Aus der

Poliklinik für Zahnärztliche Prothetik

Klinikum der Ludwig-Maximilians-Universität München

Einfluss mechanischer und chemischer Oberflächenbehandlung auf die Verbundfestigkeit von verschieden gereinigtem 3D gedrucktem Harz

Dissertation

zum Erwerb des Doktorgrades der Zahnmedizin

an der Medizinischen Fakultät der

Ludwig-Maximilians-Universität München

vorgelegt von

Valerie Maria-Sophie Lankes

aus

Regensburg

Jahr

2024

Mit Genehmigung der Medizinischen Fakultät der

Ludwig-Maximilians-Universität zu München

Erster Gutachter:	Prof. Dr. Bogna Stawarczyk, M.Sc.
Zweiter Gutachter:	Priv. Doz. Dr. Marcel Reymus
Dritter Gutachter:	Priv. Doz. Dr. Matthias Woiczinski
Mitbetreuung durch den promovierten Mitarbeiter:	_____
Dekan:	Prof. Dr. med. Thomas Gudermann
Tag der mündlichen Prüfung:	17.06.2024

LMU LUDWIG-MAXIMILIANS-UNIVERSITÄT MÜNCHEN

Dekanat Medizinische Fakultät
Promotionsbüro

Eidesstattliche Versicherung

Lankes, Valerie Maria-Sophie

Name, Vorname

Ich erkläre hiermit an Eides statt, dass ich die vorliegende Dissertation mit dem Thema

Einfluss mechanischer und chemischer Oberflächenbehandlung auf die Verbundfestigkeit von verschieden gereinigtem 3D gedrucktem Harz

selbständig verfasst, mich außer der angegebenen keiner weiteren Hilfsmittel bedient und alle Erkenntnisse, die aus dem Schrifttum ganz oder annähernd übernommen sind, als solche kenntlich gemacht und nach ihrer Herkunft unter Bezeichnung der Fundstelle einzeln nachgewiesen habe.

Ich erkläre des Weiteren, dass die hier vorgelegte Dissertation nicht in gleicher oder in ähnlicher Form bei einer anderen Stelle zur Erlangung eines akademischen Grades eingereicht wurde.

München, 23.06.2024
Ort, Datum

Lankes Valerie Maria-Sophie
Unterschrift Valerie Maria-Sophie Lankes

Inhaltsverzeichnis

Abkürzungsverzeichnis

CAD – Computer-aided design

CAM – Computer-aided manufacturing

AM – Additive manufacturing

SLA – Stereolithographie

DLP – Digital light processing

Al_2O_3 – (Di-)Aluminium(tri)oxid

MMA – Methylmethacrylat

10-MDP – 10-Methacryloyloxydecyl-Dihydrogenphosphat

Publikationsliste

Lankes V, Reymus M, Liebermann A, Stawarczyk B. Bond strength between temporary 3D printable resin and conventional resin composite: influence of cleaning methods and air-abrasion parameters. Clin Oral Investig 2023; 27:31-43 (doi: 10.1007/s00784-022-04800-7)

IF 2023: 3.607

Lankes V, Reymus M, Mayinger F, Coldea A, Liebermann A, Hoffmann M, Stawarczyk B. Three-Dimensional Printed Resin: Impact of Different Cleaning Protocols on Degree of Conversion and Tensile Bond Strength to a Composite Resin Using Various Adhesive Systems. Materials 2023, 16(9), 3580 (doi: 10.3390/ma16093580)

IF 2023: 3.748

Beitrag zu den Veröffentlichungen

Der eigene Beitrag zu den Publikationen „Bond strength between temporary 3D printable resin and conventional resin composite: influence of cleaning methods and air-abrasion parameters" sowie „Three-Dimensional Printed Resin: Impact of Different Cleaning Protocols on Degree of Conversion and Tensile Bond Strength to a Composite Resin Using Various Adhesive Systems" kann in der nachstehenden Übersicht entnommen werden.

	Valerie Lankes	**Prof. Dr. Bogna Stawarczyk**	**Co-Autoren**
Literaturrecherche	100%	-	-
Projektidee	-	80%	20%
"Bond strength between temporary 3D printable resin and conventional resin composite: influence of cleaning methods and air-abrasion parameters"			
Prüfkörperherstellung und Alterung	95%	5%	-
Datenerhebung	90%	10%	-
Deskriptive statistische Analyse	85%	15%	-
Explorative statistische Analyse	10%	90%	-
Tabellen und Abbildungen	100%	-	-
Manuskripterstellung	80%	10%	10%
Einreichen des Manuskripts	100%	-	-
"Three-Dimensional Printed Resin: Impact of Different Cleaning Protocols on Degree of Conversion and Tensile Bond Strength to a Composite Resin Using Various Adhesive Systems"			
Prüfkörperherstellung und Alterung	90%	5%	5%
Datenerhebung	95%	-	5%
Deskriptive statistische Analyse	100%	-	-
Explorative statistische Analyse	70%	30%	-
Tabellen und Abbildungen	100%	-	-
Manuskripterstellung	80%	10%	10%
Einreichen des Manuskripts	100%	-	-

1. Einleitung

In der Zahnmedizin wird die CAD/CAM-Technologie (computer-aided design/computer-aided manufacturing) im Sprachgebrauch bisher hauptsächlich mit subtraktiven (fräsen, schleifen) Verfahren gleichgesetzt. Die additive Fertigung (AM – additive manufacturing) rückt jedoch immer mehr in den wissenschaftlichen Fokus. Gründe dafür sind eine größere Freiheit in Bezug auf die Objektgeometrie sowie wirtschaftliche Vorteile durch deutliche Materialeinsparungen sowie das Wegfallen von Verschleißteilen wie Fräsen. Etabliert hat sich der 3D Druck in der Praxis bereits bei der Herstellung von Aufbisschienen individuellen Abformlöffeln, chirurgischen Bohrschablonen sowie in der Lehre an Hochschulen (Schweiger et al., 2021).

Zu den führenden additiven Herstellungsverfahren zählen 3D Drucker mit SLA (Stereolithographie) oder DLP (digital light processing) Technologie (Alammar et al., 2022). Diese Technologien unterscheiden sich in der Art der Lichtquelle, denn bei beiden Verfahren befindet sich das photopolymerisierbare flüssige Harz in einer Wanne und wird durch die Lichtquelle Schicht für Schicht auf die Bauplattform, die in die Wanne eintaucht, gezielt polymerisiert. Das fertigte Objekt befindet sich nach dem Druckvorgang an Hilfs- bzw. Stützstrukturen auf der Bauplattform, die anschließend im sogenannten Post-Processing abgetrennt werden müssen. Dies beinhaltet zudem eine Reinigung des Objekts von anhaftendem nicht-polymerisiertem Harz (Mayer et al., 2021) und eine Nachbelichtung mit speziellen Geräten, um eine möglichst hohe Umsetzungsrate der Kohlenstoffdoppelbindung im Objekt zu erreichen (Reymus and Stawarczyk, 2020). Im Allgemeinen bestehen die Harzmaterialien aus einer Harzmatrix aus polymerisierbaren Methacrylaten, anorganischen Füllstoffen, (Photo-)Initiatoren und Farbstoffen. Die Entwicklung von keramisch gefüllten Hybridmaterialien ermöglicht die Verwendung von gedruckten Restaurationen als festsitzenden Zahnersatz, da durch den erhöhten Anteil anorganischer Füllstoffe (z.B. Glaskeramikfüller), die mechanischen Eigenschaften entsprechend gesteigert werden (Zimmermann et al., 2020). Ebenso ermöglicht der wissenschaftliche Fortschritt das Drucken mit einer sehr hohen Präzision (Sampaio et al., 2021). Beides sind Erfordernisse im klinischen Einsatz von zahnfarbenen festsitzenden Restaurationen von (Langzeit-)Provisorien, Kronen und Brücken.

Ausschlaggebend für den klinischen Erfolg sind neben Biokompatibilität und mechanischen Eigenschaften, ein dauerhaft stabiler Verbund an der Zahnhartsubstanz. Durch die Nachbelichtung von 3D gedruckten Objekten kommt es zu einer weiteren Polymerisation und folglich zu einem geringen Restmonomergehalt an der Oberfläche. Die überwiegend inerte Oberfläche verhindert das Ko-polymerisieren von adhäsiven Befestigungsmaterialien und macht deshalb eine

Vorbehandlung der Klebefläche vor dem Einsetzen der Restauration notwendig (Mayinger et al., 2021, Borges et al., 2021). Zu den bekanntesten Vorbehandlungen zählt das Abstrahlen mit Aluminiumoxidpartikeln (Korund). Das Korundstrahlen reinigt und verändert die Restaurationsoberfläche in ihrem Rauheitsprofil (Kern, 2015, Nejat et al., 2018, Özcan and Bernasconi, 2015). Eine bessere Benetzbarkeit von Adhäsivsystemen und Befestigungsmaterialien wird ermöglicht und zudem wirken sich Mikroretentionen positiv auf die Verbundfestigkeit aus (Kuscu et al., 2021). Zusätzlich zum Abstrahlen ist die chemische Zusammensetzung der verwendeten Adhäsivsysteme wichtig für den langfristigen Erfolg. Sogenannte Universaladhäsive enthalten säuremodifizierte Monomere mit bifunktionellen Eigenschaften und versprechen dem Anwender oft den Verbund auf allen Materialoberflächen (Ye et al., 2022). Silanhaltige Adhäsive bilden durch eine Kondensationsreaktion mit reaktiven Hydroxylgruppen eine kovalente Bindung mit glaskeramischen Füllstoffen (Hagino et al., 2021). Inhaltsstoffe wie Methylmethacrylate (MMA) greifen die Oberfläche an und lösen bereits bestehende Doppelbindungen, die anschließend für eine erneute Polymerisation mit dem Befestigungskomposit zur Verfügung stehen, dies ist v.a. bei subtraktiv hergestellten Restaurationen aus Kompositen von Bedeutung (Reymus et al., 2019).

Viele Materialhersteller haben bereits 3D druckbare Harze für festsitzende (Langzeit-)Provisorien in ihrem Portfolio. Bisher sind wenige davon als Material für definitive Restaurationen freigegeben. Allerdings sind die Befestigungsstrategien noch nicht ausreichend wissenschaftlich erforscht.

2. Zielsetzung

In den zwei dieser Arbeit zugrundeliegenden international veröffentlichten Publikationen wurde die Verbundfestigkeit von einem 3D druckbarem Harz und einem adhäsiven Befestigungskomposit in-vitro untersucht. Als Harz wurde printodent® GR-17.1 temporary It (pro3dure medical GmbH, Iserlohn, Germany) verwendet, das für 3D gedruckte Langzeitprovisorien zugelassen ist.

Insbesondere wurde der Einfluss von unterschiedlichen Strahlpartikeln, -drücken und Adhäsivsystemen untersucht. Zudem wurden verschiedene Reinigungsmethoden im Post-Processing, die von Herstellern empfohlen oder für die Reinigung speziell entwickelt wurden, berücksichtigt. Um die in-vitro Verbundfestigkeit möglichst kliniknah zu simulieren, wurde zusätzlich eine künstliche Alterung in das Studiendesign aufgenommen.

3. Material und Methoden

Insgesamt wurden 1.260 Prüfkörper (Geometrie 15x15x4 mm) mit der DLP-Drucktechnologie hergestellt. Das anhaftende nicht-polymerisierte Harz wurde entweder chemisch in 100%igen Isopropanol, oder in einer Butyldiglykol-Lösung im Ultraschallbad abgewaschen oder durch Zentrifugieren physikalisch entfernt. Die Nachbelichtung erfolgte nach Harzherstellerangaben.

In der ersten Untersuchung wurde die mechanische Vorbehandlung untersucht. Dabei wurde die Klebefläche der unterschiedlich gereinigten Prüfkörper entweder mit 50 µm Aluminiumoxid (0,1 MPa / 0,4 MPa) oder mit 50 µm Glasperlen (0,1 MPa / 0,4 MPa) gestrahlt. Anschließend wurden die Oberflächenenergie und das Rauheitsprofil gemessen. Ein konfektionierter Acrylzylinder mit einer definierten Klebefläche von 2,9 mm^2 wurde mit einem adhäsiven dualhärtenden Befestigungskomposit (Panavia V5, Kuraray Noritake, Okyama, Japan) auf der Prüfkörperoberfläche verklebt. Die Hälfte der Prüfkörper wurden einer künstlichen Alterung in einem Thermolastwechsel (10.000 Zyklen, zwischen 5° und 55°C) ausgesetzt. Initial und nach Alterung wurden die Scher-und Zugfestigkeiten in einer Universalprüfmaschine ermittelt und die Bruchbilder analysiert. Die globale univariate Varianzanalyse mit partiellem Eta-Quadrat wurde angewandt, um die Effektstärke der getesteten Parameter zu bestimmen. Die nicht-parametrischen Tests Kruskal-Wallis-H und Mann-Whitney-U verglichen die untersuchten Gruppen miteinander.

Bei der zweiten Untersuchung lag der Fokus auf der chemischen Konditionierung. Mit einem Raman-Mikroskop wurde zunächst die Umsetzungsrate der Kohlenstoffdoppelbindungen von Prüfkörpern unmittelbar nach der Reinigung und Nachbelichtung gemessen und anschließend mit gestrahlten (Al_2O_3, 0,1 MPa) Prüfkörperoberflächen verglichen. Auf die Klebefläche wurde entweder ein Keramikprimer (Clearfil Ceramic Primer Plus, Kuraray Noritake, Okayama, Japan), zwei unterschiedliche Universaladhäsive (Clearfil Universal Bond Quick, Kuraray Noritake Okayama, Japan oder Scotchbond Universal Plus, 3M, Saint Paul, Minnesota, USA) oder ein MMA-Primer (Visio.link, Bredent, Senden, Germany) nach Herstellerangaben aufgetragen. Die Verklebung, Alterung und die Zugfestigkeitsprüfung der Prüfkörper erfolgten analog zur ersten Untersuchung. Um den Einfluss der Reinigungsmethoden und der chemischen Vorbehandlung auf die Zugfestigkeit zu ermitteln, wurde eine einfaktorielle Varianzanalyse mit partiellem Eta-Quadrat und anschließendem Scheffé-Post-hoc-Test berechnet. Ein t-Test untersuchte die Auswirkungen der künstlichen Alterung.

4. Ergebnisse

Die Vorbehandlung mit Aluminiumoxid mit dem Druck von 0,4 MPa zeigte die höchste Oberflächenrauheit im Vergleich zu einer Vorbehandlung mit Glasperlen oder niedrigerem Druck. Der Strahldruck hatte einen größeren Einfluss auf die Verbundfestigkeit als die Art des Strahlpulvers. Die Vorbehandlung mit Glasperlen mit dem Druck von 0,1 MPa zeigte die niedrigsten Scher- (23 MPa) und Zugfestigkeiten (10 MPa). Ebenso wurden überwiegend adhäsive Bruchbilder erfasst. Unabhängig der Reinigungsmethode zeigte die Vorbehandlung mit Aluminiumoxid mit 0,4 MPa die höchsten Scher- (37 MPa) und Zugfestigkeiten (26 MPa). Der Vergleich der Reinigungsmethoden zeigte, dass zentrifugierte Prüfkörper initial höhere Verbundfestigkeiten unabhängig der Strahlparameter aufwiesen.

Zentrifugierte Prüfkörper zeigten vor dem Korundstrahlen (Al_2O_3, 0,1 MPa) verglichen mit der chemischen Reinigung (> 95%) niedrigere Kohlenstoffumwandlungsraten (88%). Nach dem Korundstrahlen erreichten die Prüfkörper ähnliche Kohlenstoffumwandlungsraten (92%) wie nach der chemischen Reinigung. Die niedrigsten Zugfestigkeiten wies die Vorbehandlung mit dem Keramikprimer (16 – 19 MPa) auf. Allerdings konnte die Verbundfestigkeit signifikant erhöht werden, wenn die Prüfkörper zentrifugiert waren (27 – 33 MPa). Bei nicht gealterten Prüfkörpern konnten unabhängig der Reinigungsmethode höhere Werte (36 – 40 MPa) unter Verwendung von den Universaladhäsiven Clearfil Universal Bond Quick oder Scotchbond Universal Plus im Vergleich zu dem MMA-Primer (24 – 27 MPa) gemessen werden. Nach der künstlichen Alterung erreichte die Konditionierung mit dem MMA-Primer (29 – 34 MPa) ähnlich hohe Zugfestigkeitswerte wie die der Universaladhäsive (33 – 36 MPa).

5. Diskussion

Nach der physikalischen Reinigung verbleiben Rückstände von nicht polymerisiertem klebrigem Harz auf der Oberfläche. Die Nachbelichtung erzeugt eine glänzende, aber inerte Oberfläche. Die Vorversuche zeigten, dass ohne Oberflächenvorbehandlung keine Verbundfestigkeit zum Befestigungskomposit Panavia V5 erreicht werden kann. Wird allerdings die oberste Schicht durch Abstrahlen entfernt, befindet sich darunter ein höherer Restmonomeranteil verglichen mit der chemischen Reinigung. Dies ermöglicht bessere Verbundfestigkeiten auch bei der Verwendung von rundlichen Glasperlen mit einem geringen Druck kombiniert. Auch bei der Wahl des Adhäsivsystems konnte die physikalische Reinigung kombiniert mit dem Keramikprimer deutlich höhere Verbundfestigkeiten im Gegensatz zur chemischen Reinigung erreichen.

