fluids. Many different luting materials are used by the date with different properties: zinc phosphate, polycarboxylate, glass ionomer, resin ionomer, composites and adhesive resin. The new materials have usually better adhesion to natural bone than phosphate cements and have less solubility into surroundings as well are faster to harden decreasing the patient time in the chair and but they are also more expensive than the traditional phosphate cements and the excess cement is more difficult to remove and they have also shown pulp irritation.

Even though the adhesion with calcium and zinc phosphate cements are lower than newer luting agents they are still widely used. Zinc phosphate cement anchors the prosthesis purely mechanically and has a god compressive strength but low tensile strength and shows dissolution/chemical changes in the cement in oral environment but despite or thanks to these problems it has shown to be reliable cement with success rate of incredible 74% after 15 years with conventional fixed partial dentures and there are restorations with over 20 and even up to 45 years working time.

Despite the used cement the cementation gap is always present when restoration/luting is done and its width is determined by the cement, the design of the abutment and crown as well the preparation method and the skills of the dentist. The marginal gap effects the bonding strength, the dissolution of the cement and marginal leakage. Different luting agents affects the sealing ability and the possible obstructions of molecule and dental fluid penetration into the marginal leakage as well the resistance to varying stresses.

McLean and von Fraunhofer, suggested that the maximum tolerable cementation gap should be 120 μm but this figure was questioned by Kydd et al. who showed that even the marginal gaps in gold crown/zinc phosphate up to width of 244 μm lasted longer than 20 years. The width of the cementation gap will affect the microleakage that is depending on the cement layer thickness. When the thickness of the layer was 25-75 μm there was not seen any changes in the microlakage and when the thickness is greater than 150 μm the dissolution becomes significantly higher.

Even though the zinc phosphate cemented restorations have shown to last long time, the marginal leakage in restorations is associated to different failures of restorations caused by the deposit of bacterial colonies that in minor case can result in marginal discoloration and in severe cases lead to pulpal pathosis, periodontal disease and microbiological ingress and secondary caries. Not only has the marginal gap caused problem to the restoration but also the bacterial adhesion on the excess cement. The excess cement gives a rough surface in the gingiva that is perfect for the bacterial adhesion and can work as the origin to peri-implant mucosities and peri-implantitis.
been shown that surface finish and proper removal of the excess cement will affect the bacterial adhesion positively.

A close inspection of the in vivo aged samples provides insights to the margins and to the microleakage and would sharpen the understanding and inspire the future development of the cements and interfaces between the crown and abutment. This study concentrates on the phosphate cements with some discussion of the resin cement as well.

2. Materials and Methods

2.1 Collection of the samples

Prosthesis after a varying time of use were removed from the patients during a five months period by the dentist. The detailed list of the collected in vivo aged prosthesis is presented in the Table 1. It is noted that the prosthesis b and f were fractured during removal and e was removed due to the infections. The prosthesis a, c, and d were in good conditions but there are no information available of the patient’s condition, sex or age, however it is noted that the loss of bonding between the crown and abutment was not the reason.

The collected prosthesis had different in vivo times varying from 6 to 25 years. The materials used for crown and abutment changed between the samples and also the type of phosphate cement and the use of the phosphate cement. Both calcium and zinc phosphates are present in the samples. The phosphate cements were used both in luting and cavity lining.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crown</th>
<th>Cement Abutment</th>
<th>Age Luting/lining</th>
<th>Abutment</th>
<th>Age (years)</th>
<th>Luting/lining</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Cobalt (Co), Chromium (Cr)</td>
<td>Zinc phosphate</td>
<td>Titanium (Ti)</td>
<td>6</td>
<td>Luting</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>Alumina (Al2O3), Silica (SiO2)</td>
<td>Calcium phosphate</td>
<td>Tooth</td>
<td>25</td>
<td>Luting</td>
<td></td>
<td>Fractured</td>
</tr>
<tr>
<td>c</td>
<td>Gold (Au), Palladium (Pd)</td>
<td>Zinc phosphate</td>
<td>Tooth</td>
<td>9</td>
<td>Luting</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>Gold (Au), Palladium (Pd)</td>
<td>Calcium phosphate</td>
<td>Tooth</td>
<td>21</td>
<td>Luting, cavity lining</td>
<td></td>
<td>Fractured</td>
</tr>
<tr>
<td>e</td>
<td>Nickel (Ni), Chromium (Cr), Molybdenum (Mo)</td>
<td>Zinc phosphate</td>
<td>Tooth</td>
<td>6</td>
<td>Cavity lining</td>
<td></td>
<td>Resin based cement for luting</td>
</tr>
<tr>
<td>f</td>
<td>Cobalt (Co), Chromium (Cr)</td>
<td>Calcium phosphate</td>
<td>Gold (Au), Palladium (Pd)</td>
<td>20</td>
<td>Cavity lining</td>
<td></td>
<td>Resin based cement for luting</td>
</tr>
</tbody>
</table>

