ORIGINAL RESEARCH

Dental Alloy Adhesive Primers and Bond Strength at Alloy–Resin Interface: A Systematic Review and Meta-analyses

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Abstract

Aim: The present systematic review aimed to report the studies concerning the primers in improving bond strength and identifying pertinent primers for a particular dental alloy by adhering to PRISMA precepts.

Materials and methods: PubMed and Semantic Scholar databases were scoured for articles using 10 search terms. *In vitro* studies satisfying the inclusion criteria were probed which were meticulously screened and scrutinized for eligibility adhering to the 11 exclusion criteria. The quality assessment tool for *in vitro* studies (QUIN Tool) containing 12 criteria was employed to assess the risk of bias (RoB).

Results: A total of 48 studies assessing shear bond strength (SBS) and 15 studies evaluating tensile bond strength (TBS) were included in the qualitative synthesis. Concerning SBS, 33.4% moderate and 66.6% high RoB was observed. Concerning TBS, 26.8% moderate and 73.2% high RoB was discerned. Seventeen and two studies assessing SBS and TBS, respectively, were included in meta-analyses.

Conclusions: Shear bond strength and TBS increased for the primed alloys. Cyclic disulfide primer is best-suited for noble alloys when compared with thiol/thione primers. Phosphoric acid- and phosphonic acid ester-based primers are opportune for base alloys.

Clinical significance: The alloy–resin interface (ARI) would fail if an inappropriate primer was selected. Therefore, the selection of an appropriate alloy adhesive primer for an alloy plays a crucial role in prosthetic success. This systematic review would help in the identification and selection of a congruous primer for a selected alloy.

Keywords: Alloy adhesive primers, Alloy–resin interface, Base alloys, Bond strength, Noble alloys.

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Introduction

The interaction between dental alloy and dental resin is not uncommon in the fabrication of dental prostheses, restorations, and appliances. Sufficient bonding integrity is mandatory between the alloy frameworks/substructures and the resins or alloy–resin interface (ARI) for the clinical longevity of a prosthesis. Poor chemical bonding at ARI due to the coefficient of thermal expansion (CTE) mismatch between alloy and resin is a significant clinical problem, which often introduces adhesive failure and increases microleakage of oral fluids in the finish lines, which causes the accumulation of oral debris, bacterial/fungal colonization, adherence of dental plaque and stains.[1,2] As a result, the propagation of microorganisms contributes to an unfavorable soft tissue response including denture-induced stomatitis.[3] The low bond strength of the resin often results in its disruption and subsequent fracturing due to repeated occlusal stress.[4]

Several alloy–resin bonding methods, such as macro and micromechanical retention, chemical bonding, or a combination, have been employed to circumvent these limitations.[5,6] Constraints in mechanical retention, including colossal substructure and microleakage at the ARI cause compromised retention.[6] The various chemical bonding strategies are technique-sensitive, acutely laborious, and demand appropriate singular devices.[7] Nevertheless, tarnished alloy surfaces also significantly affect ARI adhesion.[8] Various alloy surface treatments have been used to provide a strong and durable alloy–resin bond. Chemical bonding systems were divided into three main categories according to their mechanisms of chemical adhesion to alloy.[9] Silicoating the alloy surface[10–12] and tin/oxide layer coating, however, require expensive equipment, prolonged time, and exhaustive techniques.[13]

Several alloy priming agents/monomers capable of improving the bonding at ARI have been synthesized and introduced to the field of dentistry.[14–18] Compared with traditional silicoating and

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oxidation methods, the primer system is simpler, easier, and more economical because it does not require special equipment and is not technique-sensitive.[19,20] Representative priming agents for base alloys contain an acidic monomer, while primers for noble alloys include a sulfur-containing monomer.[7] Some methacrylates containing phosphoric acid or carboxylic acid groups promote adhesion to base alloys. These monomers, however, are not effective in promoting adhesion to noble alloys without some surface preparation due to the absence of a defined passive oxide surface. Several sulfur-containing primers, such as thiol, thiophenol, disulfide thiophosphoric acid, thiobarbituric acid, triazinedithione, sulfide, dithiolane, and thiouracil are known to possess chemical affinity toward precious alloy adherend. However, determining the most effective functional primer for bonding and the effects of primer application on bond strength remains in debate.[21–24]

Although there are humongous studies available concerning alloy primers in dentistry, there are hardly any reviews on this topic. Hence, the purpose of this study was to review the published literature systematically concerning the utility of alloy primers in prosthodontics in improving bond strength and identifying the best-suited alloy primer for a particular dental casting alloy. The null hypothesis was that priming the alloy surface does not have any effect on the alloy–resin bond strength. The second null hypothesis was that there would be no significant differences between the selected primers used on the included alloys.