Die Biokompatibilität von Materialien hängt im Wesentlichen vom Grad der Umwandlung der Kohlenstoff-Doppelbindungen ab, da Restmonomere als auslaugbare Bestandteile vorliegen und im Speichel in Lösung gehen können (dos Santos et al., 2014). Unmittelbar nach der Nachbelichtung wiesen die zentrifugierten Prüfkörper eine geringere Umsetzungsrate im Vergleich zur chemischen Reinigung auf. Nach dem Abstrahlen wiesen allen Reinigungsmethoden vergleichbar hohe Umsetzungsraten auf. Bei zahnmedizinischen Restaurationen wird die Oberfläche routinemäßig finiert und poliert. Es ist anzunehmen, dass die initial gemessen Umsetzungsraten vernachlässigbar sind.

Die Vorbehandlung mit Aluminiumoxid mit einem hohen Druck von 0,4 MPa zeigte hohe Verbundfestigkeiten. Klinisch könnte die Oberfläche bei hohen Druck beschädigt werden, die anorganischen Füllstoffe (Gläser) könnten aus der Harzmatrix desintegrieren und zu einem Verlust der mechanischen Eigenschaften führen (Yoshihara et al., 2017). Auch ein unachtsames Strahlen könnte den Restaurationsrand stark beschädigen und die Restauration schließlich unbrauchbar machen. Ein Abstrahlen mit Glasperlen mit dem Druck von 0,1 MPa erreichte in den Versuchen keinen zuverlässigen Verbund. Durch die rundliche Geometrie des Strahlguts kann kaum bis geringfügig mikromechanisch Retentionen zur Verankerung des Befestigungskomposits geschaffen werden (Nobuaki et al., 2015).

Die verwendeten Universaladhäsive (Clearfil Universal Bond Quick und Scotchbond Universal Plus) zeigten die höchsten Verbundfestigkeiten. Bifunktionelle Monomere wie das saure phosphorhaltige Monomere 10-MDP interagieren ionisch mit den oxidkeramischen Füllstoffen in

der Harzmatrix (Klaisiri et al., 2021). Darüber hinaus bilden enthaltene silanreaktive Hydroxylgruppen zu den glaskeramischen Füllstoffen eine kovalente Bindung und können durch Methacrylatgruppen mit dem Befestigungskomposit polymerisieren.

Im Gegensatz zu den Universaladhäsiven erreichte der 10-MDP haltige Keramikprimer niedrigere Verbundfestigkeiten. Da der Primer hauptsächlich Silan enthält wird der Verbund stark auf den Verbund zu glaskeramischen Füllstoffen reduziert und gleichzeitig wird die Bildung von Kohlenstoffverbindungen zwischen Harzmatrix und Befestigungskomposit blockiert (Lima et al., 2022). Aufgrund der niedrigen bis mittleren Viskosität des 3D Harzes, die für die Verarbeitung im Drucker wichtig ist, hat es die Eigenschaften eines fließfähigen Komposit und besteht nach Herstellerangaben hauptsächlich aus der Harzmatrix (60 %) und einer reduzierten Anzahl von Füllstoffen (40 %). Dadurch konnte der MMA-Primer visio.link zwar höhere Verbundfestigkeiten als der Keramikprimer erzielen, allerdings entfällt die chemische Haftung an anorganischen Füllstoffen (Palitsch et al., 2012).

6. Zusammenfassung

Ziel der vorliegenden Arbeit war es die in-vitro Verbundfestigkeit zwischen einem für Langzeitprovisorien zugelassen 3D druckbarem Harz und einem adhäsiven dualhärtenden Befestigungskomposit zu ermitteln. Untersucht wurde der Einfluss der Reinigungsmethode, die Bestandteil des Post-Processing ist, das Abstrahlen der gedruckten Oberflächen mit verschiedenen Strahlparametern und die chemische Konditionierung mit unterschiedlichen Adhäsivsystemen. Die Art der Reinigung beeinflusste, sowohl an abgestrahlten Prüfkörperoberflächen als auch an chemisch vorbehandelten, die Verbundfestigkeit. Die physikalische Reinigung (Zentrifugation) steigerte die Verbundfestigkeit verglichen mit der Reinigung in Lösungsmitteln (Isopropanol bzw. Butyldiglykol-haltige Lösung) bei Abstrahlen mit Glasperlen und 0,1 MPa und bei Verwendung des Keramikprimers (Clearfil Ceramic Primer). Da viele 3D Druckhersteller die Reinigung in Isopropanol empfehlen, konnten die Untersuchungen zeigen, dass unabhängig der untersuchten Reinigungsmethoden die mechanische Vorbehandlung mit Aluminiumoxid mit 0,4 MPa, die Universaladhäsive (Clearfil Universal Bond und Scotchbond Universal Plus) und der MMA-Primer (Visio.Link) hohe Verbundfestigkeiten erreichten.

7. Abstract (English)

The aim of the present research was to determine the in-vitro bond strength between a 3D printable resin approved for long-term temporaries and an adhesive dual-curing luting composite. The influence of the cleaning method, which is part of the post-processing, the air-abrasion of the printed surfaces with different air-abrasion parameters and the chemical conditioning with various adhesive systems were investigated. The type of cleaning, both on air-abraded specimen surfaces and on chemically pretreated ones, influenced the bond strength. Physical cleaning (centrifugation) increased bond strength compared to solvent cleaning (isopropanol or butyl diglycol containing solution) when air-abrasion occurred with glass pearls at 0.1 MPa or using the ceramic primer (Clearfil Ceramic Primer). Since many 3D printing manufacturers recommend cleaning in isopropanol, the investigations showed that regardless of the cleaning methods investigated, the mechanical pretreatment with alumina powder at 0.4 MPa, the universal adhesives (Clearfil Universal Bond and Scotchbond Universal Plus) and the MMA primer (Visio.Link) achieved high bond strengths.

Veröffentlichung I

Clinical Oral Investigations
https://doi.org/10.1007/s00784-022-04800-7

REVIEW

Bond strength between temporary 3D printable resin and conventional resin composite: influence of cleaning methods and air-abrasion parameters

Valerie Lankes[1] · Marcel Reymus[2] · Anja Liebermann[1,3] · Bogna Stawarczyk[1]

Received: 2 September 2022 / Accepted: 17 November 2022

Abstract

Objectives The influence of different cleaning methods, air-abrasion parameters, and aging on shear bond strength (SBS) and tensile bond strength (TBS) of 3D resin luted to composite resin.

Materials and methods Nine hundred resin substrates were 3D printed (D20II, Rapid Shape) and cleaned with either isopropanol (ISO), butyldiglycol-based solution (BUT), or centrifugation (CEN). After 24-h storage in 37 °C water, specimens were air-abraded (mean particle size 50 µm; $n=60$) with either alumina at 0.1 MPa (AL0.1) or 0.4 MPa (AL0.4) and glass pearls at 0.1 MPa (GP0.1) and 0.4 MPa (GP0.4) or conditioned with visio.link (control) and luted with PanaviaV5. Initially (24 h, 37 °C water storage) or after aging (10,000 thermal cycles), SBS and TBS were measured, and fracture types were examined. Surface free energy (SFE) and roughness (Ra) were determined after air-abrasion. Kolmogorov–Smirnov, Kruskal–Wallis H, Mann–Whitney U, chi-square, and partial eta-squared were computed.

Results SBS measurements presented higher values than TBS ($p<0.001$–0.033). Within the pretreatment groups, CEN showed the highest SBS and TBS values compared to cleaning with ISO or BUT ($p<0.001$–0.040). Pretreatment with GP0.1 displayed the lowest bond strength values ($p<0.001$–0.049), and mostly adhesive fractures occurred. The highest Ra values ($p<0.001$) were observed for AL0.4 pretreatment.

Conclusions Pretreatment with AL0.4 and the control group mainly presented the highest bond strength values. Thermocycling had a positive effect on the bond strength.

Clinical relevance According to this study, 3D-printed restorations should be pretreated with AL0.4 or with visio.link before adhesive luting, regardless of their cleaning.

Keywords 3D resin · Cleaning · Air-abrasion · Surface properties · Bond strength · Fracture types

Introduction

The computer-aided design/computer-aided manufacturing (CAD/CAM) technology allows composite resin materials to be used for permanent indirect restorations. The term CAD/CAM stands for a variety of digitally supported techniques. For CAD/CAM polymers and composite resins, CAM is traditionally equivalent with the subtractive (milling) way of manufacturing [1]. Nowadays, additive manufacturing (AM), commonly known as 3D printing, is increasingly appreciated. Usually, the printing object is built up three-dimensional, layer by layer out of a vat of light-polymerizing resin by action of light, using stereolithography (SLA) or digital light processing (DLP) technology [2]. In contrast to milling and grinding, there is less restriction in object-geometry and waste of material. AM is already now well established in the prosthetic pretreatments such as bite splints, customized impression trays, surgical guides, and removable dental protheses. The latest material and printing research confirms that 3D-printed resin-based temporaries are suitable for long-term use [3]. Printed long-term

✉ Valerie Lankes
V.Lankes@med.uni-muenchen.de

1 Department of Prosthetic Dentistry, University Hospital, LMU Munich, Goethestraße 70, 80336 Munich, Germany

2 Department of Conservative Dentistry and Periodontology, University Hospital, LMU Munich, Goethestraße 70, 80336 Munich, Germany

3 Department of Prosthetic Dentistry, Faculty of Medicine and University Hospital Cologne, University of Cologne, Kerpener Str. 32, 50931 Cologne, Germany

Published online: 28 November 2022

temporaries present higher accuracy, better marginal fit [4], higher fracture resistance [5], and biocompatibility [6] compared to the conventionally manufactured ones. Up to now, only few 3D printable materials are available for fixed permanent restorations [7], but many manufacturers of 3D printable resins for long-term temporaries strive to obtain an approval under the medical device regulation, for the application as fixed dental protheses.

Besides mechanical and biological properties, a durable bond between restoration and the luting material is a crucial factor for a sufficient clinical long-term stability. The adhesion of composite material to tooth structure has already been extensively clarified and documented [8, 9]. In general, composite resin materials consist of a resin matrix of polymerized methacrylate, inorganic fillers, and (photo-)initiators. For milled composite resin restorations, the removed smear layer and unpolymerized carbon–carbon double bonds (free methacrylate) are important to create a strong adhesive bond by co-polymerizing the luting composite resin. The mechanical pretreatment of the bonding area is the most popular method for eliminating the smear layer, enlarging the surface area, and creating micro-mechanical retentions. Various air-abrasion powders with different mean sizes and pressures are described in literature [10–12]. Alumina powder displayed especially promising results [13] but has been criticized for damaging the surface, whereas air-abrasion with glass pearls would be sufficient [14]. Only a few in vitro studies have been concerned with the influence of air-particle abrasion on the surface properties of 3D printable resin restorations [15, 16]. None of them though takes air-abrasion pressure into account. However, with AM, there is no smear layer due to grinding or milling. Here, the post-processing procedures are important to be considered.

After the printing process, the objects must be freed from excess adherent uncured resin. Various cleaning methods are described in literature, whereby most resin manufacturers, despite lacking the scientific basis, suggest to simply rinse with isopropanol [17, 18]. This recommendation needs to be questioned, since solutions in particular may lead to changes in the surface structure of the printed object [18]. It is a necessity that the cleaned objects are being post-polymerized [19] by increasing converted carbon–carbon double bonds to stabilize mechanical and especially biological properties [19]. There is no literature yet, concerning the potential or limitations of post-processing procedures in combination with mechanical pretreatment with regard to the adhesion bond between the 3D resin and the luting composite resins. Therefore, the study at hand has been conducted.

The aim was to investigate the influence between three different cleaning methods and four different air-abrasion procedures, varying in pressure and air-abrasion agents, on the shear (SBS) and tensile (TBS) bond strength between 3D-printed temporary resin and a dual curing resin composite. The selected cleaning solution was either suggested by a manufacturer (isopropanyl alcohol) or specially developed for cleaning 3D-printed objects (InovaPrint wash). Additionally, centrifugation, as a physical cleaning method, was used since it is also recommended by some manufacturers. The centrifugal force has already been researched with regard to cleaning and mechanical properties of printed objects and has displayed promising results [18]. As a control group, a protocol with visio.link combined with 0.1 MPa alumina air-abrasion was chosen as this combination demonstrated good bond strength values (23.7–25.7 MPa) in various studies concerning the luting of CAD/CAM composite blocks [20, 21]. To investigate the bond strength of fixed dental prostheses, it is essential for in vitro studies to be as close to the clinic as possible; therefore, thermocycling as artificial aging was also included.

The null hypothesis stated that neither the cleaning method nor the pretreatment (air-abrasion powder and pressure) nor the aging regime nor the test method has an impact on the bond strength. Furthermore, the null hypothesis was that the air-abrasion shows no impact on the surface roughness and surface free energy.

Material and methods

A specimen geometry (4 × 15 × mm) was digitally designed (Meshmixer software, Autodesk Inc., San Rafael, CA, USA) and exported as a STL file. A total of 900 resin specimens (printodent Generative Resin GR-17.1 temporary lt, Pro3dure medical GmbH, Iserlohn, Germany) were additively produced, vertically to the printer's platform in a layer thickness of 50 µm by using the digital light processing (DLP) printer D20II (Rapidshape, Heimsheim, Germany) according to the manufacturer's instructions. Before printing, the 3D resin was processed on a roller stirring device (LC-3D Mixer, NextDent, Soesterberg, Netherlands) for 30 min to achieve a sufficiently homogeneous distribution of the ingredients. An overview of the study design is presented in Fig. 1.

The printed specimens were divided into three groups ($n = 300$) and cleaned as follows:

1. Isopropanol (ISO) (100%, SAV LP GmbH, Flintsbach, Germany) for 4 min in an ultrasonic bath (Sonorex Super RK 102H, Bandelin, Berlin, Germany). The residue of the liquid was removed with compressed air.
2. Butyldiglycol-based cleaning solution (BUT) (InovaPrint Wash, hpdent GmbH, Gottmadigen, Germany) for 2 min in an ultrasonic bath as recommended by the manufacturer. The residue of the liquid was removed with compressed air.
3. Centrifugation (CEN) (Allegra X-15R, Beckman Coulter GmbH, Krefeld, Germany). Two specimens in

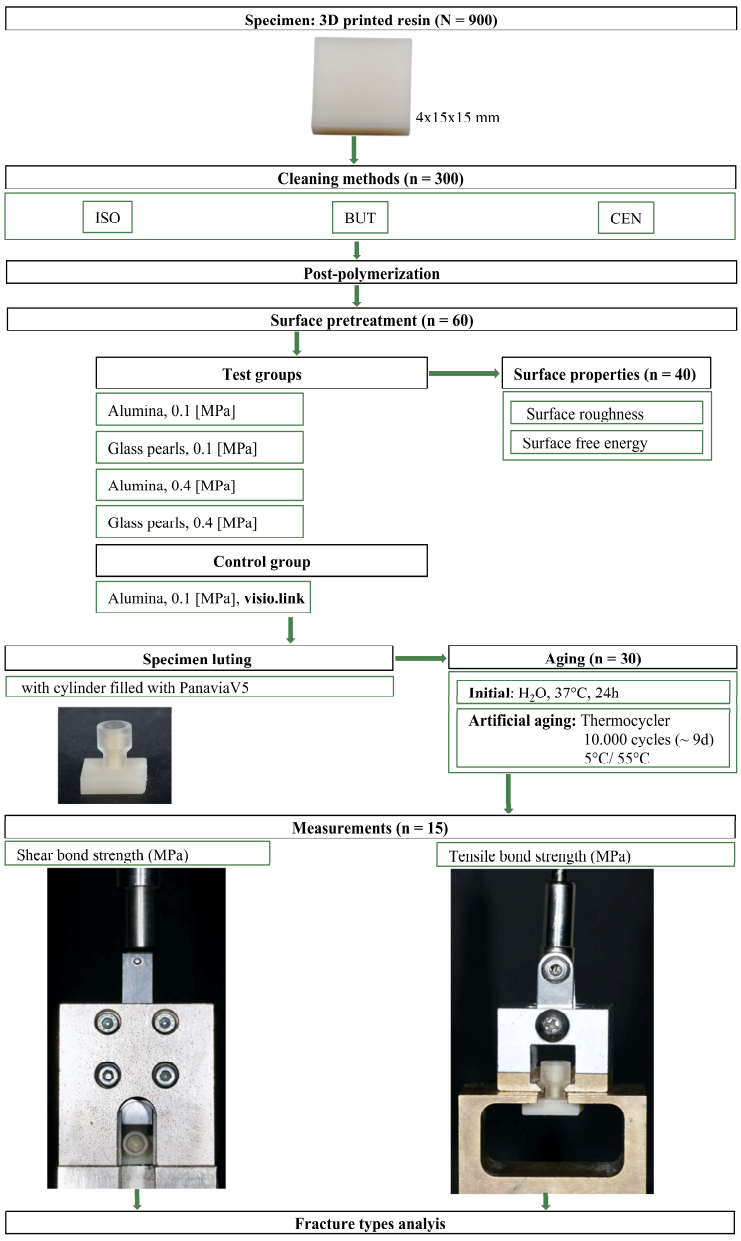


Fig. 1 Study design

each polypropylene conical tube (Cellstar Tubes 50 ml, Greiner Bio-One, Austria) were centrifugated with 600 G for 10 min.