The prosthesis were illustrated with a light microscope (S8APO, Leica Microsystems, Germany) followed the characterization in scanning electron microscopes (SEM). The as received prosthesis were washed with ethanol in ultra-sonic bath prior SEM where the outside surface and interfaces between the crown/cement/abutment were investigated. After the outside surface characterization the prosthesis were cut horizontally or/and vertically with low speed saw and investigated with SEM.

More detailed investigation of the interfaces was conducted on the cross section polished surfaces (CP-09010, JEOL, Japan with argon beam and the acceleration voltage of 5 kV for 15 hours). A field emission scanning electron microscope (SEM) (JSM-7000F, Jeol, Japan) equipped with an energy dispersive spectroscopy (EDS) detector (INCAx-sight, Oxford Instruments, United Kingdom) and a tabletop scanning electron microscope (TM3000, JEOL) were used for SEM investigations.

After the microstructure characterization the polished surface was investigated with XRD and the cement was carefully removed from the polished surfaces and analyzed using XRD with Cuα1 radiation (X’Pert Pro, PANalytical, Netherlands) and Raman spectras were normalized to the top at
110 cm\(^{-1}\) (785 nm red laser, LabRAM HR, HORIBA, United States of America). XRD and raman was used for analyzing the phase assembly in \textit{in vivo} aged cements and zinc phosphate cement was compared to freshly made cement prepared according the instruction from the producer (Harward cement, Hoppegarten, Germany).

3. Results

3.1 Pores and porosity,

Both freshly made and aged cement shows holes and pores created during the mixing and setting of the cement as seen in the figure 1. There are two types of porosity where most of them have spherical shapes and show the formation of the crystals and the others with irregular shapes having smooth surfaces without crystals. The origin of the pores can be connected to the inclusion of the air bubbles during the mixing or evaporation of the water during the setting. Latter most likely leads to micropores up to 10 µm diameter size while the former produces pores up to 172 µm. The spherical pores shows crystal formation independently the size. It is noted that the pores and holes on the surface of the phosphate cemented samples are covered with body tissue in the areas where the cement has been in contact with gingiva or oral liquids, indicating a good biocompatibility of the cement.

3.1 Crystallization and growth of hopeite

The uneven reaction during setting gives possibility for crystal growth in the pores and is seen in figure 1 for freshly made zinc phosphate cement. Similar crystals are seen in the \textit{in vivo} aged zinc phosphate samples as seen in Figure 2c and it is obvious that the crystals have grown in size during the aging. The crystal can be attributed to the hopeite formation inside the cement and has been reported also by Jakeman et al. and Crisp et al. This is shown for the aged samples with zinc phosphate where the XRD confirms that the crystals can be attributed to the crystalline form of zinc phosphate Zn\(_3\)(PO\(_4\))\(_2\), 4H\(_2\)O (“hopeite”), Fig 3a. The XRD on the freshly made zinc phosphate cement did no show peaks for hopeite even though the visual investigation reveals the crystals indicating a larger formation and growth of the hopeite during the aging. The XRD shows the typical peaks for unreacted ZnO and MgO in an amorphous matrix as expected, these peaks are present in the \textit{in vivo} aged samples as well.