Materials and Methods

Question of Cynosure

Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines were adhered to for this review.[25] The question of cynosure was: "Does priming the alloys with alloy primers impact the bond strength between superjacent resin materials and alloys?" This question was deduced based on the PICO model (participant, intervention, comparator, and outcome), in which, the dental alloy was the participant; the priming alloy surface was the intervention; the non-primed alloy surface was the control, and the outcome was the *in vitro* studies assessing shear bond strength (SBS) and tensile bond strength (TBS).

Search Strategy

For publication searching, PubMed and semantic scholar databases were chosen. The research commenced on 30th March 2022 and the studies published from 1985 to 2021 were selected. The subsequent search terms were employed to acquire and extract studies: "Dental metal primers," "Dental alloy primers," "Dental adhesive primers," "Alloy primer in prosthodontics," "Dental alloy primers in cast partial dentures," "Dental thione primer," "Dental thiol primer," "Dental silane alloy primer," "Dental phosphate alloy primer," "Dental sulfur alloy primer." The systematic review included only the *in vitro* laboratory studies.

Study Selection

The studies evaluated SBS and TBS between dental alloys and resins by using alloy primers were considered in the inclusion criterion. The studies selected were then put through full-text reading for conclusive admittance in the systematic review, and eleven exclusion criteria were stipulated: Other languages, non-alloy adherends, methodical complications, primers in commercial adhesive resins, reviews, case reports, inadequate information/incomplete data, other than bond strength analysis, orthodontic bracket studies, nonmetallic/alloy primers, pure metals, and non-disclosure of the primers chemical name. The references of each admitted study were manually searched to retrieve all potentially relevant studies.

Data Extraction and Formation of Matrices

Extracted data from included studies were documented by an analyst in a standardized matrix form. For each study, the publication's data (title, authors, publication year, and the first author), methodology details (the alloy, alloy surface treatments, primer, bonding surface area (BSA), superjacent resin adherends, thermocycling, and mechanical test), intervention (non-primed alloy surface as control and primed alloy) and the outcome (bond strength in MPa) were recorded. The corresponding authors of certain studies where results depicted in bar/line figures were contacted through e-mail to obtain clear bond strength values. Upon nil response, the studies were excluded from the meta-analyses.

Risk of Bias (RoB) Assessment

The quality of the method execution in each included study was evaluated by the two unfettered analysts. Quality assessment tool for *In vitro* studies (QUIN Tool)[26] containing 12 criteria was employed to assess the RoB. The criteria were (1) clearly stated aims/objectives, (2) sample size calculation, (3) sampling technique, (4) control group, (5) methodology explanation, (6) operator details, (7) randomization, (8) outcome measurement method, (9) outcome assessor details, (10) blinding, (11) statistical analysis, and (12) results presentation. The included studies were scored for each criterion as adequately specified = 2 points (low), inadequately specified = 1 point (moderate/some concerns), and not specified = 0 point (high). The scores were then summed up to obtain a total score for a particular *in vitro* study. The scores thus obtained were used to grade the *in vitro* study as high, medium, or low risk (>70%: low RoB, 50–70%: medium RoB, and <50%: high RoB) by using the following formula:[26]

$$\text{Final score} = \frac{(\text{Total score} \times 100)}{2(\text{No. of criteria applicable})}.$$

Data Analysis

Standardized mean differences were evaluated through a random-effects model, between experimental (primed alloy surface/primer (A) and control groups (non-primed alloy surface/primer (B). Subgroup meta-analyses were conducted considering the alloy priming (non-primed vs primed) and the type of primer (primer A vs primer B). Statistical heterogeneity among studies was considered using the Cochrane's Q test and the inconsistency I^2 test (>50% indicates high heterogeneity). Meta-analyses were conducted using Review Manager (RevMan version 5.4; Cochrane Collaboration, London, UK) with a significance level of 5%.