All specimens were post-cured using OtoFlash G171 (NK-Optik, Baierbrunn, Germany) for 2000 flashes from each side (flashlight; wavelength range 280–700 nm, peaks

at approximately 400 and 500 nm) and subsequently stored for 24 h in distilled water at 37 °C. The specimens were further divided into five subgroups ($n = 60$) and air-abraded with alumina or glass pearls with a mean particle size of 50 µm for 10 s (basis Quattro IS, Renfert, Hilzingen, Germany). The execution duration was controlled manually via a timer. The evaluated air-abrasion powders combined with specific pressures are listed in Table 1.

A blasting tool ensured 10 mm distance between the noodle and the specimen's surface with an angle of 45°.

Then, all specimens were ultrasonically cleaned for 3 min in distilled water and carefully dried with compressed air.

As the control group, 180 specimens were, after air-abrasion with alumina at 0.1 MPa, additionally treated with visio.link (bredent, Senden, Germany). The conditioning agent was applied with a microbrush and then light cured for 90 s with a manufacturer-recommended light curing unit (bre.Lux Power unit, bredent) on the specimen's surface. The pretreatment was performed immediately before bonding of the specimens.

An acrylic cylinder (SD Mechatronik, Feldkirchen-Westerham, Germany) with an inner diameter of 2.9 mm was positioned on each pretreated specimen's surface, filled with a luting composite resin in shade A2 (Panavia V5, Kuraray Noritake, Okyama, Japan). Excess luting material around the cylinder on the luting area was carefully removed with a microbrush before polymerizing for 40 s (10 s from four different sides) using a LED light unit (Elipar Deep Cure-S, 3 M, Seefeld, Germany) with a wavelength of 430–480 nm and a light intensity of 1.480 mW/cm^2. The cylinder was not disconnected before conducting the bond strength tests.

All specimens were subsequently stored in distilled water for 24 h at a temperature of 37 °C before half of the specimens were aged by a thermocycling process (Thermocycler, SD Mechatronik, Feldkirchen-Westerham, Germany). The artificial aging completed 10,000 thermal cycles between 5° and 55 °C remaining for 20 s in each bath.

SBS and TBS measurements

SBS and TBS were carried out in a universal testing machine (Zwick 1445, Zwick, Ulm, Germany). For SBS, the compound surface was parallel to the loading direction, and the acrylic cylinder to the horizontal direction. The specimens were vertically loaded at a rate of 1 mm/min until fracture. For TBS, the specimens were fixed in a special holding device pulled apart by an upper chain with a crosshead speed of 5 mm/min until bond failed and calculated as follows: fracture load/bonding area (N/mm^2 = MPa).

Fracture types

The deboned area of each specimen was evaluated using a digital microscope magnification of 50 × (VHX-970F, Keyence, Osaka, Japan), and fractures were classified as follows:

i. Adhesive between the substrate and the luting composite
ii. Cohesive within the luting composite resin
iii. Cohesive within the 3D-printed resin
iv. Mixed cohesive

SFE and Ra

From each of the four air-abrasion groups, 10 specimens were taken to conduct angle measurements (Easy Drop, Krüss, Hamburg, Germany) to determine SFE. Measurements were performed at room temperature by the sessile drop method with a defined volume of the test liquids which were distilled water and diiodomethane (CAS 75–11-6, Sigma-Aldrich, St. Louis, USA). Three drops of each liquid were generated on each specimen's surface. After 5 s, a picture was taken, and the drop was analyzed with the tangent 1 method for distilled water or the circle method for diiodomethane by the used software (DSA 4, Drop Shape Analysis, Krüss). After specifying the baseline of the drop, the contact angle was calculated with the

Table 1 Summary of pretreatment with abbreviations, material, manufacturers, composition, and lot numbers

Abbreviation	Pretreatment	Material	Manufacturers	Composition	Lot
AL0.1	Powder: alumina Pressure: 0.1 MPa	Strahlkorund	Orbis Dental Handelsgesellschaft mbH, Münster, Germany	Aluminia powder, mean particle size 50 µm	20,190,288
AL0.4	Powder: alumina Pressure: 0.4 MPa				
GP0.1	Powder: glass pearls Pressure: 0.1 MPa	Perlablast micro	Bego Bremer Goldschlägerei, Bremen, Germany	Lead-free sodium hydrogencarbonate glass pearls, mean particle size 50 µm	A46518
GP0.4	Powder: glass pearls Pressure: 0.4 MPa				

Owens–Wendt–Rabel–Kaelble method. Further, the same specimens were used for tactile Ra measurements by a profilometer (MarSur M 400, Mahr, Göttingen, Germany). Six measurements (3 × horizontal, 3 × vertical) were conducted on each specimen, with a length of 5.6-mm and 3-mm distance between the single tracks, determined Ra.

Statistical analysis

The data were analyzed statistically with SPSS version 26.0 (IBM, SPSS, Statistics, Armonk, NY, USA). The normal distribution was analyzed using the Kolmogorov–Smirnov test. The global univariate ANOVA with partial eta-squared (η_P^2) were applied to figure out the impact of the tested parameters. The differences between the groups were analyzed non-parametrically with the Kruskal–Wallis *H* and multiple pairwise Mann–Whitney *U* test. For the correlation between SBS and TBS, the Spearman rho test was applied. The frequency of fracture types was analyzed by the chi-square test and Ciba-Geigy table. *p* values less than 0.05 were interpreted as statistically significant.

Results

A deviation of the normal distribution was observed; therefore, the data were analyzed non-parametrically. Descriptive statistics with standard deviation (SD); 95% confidence intervals; and minimum, medium, and maximum are summarized in Tables 2 and 3. The highest impact on SBS and TBS was exerted by the test method ($\eta_P^2 = 0.454$, $p < 0.001$), followed by the cleaning methods ($\eta_P^2 = 0.160$, $p < 0.001$), the pressure during the air-abrasion ($\eta_P^2 = 0.142$, $p < 0.001$), the air-abrasion powder ($\eta_P^2 = 0.099$, $p < 0.001$), and aging ($\eta_P^2 = 0.027$, $p < 0.001$). SBS showed higher values than TBS ($p = 0.001 - 0.033$), except for initial measurements within specimens cleaned with BUT and pretreated with GP0.1 ($p = 0.285$). A positive correlation between SBS and TBS was found (*R*, 0.424, $p < 0.001$).

SBS measurements

Regarding the cleaning methods, CEN led to higher values for groups pretreated with AL0.1 ($p < 0.001$–0.014), initially tested specimens pretreated with AL0.4 ($p < 0.001$–0.036), and the aged group pretreated with GP0.4 ($p = 0.003$–0.021). Specimens tested in the initial state and pretreated with GP0.4, cleaned with CEN, presented higher values compared to ISO ($p = 0.006$). ISO showed higher values for specimens tested in the initial state and pretreated with GP0.1 ($p = 0.001$) compared to BUT. The aged groups pretreated with GP0.1 or AL0.4 and the initially tested control group ($p > 0.092$) showed no difference in cleaning methods, whereas the aged control group showed higher values when cleaned with BUT compared to CEN ($p = 0.002$).

Regarding the pressure, 0.4 MPa led to higher values in artificially aged groups cleaned with ISO and pretreated with alumina ($p = 0.006$) or cleaned with CEN and pretreated with glass pearls ($p = 0.029$). In addition, groups cleaned with BUT and air-abraded at 0.4 MPa increased values in

Table 2 Descriptive statistics (median, min/max) and 95% confidence intervals (CI) for SBS per cleaning method, pretreatment, and aging

	ISO			BUT			CEN		
	Median	Min/max	95% CI	Median	Min/max	95% CI	Median	Min/max	95% CI
Pretreatment	Initial								
AL0.1	$35.5^{b\alpha II}$	13.5/54.6	(26; 39)	$34.4^{b\beta i}$	10.1/52.5	(35; 41)	$46.0^{a\alpha II}$	25.4/56.3	(37; 50)
GP0.1	$36.0^{a\alpha}$	16.1/50.3	(29; 41)	$23.3^{*bB\gamma ii}$	1.6/34.9	(10; 28)	$44.0^{a\alpha\beta}$	7.9/64.5	(28; 48)
AL0.4	$43.3^{b\alpha II}$	7.9/58.6	(30; 48)	$37.1^{b\beta iiII}$	28.3/51.6	(34; 43)	$49.2^{a\alpha II}$	36.5/61.1	(45; 54)
GP0.4	$38.4^{b\alpha}$	8.0/49.5	(26; 43)	$44.0^{abA\alpha i}$	36.6/48.3	(40; 46)	$45.2^{a\alpha}$	38.0/62.0	(42; 52)
Control	$34.3^{a\alpha II}$	30.0/45.6	(31; 38)	$38.2^{a\beta II}$	23.2/52.9	(33; 43)	$33.1^{a\beta II}$	25.9/45.5	(31; 37)
Pretreatment	Artificial aging								
AL0.1	$38.7^{bB\beta I}$	28.6/57.1	(35; 45)	$45.7^{bB\beta i}$	10.1/62.6	(33; 51)	$61.5^{a\alpha iI}$	49.1/75.3	(57; 67)
GP0.1	$36.2^{*a\beta}$	22.4/66.2	(31; 47)	$22.4^{*aB\gamma ii}$	3.1/53.0	(12; 35)	$36.0^{aB\gamma ii}$	8.7/75.7	(26; 50)
AL0.4	$55.0^{aA\alpha iI}$	24.1/75.7	(44; 61)	$56.8^{aA\alpha iI}$	46.2/76.7	(52; 67)	$67.0^{*a\alpha iI}$	43.6/75.7	(56; 70)
GP0.4	$41.3^{b\beta ii}$	26.0/54.6	(37; 48)	$42.3^{bA\beta ii}$	15.0/55.0	(31; 46)	$50.5^{aA\beta ii}$	40.3/62.8	(46; 55)
Control	$60.4^{ab\alpha I}$	38.4/75.5	(37; 48)	$62.8^{a\alpha I}$	52.7/75.7	(57; 67)	$45.3^{b\beta\gamma I}$	33.7/75.7	(41; 56)

*Not normally distributed. ^{ab}Different lowercase letters present significant differences between the cleaning methods within one pressure, powder, and aging group. ^{AB}Different uppercase letters present significant differences between the applied pressure within one powder, cleaning method, and aging group. $^{\alpha\beta\gamma\delta}$Different letters present significant differences between pretreatments (1–5) within one cleaning method and aging group. ^{i,ii}Different letters present significant differences between the applied powder within one pressure, cleaning method, and aging group. ^{I,II}Different letters present significant differences between the aging regime within one pressure, powder, and cleaning group

Table 3 Descriptive statistics (median, min/max) and 95% confidence intervals (CI) for TBS per cleaning method, pretreatment, and aging

	ISO			BUT			CEN		
	Median	Min/max	95% CI	Median	Min/max	95% CI	Median	Min/max	95% CI
Pretreatment	Initial								
AL0.1	$21.2^{bB\beta I}$	11.3/36.6	(16; 27)	$16.2^{b\beta}$	8.0/35.6	(11; 23)	$30.6^{aB\beta\gamma}$	18.6/37.7	(25; 34)
GP0.1	$19.5^{ab\beta}$	1.7/32.7	(12; 24)	$13.9^{bB\gamma}$	2.6/27.4	(8; 20)	$26.0^{a\delta}$	6.2/39.1	(18; 31)
AL0.4	$25.7^{bA\alpha}$	17.3/48.0	(22; 35)	$27.6^{b\alpha}$	13.5/40.6	(21; 34)	$38.0^{aA\alpha}$	31.5/44.2	(34; 40)
GP0.4	$20.7^{*b\alpha\beta}$	10.8/44.1	(16; 30)	$18.6^{bA\beta}$	8.5/38.8	(16; 30)	$33.5^{a\alpha\beta}$	20.1/46.5	(27; 37)
Control	$27.4^{a\alpha II}$	17.6/42.2	(23; 33)	$31.0^{a\alpha II}$	21.5/41.5	(26; 34)	$24.8^{a\gamma\delta II}$	20.3/36.2	(22; 30)
Pretreatment	Artificial aging								
AL0.1	$13.9^{bB\gamma II}$	5.3/25.3	(10; 18)	$17.6^{bB\beta\gamma}$	1.7/36.6	(10; 33)	$26.7^{aB\beta\gamma}$	17.1/38.6	(24; 34)
GP0.1	$18.8^{a\beta\gamma}$	10.2/34.7	(14; 25)	$9.5^{bB\gamma}$	0.5/25.7	(4; 18)	$20.4^{aB\gamma}$	9.8/41.8	(17; 29)
AL0.4	$35.6^{aA\alpha i}$	25.0/43.7	(30; 38)	$35.3^{aA\alpha i}$	23.8/41.0	(29; 37)	$35.7^{aA\alpha i}$	29.5/49.5	(32; 41)
GP0.4	$17.9^{b\beta II}$	8.3/22.7	(14; 20)	$15.9^{bA\beta II}$	10.3/28.6	(13; 22)	$30.3^{aA\beta II}$	19.0/38.8	(25; 33)
Control	$36.8^{a\alpha I}$	23.3/41.9	(31; 39)	$35.0^{a\alpha I}$	29.0/41.0	(31; 37)	$34.8^{a\alpha I}$	26.3/44.2	(30; 38)

*Not normally distributed. [ab]Different lowercase letters present significant differences between the cleaning methods within one pressure, powder, and aging group. [AB]Different uppercase letters present significant differences between the applied pressure within one powder, cleaning method, and aging group. [αβγδ]Different letters present significant differences between pretreatments (1–5) within one cleaning method and aging group. [i,ii]Different letters present significant differences between the applied powder within one pressure, cleaning method, and aging group. [I,II]Different letters present significant differences between the aging regime within one pressure, powder, and cleaning group

groups pretreated with glass pearls ($p < 0.001$–0.026) or pretreated with alumina after thermocycling ($p = 0.004$).

When comparing the different pretreatments 1 to 5, the highest values were observed in groups pretreated with AL0.4 ($p < 0.001$–0.019), except for BUT-cleaned initially tested specimens ($p < 0.017$), while pretreatment with GP0.1 showed the lowest values ($p < 0.001$–0.029).

Regarding the powder, pretreatment with AL0.4 showed higher values than GP0.4 ($p < 0.001$–0.010) in aged groups. Thermocycled groups cleaned with CEN or BUT and pretreated with AL0.1 presented higher values than GP0.1 ($p < 0.001$–0.012). BUT-cleaned initially tested specimens, pretreated with AL0.1, led to higher values than GP0.1 ($p = 0.010$), whereas pretreatment with GP0.4 ($p = 0.019$) led to higher values compared to AL0.4.

Regarding the aging regime, thermocycling increased SBS values ($p < 0.001$–0.029) when cleaned with ISO or CEN and pretreated with alumina. In addition, the control group ($p < 0.001$–0.002) and BUT-cleaned specimens pretreated with AL0.4 ($p < 0.001$) showed higher values after artificial aging.

TBS measurements

Regarding the cleaning methods, CEN showed the highest values ($p < 0.001$–0.024) except for the control group ($p > 0.220$) and aged specimens pretreated with AL0.4 ($p = 0.415$). Cleaning with ISO compared to BUT led to higher values for thermocycled specimens pretreated with GP0.1 ($p < 0.036$). Significant differences between CEN and ISO were detected in groups pretreated with AL0.1 ($p < 0.003$) or GP0.4 ($p < 0.011$) and for initially tested specimens pretreated with AL0.4 ($p = 0.017$). Cleaning with CEN showed higher values compared to BUT for groups pretreated with AL0.1 ($p < 0.001$–0.004), GP0.1 ($p = 0.003$–0.007), or GP0.4 ($p < 0.001$–0.029) and for initially tested specimens pretreated with AL0.4 ($p = 0.007$).

Regarding the pressure level, 0.4 MPa increased TBS values in groups cleaned with ISO and pretreated with alumina ($p < 0.001$–0.034) and in artificially aged groups cleaned with BUT or CEN ($p < 0.001$–0.049). In addition, initially tested, 0.4 MPa led to higher values for BUT-cleaned specimens pretreated with glass pearls ($p = 0.029$) and centrifugated specimens pretreated with alumina ($p = 0.002$).

When comparing the different pretreatments 1 to 5, pretreatment with AL0.4 led to the highest values ($p < 0.001$–0.033), whereas GP0.1 showed the lowest values ($p < 0.001$–0.049) (Fig. 2).

Regarding the powder, after artificial aging, pretreatment with AL0.4 led to higher values than pretreatment with GP0.4 ($p < 0.005$). As for the aging regime, ISO-cleaned specimens pretreated with AL0.1 showed lower values ($p = 0.010$) after artificial aging. The control group presented higher values ($p < 0.001$–0.026) after 10,000 thermal cycles.

