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RESEARCH AND EDUCATION

Bond strength and interactions of machined titanium-based alloy with dental cements

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ABSTRACT

Statement of problem. The most appropriate luting agent for restoring cement-retained implant restorations has yet to be determined. Leachable chemicals from some types of cement designed for teeth may affect metal surfaces.

Purpose. The purpose of this in vitro study was to evaluate the shear bond strength and interactions of machined titanium-based alloy with dental luting agents.

Material and methods. Eight dental luting agents representative of 4 different compositional classes (resin, polycarboxylate, glass ionomer, and zinc oxide-based cements) were used to evaluate their effect on machined titanium-6 aluminum-4 vanadium (Ti-6Al-4V) alloy surfaces. Ninety-six paired disks were cemented together (n=12). After incubation in a 37°C water bath for 7 days, the shear bond strength was measured with a universal testing machine (Instron) and a custom fixture with a crosshead speed of 5 mm/min. Differences were analyzed statistically with 1-way ANOVA and Tukey HSD tests (α=.05). The debonded surfaces of the Ti alloy disks were examined under a light microscope at ×10 magnification to record the failure pattern, and the representative specimens were observed under a scanning electron microscope.

Results. The mean ±SD of shear failure loads ranged from 3.4 ±0.5 to 15.2 ±2.6 MPa. The retention provided by both polycarboxylate cements was significantly greater than that of all other groups ($P<.05$). The scanning electron microscope examination revealed surface pits only on the bonded surface cemented with the polycarboxylate cements.

Conclusions. Cementation with polycarboxylate cement obtained higher shear bond strength. Some chemical interactions occurred between the machined Ti-6Al-4V alloy surface and polycarboxylate cements during cementation. (J Prosthet Dent 2015;114:660-665)

Titanium-6 aluminum-4 vanadium (Ti-6Al-4V) alloy is considered a useful dental restorative material because of its biocompatibility, high mechanical strength, and good corrosion resistance, as well as its lower cost compared with the noble metal alloys. The spontaneous formation of a protective oxide film when titanium and its alloys are exposed to oxygen provides the corrosion resistance that has made this one of the materials of choice for implant components.[1,2] Abutments intended to support implant restorations are commonly fabricated by machining Ti-6Al-4V rods with a lathe. Metal frameworks intended for porcelain application are milled from disks of this alloy with computer-aided design/computer-aided manufacturing (CAD/CAM).[3] These restorations are cemented with a variety of traditional dental luting agents.[4-6] The clinical performances of both CAD/CAM titanium-ceramic crowns and fixed dental prostheses appear to be acceptable at 3 years with no apparent biologic complications and a high cumulative survival rate.[7,8] However, no guidelines exist as to the most appropriate luting agent to use. Several studies have also reported unexpectedly high bonding values of polycarboxylate cements with titanium structures, leading the authors to speculate that a bonding mechanism to titanium exists.[9-12] Several reports indicate that some dental cements alter the protective titanium oxide layer, resulting in color changes to the titanium surface.[12,13] The instructions for use with one polycarboxylate cement (Durelon; 3M ESPE) state that "a discoloration effect may result when used with titanium." Color change has been associated with corrosion of the titanium alloy,[14] which may account for the higher than expected bond strength values. Although this may be of benefit mechanically,[15] the corrosion effects have

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Clinical Implications

Polycarboxylate cement should be carefully considered when used with titanium alloy abutments or restorative frameworks because of the pit-corrosion reaction.

been linked to implant failure[16] and an increase in pathogenic microbial adherence to the alloy.[17] Also, fluorinated acidic dental cements increase titanium corrosion susceptibility.[18,19]

These interactions require investigation not only for the physical and chemical interactions with cements but also to determine whether alloy preparation (turned or milled) may be a factor.

The purpose of this study was to determine the shear bond strength of CAD/CAM turned and milled Ti-6Al-4V with different cements and to examine with scanning electron microscopic (SEM) images any surface physical changes that may occur on the differently prepared surfaces. The null hypotheses tested were that the types of cement do not affect shear bond strength and do not react with titanium alloy surfaces.