Results

Data Selection

PRISMA flow chart presents the study selection process (Flowchart 1). A grand summation resulted in 2,728 potentially eligible studies from the research databases (Table 1). After excluding duplicates, 1,868 studies were evaluated regarding the inclusion criteria. Most of the inappropriate studies (512 studies) were excluded after screening titles and abstracts by two unfettered analysts. As a consequence, 1,356 studies were selected for full-text screening

Flowchart 1: Systematic review PRISMA flowchart

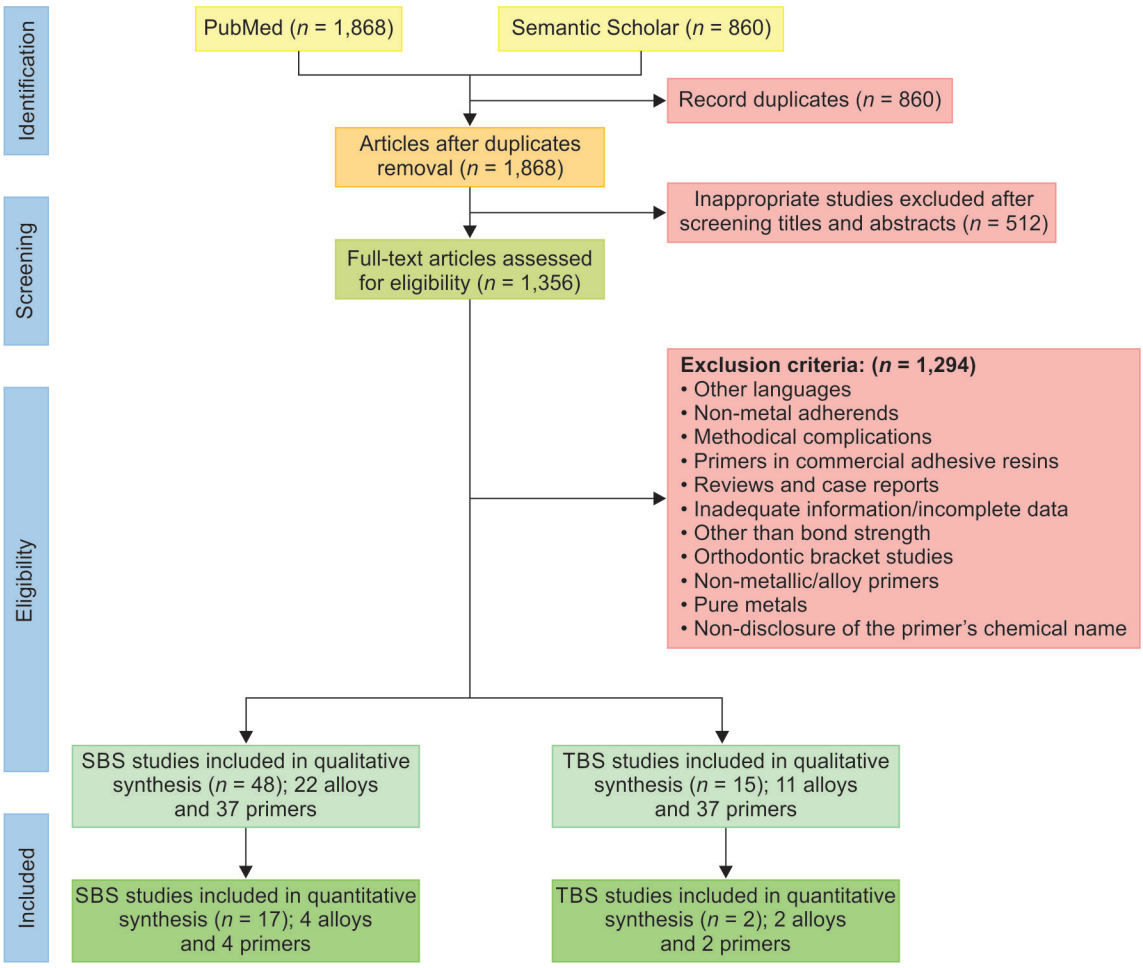


Table 1: Studies retrieved from databases

		Articles	
Search	*Term*	*PubMed/ Medline*	*Semantic Scholar*
1	Dental metal primers	864	204
2	Dental alloy primers	403	222
3	Dental adhesive primers	284	280
4	Alloy primer in prosthodontics	102	3
5	Dental alloy primers in cast partial dentures	12	7
6	Dental thione primer	83	26
7	Dental thiol primer	20	30
8	Dental silane alloy primer	35	28
9	Dental phosphate alloy primer	57	47
10	Dental sulfur alloy primer	8	13
Total		1,868	860

by unfettered two pairs of analysts. Disagreements between the analysts about the study's inclusion eligibility were resolved by an accord by a third analyst. An inter-reviewer agreement was obtained during study selection (Cohen's κ, 0.91). After excluding 1,294 studies adhering to the stipulated 11 exclusion criteria, 48 and 15 studies were included in the qualitative analysis concerning SBS and TBS, respectively. Also, 17 and 2 studies were included in the quantitative analysis concerning SBS and TBS, respectively.