SFE and Ra

The highest impact on Ra was exerted by pressure (Ra: $\eta_p^2 = 0.610$, $p < 0.001$) and followed by powder (Ra: $\eta_p^2 = 0.382$,

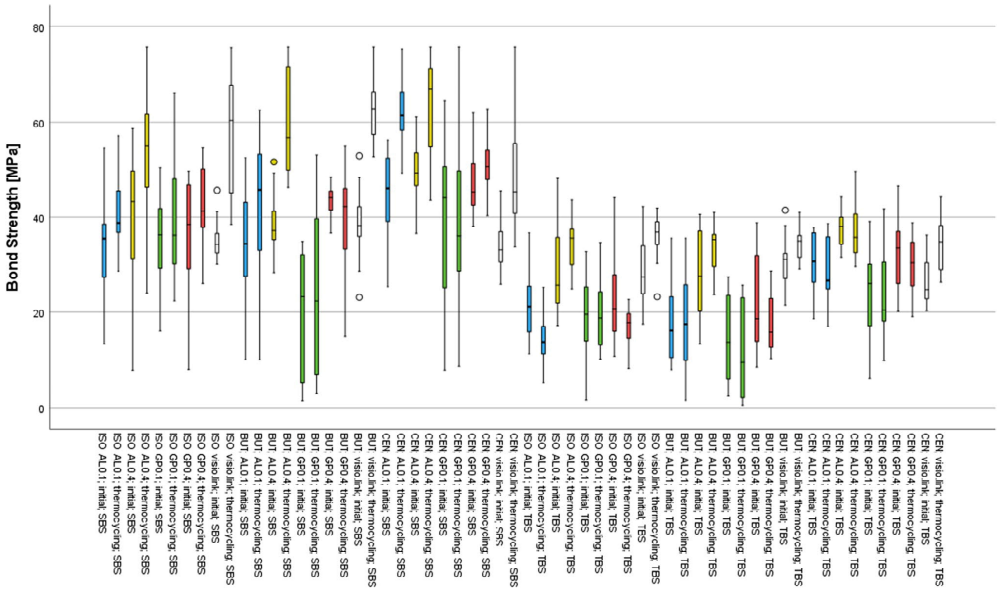


Fig. 2 Bond strength values (MPa) of all tested groups

$p < 0.001$). Air-abrasion with alumina ($p < 0.001$) or pressure at 0.4 MPa ($p < 0.001$) presented higher Ra values compared to specimens pretreated with glass pearls or 0.1 MPa pressure. The highest Ra values were observed by pretreatment with AL0.4 (Table 4).

Fracture types

Digital microscopic images show the four fracture types evaluated (Fig. 3). 95% CI and percentage of investigated fracture types are summarized in Tables 5 and 6.

For SBS, predominantly, cohesive fractures within the 3D-printed resin were observed (40–100%), except for groups cleaned with BUT or CEN and pretreated with GP0.1 where adhesive failures occurred (27–80%). Mostly mixed cohesive fractures were observed in centrifugated specimens pretreated with AL0.4. For TBS, groups showed predominantly cohesive fractures within the 3D-printed resin or cohesive fractures within the luting composite, except for groups pretreated with GP0.1, where adhesive fractures occurred (40–80%).

Discussion

The range of applications of 3D printable resins in dental practice is excelling fast. However, the use of it as fixed dental protheses requires a permanently stable and durable adhesive bond via a luting composite resin. The bond between the luting composite resin and 3D-printed resin might depend

Table 4 Descriptive statistics (median, min/max) and 95% confidence intervals (CI) of measured surface roughness Ra (µm) and SFE on particle-abraded specimens

	Ra			SFE		
Pretreatment	Median	Min/max	95% CI	Median	Min/max	95% CI
AL0.1	1.36[ab]	1.19/1.87	(1.23;1.53)	50.55[a]	45.60/56.10	(48.84;53.21)
GP0.1	1.31[b]	1.02/1.61	(1.21;1.51)	49.80[a]	46.70/54.50	(48.25;52.34)
AL0.4	2.23[a]	2.03/2.59	(2.12;2.38)	49.95[a]	46.30/50.90	(48.26;50.59)
GP0.4	1.52[b]	1.12/2.18	(1.34;1.83)	49.90[a]	43.90/50.80	(46.59;50.42)

*Not normally distributed. [ab]Different letters present significant differences between pretreatment groups (1–4)

Fig. 3 Digital microscope images of adhesive (top left), cohesive within the luting composite resin (top right), cohesive within the 3D-printed resin (bottom left), and mixed cohesive (bottom right) fractures

on the post-processing procedures applied to the resin. A variety of cleaning methods and air-abrasion possibilities exists to be used with 3D-printed resin, all of which have not been researched so far in this context. With the present investigation, some of most promising combinations of these have been considered. Based on the results presented, the proposed hypothesis is rejected in all cases. Overall, among the cleaning methods, the highest SBS and TBS values were observed in combination with centrifugation. Using centrifugation, it was observed that a visibly thin layer of residual monomer covered the surface of the specimen, whereas the other two cleaning methods only left a blank surface and consequently a visibly more effective cleaning [18].

It is assumed that the higher concentration of residual monomers with unreacted double bonds on the resin surface, after post-polymerization in Otoflash G171 under nitrogen atmosphere, which improves the degree of conversion [19], could be exposed again by the mechanical pretreatment of the surface and have a positive influence on the bond between the 3D resin matrix and luting composite. This may be attributed to the unconverted double bonds following copolymerization. Preliminary measurements with cleaned substrates and without mechanical pretreatment already showed insufficient bond strengths initially, especially centrifuging, and non-pretreated substrates achieved bond strength values of zero. An investigation regarding the repair of 3D-printed resin substrates resulted in the recommendation to repair the printed substrates with temporary composite resin without mechanical pretreatment, but the substrates were not chemically or physically cleaned [15].

Studies done on splints created via AM have shown that conditioners containing methyl methacrylate (MMA) play a vital role in the durability of bond strengths [13]. Convincing results were also achieved with MMA in the bonding of CAD/CAM composite resin blocks [22]. Therefore, visio.link has been used as a positive control. visio.link consists of MMA, dimethacrylate, and pentaerythritol acrylate and thus generate an adhesive bond to the resin matrix. Contrary to the assumption that this use might have a positive impact on the bond strength, the results have shown that this control had a negative impact when combined with centrifugation as a cleaning method, whereas centrifugation in combination with any other air-abrasion pretreatment displayed the best results. A possible explanation could be that the 3D resin used contains 40% inorganic glass–ceramic fillers which may hinder the conditioning with MMA and therefore the bonding qualities. This assumption is reinforced via further investigations where resins containing less fillers in combination with the use of MMA conditioning displayed better bonding features [23]. In this investigation, the chemical cleaning methods in combination with MMA displayed higher bond strength. A possible explanation for this could be that these cleaning methods had a higher cleaning capacity than centrifugation since the chemical cleaning releases some of the fillers from the resin matrix [24], with which MMA

Table 5 Percentage of evaluated fracture types and 95% CI for SBS per cleaning method, pretreatment, and aging

Initial		% adhesive and 95% CI	% cohesive within luting composite and 95% CI	% cohesive within 3D resin and 95% CI	% mixed and 95% CI
Cleaning	Pretreatment				
ISO					
	AL0.1	13 (0; 41)	13 (0; 41)	73 (43, 93)*	0 (0; 22)
	GP0.1	13 (0; 41)	20 (3; 49)	67 (37; 89)*	0 (0; 22)
	AL0.4	7 (0; 32)	33 (10; 62)	47 (20; 74)	13 (0; 41)
	GP0.4	20 (3; 49)	13 (0; 41)	67 (37; 89)*	0 (0; 22)
	Control	0 (0; 22)	0 (0; 22)	100 (77; 101)*	0 (0; 22)
BUT					
	AL0.1	20 (3; 49)	13 (0; 41)	60 (31; 84)*	7 (0; 32)
	GP0.1	53 (25; 79)	0 (0; 22)	47 (20; 74)	0 (0; 22)
	AL0.4	0 (0; 22)	0 (0; 22)	73 (43; 93)*	27 (6;56)
	GP0.4	7 (0; 32)	13 (0; 41)	67 (37; 89)*	13 (0; 41)
	Control	0 (0; 22)	0 (0; 22)	100 (77; 101)*	0 (0; 22)
CEN					
	AL0.1	0 (0; 22)	27 (6; 56)	47 (20; 74)	27 (6; 56)
	GP0.1	47 (20; 74)	27 (6; 56)	20 (3; 49)	7 (0; 32)
	AL0.4	0 (0; 22)	33 (10; 62)	40 (15; 68)	27 (6;56)
	GP0.4	0 (0; 22)	0 (0; 22)	73 (43; 93)*	27 (6; 56)
	Control	0 (0; 22)	0 (0; 22)	100 (77; 101)*	0 (0; 22)
Artificial aging		% adhesive and 95% CI	% cohesive within luting composite and 95% CI	% cohesive within 3D resin and 95% CI	% mixed and 95% CI
Cleaning	Pretreatment				
ISO					
	AL0.1	0 (0; 22)	27 (6; 56)	73 (43; 93)*	0 (0; 22)
	GP0.1	0 (0; 22)	40 (15; 68)	60 (31; 84)	0 (0; 22)
	AL0.4	0 (0; 22)	13 (0; 41)	60 (31; 84)*	27 (6;56)
	GP0.4	0 (0; 22)	20 (3; 49)	80 (50; 96)*	0 (0; 22)
	Control	13 (0; 41)	13 (0; 41)	73 (43; 93)*	0 (0; 22)
BUT					
	AL0.1	20 (3; 49)	33 (10; 62)	47 (20; 74)	0 (0; 22)
	GP0.1	47 (20; 74)	13 (0; 41)	40 (15; 68)	0 (0; 22)
	AL0.4	0 (0; 22)	27 (6; 56)	53 (25; 79)	20 (3; 49)
	GP0.4	13 (0; 41)	20 (3; 49)	67 (37; 89)*	0 (0; 22)
	Control	0 (0; 22)	73 (43; 93)*	27 (6; 56)	0 (0; 22)
CEN					
	AL0.1	0 (0; 22)	33 (10; 62)	40 (15; 68)	27 (6; 56)
	GP0.1	27 (6; 56)	13 (0; 41)	60 (31; 84)*	0 (0; 22)
	AL0.4	0 (0; 22)	7 (0; 32)	40 (15; 68)	53 (25; 79)
	GP0.4	7 (0; 32)	40 (15; 68)	47 (20; 74)	7 (0; 32)
	Control	0 (0; 22)	40 (15; 68)	60 (31; 84)	0 (0; 22)

can copolymerize, without fillers hindering. In particular when pretreated with glass pearls or low pressure, visio.link increases the bond strength, as higher pressure or alumina particles could expose the fillers again, which would impair the bond with visio.link. Regarding the fracture types, for conditioning with visio.link, mostly cohesive fractures within the 3D resin occurred, which indicates that the bond strength is higher than the flexural strength of the printed material. Pretreatment with alumina predominately produced better bonding features than a pretreatment with glass particles. When comparing the two pretreatment materials with regard to the shape, alumina, in unstructured

Table 6 Percentage of evaluated fracture types and 95% CI for TBS per cleaning method, pretreatment, and aging

Initial		% adhesive and 95% CI	% cohesive within luting composite and 95% CI	% cohesive within 3D resin and 95% CI	% mixed and 95% CI
Cleaning	Pretreatment				
ISO					
	AL0.1	40 (15; 68)	13 (0; 41)	40 (15; 68)	7 (0; 32)
	GP0.1	67 (37; 89) *	0 (0; 22)	33 (10; 62)	0 (0; 22)
	AL0.4	33 (10; 62)	13 (0; 41)	53 (25; 79)	0 (0; 22)
	GP0.4	40 (15; 68)	20 (3; 49)	40 (15; 68)	0 (0; 22)
	Control	0 (0; 22)	33 (10; 62)	67 (37; 89)*	0 (0; 22)
BUT					
	AL0.1	67 (37; 89) *	0 (0; 22)	33 (10; 62)	0 (0; 22)
	GP0.1	67 (37; 89) *	0 (0; 22)	33 (10; 62)	0 (0; 22)
	AL0.4	13 (0; 41)	20 (3; 49)	60 (31; 84)*	7 (0; 32)
	GP0.4	40 (15; 68)	20 (3; 49)	40 (15; 68)	0 (0; 22)
	Control	7 (0; 32)	27 (6; 56)	67 (37; 89)	0 (0; 22)
CEN					
	AL0.1	0 (0; 22)	20 (3; 49)	73 (43; 93)*	7 (0; 32)
	GP0.1	53 (25; 79)	20 (3; 49)	27 (6; 56)	0 (0; 22)
	AL0.4	0 (0; 22)	73 (43; 93)*	27 (6; 56)	7 (0; 32)
	GP0.4	7 (0; 32)	53 (25; 79)	40 (15; 68)	0 (0; 22)
	Control	0 (0; 22)	7 (0; 32)	93 (67; 100)*	0 (0; 22)
Artificial aging		% adhesive and 95% CI	% cohesive within luting composite and 95% CI	% cohesive within 3D resin and 95% CI	% mixed and 95% CI
Cleaning	Pretreatment				
ISO					
	AL0.1	73 (43; 93) *	0 (0; 22)	27 (6; 56)	0 (0; 22)
	GP0.1	40 (15; 68)	7 (0; 32)	53 (25; 79)	0 (0; 22)
	AL0.4	0 (0; 22)	40 (15; 68)	60 (31; 84)	0 (0; 22)
	GP0.4	47 (20; 74)	0 (0; 22)	53 (25; 79)	0 (0; 22)
	Control	13 (0; 41)	80 (50; 96)*	7 (0; 32)	0 (0; 22)
BUT					
	AL0.1	40 (15; 68)	13 (0; 41)	47 (20; 74)	0 (0; 22)
	GP0.1	73 (43; 93) *	0 (0; 22)	27 (6; 56)	0 (0; 22)
	AL0.4	0 (0; 22)	53 (25; 79)	47 (20; 74)	0 (0; 22)
	GP0.4	67 (37; 89) *	0 (0; 22)	33 (10; 62)	0 (0; 22)
	Control	0 (0; 22)	80 (50; 96)*	20 (3; 49)	0 (0; 22)
CEN					
	AL0.1	13 (0; 41)	13 (0; 41)	73 (43; 93)*	0 (0; 22)
	GP0.1	80 (50; 96) *	7 (0; 32)	13 (0; 41)	0 (0; 22)
	AL0.4	0 (0; 22)	40 (15; 68)	60 (31; 84)	0 (0; 22)
	GP0.4	0 (0; 22)	33 (10; 62)	67 (37; 89)*	0 (0; 22)
	Control	7 (0; 32)	67 (37; 89)*	27 (6; 56)	0 (0; 22)

shape of particles, displays a rougher surface than glass pearls, which are microspheres. This could lead to a better penetration of the resin which in turn could lead to a better bonding with the luting composite due to an improved interlocking [20, 23, 25]. This possible explanation is also supported by the different pressures used where higher pressures displayed better bonding features presumably due to the higher pressures resulting also in a deeper penetration of the resin surface. However, it is important to note that high pressure can damage the surface, resulting in the falling out of fillers and leading clinically to a possibly poorer fit of the restoration [26].

Thermocycling has established itself as suitable for simulating temperature changes in the oral cavity [27, 28]. In this study, half of the bond strength measurements were performed after thermal aging of 10,000 cycles between 5 and 55 °C. Ten thousand cycles are equivalent to about 1 year of use [27], but thermocycling is only an approximation for certain intraoral situations to simulate, e.g., hot food or ice cream. In this study, different results were found after aging on the SBS and TBS values. Increasing SBS values after thermal aging were reported in the previous investigation [29]. Lower values after artificial aging may be caused by mechanical stress in the bonding interface, caused by volumetric changes [30]. An increased bond strength can be explained by the upper temperature which can promote post-polymerization of the luting area. In addition, the absorption of water during thermal cycling causes 3D resin material to expand which may affect the anchorage of the luting composite resin.

In general, several bond strength measurement methods can be considered when evaluating adhesive properties. Among others, these can be macro-shear bond and macro-tensile bond strength tests [31] as well as micro-shear and micro-tensile tests. Micro-tests provide higher bond strength values than their equivalent macro-tests [32, 33] and work well for evaluating the dentin bond [34]. There are investigations questioning the clinical validity of bond strength in vitro tests [32, 35, 36]. However, due to their simplicity and being low technique-sensitive, the more commonly used macro-tests were applied [37, 38]. For macro-SBS and macro-TBS measurements, this study used the same specimen geometry and defined diameter of acrylic cylinders and thus an identical bonding area but different crosshead speeds. Within the limits suggested by ISO/TS 11,405, the crosshead speed does not seem to have any influence on the bond strength values [39]. Nevertheless, higher bond strength values were observed by SBS measurements than by TBS measurements; however, SBS (19–63 MPa) and TBS (12–38 MPa) showed similar tendencies. This was also reported earlier [40]. However, the measured values showed similar trends in the groups studied and can be compared with each other. It can be assumed that the differences of the qualitative test methods in the mean values are caused by the different types of force application. In the tensile test, the stresses at the bonding interface are much more homogeneous than those in the shear test, so that the maximum principal stress values are much closer to the nominal strength [39].