MATERIAL AND METHODS

Eight commercially available cements were used in this study (Table 1). They were representative of 4 different compositional chemistry classes: resin, ML (Multilink Implant; Ivoclar Vivadent) and PI (Premier Implant Cement; Premier Dental); polycarboxylate, D (Durelon; 3M ESPE) and PF (Poly-F Plus; Dentsply DeTrey); glass ionomer, K (Ketac Cem; 3M ESPE) and R (RelyX Luting Plus; 3M ESPE); and zinc oxide-based cements, T (TempoCem; DME America) and FL (Fleck's Zinc Phosphate cement; Keystone Industries). One hundred ninety-two cylindrical disks (4 mm width × 6.6 mm diameter) were cut from stock Ti-6Al-4V alloy rods, also referred to as ASTM F136 ELI (extra low interstitial). Half the disks were chosen to have 1 surface machined producing a turned surface and representing the manufactured surface used for implant abutment components (Nobel Biocare USA). The remaining disks had 1 surface machined by milling and represented the process used to fabricate titanium alloy copings (Procera abutment; Nobel Biocare USA). One turned surface was assembled with 1 milled surface. Twelve cylinder pairs were selected and assigned to each of the 8 test cement groups. Representative photographic and SEM images were made of both types of titanium disk surfaces (Fig. 1).

The cements were mixed according to the manufacturer's instructions, and a thin layer was applied to the turned cylinder surface with a microbrush (Benda Micro applicators; Centrix Inc). The milled cylinder surface was adhered to this cement-loaded surface, the excess was removed, and the 2 joined cylinders axially loaded with a 49-N force for 10 minutes at room temperature. Once set, the cylinder pairs were incubated in a water bath at 37°C for 7 days. The cemented cylinders for each test cement (n=12) were subjected to a shear bond test, with the testing setup reported in a previous study,[16] and the peak shear force was recorded. The debonded surfaces of the Ti alloy disks were examined under a light microscope (BX51 TRF; Olympus Corp) at ×10 magnification to record and compare the mode of failure. Representative specimens were selected and observed after sputtering with a carbon conductive layer of approximately 30 nm with a scanning electron microscope (JSM 7000F; JEOL Ltd). Differences among groups were identified with 1-way ANOVA (α=.05) and a post hoc Tukey HSD test.

Table 1. Cements, manufacturers and batch numbers used

Code	Material	Manufacturer	Lot No.
T	TempoCem, Automix	DMG America	686255
R	RelyX Luting Plus	3M ESPE Dental Products	N353126
D	Durelon	3M ESPE Dental Products	499443
PF	Poly-F Plus	Dentsply, DeTrey GmbH	1204000271
FL	Fleck's Zinc Phosphate	Mizzy, Keystone Industries	L79
K	Ketac Cem	3M ESPE Dental Products	496388
ML	Multilink Implant	Ivoclar Vivadent	R56681
PI	Premier Implant Cement	Premier Dental	4186CI

RESULTS

The mean ±standard deviation shear bond strength values ranged from 15.2 ±2.7 MPa for D to 3.4 ±0.6 MPa for T (Fig. 2). Statistical analysis with ANOVA (df=95, F=59.4, P<.001) followed by a Tukey HSD test indicated significant differences among the groups (P<.05).

A general trend could be seen with each cement having a similar shear bond strength to its paired cement composition (resins, glass ionomers, and polycarboxylates) variant and not having significant differences (P>.05) from each other. The zinc oxide-based cement (T) had the lowest cement bond strength, significantly less than all other test groups (P<.05). The shear strength values of the polycarboxylate cements were significantly higher than all the other tested cements (P<.05), but no difference was detected between the 2 brands within the group. All fracture surfaces showed combined adhesive and cohesive failure patterns, with cement attached to both milled and turned surfaces, suggesting no major differences between the methods of alloy fabrication.