Descriptive Analysis

The grand descriptive data matrices concerning SBS and TBS are furnished in Tables 2 and 3, respectively. The alloy primers may be conveniently categorized based on the reactive acidic moieties present. For the description convenience, an elaborate classification system of the dental alloy primers was devised and exhibited in Table 4. Primers are carboxylic acid-based or their anhydrides,[2,3,8,18,19,27–41] sulfur-containing/ thione–thiol-based,[3,8,14,17,23,24,27,30,32,38,40,42–61] phosphoric acid-based,[3,19,27–33,36–38,42,50,54–56,58,62–66] silicic acid-based,[3,35] and phosphonic acid ester-based.[35,67,68] Combinations of the above primers (binary primers: two monomers with different reactive functional groups; ternary primers: three monomers with different reactive functional groups) were also been employed in the studies. Hybrid primers are structurally altered and contain two reactive functional moieties in a single primer/monomer. In the included studies, VBATDT + 10-MDP and MTU-6 were found to be the common alloy primers with comparatively high bond strength with noble alloys. Likewise, 10-MDP, MEPS, and VBATDT + 10-MDP were the common high bond strength yielding alloy primers with base alloys.

The superjacent adherends were autocure (AC) resin,[3,14,27–29,33,35,38,41,45,50,52,54,56,64,65,68–71] corresponding alloys

Table 2: Descriptive data of the included studies (n = 48) concerning shear bond strength (SBS)

Authors (Year)	*Alloy adherends*, dimensions and surface treatments (ST)*	*Alloy primers and bonding surface area (BSA)*	*Superjacent adherends and dimensions*	*Number of specimens per group/ condition (n), sample treatment, standards, and crosshead speed (CHS)*	*Results and Conclusion*
Jacobson et al. (1988)[2]	Co-Cr Dimension: 3.17 × 3.17 × 0.16 cm^3 ST: Sandblasted (SB) with 50 µm Al_2O_3 for 30 s Electropolished for 20 min Ultrasonic treatment for 5 min	4-META BSA: 1.27 × 0.64 cm^2	Heat-cure (HC) denture base material (1.27 × 0.64 × 0.95 cm^3)	n = Not mentioned Thermocycle (TC): Not performed Standards: Not specified CHS: 5 mm/min	Highest SBS was observed between resin and a plain flat alloy plate with 4-META
Ohkubo et al. (2000)[3]	1. Co-Cr 2. Ti-Al-V Dimension: 6 mm Ø × 2.5 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 10 s	1. MEPS 2. 10-MDP 3. 4-META 4. EP8MA (10-epithiodecyl methacrylate) 5. γ-MPTS BSA: 5 mm Ø	AC resin PMMA-MMA (6 mm Ø × 2 mm thick)	n = 10 TC: 4°C and 60°C DT: 1 minute No. of cycles: 2000 Standards: Not specified CHS: 0.5 mm/min	10-MDP and MEPS exhibited significantly higher bond strengths than 4-META and γ-MPTS. SBS by EP8MA exhibited no statistical difference when compared with 10-MDP and MEPS
Choo et al. (2015)[8]	1. Co-Cr 2. Ti-Al-V 3. Au-Pd-Ag Dimension: 8 mm Ø × 1.5 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 10 s	1. VBATDT + 10-MDP 2. MAC-10 3. VBATDT BSA: 5 mm Ø	Veneer composite LC resin (5 mm Ø × 2 mm thick)	n = 12 TC: 5°C and 55°C DT: 30 s No. of cycles: 5000 Standards: Not specified CHS: 0.5 mm/min	VBATDT + 10-MDP showed significantly higher SBS
Atsuta et al. (1992)[14]	1. Au-Ag-Cu-Pd 2. Ag-Pd-Cu-Au Dimension: 10 mm Ø × 2 mm thick. ST: #600 silicon-carbide (SiC) paper, SB with 50 µm Al_2O_3 for 10 s	VBATDT. BSA: 5 mm Ø	Autocure (AC) opaque resin (PMMA + MMA-4-META/TBB) + Light-cure (LC) resin. (6 mm Ø × 2 mm thick)	n = Not mentioned TC: 4°C and 60°C Dwell time (DT): 1 min No. of cycles: 20,000, 50,000,, 100,000. Standards: Not specified CHS: 0.5 mm/min	VBATDT and PMMA + MMA-4-META/TBB resin effectively bonded light-cured composite and alloys used
Matsumura et al. (2000)[17]	1. Ag-In-Zn-Pd. 2. Ag-Pd-Cu-Au 3. Au-Pt-Pd 4. Pd-Ga-Co. 5. Au-Cu-Ag-Pt-Pd Dimension: 10 mm Ø × 2.5 mm thick. ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 10 s	1. VBATDT + 10-MDP 2. MTU-6 BSA: 5 mm Ø	8 mm Ø × 2 mm thick alloys luted with AC adhesive resin PMMA + MMA-4-META/TBB	n = 16 TC: 4°C and 60°C DT: 1 min No. of cycles: 100,000 Standards: Not specified CHS: 0.5 mm/min	Au-Pt-Pd and Pd-Ga-Co alloys conditioned with the VBATDT + 10-MDP primer exhibited greater bond strength
Kim et al. (2009)[18]	1. Ti-Al-V 2. Co-Cr Dimension: 10 mm Ø × 2.5 mm thick ST: #600 SiC paper, SB with 250 µm Al_2O_3 for 5 s	1. VBATDT + 10-MDP 2. MAC-10 BSA: Not mentioned	HC denture base resin	n = 5 TC: Not performed Standards: Not specified CHS: 1 mm/min	The specimens primed with the 10-MDP showed higher bond strength