The crystals are also formed on the calcium phosphate cement in contact with gingiva as shown in the figure 2d, the composition of these crystals could not be confirmed due the difficulties to take the XRD but are presumably hydroxyapatite. However similar cement in the oral environment did not show such crystals in SEM but the XRDP in Figure 3b shows increased intensity of the peaks for hydroxyapatite (~ 26° and 32°) and α-tricalcium phosphate (~ 47°) in otherwise amorphous cement confirming the good biocompatibility as already seen in the SEM (fig 1a). It is also noted that no significant crystalline peaks attributed to solid filler particles (alumina, silica, fluorine) were detected after \textit{in vivo} aging indicating the retention of the calcium phosphate cement in the oral environment.
Fig 1: The holes and pores on the surface of the cement after 25 years (sample b) when exposed to oral environment they are covered with body tissues as seen as the dark color in BS mode (a). Crystal growth in the pore of freshly made zinc phosphate cement (b). Crystal growth in the zinc phosphate cement after 6 years in vivo, sample a (c). Crystal growth on the calcium phosphate cement in contact with gingiva for 25 years, sample b (d).
Fig 3. XRDP for zinc phosphate cement in vivo 6(sample a) years from the horizontally cut surface (a). XRDP for calcium phosphate after 25(sample b) and 21(sample d) years in oral environment (b).

3.2 Cracks

All in vivo aged phosphate cements had cracks in the matrix and also on the interfaces between the crown and/or abutment. The location of the detached interface (gap) depended on the materials used. This will be described in more details below. The most severe cracking in the cement is located in the margin end of the prosthesis between crown and abutment as demonstrated in the Figure 4 where a vertically cross sectioned sample a is presented. Close to the margin end the cement is severely cracked and shows no typical structure of the zinc phosphate cement. The cracks in the cement expose the cement to the oral environment and thus affects the chemical composition of the cement. Zinc oxide particles in the zinc phosphate cement are known to decompose/dissolve [ref] in oral environment and this is also the case here. The EDS confirms the chemical changes of the cement. The decrease of zinc closer to the margin end of the prosthesis is shown in figure 5 and the typical microstructure of zinc phosphate remains deeper in the margin as see in the inset in Figure 4.

The dissolution process is time depended; the longer time the prosthesis is in use the larger dissolution of zinc oxide and deterioration of the mechanical properties of the cement. It is also noted that the chemical composition of the phosphate cement remains intact and only ZnO particles are removed. The calcium phosphate cement shows similar retention behavior close to the margin end of the prosthesis showing cracked cement and EDS revealed also a chemical change where the filler materials based on aluminum, fluoride and silicon are not detected close to the margin end. They can be detected again at similar distances from the margin end as Zn for zinc phosphate cement shown in Figure 5.

Figure 4: The cracking of the cement at the margin end of the in vivo aged (6 years) zinc phosphate cement.
Figure 5: EDS results of the zinc phosphate cement at the margin end for 9 years in vivo aged prosthesis (sample c) showing dissolution of ZnO and the carbon content in the cement.

3.3 Interfacial debonding and marginal gaps

As mentioned above the interfaces are accompanied with gaps between cement and crown/abutment and the gaps are found in all investigated prosthesis. The placement of the gap varies depending on the cement. The zinc phosphate cement is detached from the cement/tooth interface (Figure 6a) while the interface between the crown and cement was good. It must be noted that the interfaces between metal and zinc phosphate are generally good and the cracking of the cement occurs mainly inside the cement matrix, not on the interfaces. The interface debonding occurs when tooth is used as abutment and the interface is good when metals are used as shown in the Figure 2b where the Titanium was used as abutment and CoCr as crown. Calcium phosphate cement detached from cement/tooth interface and also in some cases at the cement/crown interface. Prosthesis e had aluminum and silicon based resin for luting and zinc phosphate was only used at the top of the prosthesis for lining. The resin detached on the cement/crown interface but when the gap got closer to zinc phosphate lining the interfacial debonding moved to the cement/tooth interface as seen in Figure 6b. It is also noted that there was always found an interface debonding between the different types of cements.