Representative fracture surfaces were observed and photographed, then additionally examined with SEM. Discoloration or blackening of the titanium alloy on both the turned and milled specimens for D and PF was observed. No other test cements produced discoloration. SEM examination revealed no surface detail change for

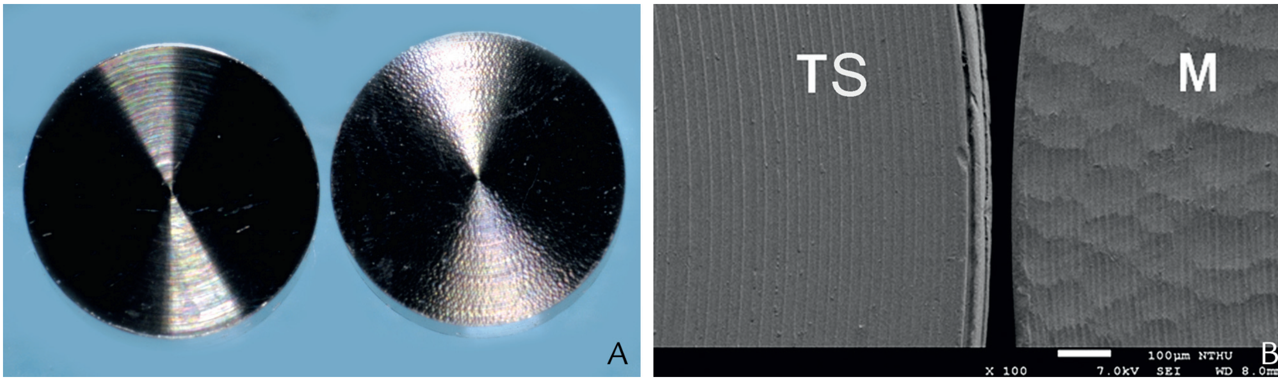

Figure 1. A, Ti-6Al-4V pair disk specimen, 1 turned surface (left) and 1 milled surface (right), before cementation. B, Surface preparations (original magnification ×100). TS, turned; M, milled.

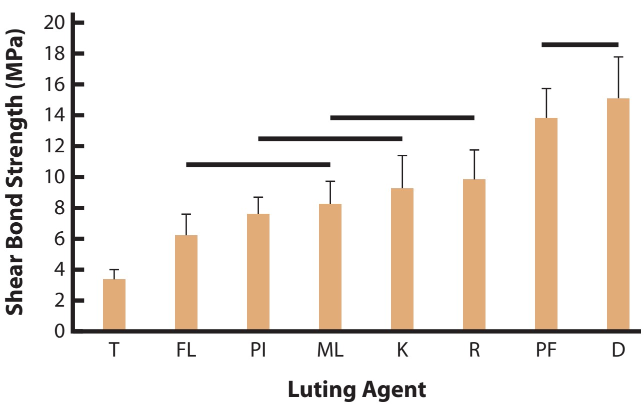

Figure 2. Ordered results of shear bond test and statistical analyses (n=12). Dental cements: T, TempoCem; FL, Fleck's Zinc Phosphate; PI, Premier Implant Cement; ML, Multilink Implant; K, Ketac Cem; R, RelyX Luting Plus; PF, Poly-F Plus; D, Durelon. No statistically significant differences between groups are linked by horizontal lines (*P*>.05).

the T, R, FL, K, ML, and PI groups (Figs. 3-5). In contrast, the D and PF specimens showed some surface alterations after debonding with microscopic amorphous structure changes and multiple micropits on both machined titanium alloy surfaces (Fig. 6).

DISCUSSION

The results support the rejection of both null hypotheses, as significant differences in shear bond strength were found within the test cement groups and surface reactions were noted on the specimen surfaces of the polycarboxylate cement group.