Another limitation of the study at hand is the fact that no a priori power analysis was performed to determine the sample size. The groups for post hoc power analysis were selected within isopropanol, as this is the most used cleaning procedure for 3D-printed objects and with the smallest dispersion. The post hoc power analysis comparing the results of aged specimens cleaned with ISO and pretreated at 0.1 MPa with glass pearls and the control group with VL within TBS measurements yielded a power of a two-sided two-sample t test of 100%, with a sample size of 15 specimens in each group, an observed effect of 16.64 MPa, and a pooled standard deviation of 7.34. However, it must be taken into account that for a few groups, especially the comparisons between the control group and the group pretreated with AL0.4 MPa, a smaller effect was observed, leading to a reduced power of the statistical analysis.

As new materials for dental restorations are launched every day, the optimal combination of substrates and bonding procedures is constantly evolving. In the present study, it was observed that the interaction between cleaning and pretreatment has an impact on the bond strength. Material combinations that passed the in vitro tests should be further investigated in long-term clinical trials.

Conclusions

Within the limitations of the present in vitro study, the following conclusions could be drawn:

- The test methods, i.e., SBS and TBS, had the highest impact on bond strength values, whereby SBS overall resulted in higher values than TBS.
- Within the pretreatment groups, centrifuged specimens showed higher bond strength compared to the chemical cleaning methods investigated.
- The pressure has a greater influence on the bond strength than the type of air-abrasion powder. The pretreatment with GP0.1 showed the lowest bond strengths and the highest number of adhesive fractures.
- The pretreatment with AL0.4 seemed to have the highest bond strengths among the tested groups. Although SFE was not affected, air-abrasion with AL0.4 showed the highest Ra values.
- The control group presented equally high bond strengths as the pretreatment with AL0.4. The very high number of cohesive fractures in the 3D-printed material highlights the high bond strength.
- Artificial aging positively influenced the bond strength in almost all tested groups.

Acknowledgements The authors would like to thank Pro3Dure, HPdent, and Kuraray Noritake for supporting this study with material.

Author contribution Valerie Lankes performed the experiments, prepared figures and tables, and wrote the main manuscript text. Marcel Reymus provided the infrastructure and approved the final manuscript. Anja Liebermann wrote manuscript text and approved the final manuscript. Bogna Stawarczyk had the idea, performed statistical analysis, wrote the manuscript, and approved the final manuscript.

Funding Open Access funding enabled and organized by Projekt DEAL.

Data Availability All data generated or analysed during this study are included in this published article.

Declarations

Competing interests The authors declare no competing interests.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

Consent to participate For this type of study, formal consent was not required.

Conflict of interest The authors declare no competing interests.

References

1. Giordano R (2006) Materials for chairside CAD/CAM-produced restorations. J Am Dent Assoc 137:14s–21s. https://doi.org/10.14219/jada.archive.2006.0397
2. Schweiger J, Edelhoff D and Güth JF (2021) 3D printing in digital prosthetic dentistry: an overview of recent developments in additive manufacturing. J Clin Med 10. https://doi.org/10.3390/jcm10092010
3. Sampaio CS, Niemann KD, Schweitzer DD, Hirata R, Atria PJ (2021) Microcomputed tomography evaluation of cement film thickness of veneers and crowns made with conventional and 3D printed provisional materials. J Esthet Restor Dent 33:487–495. https://doi.org/10.1111/jerd.12651
4. Peng CC, Chung KH, Yau HT, Ramos V Jr (2020) Assessment of the internal fit and marginal integrity of interim crowns made by different manufacturing methods. J Prosthet Dent 123:514–522. https://doi.org/10.1016/j.prosdent.2019.02.024
5. Reeponmaha T, Angwaravong O, Angwarawong T (2020) Comparison of fracture strength after thermo-mechanical aging between provisional crowns made with CAD/CAM and conventional method. J Adv Prosthodont 12:218–224. https://doi.org/10.4047/jap.2020.12.4.218
6. Anthony T, MaryCatherine M, Ana PF, Despoina B, Avathamsa A, Carmem SP, Jack LF, Luiz EB (2018) 3D printed versus conventionally cured provisional crown and bridge dental materials. Dent Mater 34:192–200. https://doi.org/10.1016/j.dental.2017.10.003
7. Zimmermann M, Ender A, Egli G, Ozcan M, Mehl A (2019) Fracture load of CAD/CAM-fabricated and 3D-printed composite crowns as a function of material thickness. Clin Oral Investig 23:2777–2784. https://doi.org/10.1007/s00784-018-2717-2
8. Lad PP, Kamath M, Tarale K, Kusugal PB (2014) Practical clinical considerations of luting cements: a review. Journal of international oral health : JIOH 6:116 120
9. Elbahie E, Beitzel D, Mutluay MM, Majd H, Yahyazadehfar M, Arola D (2018) Durability of adhesive bonds to tooth structure involving the DEJ. J Mech Behav Biomed Mater 77:557–565. https://doi.org/10.1016/j.jmbbm.2017.10.001
10. Kern M (2015) Bonding to oxide ceramics—laboratory testing versus clinical outcome. Dent Mater 31:8–14. https://doi.org/10.1016/j.dental.2014.06.007
11. Nejat AH, Lee J, Shah S, Lin CP, Kulkarni P, Chavali R, Lawson NC (2018) Retention of CAD/CAM resin composite crowns following different bonding protocols. Am J Dent 31:97–102
12. Özcan M, Bernasconi M (2015) Adhesion to zirconia used for dental restorations: a systematic review and meta-analysis. J Adhes Dent 17:7–26. https://doi.org/10.3290/j.jad.a33525
13. Kuscu E, Klink A, Spintzyk S, Kraemer Fernandez P, Huettig F (2021) Bonding interface and repairability of 3D-printed intraoral splints: shear bond strength to current polymers, with and without ageing. Materials 14:3935. https://doi.org/10.3390/ma14143935
14. Nobuaki A, Keiichi Y, Takashi S (2015) Effects of air abrasion with alumina or glass beads on surface characteristics of CAD/CAM composite materials and the bond strength of resin cements. J Appl Oral Sci 23:629–636. https://doi.org/10.1590/1678-775720150261
15. Lim NK, Shin SY (2020) Bonding of conventional provisional resin to 3D printed resin: the role of surface treatments and type of repair resins. J Adv Prosthodont 12:322–328. https://doi.org/10.4047/jap.2020.12.5.322
16. Holmer L, Othman A, Lührs AK, von See C (2019) Comparison of the shear bond strength of 3D printed temporary bridges materials, on different types of resin cements and surface treatment. J Clin Exp Dent 11:e367–e372. https://doi.org/10.4317/jced.55617
17. Taormina G, Sciancalepore C, Messori M, Bondioli F (2018) 3D printing processes for photocurable polymeric materials: technologies, materials, and future trends. J App Biomater Funct Mater 16:151–160. https://doi.org/10.1177/2280800018764770
18. Mayer J, Reymus M, Wiedenmann F, Edelhoff D, Hickel R and Stawarczyk B (2021) Temporary 3D printed fixed dental prosthesis materials: impact of post printing cleaning methods on degree of conversion as well as surface and mechanical properties. Int J Prosthodont. https://doi.org/10.11607/ijp.7048
19. Reymus M, Lümkemann N, Stawarczyk B (2019) 3D printed material for temporary restorations: impact of print layer thickness and post-curing method on degree of conversion. Int J Comput Dent 22:231–237
20. Bähr N, Keul C, Edelhoff D, Eichberger M, Roos M, Gernet W, Stawarczyk B (2013) Effect of different adhesives combined with two resin composite cements on shear bond strength to polymeric CAD/CAM materials. Dent Mater J 32:492–501. https://doi.org/10.4012/dmj.2012-329
21. Keul C, Kohen D, Eichberger M, Roos M, Gernet W, Stawarczyk B (2015) The effect of different pretreatment methods of PMMA-based crowns on the long-term tensile bond strength to dentin abutments. Clin Oral Investig 19:35–43. https://doi.org/10.1007/s00784-014-1215-4
22. Reymus M, Roos M, Eichberger M, Edelhoff D, Hickel R, Stawarczyk B (2019) Bonding to new CAD/CAM resin composites: influence of air abrasion and conditioning agents as pretreatment strategy. Clin Oral Investig 23:529–538. https://doi.org/10.1007/s00784-018-2461-7
23. Keul C, Martin A, Wimmer T, Roos M, Gernet W, Stawarczyk B (2013) Tensile bond strength of PMMA- and composite-based CAD/CAM materials to luting cements after different conditioning methods. Int J Adhes Adhes 46:122–127. https://doi.org/10.1016/j.ijadhadh.2013.06.003

24. Han L, Okamoto A, Fukushima M, Okiji T (2008) Evaluation of flowable resin composite surfaces eroded by acidic and alcoholic drinks. Dent Mater J 27:455–465. https://doi.org/10.4012/dmj.27.455
25. Stawarczyk B, Basler T, Ender A, Roos M, Ozcan M, Hämmerle C (2012) Effect of surface conditioning with airborne-particle abrasion on the tensile strength of polymeric CAD/CAM crowns luted with self-adhesive and conventional resin cements. J Prosthet Dent 107:94–101. https://doi.org/10.1016/S0022-3913(12)60031-6
26. Yoshihara K, Nagaoka N, Maruo Y, Nishigawa G, Irie M, Yoshida Y, Van Meerbeek B (2017) Sandblasting may damage the surface of composite CAD-CAM blocks. Dent Mater 33:e124–e135. https://doi.org/10.1016/j.dental.2016.12.003
27. Gale MS, Darvell BW (1999) Thermal cycling procedures for laboratory testing of dental restorations. J Dent 27:89–99. https://doi.org/10.1016/S0300-5712(98)00037-2
28. Bayne SC (2012) Correlation of clinical performance with "in vitro tests" of restorative dental materials that use polymer-based matrices. Dent Mater 28:52–71. https://doi.org/10.1016/j.dental.2011.08.594
29. Piwowarczyk A, Lauer HC, Sorensen JA (2004) In vitro shear bond strength of cementing agents to fixed prosthodontic restorative materials. J Prosthet Dent 92:265–273. https://doi.org/10.1016/j.prosdent.2004.06.027
30. Torstenson B, Brännström M (1988) Contraction gap under composite resin restorations: effect of hygroscopic expansion and thermal stress. Oper Dent 13:24–31
31. Della Bona A, van Noort R (1995) Shear vs. tensile bond strength of resin composite bonded to ceramic. J Dent Res 74:1591–1596. https://doi.org/10.1177/00220345950740091401
32. Schreier SS, Cesar PF, Swain MV (2010) Direct comparison of the bond strength results of the different test methods: a critical literature review. Dent Mater 26:e78–e93. https://doi.org/10.1016/j.dental.2009.12.002
33. Placido E, Meira JB, Lima RG, Muench A, de Souza RM, Ballester RY (2007) Shear versus micro-shear bond strength test: a finite element stress analysis. Dent Mater 23:1086–1092. https://doi.org/10.1016/j.dental.2006.10.002
34. Sano H, Shono T, Sonoda H, Takatsu T, Ciucchi B, Carvalho R, Pashley DH (1994) Relationship between surface area for adhesion and tensile bond strength–evaluation of a micro-tensile bond test. Dent Mater 10:236–240. https://doi.org/10.1016/0109-5641(94)90067-1
35. Braga RR, Meira JB, Boaro LC, Xavier TA (2010) Adhesion to tooth structure: a critical review of "macro" test methods. Dent Mater 26:e38-49. https://doi.org/10.1016/j.dental.2009.11.150
36. Sirisha K, Rambabu T, Ravishankar Y, Ravikumar P (2014) Validity of bond strength tests: a critical review-part II. J Conserv Dent 17:420–426. https://doi.org/10.4103/0972-0707.139823
37. Eren D, Bektaş Ö, Siso SH (2013) Three different adhesive systems; three different bond strength test methods. Acta Odontol Scand 71:978–983. https://doi.org/10.3109/00016357.2012.741696
38. Armstrong S, Geraldeli S, Maia R, Raposo LH, Soares CJ, Yamagawa J (2010) Adhesion to tooth structure: a critical review of "micro" bond strength test methods. Dent Mater 26:e50-62. https://doi.org/10.1016/j.dental.2009.11.155
39. Sirisha K, Rambabu T, Shankar YR, Ravikumar P (2014) Validity of bond strength tests: a critical review: part I. J Conserv Dent 17:305–311. https://doi.org/10.4103/0972-0707.136340
40. Leloup G, D'Hoore W, Bouter D, Degrange M, Vreven J (2001) Meta-analytical review of factors involved in dentin adherence. J Dent Res 80:1605–1614. https://doi.org/10.1177/00220345010800070301

Veröffentlichung II

materials

MDPI

Article

Three-Dimensional Printed Resin: Impact of Different Cleaning Protocols on Degree of Conversion and Tensile Bond Strength to a Composite Resin Using Various Adhesive Systems

Valerie Lankes [1,*], Marcel Reymus [2], Felicitas Mayinger [1], Andrea Coldea [1], Anja Liebermann [3], Moritz Hoffmann [1] and Bogna Stawarczyk [4]

[1] Department of Prosthetic Dentistry, University Hospital, LMU Munich, 80336 Munich, Germany; felicitas.mayinger@med.uni-muenchen.de (F.M.); andrea.coldea@med.uni-muenchen.de (A.C.); moritz.hoffmann@med.uni-muenchen.de (M.H.)
[2] Department of Conservative Dentistry and Peridontology, University Hospital, LMU Munich, 80336 Munich, Germany; marcel.reymus@med.uni-muenchen.de
[3] Head of the Department of Prosthetic Dentistry, Faculty of Medicine and University Hospital Cologne, 50931 Cologne, Germany; anja.lieberman@uk-koeln.de
[4] Scientific Head Dental Material Unit, Department of Prosthetic Dentistry, University Hospital, LMU Munich, 80336 Munich, Germany; bogna.stawarczyk@med.uni-muenchen.de
* Correspondence: v.lankes@med.uni-muenchen.de; Tel.: +49-(0)-89-4400-59544; Fax: +49-(0)-89-4400-59502

Abstract: The present investigation tested the effect of cleaning methods and adhesives on the tensile bond strength (TBS) of a resin-based composite luted to a temporary 3D printed resin. Substrates (n= 360) were printed using a Rapidshape D20II and cleaned with a butyldiglycol-based solution, isopropanol, or by centrifugation. Specimens were air-abraded with Al_2O_3 (mean particle size 50 µm) at 0.1 MPa followed by pretreatment (n = 30/subgroup) with: (1) Clearfil Ceramic Primer (CCP); (2) Clearfil Universal Bond (CUB); (3) Scotchbond Universal Plus (SUP) or 4. Visio.link (VL) and luted to PanaviaV5. TBS (n = 15/subgroup) was measured initially (24 h at 37 °C water) or after thermal cycling (10,000×, 5/55 °C). The degree of conversion (DC) for each cleaning method was determined prior and after air-abrasion. Univariate ANOVA followed by post-hoc Scheffé test was computed ($p < 0.05$). Using Ciba-Geigy tables and chi-square, failure types were analyzed. The DC values were >85% after all cleaning methods, with centrifugation showing the lowest. CCP pretreatment exhibited the lowest TBS values, with predominantly adhesive failures. The combination of CCP and centrifugation increased the TBS values ($p < 0.001$) compared to the chemical cleaning. CUB, SUP, and VL, regardless of cleaning, can increase the bond strength between the 3D printed resin and the conventional luting resin.

Keywords: cleaning; 3D temporary resin; degree of conversion; adhesives; tensile bond strength; failure types

Citation: Lankes, V.; Reymus, M.; Mayinger, F.; Coldea, A.; Liebermann, A.; Hoffmann, M.; Stawarczyk, B. Three-Dimensional Printed Resin: Impact of Different Cleaning Protocols on Degree of Conversion and Tensile Bond Strength to a Composite Resin Using Various Adhesive Systems. *Materials* **2023**, *16*, 3580. https://doi.org/10.3390/ma16093580

Academic Editor: Jeremie Soulestin

Received: 6 April 2023
Revised: 3 May 2023
Accepted: 5 May 2023
Published: 7 May 2023

1. Introduction

In the last decade, the application of tooth-colored resin-based materials manufactured with CAD (computer-aided design)/CAM (computer-aided manufacturing) technology has increased in all fields of dentistry. Additive manufacturing (AM) supports maxillofacial surgery with surgical templates, orthodontics benefits from individualized brackets, students practice root canals treatments on printed teeth, and dental prosthetics applies printed bite splints and dentures [1]. The development of ceramic-filled hybrid materials enables the use of printed restorations as permanent fixed restorations, as they contain varying amounts of inorganic fillers (e.g., glass–ceramic fillers) in addition to a resin matrix and initiators [2]. Within AM, the most commonly used manufacturing technique is VAT polymerization, in which the liquid, light-curing resin is added to a vat of the printer and cured by a controlled supply of ultraviolet light, and, layer by layer, the object is built

up on the building platform [3], requiring a subsequent cleaning of the printed objects. Chemical cleaning, especially with isopropanol, is the most used method, as such liquids are easy to obtain. Some companies have addressed the purification of 3D printed objects and launched specifically developed solutions (e.g., InovaPrint wash). Physical cleaning by using centrifugal force has shown an additional positive influence on the material quality of the printed objects [4]. For the long-term use of dental materials in the oral cavity, their biocompatibility is of utmost importance. The biocompatibility of resin-based materials essentially depends on the degree of conversion of the carbon double bonds, since non-polymerized residual monomers in the resin structure present themselves as leachable components and can go into solution in liquid media [5]. Leachable substances can trigger systemic and local immune reactions in the organism, as well as induce allergies in dentists and dental technicians [6]. In printed restorations, there are several parameters that influence the degree of conversion of carbon–carbon double bonds [7]. It has already been shown that the polymerization device Otoflash G171, which polymerizes under oxygen-free conditions using a nitrogen atmosphere, has a higher carbon double bond rate than comparable devices [8,9]. To date, the degree of conversion after surface finishing has not been investigated, although this is clinically important as the restoration is routinely finished by polishing or grinding.