Figure 6: The interfacial debonding of the cements. Zinc phosphate detached on the cement/tooth interface, sample c (a), Resin detached on the cement/crown interface and the
crack is moved to cement/tooth interface when Zinc phosphate cement is used for lining (upper right corner), sample e (b)

3.4 Carbon contamination

The outer surface of the prosthesis showed a gap between the abutment and crown and a closer look in the SEM revealed that the gap is filled with biological growth, see Figure 7. At the cementation gap the prosthesis can be exposed to oral environment that will give an effect not only on the chemical composition and mechanical properties of the cements but also it will give access to biological growth on the prosthesis. This is seen in all the samples as demonstrated in the Figures 1 and 5, where backscatter pictures reveals carbon contamination in the pores of the cement and also carbon infiltration in the gap at the margin end of the prosthesis. The carbon contamination does not stay only in the marginal end of the prosthesis but can even reach the top of the prosthesis as is seen in Figure 8 where the zinc phosphate lining at the very top of the prosthesis is contaminated with carbon. The carbon infiltrates to the top through the gaps in the resin/crown interfaces. Furthermore it must be mentioned that the zinc phosphate lining shows very poor mechanical properties with severe cracks in the lining.

Figure 7+ The biological growth in the gap on the outer surface of the 6 years in vivo aged prosthesis
3.5 Dissolution of zinc oxide

As known the zinc phosphate cement dissolves in the marginal end and change the composition of the cement. The same phenomena is seen in this study. The dissolution inside the prosthesis starts where there is an access to the oral environment. So the ZnO starts to dissolve in the interfacial gaps between the cement crown/abutment, starting from the gap side as seen in the Figure 9 where the mapping of Zn shows only very little traces of Zn very close to the interfacial gap. The chemical change is also seen in raman investigation. The raman shift for the 25 years in vivo aged sample are shown in Figure 10. The raman shift connected to ZnO (101, 388 and 437 cm⁻¹) are decreased during aging when compared to a freshly made cement confirming the EDS results.
Figure 10: Normalized raman shifts for fresh zinc phosphate cement and 25 years in vivo aged sample (b)

3.6 Excess cements

The margin end of the prosthesis with phosphate cement had cracks, but none of the investigated samples showed any excess of the cement outside the margin end. This was not the case for the resin luted samples. Even though the aluminum, silicon based resin did not show any chemical change during in vivo it showed an excess of resin outside the marginal gap, as seen in the Figure 11. It is clear that this excess in contact with gingiva will give rise to a bacterial growth near the margin and may cause severe problems to patient in the form of infections and indeed this was the case with the samples e which was removed from the patient due the infections.

4. Discussions

4.1 Cracking, interfacial debonding and retention

From the results it is clear that the phosphate cements are sensitive to cracking in the matrix unlike resin cement that did not show major cracking at the marginal ends. The problems at the marginal end depends on the cementation material used and mechanical stresses affecting the prosthesis. Oilo et al. showed that the chewing causes tensile hoop stresses on the tip of the crowns that will
effects the cracking and the debonding of the cement. All three cements showed debonding from the crown and/or abutment as is known from the literature. According to the literature the zinc phosphate debonds on the cement/tooth interface that is in the line with this study: the zinc phosphate preferred the metallic bonding beyond the bonding to the natural tooth. The different metals used for abutments and crowns made it difficult to draw final conclusions on the calcium phosphate and resin cements. There is a small uncertainty in the investigation concerning the interface debonding caused by the drying of the natural bone during the preparation work. The drying might increase the stresses in the interface and increase the cracking/debonding behavior. But the infiltration of the carbon to the top of the restoration shows that the cracking and the debonding phenomena is an existing problem in the prosthesis. The cracking and debonding create problems in causing the microleakage of intraoral fluids into to the margin and possible contamination of biological and or bacterial growth on the surface, marginal ends and even inside the prosthesis.