The shear bond strength test results indicated the retentive capabilities of both PF and D polycarboxylate cements, giving significantly higher values than other test cements in this study. Visual examination revealed discoloration with both the PF and D specimens, though this was difficult to determine quantitatively and qualitatively. However, no other tested cements appeared to be affected. SEM images of D and PF specimens revealed the titanium alloy surface was physically altered by the cements, causing pitting corrosion on both the turned and milled surfaces (Fig. 6). The chemical reaction could be due to the addition of stannous fluoride to both of these products; this must be further evaluated. Fluoride is a corrosive agent known to affect titanium and its alloys, with hydrofluoride etchant commonly used to clean and etch titanium.[17] Both of these polycarboxylate cements have been reported to increase restoration retention when used with titanium abutments,[9-12] caused perhaps by a chemical interaction.[10,11] However, aside from speculation, this has not been investigated. The instructions for the use of Durelon cement (3M ESPE) state, "Durelon is not suitable for cementation from/to titanium-based restorations, since cement discoloration can occur on the points which come into contact with titanium." A 2010 survey of US dental schools reported the use of various types of cements for the definitive cementation of implant-supported restorations. Cement selection was thought to be somewhat arbitrary and often based on the materials used for tooth-supported restorations. The study indicated that 17% of the schools used a polycarboxylate cement, though the specific brand was not identified.[6] If Durelon cement was the polycarboxylate used, it suggests the instructions for use are not being followed. Similarly, the studies involving Durelon with titanium as a cementing medium should state that the procedure is for off-label use and clarify exactly why the material is being investigated. The instructions for use for all other cements chosen for this study, including the other polycarboxylate cement (PF), make no mention of any effect on titanium surfaces. Some other brands of polycarboxylate cement do not have any fluoride additive and should be tested to confirm the suspicion that the stannous fluoride is of concern.

The glass ionomer-based groups (K, R) tested also contain the fluoride ion but not in the form of stannous fluoride, and no reaction with the titanium alloy surfaces was observed. However, this is contrary to other studies that have also evaluated glass ionomers with respect to titanium corrosion.[13,18,19] One of these studies[13]

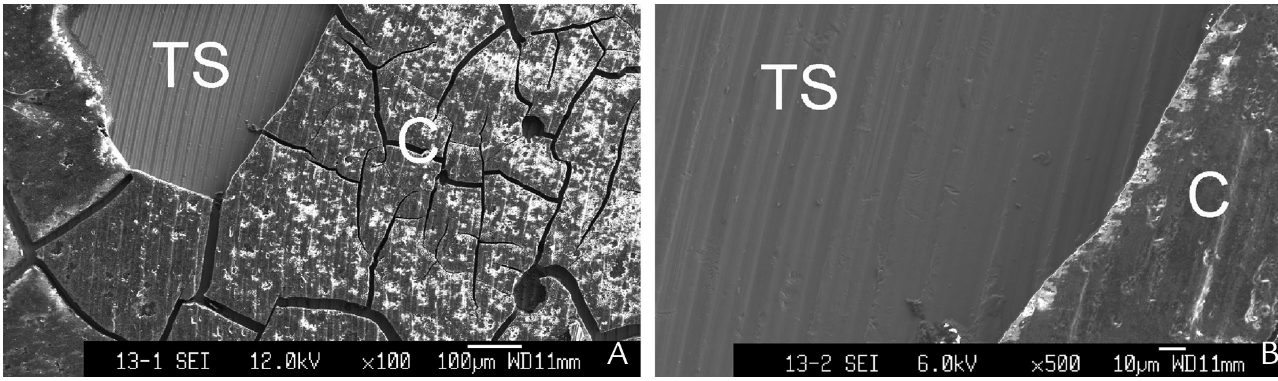

Figure 3. Representative of zinc oxide cements: TempoCem cement fracture surface. SEM of fracture patterns. Turned surface (TS) of titanium alloy is visible, as is imprint of milled surface on cement (C). A, Original magnification ×100; B, original magnification ×500.