For the successful and long-term luting of additively manufactured resin-based restorations, the bond strength of the bonding area can be considerably increased by mechanical pretreatment with aluminum oxide (Al_2O_3) particles, as the surface area is enlarged, and micromechanical retention promotes the wetting of the luting composite [10]. Additional conditioning with adhesive systems enables the chemical bond to the organic resin matrix in both the object and the luting composite. Progress in the field of the different adhesive systems has allowed the successful implementation of universal adhesives, which are particularly easy and variable to use. Investigations on the bonding properties of universal adhesives employed using self-etch mode or with an additional phosphoric acid etching on enamel and dentin have been carried out [11,12]. Functional acid-modified methylmethacrylates, such as 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP), and silanes provide a chemical bond to zirconia [13], glass-ceramics [14], metals [15], and composites [16]. The chemical structure of the adhesives is equally important [17], as the increased cross-linking and the formation of hydrogen bonds increase its stability and thus its bonding performance [18,19].

New materials such as 3D printable resins are increasingly being introduced to the dental market by manufacturers and the indications are steadily increasing. However, especially when used as fixed prostheses, adhesive luting is a decisive factor for long-term success [20,21]. To the best of the authors' knowledge, the influence of the cleaning protocol of the printed objects in combination with the application of differently chemically structured adhesive systems and an additional artificial aging on the bond strength between a 3D printed resin and a luting composite resin has not yet been investigated. Therefore, the aim of this investigation was to examine the degree of conversion (DC) and the tensile bond strength (TBS) between a 3D printed resin and a conventional resin-based luting composite following various cleaning procedures and the application of different adhesive systems after varying aging regimens. The first null hypothesis stated that neither the choice of cleaning protocol, nor the use of different adhesive systems, nor the aging regimen show an impact on TBS. The second null hypothesis was that the different cleaning procedures show no impact on the degree of conversion before and after air abrasion.

2. Materials and Methods

Square specimens ($4 \times 15 \times 15$ mm^3) were fabricated using a CAD software (Autodesk Netfabb Basic 2022.0, San Rafael, CA, USA) and exported as STL file. A total of 360 specimens (printo dent Generative Resin GR-17.1 temporary lt, Pro3dure medical, Iserlohn, Germany) were aligned vertically to the printer building platform and additively manufactured with a layer thickness of 50 µm using a 3D printer with digital light processing (DLP)

technology (D20 II, Rapid Shape, Heimsheim, Germany). An overview of the study design is shown in Figure 1.

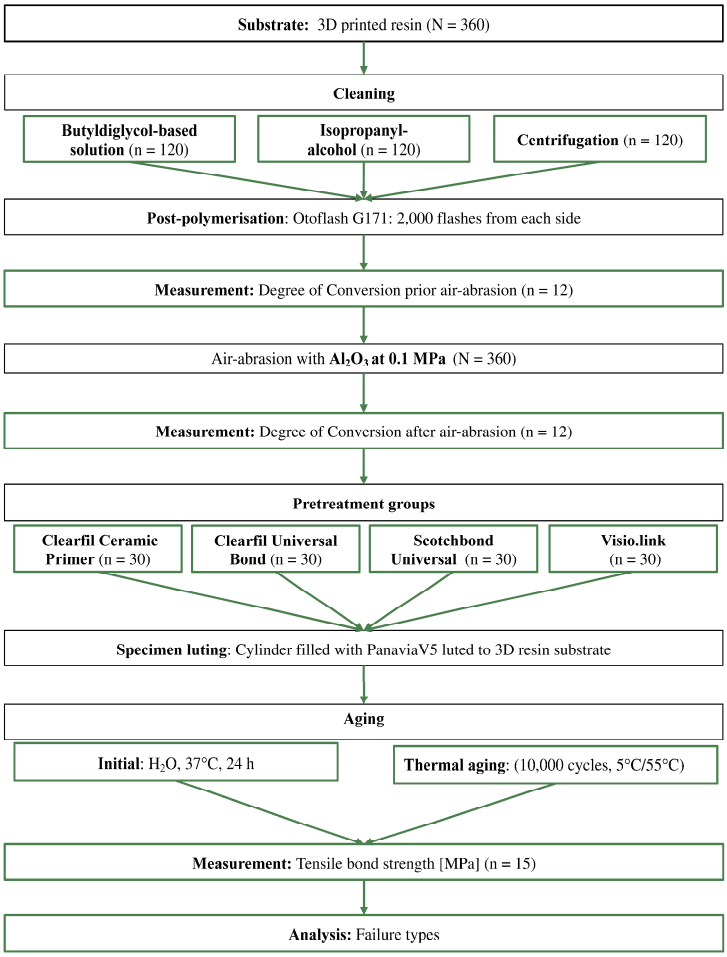


Figure 1. Study design.

Directly after 3D printing, the specimens were cleaned to remove remaining unpolymerized monomers, either chemically with butyldiglycol-based solution (BUT) or 100% isopropanol (ISO), or mechanically by centrifugation (CEN). Specimens (n = 120) cleaned with BUT (InovaPrint wash, hpdent GmbH; Gottmadingen, Germany) were ultrasonically (Sonorex Super RK 102H, Bandelin, Berlin, Germany) cleaned for 2 min according to manufacturer's recommendation, whereas specimens (n = 120) cleaned with ISO (SAV LP, Flintsbach Germany) were activated for 4 min in an ultrasonic bath. Specimens were dried using compressed air. For the mechanical cleaning method, the specimens (n = 120) were individually positioned into centrifugal tubes (Polypropylene Conial Tube, BD Falcon, Franklin Lakes, NJ, USA) and centrifugated at 600 G for 10 min (Allegra X-15R, Beckmann Coulter GmbH, Krefeld, Germany). The specimens were then post-cured (Otoflash G171, NK Optik, Baierbrunn, Germany) from both sides with 2000 light flashes in the wave-

length range of 280–580 nm under a nitrogen atmosphere to prevent oxygen inhibition on the surfaces.

After storage in distilled water (37 °C) for 24 h in an incubator (HeraCell 150, Heraeus, Hanau, Germany) the bonding areas of the specimens were air-abraded (basis Quattro IS, Renfert GmbH, Hilzingen, Germany) with Al_2O_3 (Orbis Dental Handelsgesellschaft mbH, Münster, Germany) with a mean particle size of 50 µm at 0.1 MPa pressure (10 s, 45°, 10 mm distance) followed by cleaning for 3 min in an ultrasonic bath.

Thereafter, the specimens were randomly divided into groups with pretreatment of the bonding area as follows (n = 30):

1. Clearfil Ceramic Primer Plus [CCP] (Kuraray Noritake, Okayama, Japan):
   The primer was applied in a thin layer with a microbrush and waited for 20 s.
2. Clearfil Universal Bond Quick [CUP] (Kuraray Noritake Okayama, Japan):
   The universal adhesive was mixed 1:1 with Clearfil DC-Activator (Kuraray Noritake Okayama, Japan), then applied with a microbrush, and subsequently air dried for 5 s.
3. Scotchbond Universal Plus [SUP] (3M, Saint Paul, MN, USA):
   The universal adhesive was applied, massaged for 20 s with a microbrush, and then air dried for 5 s.
4. Visio.link [VL] (Bredent, Senden, Germany):
   The resin primer was applied with a microbrush, then light cured for 90 s with a manufacturer-recommended light-curing unit (bre.Lux Power unit, bredent, Senden, Germany).

The compositions of the used materials are presented in Table 1. Acrylic cylinders (SD Mechatronik, Feldkrichen-Westerham, Germany) with an inner diameter of 2.9 mm were filled with dual adhesive-curing resin-based composite (Panavia V5, Kuraray Noritake, Okayama, Japan) via automix syringe, placed on the bonding area, and light-cured (Elipar Deep Cure-S, 3M, Seefeld, Germany) at room temperature (23 °C, 60% humidity) for a total of 40 s (10 s from the three different sides and 10 s from the top).

Table 1. Summary of the adhesive and luting materials, compositions, LOT-Numbers, and expiration.

	Material	Abbreviation	Composition	Manufacturer	LOT	Expiry
Conditioning method	Clearfil Ceramic Primer Plus	CCP	Ethanol, 3-Methacryloyloxypropyltrimethoxysilan, 10-MDP [a]	Kuraray Noritake Okayama, Japan	5D0063	29.2.24
	Clearfil Universal Bond Quick	CUB	Bisphenol A diglycidylmethacrylat, ethanol, 2-hydroxyethylmethacrylat, 10-MDP, hydrophilic amide monomers, colloidal silica, silane, water [b]	Kuraray Noritake Okayama, Japan	4N0301	30.9.24
	Scotchbond Universal Plus	SUP	MDP, Vitrebond-Copolymer, silica fillers, ethanol, water, initiators, amino functional silane, dimethacrylate (bisphenol A-free), pH = 2.7 [c]	3M, Seefeld, Germany	7172629	30.4.24
	Visio.link	VL	MMA, 2-Propenoic acid, bisphenol-A diglycidyl-methacrylate, diphenyl(2,4,6-trimethylbenzyl) phosphinoxidec [d]	Bredent, Senden, Germany	193211	31.8.24
Resin-based composite	Panavia V5		Bisphenol-A-diglycidylmethacrylat, triethylenegycol-dimethacrylat, titanoxide, colloidal silica, silanised barium glass filler, silanised fluoroaluminosilicate, alumina filler, hydrophobic aromatic dimethylacrylate, aliphatic dimethylacrylate, initiatiors, pigments [e]	Kuraray Noritake Okayama, Japan	760165	30.4.24
3D printable resin	printo dent Generative Resin GR-17.1 temporary lt		Methacrylic resins < 60% (mainly Bisphenol-A ethoxylate dimethacrylate), metal oxides, photoinitiators < 2% (mainly TiO_2, TPO), UV inhibitors < 0.1%, inorganic glass fillers 40% [f]	Pro3dure medical, Iserlohn, Germany	03082017	03.8.23

[a] Kuraray Noritake, Clearfil Ceramic Primer Plus, safety data sheet, 2015, status 23 October 2022. [b] Kuraray Noritake, Clearfil Universal Bond Quick, safety data sheet, 2021, status 23 October 2022. [c] 3M, Scotchbond Universal Plus Adhesive, Technical Product Profile, 2021, status 23 October 2022. [d] bredent, Visio.Link, safety data sheet, 2020, status 23 October 2022. [e] Kuraray Noritake, Panavia V5, safety data sheet, 2021, status 23 October 2022. [f] Pro3dure medical manufacturer information, status 05 April 2022.

All specimens were stored for 24 h in distilled water (37 °C). Half of the specimens were then thermocycled (SD Mechatronik, Feldkirchen-Westerham, Germany) with 10,000 cycles between 5 and 55 °C, each with a drip-off time of 5 s, remaining in each bath for 20 s.

TBS measurements (Figure 2) were performed at room temperature (22 °C, 60% humidity) using a universal testing machine (Zwick 1445, Zwick, Ulm, Germany). The bonded acrylic cylinders were passively fixed into a holding device and pulled with a crosshead speed of 5 mm/min until debonding occurred. The force was applied perpendicular to the bonding area.

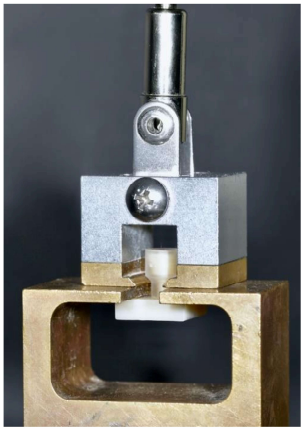


Figure 2. TBS method.

TBS was determined according to the following equation, where s is the TBS [MPa], F is the load at fracture [N], and A is the bonding area [mm^2]:

$$s = \frac{F}{A}$$

The failure types were analyzed under a digital microscope with a 30× magnification (VHX-970F, Keyence, Osaka, Japan) and classified as follows: (i) adhesive between the substrate and the luting composite, (ii) cohesive within the luting composite, and (iii) cohesive within the 3D printed resin (Figure 3).

Figure 3. Overview of failure types: Adhesive between the substrate and the luting composite (**left**), cohesive within the luting composite (**middle**), and cohesive within the 3D printed resin (**right**).

The degree of conversion (DC) of the three differently cleaned groups were determined using Raman spectra recorded on a confocal Raman spectrophotometer (inVia Qontor, Renishaw, New Mills, UK). Twelve specimens of non-polymerized 3D resin, spread on a microscope slide, and twelve specimens per group, examined directly after post-polymerization and after air-abrasion, were exposed to a high-power near infra-red (HPNIR) laser at a wavelength of 785 nm and a spectral resolution of 1 cm^{-1} through a microscope objective (50×). Each measurement was completed with five accumulations at a laser power of 100%

and an irradiation time of 5 s. The recorded spectra were edited in the software WiRE 4.2 (Renishaw, New Mills, UK) in a spectral region of 1500–2000 cm^{-1}, including the removal of a baseline, fitting of the determined curves, and the determination of the height of the different peaks. The peak values at 1640 cm^{-1} and 1610 cm^{-1} were analyzed. The degree of conversion (DC) was calculated with the following equation:

$$DC(\%) = 100 \times \left(1 - \frac{(1640cm^{-1}/1610cm^{-1})_{polymerized}}{(1640cm^{-1}/1610cm^{-1})_{unpolymerized}}\right)$$

A statistical evaluation of the data were performed using descriptive analysis followed by Kolmogorov–Smirnov to test the violation of normal distribution. Parametric tests were performed, as all groups were normally distributed. To determine the influence of the cleaning methods and pretreatment on TBS, one-way ANOVA with partial eta-squared (η_P^2) followed by Scheffé post-hoc test was computed. A two-group *t*-test investigated the impact of the aging regimen. The data were analyzed with SPSS version 26.0 (IBM, SPSS, Statistics, Armonk, NY, USA). The frequency of fracture types was analyzed by chi-square test and Ciba-Geigy table. Statistical significance was inferred when *p*-values < 0.05.

3. Results

The results of the descriptive analyses are presented in Tables 2 and 3.

Table 2. DC for all tested cleaning groups with descriptive statistics (Mean ± SD, Min/Med/Max) and 95% confidence intervals (CI).

Cleaning	Mean ± SD	95% CI	Min/Med/Max
Prior to air abrasion			
BUT	96.6 ± 0.9 ^{bA}	(95.9/97.1)	95.2/96.8/97.7
ISO	95.5 ± 0.7 ^{bB}	(96.0/96.9)	95.4/96.3/97.9
CEN	88.4 ± 0.7 ^{aA}	(87.8/88.8)	87.3/88.5/89.3
After air abrasion			
BUT	95.1 ± 1.4 ^{bA}	(94.2/95.9)	92.6/95.4/96.9
ISO	94.4 + 2.6 ^{abA}	(92.7/96.0)	89.7/94.6/98.5
CEN	92.7 ± 1.9 ^{aB}	(91.4/93.9)	90.1/93.0/95.4

^{ab}: different letters indicate significant differences between cleaning groups within one pretreatment group (prior to air abrasion or after air abrasion). ^{AB}: different letters indicate significant differences between the pretreatment groups within one cleaning group.

Table 3. Descriptive statistics with mean and standard deviation (SD), the minimum/median/maximum (Min/Med/Max) and 95% confidence intervals (CI) for TBS in MPa per cleaning, pretreatment, and aging group.