Zinc phosphate samples were not removed due the infections which indicates that the microleakage is not a problem for phosphate cements as is also stated in several earlier studies. But if the cracks/microleakage are large enough (>50 µm) they might make possible a bacterial ingress and secondary caries not only close to gingiva but even inside the prosthesis. The major cracking for phosphate occurs at the margin end where most the cement is exposed to oral fluids as well where micro movements during the biting occurs increasing the stresses. Both phenomena will increase the cracking/dissolution of the cement and in that way increase the microleakage. The microleakage is also depended on the thickness of the cement layer. According to the literature the layer thickness above 150 µm will increase the dissolution speed of the zinc oxide and thus microleakage. The measured layer thicknesses in the study showed larger layer thicknesses than 150 µm but here the sample preparation and bone drying will certainly effect the results. The samples were not fixed with the resin prior the cutting and polishing that will most probably increase the apparent layer thickness. The measured layer thickness of the cement varied from 150-340 µm. Even though the measured layer thicknesses exceeds the limit of 150 µm the secondary caries was not the reason for the removal of the prostheses with zinc phosphate cement.

The microleakage changes the chemical composition of the zinc phosphate cement by dissolving the zinc oxide from zinc phosphate as is widely reported for this cement. The dissolution might be one of the reason why the zinc phosphate luted restorations can be used over 20 years without any bacterial issues and increased inflammatory failures compared to resin luted restorations. Another issue is the removal of the alumina and silica particles at the margin end in the calcium phosphate cement. It is hardly possible for oral environment to dissolve alumina and silica particles so it is most likely to be connected to the poorer mechanical properties of the calcium phosphate cement and the chemical retention of the phosphate cement during the aging and the physical movement of the cement during biting causing pullout of the particles during the movement.

The success of the zinc phosphate cement might also be connected to the easier removal of the excess cement. The cleaner surface towards gingiva gives a smoother surface and less possibilities to bacterial adhesion at the marginal end opposite to the resin luted restorations. The removal of the excess resin cement is difficult and also it is more difficult to detect with radiographic method. In this study both resin luted samples showed excess cement facing gingiva or close to gingiva. The excess cement outside the marginal end will give an excellent growing platform for bacterial adhesion and origin for the secondary caries as well increase the risk for infections as already seen in this study: one of the resin luted samples was removed because of inflammation. The excess cement is also connected to the peri-implant disease. Linkevicius et al. showed that 85% of 72 implants developed peri-implant disease when there was found excess cement and that all the patients with excess cement and with earlier problems with periodontitis developed peri-implantitis.

In order to decrease the problems caused by excess cement, marginal leakage and debonding on the margins a better marginal fit should be achieved together with the better mixing and working habits.
with the cements. With proper cement preparation the content of pores with hopeite caused by air or water evaporation during the mixing will decrease and thus the mechanical strength of the cement will increase. This will decrease the cracking of the cement. Another fact when working with the resin is to reduce the excess cement at the margin end that is one of the highest risk factors to develop peri-implant disease as discussed in review of Valente et al.

5. Conclusions

(1) Crack formation in the matrix is a common feature in all phosphate cements, but not in resin composite cements;
(2) Air bubbles or pores were observed in all samples, with apparently higher concentration in zinc phosphate cement;
(3) The formation of platelet tertiary zinc phosphate ("hopeite") crystals was found confined inside the pores, in which the growth of these crystals continued during aging.
(4) Interfacial debonding was observed at one of the two interfaces between crown and cement respectively between cement and tooth/abutment, i.e. at the cement-tooth interface when zinc phosphate cement was used, and at both the cement-crown and cement abutment interface when calcium phosphate and resin composite cements were used.
(5) Severe cracking and loss of cement was observed at the marginal end of the cementation gap of all the samples, which may indicate the risk of marginal leakage after long-term aging.
(6) The unreacted zinc oxide particles initially imbedded in the zinc phosphate cements matrix dissolved on the surface of the interfacial debonding gaps close to the margin side.
(7) The detected carbon infiltrated along the interfacial debonding gaps and cracks from the marginal surface up to the restorations top may indicate the penetration of protein-containing saliva or possibly even bacteria.
(8) The excess calcium phosphate cement piece stuck on the outside of porcelain surface of the crown sample b was stable and showed significant retention after a 25 years period in the oral cavity.
(9) When resin composite cements was used, excess cement piece was observed in gingiva gap outside the marginal end of the cementation gap, which rationalized the difficulty commonly faced in daily practice in cleaning up the cement leaked into the gingiva gap.

Acknowledgements

References