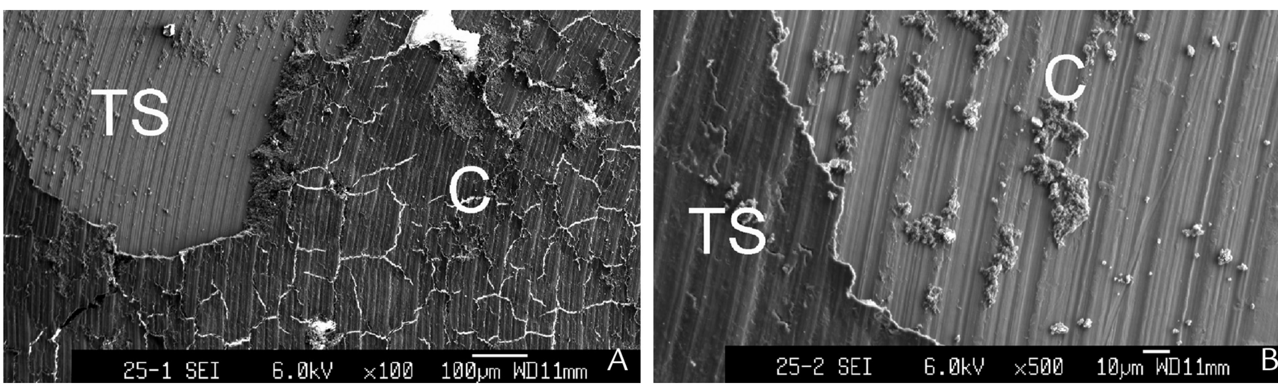

Figure 4. Representative of glass ionomer cements: RelyX Luting Plus cement fracture surfaces. SEM of fracture patterns. Turned surface (TS) of titanium alloy visible, as is imprint of milled surface on cement (C). A, Original magnification ×100; B, original magnification ×500.

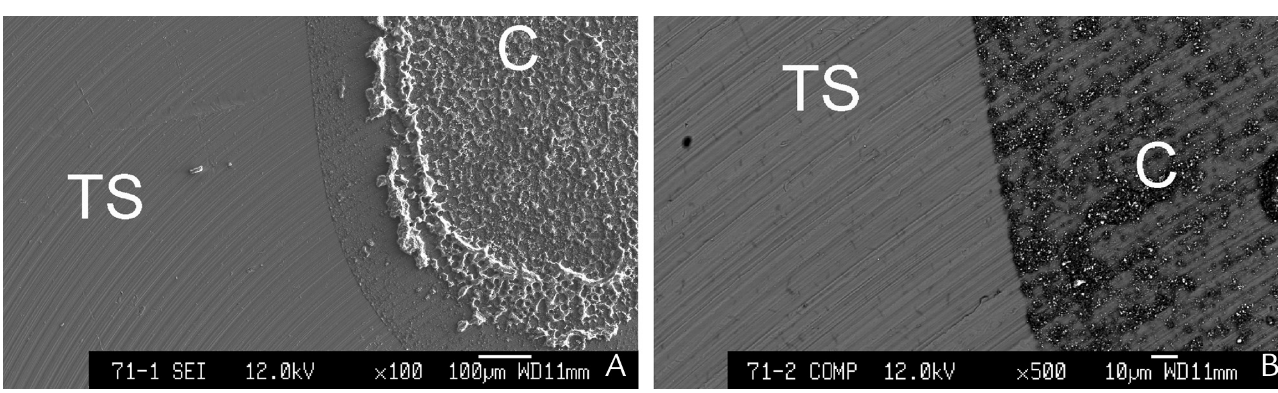

Figure 5. Representative of resin cement pair: Multilink Implant cement fracture surfaces. SEM of fracture patterns. Turned surface (TS) of titanium alloy is visible, as is imprint of milled surface on cement (C). A, Original magnification ×100; B, original magnification ×500.