	BUT			ISO			CEN		
	Mean ± SD	95% CI	Min/Med/Max	Mean ± SD	95% CI	Min/Med/Max	Mean ± SD	95% CI	Min/Med/Max
Pretreatment					Initial				
CCP	16 ± 7 ^{aAi}	(11; 21)	3/15/30	17 ± 6 ^{aAi}	(12; 21)	8/43/59	27 ± 8 ^{aBi}	(21; 32)	14/25/40
CUB	40 ± 5 ^{cAii}	(36; 44)	28/41/48	36 ± 8 ^{cAi}	(30; 41)	18/36/45	36 ± 6 ^{bAi}	(31; 40)	27/35/46
SUP	36 ± 4 ^{cAi}	(33; 38)	28/36/41	36 ± 9 ^{cAi}	(30; 42)	21/34/51	38 ± 5 ^{bAi}	(34; 41)	27/37/46
VL	24 ± 3 ^{bAi}	(20; 25)	19/23/30	27 ± 6 ^{bBi}	(26; 43)	20/29/35	25 ± 3 ^{aABi}	(22; 27)	20/26/30
					Artificial aging				
CCP	19 ± 7 ^{aAi}	(14; 23)	9/18/31	18 ± 6 ^{aAi}	(13; 21)	8/15/28	33 ± 5 ^{aBii}	(29; 37)	23/33/40
CUB	33 ± 4 ^{bAi}	(27; 33)	25/30/38	34 ± 5 ^{bcAi}	(30; 37)	24/33/41	34 ± 4 ^{aAi}	(30; 36)	28/34/40
SUP	36 ± 4 ^{cAi}	(32; 39)	29/37/42	36 ± 4 ^{cAi}	(32; 38)	30/36/42	35 ± 4 ^{aAi}	(33; 37)	29/35/41
VL	31 ± 7 ^{bcAii}	(27; 35)	17/32/42	29 ± 7 ^{bAi}	(24; 33)	19/29/40	34 ± 6 ^{aAii}	(29; 38)	22/36/41

BUT: butyldiglycol-based solution; ISO: isopropanol; CEN: centrifugation; CCP: Clearfil Ceramic Primer; CUB: Clearfil Universal Bond; SUP: Scotchbond Universal Plus; VL: Visio.link. ^{abc}: different lowercase letters indicate significant differences between the pretreatment methods within one cleaning and the aging group. ^{AB}: different uppercase letters indicate significant differences between the cleaning methods within one pretreatment and the aging group. ^{i,ii}: different letters indicate significant differences between the aging regimen within one cleaning and the pretreatment group.

3.1. Degree of Conversion

Directly after post-polymerization, CEN showed lower DC values than BUT and ISO ($p < 0.001$). After air abrasion, BUT showed higher DC values compared to CEN ($p = 0.024$). CEN presented a higher DC after air abrasion ($p < 0.001$) than prior to air abrasion, whereas ISO showed lower DC values after air abrasion ($p = 0.016$).

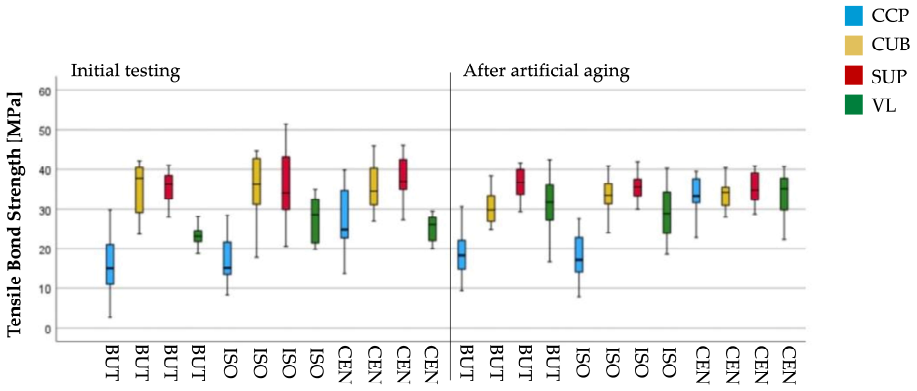
3.2. Tensile Bond Strength

The highest impact on TBS was exerted by the pretreatment method ($\eta_P^2 = 0.497$, $p < 0.001$), followed by the cleaning procedure ($\eta_P^2 = 0.104$, $p < 0.001$), and aging ($\eta_P^2 = 0.015$, $p = 0.026$). Furthermore, the effect of the combination of the three parameters was significant for cleaning coupled with pretreatment methods ($\eta_P^2 = 0.155$, $p < 0.001$) and for pretreatment methods coupled with aging ($\eta_P^2 = 0.088$, $p < 0.001$).

Regarding the pretreatment methods, CCP presented the lowest TBS values ($p < 0.001$–0.012) for groups cleaned with BUT or ISO. Pretreatment with CUB ($p < 0.001$–0.034) or SUP ($p < 0.001$–0.023) showed initially higher values than CCP and VL. Pretreatment with SUP led to higher values than CUB ($p = 0.048$) for artificially aged BUT-cleaned specimens. VL presented lower values compared to SUP ($p = 0.027$) for thermocycled ISO-cleaned specimens. No impact of the pretreatment method ($p = 0.703$–0.998) on TBS could be observed for aged, centrifuged groups.

Regarding the cleaning methods, CEN led to higher values for groups pretreated with CCP ($p < 0.001$). Cleaning with BUT initially showed lower values ($p = 0.024$) compared to ISO, when pretreated with VL.

Regarding the aging regime, thermocycling increased TBS values for groups cleaned with CEN and pretreated with CCP ($p = 0.013$) or VL ($p < 0.001$). Higher values were observed within initial measurements for specimens cleaned with BUT and pretreated with CUB ($p = 0.025$). Thermocycled specimens cleaned with BUT and pretreated with VL ($p = 0.001$) showed higher values than at the initial state (Figure 4).



BUT: butyldiglycol-based solution; ISO: isopropanol; CEN: centrifugation; CCP: Clearfil Ceramic Primer; CUB: Clearfil Universal Bond; SUP: Scotchbond Universal Plus; VL: Visio.link

Figure 4. Tensile bond strength values of all tested groups. Colors encode the four conditioning methods.

3.3. Failure Types

Groups conditioned with CUB, SUP, and VL showed predominantly cohesive failures within the luting composite resin (27–80%) or cohesive failures within the 3D printed resin substrates (20–73%) (Table 4). For groups conditioned with CCP, mostly adhesive failures occurred (7–80%).

Table 4. Percentage of evaluated failure types and 95% CI for TBS [MPa] per cleaning, pretreatment, and aging group.

Initial		Adhesive Failures (%) and 95% CI	Cohesive Failures within Luting Resin (%) and 95% CI	Cohesive Failures within 3D Resin (%) and 95% CI
Cleaning	Pretreatment			
BUT				
	CCP	73 (43; 93)	0 (0; 22)	27 (6; 56)
	CUB	0 (0; 22)	67 (37; 89)	33 (10; 62)
	SUP	0 (0; 22)	40 (15; 68)	60 (31; 84)
	VL	0 (0; 22)	33 (10; 62)	67 (37; 89)
ISO				
	CCP	87 (58; 99)	0 (0; 22)	13 (0; 41)
	CUB	0 (0; 22)	47 (20; 74)	53 (25; 79)
	SUP	0 (0; 22)	53 (25; 79)	47 (20; 74)
	VL	0 (0; 22)	67 (37; 89)	33 (10; 62)
CEN				
	CCP	20 (3; 47)	7 (0; 32)	73 (43; 93)
	CUB	0 (0; 22)	47 (20; 74)	53 (25; 79)
	SUP	0 (0; 22)	73 (43; 93)	27 (6; 56)
	VL	0 (0; 22)	27 (6; 56)	73 (43; 93)
Artificial Aging		**Adhesive Failures (%) and 95% CI**	**Cohesive Failures within Luting Resin (%) and 95% CI**	**Cohesive Failures within 3D Resin (%) and 95% CI**
Cleaning	Pretreatment			
BUT				
	CCP	33 (10; 62)	7 (0; 32)	60 (31; 84)
	CUB	0 (0; 22)	60 (31; 84)	40 (15; 68)
	SUP	0 (0; 22)	67 (37; 89)	33 (10; 62)
	VL	0 (0; 22)	53 (25; 79)	47 (20; 74)
ISO				
	CCP	67 (37; 89)	0 (0; 22)	33 (10; 62)
	CUB	0 (0; 22)	47 (20; 74)	53 (25; 79)
	SUP	0 (0; 22)	53 (25; 79)	47 (20; 74)
	VL	0 (0; 22)	53 (25; 79)	47 (20; 74)
CEN				
	CCP	7 (0; 32)	53 (25; 79)	40 (15; 68)
	CUB	0 (0; 22)	60 (31; 84)	40 (15; 68)
	SUP	0 (0; 22)	67 (37; 89)	33 (10; 62)
	VL	0 (0; 22)	80 (50; 96)	20 (3; 47)

4. Discussion

A reliable luting strategy for definitive restorations fabricated with novel 3D printing resin materials coupled with considerations of the highest possible biocompatibility is an important factor in fixed prosthetics. The aim of this investigation was to examine the DC proximately after post-processing of the 3D printed substrates, and the TBS between a 3D printed resin and a conventional luting composite resin following various cleaning procedures and the application of different adhesive systems after varying aging regimen. The present investigation showed that the type of cleaning, the choice of adhesive system, and the aging affect the TBS. Likewise, the measured degree of conversion showed differences according to the chemical and mechanical cleaning method. Thus, the first and the second tested null hypotheses could be rejected.

After centrifugation, a sticky surface with a visible amount of non-polymerized resin remained [4]; this was evident from a shiny surface after post-polymerization with Otoflash G171 in a nitrogen atmosphere. Since Raman spectra measure point values on the surface, it may lead to the conclusion that Otoflash G171 is not able to cure the resin as sufficiently as when polymerization is performed during the 3D printing process. After removing the shiny surface by air abrasion, the Raman spectra might measure deeper areas, resulting in comparable DC rates to chemical cleaning [8]. With the surface layers of the restoration being routinely removed by finishing and polishing, the type of cleaning may, however, play a subordinate role in biocompatibility.

Cleaning with isopropanol, on the other hand, showed a higher carbon conversion rate after post-polymerization than after sandblasting. This finding may be explained by the effective removal of the adherent liquid resin off the surface and a deterioration of the DC rate in deeper layers [22].

Air abrasion with Al_2O_3 particles exhibited good results in tensile [23,24] and shear bond strength [25] to a luting composite resin in both subtractively and additively manufactured restorations. All groups were mechanically air-abraded with Al_2O_3 particles before conditioning with adhesives, which made the results comparable.

The tested adhesive systems differ in their composition. The highest TBS values were achieved by pretreatment of the luting area with universal adhesives i.e., CUB and SUP. The universal adhesives used contain acid-modified monomers with bifunctional properties. Acidic phosphoric monomers (10-MDP) interact ionically with the oxide ceramic fillers in the restoration and additionally enable the bonding of Ca^{2+} ions in the tooth structure [26]. In addition, on one side, silane-reactive hydroxyl groups form a covalent bond with the glass-ceramic fillers through a condensation reaction and, on the other side, regular organophilic methacrylate groups can copolymerize with the luting composite resin [27],

In contrast to the universal adhesives, the 10-MDP silane primer, CCP, achieved lower TBS values. In addition, more adhesive failures were observed, although none of the specimens pretreated with CCP debonded prematurely. Reasons for this could be the chemical composition of the silane primer and the 3D printable resin. The silane primer bonds to glass–ceramic fillers, but at the same time blocks the formation of carbon bonds between the 3D resin and the luting composite resin [28].

Due to its low viscosity, which is important for processing in the printer, the 3D resin has the characteristics of a flowable composite [29] and consists mainly of the resin matrix (60%) and a reduced number of fillers (40%) according to manufacturers' specifications.

Interestingly, cleaning by centrifugation can improve the TBS values of the CCP pretreated specimens. This could be due to the mechanical cleaning, as no ingredients are dissolved in the 3D printing resin, as is the case of the chemical cleaning. With the chemical cleaning, it would be conceivable that, in addition to residual monomers, glass–ceramic fillers are also dissolved from the 3D resin matrix and are thus no longer available for chemical bonding. Visio.link containing methylmethacrylate (MMA) performed slightly better than the silane primer. MMA attacks the top layer and dissolves existing double bonds, promoting the bond to the matrix, especially for materials containing polymethylmethacrylate (PMMA) [30]. A swollen and dissolved material after application of MMA monomers to the surface of 3D printed temporary substrates has already been reported [31]. Nevertheless, no chemical interaction with the fillers is generated.

In the present investigation, artificial aging was carried out with 10,000 thermal cycles to simulate a period in the oral cavity at normal daily temperature changes (e.i. eating, drinking, and breathing). It is possible to expect that, especially after centrifugation, the increased proportion of remaining free carbon–carbon double bonds at warmer temperatures (55 °C) will promote additional co-polymerization with the luting composite resin [32]. While it can also be assumed that the aging process promotes the co-polymerization of Visio.link, it remains unclear how the cleaning method influences polymerization. On the other hand, hydrolytic degeneration and high temperature variations (5/55°) to which the specimens are exposed could increase the coefficient of thermal expansion at the bonding

interface, which could lead to cracks and result in lower TBS values [33]. However, a decrease in TBS values could only be observed in one of the tested groups (BUT-cleaned specimens pretreated with CUB). A variety of in vitro bond strength tests can evaluate the quality of adhesion. In the present study, macro tensile tests were performed as they proved to be more clinically relevant compared to shear bond strength tests, as they often indicate cohesive failures, and therefore it is assumed that this method measures not only bond strength but also overall stability [34]. In addition, macro tensile strength tests offer advantages over micro tensile strength tests, as they allow a specimen preparation without additional mechanical pre-stressing [35].

According to the TBS measurements, only cohesive failures were observed after pretreatment with CUB, SUP, and VL. It can be assumed that the bond strength is stronger than the overall stability of the 3D printed substrates or the luting composite resin. In contrast, adhesive failures of up to 80% were observed when pretreating with CCP. Thus, it can be considered that the tensile test provided a correct measurement of the bond strength.

A limitation of the present study is that a power analysis was conducted post-hoc. The post-hoc power analysis on a specimen number of 15 specimens showed that the resulting power of a two-sided *t*-test comparing the results of specimens conditioned with Visio.link and pretreated with ceramic primer and measured in the initial state is 99%, with an effect of 10.36 MPa and a pooled standard deviation of 6.22 MPa. A second post-hoc analysis was performed with the same groups (specimens conditioned with Visio.link compared to pretreatment with ceramic primer) only after artificial aging and showed that the resulting power of a two-sided *t*-test is 99%, given a sample size of 15, with an observed effect of 11.45 MPa and a pooled standard deviation of 6.76 MPa. On the one hand, the two groups were selected from the isopropanol cleaning group, as this cleaning is most frequently used for cleaning 3D printed objects and is recommended by most manufacturers. On the other hand, conditioning with Visio.link or silane coupling agents (CCP) are among the most practically relevant pretreatment methods in the dental laboratory and in practice [36–39].

The physical cleaning of fixed dental protheses by means of centrifugal force showed a comparable bond strength among the adhesives tested, especially for the aged specimens. This was in contrast to the chemical cleaning, which showed clear differences in the choice of the adhesive. The results of this study should be interpreted with caution as the in vitro design does not reflect all clinically relevant factors. In vivo studies are needed to evaluate the bond strength of additively manufactured restorations.

Author Contributions: Conceptualization, B.S.; infrastructure, M.R. and A.C.; data analysis, B.S. and V.L.; data curation, V.L.; writing—original draft preparation, V.L.; writing—review and editing, F.M., A.C., A.L. and M.H.; supervision, B.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: On reasonable request, the corresponding author will make the datasets generated during the current investigation available.

Acknowledgments: The authors would like to thank Pro3Dure, Kuraray Noritake, and HPdent for supporting this study with material.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Schweiger, J.; Edelhoff, D.; Güth, J.F. 3D Printing in Digital Prosthetic Dentistry: An Overview of Recent Developments in Additive Manufacturing. *J. Clin. Med.* **2021**, *10*, 2010. [CrossRef]
2. Zimmermann, M.; Ender, A.; Attin, T.; Mehl, A. Fracture load of three-unit full-contour fixed dental prostheses fabricated with subtractive and additive CAD/CAM technology. *Clin. Oral. Investig.* **2020**, *24*, 1035–1042. [CrossRef]