evaluated the use of both resin-modified and conventional glass ionomers, measuring the release of ions over a period of up to 24 weeks. The authors indicated that discoloration occurred if the titanium oxide layer was either thinned with the action of a high fluoride ion concentration release or thickened when a lower concentration of the ion was released from the glass ionomer. In the current study, no such effects were observed, perhaps as a result of the shorter study time of only 1 week and as a result of differing chemical reactions. In this preliminary study, time dependence and differences in fluoride additives were not studied, and more time may be required for some of the other cements to show effects. This should be considered in a future experiment. The use of 2 different surface modalities was to demonstrate the potential effect of cements when they are used with implant abutments where the turned Ti-6Al-4V surfaces exist and when milling is used to

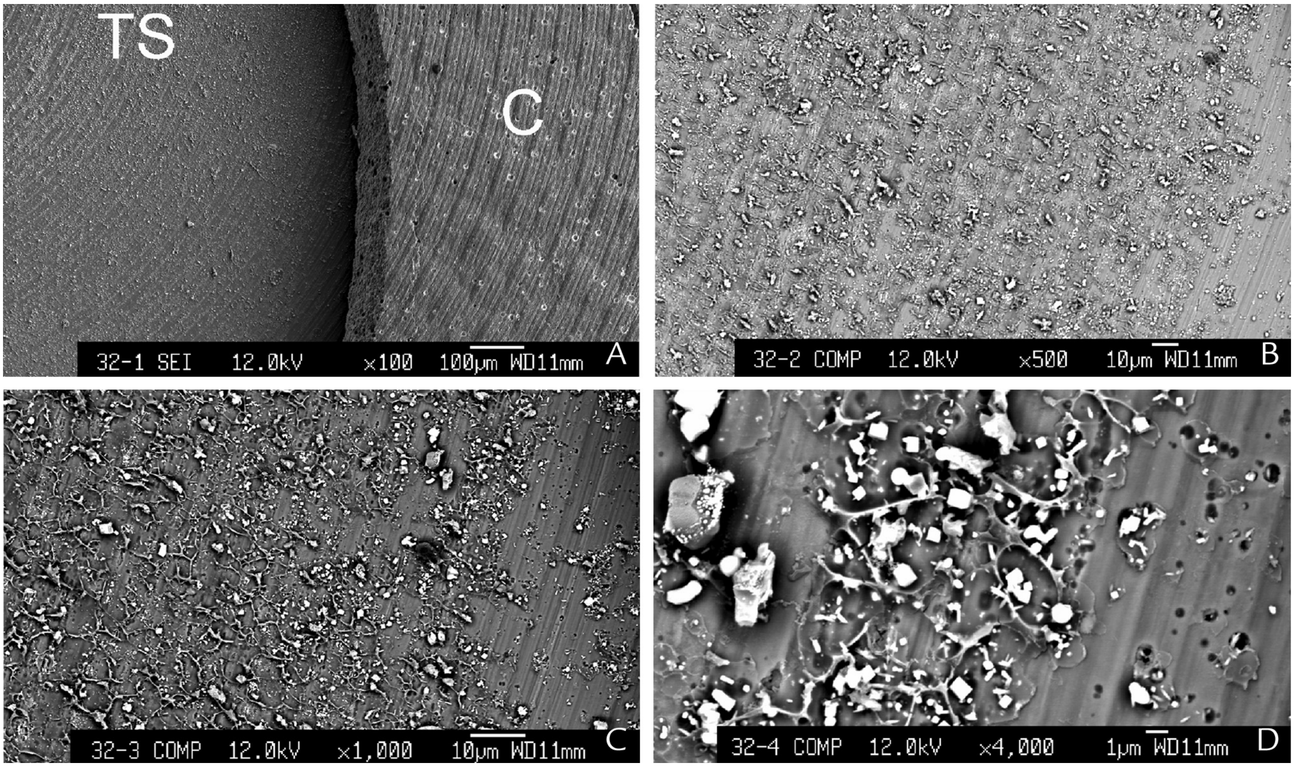

Figure 6. Representative of polycarboxylate cements: Durelon cement fracture surfaces. SEM of fracture patterns. A, Original magnification ×100. B, Original magnification ×500. C, Original magnification ×1 000. D, Original magnification ×4 000. Turned surface (TS) of titanium alloy visible, as is imprint of milled surface on cement. Note surfaces at higher magnification (C, D) show distinct surface differences with micropitting indicative of corrosion.

fabricate coping for tooth and implant restorations. Disk forms were used to provide basic information on cement interactions with machined alloy surfaces and do not simulate the true clinical situation of cement flow and distribution within a coping.