3. Alammar, A.; Kois, J.C.; Revilla-León, M.; Att, W. Additive Manufacturing Technologies: Current Status and Future Perspectives. *J. Prosthodont.* **2022**, *31*, 4–12. [CrossRef] [PubMed]
4. Mayer, J.; Reymus, M.; Wiedenmann, F.; Edelhoff, D.; Hickel, R.; Stawarczyk, B. Temporary 3D printed fixed dental prosthesis materials: Impact of post printing cleaning methods on degree of conversion as well as surface and mechanical properties. *Int. J. Prosthodont.* **2021**, *34*, 784–795. [CrossRef]
5. dos Santos, R.L.; de Sampaio, G.A.; de Carvalho, F.G.; Pithon, M.M.; Guênes, G.M.; Alves, P.M. Influence of degree of conversion on the biocompatibility of different composites in vivo. *J. Adhes. Dent.* **2014**, *16*, 15–20. [PubMed]
6. Rustemeyer, T.; Frosch, P.J. Occupational skin diseases in dental laboratory technicians. *Contact Dermat.* **1996**, *34*, 125–133. [CrossRef] [PubMed]
7. Bayarsaikhan, E.; Gu, H.; Hwangbo, N.K.; Lim, J.H.; Shim, J.S.; Lee, K.W.; Kim, J.E. Influence of different postcuring parameters on mechanical properties and biocompatibility of 3D printed crown and bridge resin for temporary restorations. *J. Mech. Behav. Biomed. Mater.* **2022**, *128*, 105127. [CrossRef] [PubMed]
8. Mayinger, F.; Reymus, M.; Liebermann, A.; Richter, M.; Kubryk, P.; Großekappenberg, H.; Stawarczyk, B. Impact of polymerization and storage on the degree of conversion and mechanical properties of veneering resin composites. *Dent. Mater. J.* **2021**, *40*, 487–497. [CrossRef] [PubMed]
9. Borges, M.G.; Silva, G.R.; Neves, F.T.; Soares, C.J.; Faria, F.S.A.L.; Carvalho, R.F.; Menezes, M.S. Oxygen Inhibition of Surface Composites and Its Correlation with Degree of Conversion and Color Stability. *Braz. Dent. J.* **2021**, *32*, 91–97. [CrossRef]
10. Lankes, V.; Reymus, M.; Liebermann, A.; Stawarczyk, B. Bond strength between temporary 3D printable resin and conventional resin composite: Influence of cleaning methods and air-abrasion parameters. *Clin. Oral. Investig.* **2023**, *27*, 31–43. [CrossRef] [PubMed]
11. Suzuki, M.; Takamizawa, T.; Hirokane, E.; Ishii, R.; Tsujimoto, A.; Barkmeier, W.W.; Latta, M.A.; Miyazaki, M. Bond durability of universal adhesives to intact enamel surface in different etching modes. *Eur. J. Oral. Sci.* **2021**, *129*, e12768. [CrossRef]
12. Yokoyama, M.; Takamizawa, T.; Tamura, T.; Namura, Y.; Tsujimoto, A.; Barkmeier, W.W.; Latta, M.A.; Miyazaki, M. Influence of Different Application Methods on the Bonding Effectiveness of Universal Adhesives to Dentin in the Early Phase. *J. Adhes. Dent.* **2021**, *23*, 447–459. [PubMed]
13. Klaisiri, A.; Krajangta, N.; Thamrongananskul, N. The Durability of Zirconia/Resin Composite Shear Bond Strength using Different Functional Monomer of Universal Adhesives. *Eur. J. Dent.* **2021**, *16*, 756–760. [CrossRef] [PubMed]
14. Lima, R.B.W.; Muniz, I.A.F.; Campos, D.E.S.; Murillo-Gómez, F.; Andrade, A.K.M.; Duarte, R.M.; de Souza, G.M. Effect of universal adhesives and self-etch ceramic primers on bond strength to glass ceramics: A systematic review and meta-analysis of in vitro studies. *J. Prosthet. Dent.* **2022**. [CrossRef] [PubMed]
15. Cuevas-Suárez, C.E.; de Oliveira da Rosa, W.L.; Vitti, R.P.; da Silva, A.F.; Piva, E. Bonding Strength of Universal Adhesives to Indirect Substrates: A Meta-Analysis of in Vitro Studies. *J. Prosthodont.* **2020**, *29*, 298–308. [CrossRef]
16. Sismanoglu, S.; Yildirim-Bilmez, Z.; Erten-Taysi, A.; Ercal, P. Influence of different surface treatments and universal adhesives on the repair of CAD-CAM composite resins: An in vitro study. *J. Prosthet. Dent.* **2020**, *124*, 238.e1–238.e9. [CrossRef]
17. Wibowo, E.S.; Park, B.-D. Crystalline Lamellar Structure of Thermosetting Urea–Formaldehyde Resins at a Low Molar Ratio. *Macromolecules* **2021**, *54*, 2366–2375. [CrossRef]
18. Yang, H.; Du, G.; Li, Z.; Ran, X.; Zhou, X.; Li, T.; Gao, W.; Li, J.; Lei, H.; Yang, L. Superstrong Adhesive of Isocyanate-Free Polyurea with a Branched Structure. *ACS Appl. Polym. Mater.* **2021**, *3*, 1638–1651. [CrossRef]
19. Liu, S.; Du, G.; Yang, H.; Su, H.; Ran, X.; Li, J.; Zhang, L.; Gao, W.; Yang, L. Developing High-Performance Cellulose-Based Wood Adhesive with a Cross-Linked Network. *ACS Sustain. Chem. Eng.* **2021**, *9*, 16849–16861. [CrossRef]
20. Scholz, K.J.; Tabenski, I.M.; Vogl, V.; Cieplik, F.; Schmalz, G.; Buchalla, W.; Hiller, K.A.; Federlin, M. Randomized clinical split-mouth study on the performance of CAD/CAM-partial ceramic crowns luted with a self-adhesive resin cement or a universal adhesive and a conventional resin cement after 39 months. *J. Dent.* **2021**, *115*, 103837. [CrossRef]
21. Tsukagoshi, K.; Hirota, M.; Nomoto, R.; Hayakawa, T. Bond strength and computational analysis for silane coupling treatments on the adhesion of resin block for CAD/CAM crowns. *Dent. Mater. J.* **2020**, *39*, 844–854. [CrossRef]
22. Horgnies, M.; Darque-Ceretti, E.; Combarieu, R. Influence of additives segregation on surface composition of automotive coatings: Effects of an ethanol cleaning. *Prog. Org. Coat.* **2003**, *47*, 154–163. [CrossRef]
23. Stawarczyk, B.; Basler, T.; Ender, A.; Roos, M.; Ozcan, M.; Hämmerle, C. Effect of surface conditioning with airborne-particle abrasion on the tensile strength of polymeric CAD/CAM crowns luted with self-adhesive and conventional resin cements. *J. Prosthet. Dent.* **2012**, *107*, 94–101. [CrossRef] [PubMed]
24. Pfeffer, S.; Jacker-Guhr, S.; Geurtsen, W.; Pfeffer, T.; Lührs, A. Microtensile bond strength of luting cements to a 3D printable composite–an in vitro study. *Sustain. Dent.* **2020**, *2*, 229–239.
25. Holmer, L.; Othman, A.; Lührs, A.K.; von See, C. Comparison of the shear bond strength of 3D printed temporary bridges materials, on different types of resin cements and surface treatment. *J. Clin. Exp. Dent.* **2019**, *11*, e367–e372. [CrossRef]
26. Ye, S.; Chuang, S.F.; Hou, S.S.; Lin, J.C.; Kang, L.L.; Chen, Y.C. Interaction of silane with 10-MDP on affecting surface chemistry and resin bonding of zirconia. *Dent. Mater.* **2022**, *38*, 715–724. [CrossRef] [PubMed]
27. Hagino, R.; Mine, A.; Matsumoto, M.; Yumitate, M.; Ban, S.; Yamanaka, A.; Ishida, M.; Miura, J.; Meerbeek, B.V.; Yatani, H. Combination of a silane coupling agent and resin primer reinforces bonding effectiveness to a CAD/CAM indirect resin composite block. *Dent. Mater. J.* **2021**, *40*, 1445–1452. [CrossRef]

28. Atsushi, M.; Tomoshige, K.; Asuka, K.-U.; Mami, H.; Yuko, T.; Ryosuke, H.; Dai, I.; Masahiro, Y.; Shintaro, B.; Mariko, M.; et al. Effectiveness of current adhesive systems when bonding to CAD/CAM indirect resin materials: A review of 32 publications. *Jpn. Dent. Sci. Rev.* **2019**, *55*, 41–50.
29. Taormina, G.; Sciancalepore, C.; Messori, M.; Bondioli, F. 3D printing processes for photocurable polymeric materials: Technologies, materials, and future trends. *J. Appl. Biomater. Funct. Mater.* **2018**, *16*, 151–160. [CrossRef]
30. Palitsch, A.; Hannig, M.; Ferger, P.; Balkenhol, M. Bonding of acrylic denture teeth to MMA/PMMA and light-curing denture base materials: The role of conditioning liquids. *J. Dent.* **2012**, *40*, 210–221. [CrossRef]
31. Lim, N.K.; Shin, S.Y. Bonding of conventional provisional resin to 3D printed resin: The role of surface treatments and type of repair resins. *J. Adv. Prosthodont.* **2020**, *12*, 322–328. [CrossRef]
32. Piwowarczyk, A.; Lauer, H.C.; Sorensen, J.A. In vitro shear bond strength of cementing agents to fixed prosthodontic restorative materials. *J. Prosthet. Dent.* **2004**, *92*, 265–273. [CrossRef]
33. Torstenson, B.; Brännström, M. Contraction gap under composite resin restorations: Effect of hygroscopic expansion and thermal stress. *Oper. Dent.* **1988**, *13*, 24–31. [PubMed]
34. Scherrer, S.S.; Cesar, P.F.; Swain, M.V. Direct comparison of the bond strength results of the different test methods: A critical literature review. *Dent. Mater.* **2010**, *26*, e78–e93. [CrossRef]
35. Sano, H.; Shono, T.; Sonoda, H.; Takatsu, T.; Ciucchi, B.; Carvalho, R.; Pashley, D.H. Relationship between surface area for adhesion and tensile bond strength–evaluation of a micro-tensile bond test. *Dent. Mater.* **1994**, *10*, 236–240. [CrossRef]
36. Stawarczyk, B.; Silla, M.; Roos, M.; Eichberger, M.; Lümkemann, N. Bonding Behaviour of Polyetherketoneketone to Methylmethacrylate- and Dimethacrylate-based Polymers. *J. Adhes. Dent.* **2017**, *19*, 331–338.
37. Liebermann, A.; Keul, C.; Bähr, N.; Edelhoff, D.; Eichberger, M.; Roos, M.; Stawarczyk, B. Impact of plasma treatment of PMMA-based CAD/CAM blanks on surface properties as well as on adhesion to self-adhesive resin composite cements. *Dent. Mater.* **2013**, *29*, 935–944. [CrossRef] [PubMed]
38. El-Damanhoury, H.M.; Elsahn, N.A.; Sheela, S.; Gaintantzopoulou, M.D. Adhesive luting to hybrid ceramic and resin composite CAD/CAM Blocks:Er:YAG Laser versus chemical etching and micro-abrasion pretreatment. *J. Prosthodont. Res.* **2021**, *65*, 225–234. [CrossRef] [PubMed]
39. Yano, H.T.; Ikeda, H.; Nagamatsu, Y.; Masaki, C.; Hosokawa, R.; Shimizu, H. Correlation between microstructure of CAD/CAM composites and the silanization effect on adhesive bonding. *J. Mech. Behav. Biomed. Mater.* **2020**, *101*, 103441. [CrossRef] [PubMed]

8. Literaturverzeichnis

ALAMMAR, A., KOIS, J. C., REVILLA-LEÓN, M. & ATT, W. 2022. Additive Manufacturing Technologies: Current Status and Future Perspectives. *J Prosthodont,* 31**,** 4-12.

BORGES, M. G., SILVA, G. R., NEVES, F. T., SOARES, C. J., FARIA, E. S. A. L., CARVALHO, R. F. & MENEZES, M. S. 2021. Oxygen Inhibition of Surface Composites and Its Correlation with Degree of Conversion and Color Stability. *Braz Dent J,* 32**,** 91-97.

DOS SANTOS, R. L., DE SAMPAIO, G. A., DE CARVALHO, F. G., PITHON, M. M., GUÊNES, G. M. & ALVES, P. M. 2014. Influence of degree of conversion on the biocompatibility of different composites in vivo. *J Adhes Dent,* 16**,** 15-20.

HAGINO, R., MINE, A., MATSUMOTO, M., YUMITATE, M., BAN, S., YAMANAKA, A., ISHIDA, M., MIURA, J., MEERBEEK, B. V. & YATANI, H. 2021. Combination of a silane coupling agent and resin primer reinforces bonding effectiveness to a CAD/CAM indirect resin composite block. *Dent Mater J,* 40**,** 1445-1452.

KERN, M. 2015. Bonding to oxide ceramics—laboratory testing versus clinical outcome. *Dent Mater,* 31**,** 8-14.

KLAISIRI, A., KRAJANGTA, N. & THAMRONGANANSKUL, N. 2021. The Durability of Zirconia/Resin Composite Shear Bond Strength using Different Functional Monomer of Universal Adhesives. *Eur J Dent*.

KUSCU, E., KLINK, A., SPINTZYK, S., KRAEMER FERNANDEZ, P. & HUETTIG, F. 2021. Bonding Interface and Repairability of 3D-Printed Intraoral Splints: Shear Bond Strength to Current Polymers, with and without Ageing. *Materials,* 14**,** 3935.

LIMA, R. B. W., MUNIZ, I. A. F., CAMPOS, D. E. S., MURILLO-GÓMEZ, F., ANDRADE, A. K. M., DUARTE, R. M. & DE SOUZA, G. M. 2022. Effect of universal adhesives and self-etch ceramic primers on bond strength to glass ceramics: A systematic review and meta-analysis of in vitro studies. *J Prosthet Dent*.

MAYER, J., REYMUS, M., WIEDENMANN, F., EDELHOFF, D., HICKEL, R. & STAWARCZYK, B. 2021. Temporary 3D printed fixed dental prosthesis materials: Impact of post printing cleaning methods on degree of conversion as well as surface and mechanical properties. *Int J Prosthodont*.

MAYINGER, F., REYMUS, M., LIEBERMANN, A., RICHTER, M., KUBRYK, P., GROSSEKAPPENBER, H. & STAWARCZYK, B. 2021. Impact of polymerization and storage on the degree of conversion and mechanical properties of veneering resin composites. *Dent Mater J,* 40**,** 487-497.

NEJAT, A. H., LEE, J., SHAH, S., LIN, C. P., KULKARNI, P., CHAVALI, R. & LAWSON, N. C. 2018. Retention of CAD/CAM resin composite crowns following different bonding protocols. *Am J Dent,* 31**,** 97-102.

NOBUAKI, A., KEIICHI, Y. & TAKASHI, S. 2015. Effects of air abrasion with alumina or glass beads on surface characteristics of CAD/CAM composite materials and the bond strength of resin cements. *J Appl Oral Sci,* 23**,** 629-36.

ÖZCAN, M. & BERNASCONI, M. 2015. Adhesion to zirconia used for dental restorations: a systematic review and meta-analysis. *J Adhes Dent,* 17**,** 7-26.

PALITSCH, A., HANNIG, M., FERGER, P. & BALKENHOL, M. 2012. Bonding of acrylic denture teeth to MMA/PMMA and light-curing denture base materials: the role of conditioning liquids. *J Dent,* 40**,** 210-21.

REYMUS, M., ROOS, M., EICHBERGER, M., EDELHOFF, D., HICKEL, R. & STAWARCZYK, B. 2019. Bonding to new CAD/CAM resin composites: influence of air abrasion and conditioning agents as pretreatment strategy. *Clin Oral Investig,* 23**,** 529-538.

REYMUS, M. & STAWARCZYK, B. 2020. Influence of Different Postpolymerization Strategies and Artificial Aging on Hardness of 3D-Printed Resin Materials: An In Vitro Study. *Int J Prosthodont,* 33**,** 634-640.

SAMPAIO, C. S., NIEMANN, K. D., SCHWEITZER, D. D., HIRATA, R. & ATRIA, P. J. 2021. Microcomputed tomography evaluation of cement film thickness of veneers and crowns made with conventional and 3D printed provisional materials. *J Esthet Restor Dent,* 33**,** 487-495.

SCHWEIGER, J., EDELHOFF, D. & GÜTH, J. F. 2021. 3D Printing in Digital Prosthetic Dentistry: An Overview of Recent Developments in Additive Manufacturing. *J Clin Med,* 10.

YE, S., CHUANG, S. F., HOU, S. S., LIN, J. C., KANG, L. L. & CHEN, Y. C. 2022. Interaction of silane with 10-MDP on affecting surface chemistry and resin bonding of zirconia. *Dent Mater,* 38**,** 715-724.

YOSHIHARA, K., NAGAOKA, N., MARUO, Y., NISHIGAWA, G., IRIE, M., YOSHIDA, Y. & VAN MEERBEEK, B. 2017. Sandblasting may damage the surface of composite CAD-CAM blocks. *Dent Mater,* 33**,** e124-e135.

ZIMMERMANN, M., ENDER, A., ATTIN, T. & MEHL, A. 2020. Fracture load of three-unit full-contour fixed dental prostheses fabricated with subtractive and additive CAD/CAM technology. *Clin Oral Investig,* 24**,** 1035-1042.

Danksagung

Ich möchte die Gelegenheit nutzen, um allen zu danken, die mich bei der Arbeit an meiner Dissertation begleitet, tatkräftig und mental unterstützt und motiviert haben.

Zunächst möchte ich mich bei Frau Prof. Bogna Stawarczyk, für ihre unermüdliche und freundschaftliche Unterstützung und Anleitung danken. Ohne Ihre Expertise und Ihr Engagement wäre diese Arbeit nicht möglich gewesen.

Ein besonderer Dank geht an Herrn PD Dr. med. dent Marcel Reymus, Frau Prof. Anja Liebermann und Frau PD Dr. med. dent. Felicitas Mayinger für ihre hilfsbereite Betreuung, wertvollen Beiträge und konstruktiven Feedbacks.

Allen Mitarbeitern und Doktoranden der Werkstoffkunde der Poliklinik für Zahnärztliche Prothetik der LMU München möchte ich mich herzlich für die schöne Zeit und immer unterstützende und kollegiale Zusammenarbeit bedanken.

Für die Bereitstellung von Materialien sowie für die hervorragende technische Unterstützung möchte ich mich bei Herrn Frank Gischer von der Firma pro3dure, Herrn Adham Elsayed von der Firma Kuraray und Herrn Henning Pielock von der Firma HPdent besonders bedanken.

Ich bin meinen Eltern zutiefst dankbar für ihre bedingungslose Liebe und Unterstützung während dieser anspruchsvollen Zeit und denen ich diese Arbeit widme. Schließlich möchte ich meinem Partner Anton von Herzen danken, der stets an meiner Seite war und mich in jeglicher Form motiviert und unterstützt hat.