If the clinician selects D or PF, a chemical reaction may occur if conditions similar to those in this investigation exist. For implant restoration, the cement selection should be carefully considered because issues related to periimplant disease[15] and implant loss[14] may be in part due to corrosion caused by cement. Corrosive changes to titanium alloy also increase the pathogenic microbial attachment of *Porphyromonas gingivalis*,[16] a known etiological agent associated with adverse tissue reactions. Because the majority of dental implants are titanium based, the effect of the polycarboxylate cements tested on the implant surface must be carefully considered in light of these results. The same considerations apply to milled Ti-6Al-4V used for metal superstructures on natural tooth restorations, though the clinical effects may differ.

CONCLUSIONS

Within the limitations of this study, the following conclusions may be drawn:

1. Cementation with polycarboxylate cement provided higher shear bond strength.
2. Titanium alloy surfaces cemented with polycarboxylate cement such as Durelon and Poly-F Plus showed surface changes with corrosion pitting on both milled and turned surfaces.

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Noteworthy Abstracts of the Current Literature

Double full-arch versus single full-arch, four implant-supported rehabilitations: A retrospective, 5-year cohort study

Maló P, Nobre MD, Lopes A, Rodrigues R

J Prosthodont 2015:24:263-270

Purpose. To report the 5-year outcome of the All-on-4 treatment concept comparing double full-arch (G1) and single-arch (G2) groups.

Materials and methods. This retrospective cohort study included 110 patients (68 women and 42 men, average age of 55.5 years) with 440 NobelSpeedy groovy implants. One hundred sixty-five full-arch, fixed, immediately loaded prostheses in both jaws were followed for 5 years. G1 consisted of 55 patients with double-arch rehabilitations occluded with implant-supported fixed prostheses, and G2 consisted of 55 patients with maxillary single-arch rehabilitations or mandibular single-arch rehabilitations occluded with natural teeth or removable prostheses. The groups were matched for age (±6 years) and gender. Primary outcome measures were cumulative prosthetic (both interim and definitive) and implant survival (Kaplan-Meier product limit estimator). Secondary outcome measures were marginal bone levels at 5 years (through periapical radiographs and using the patient as unit of analysis) and the incidence of mechanical and biological complications. Differences in survival curves (log-rank test), marginal bone level (Mann-Whitney U test), and complications (chi-square test) were compared inferentially between the two groups using the patient as unit of analysis with significance level set at $p \leq 0.05$.

Results. No dropouts occurred. Prosthetic survival was 100%. Five patients lost 5 implants (G1: n = 3; G2: n = 2) before 1 year, rendering an estimated cumulative survival rate of 95.5% (G1: 94.5%; G2: 96.4%; Kaplan-Meier, $p = 0.645$, nonsignificant). The average (SD) marginal bone level was 1.56 mm (0.89) at 5 years [G1: 1.45 mm (0.77); G2: 1.67 mm (0.99); $p = 0.414$]. The incidence rate of mechanical complications (in both interim and definitive prostheses) was 0.16 and 0.13 for G1 and G2, respectively ($p = 0.032$). The incidence rate of biological complications was 0.06 and 0.05 for G1 and G2, respectively ($p = 0.669$).

Conclusion. Based on the results, rehabilitating double- or single-arch edentulous patients did not yield significant differences on survival curves. The incidence of mechanical complications was significantly higher for double-arch rehabilitated patients but nevertheless, these mechanical complications did not affect the long-term survival of either the prostheses or the implants.