Kawaguchi et al. (2011)[19]	Co-Cr Dimension: 10 mm Ø × 2.5 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 5 s. Tribochemical silica coating system	1. 10-MDP, 2. 4-META, 3. VBATDT + 10-MDP BSA: 5 mm Ø	HC denture base resin was bonded (5.0 mm Ø × 0.5 mm thick)	*n* = 10 TC: 5°C and 55°C DT: 1 min No. of cycles: 10,000 Standards: Not specified CHS: 0.5 mm/min	VBATDT + 10-MDP is effective to bond heat-polymerized resin to Cp Ti and Co-Cr
Freitas et al. (2004)[22]	Co-Cr-Mo Dimension: 12 mm Ø × 2 mm thick ST: #600 SiC paper, SB with 100 µm Al_2O_3 for 1 min All metallic disks were submitted to four thermal cycles, under vacuum, at 960 °C to simulate the firing of the porcelain	VBATDT + 10-MDP BSA: 0.785 cm^2	10 mm Ø × 2 mm thick alloy luted with resin cement	*n* = 5 TC: Not performed Standards: Not specified CHS: 0.5 mm/min	VBATDT + 10-MDP is effective to increase the bond strength between resins and basic alloys
di Francescantonio et al. (2010)[23]	1. Co-Cr 2. Ni-Cr Dimension: 10 × 5 × 1 mm^3 ST: SB with 100 µm Al_2O_3 for 10 s	1. MTU-6 2. MEPS 3. VBATDT + 10-MDP BSA: 0.02 cm^2	Dual-cure (DC) resin cement (0.75 mm Ø × 0.5 mm height)	*n* = 6 TC: Not performed Standards: Not specified CHS: 0.5 mm/min	MEPS showed the highest SBS VBATDT + 10-MDP did not increase the SBS
Fonseca et al. (2009)[24]	Ni-Cr Dimension: 9 mm Ø × 3 mm thick ST: #320, #400, #600 SiC paper, SB with 50 µm Al_2O_3 for 20 s	1. VBATDT + 10-MDP 2. MTU-6 BSA: 5 mm Ø	Resin cements containing 10-MDP, and MAC-10 were placed on the primed alloy surface (5 mm Ø × 2 mm thick)	*n* = 10 TC: 5°C and 55°C DT: 30 s No. of cycles: 1000 Standards: Not specified CHS: 0.5 mm/min	Alloy primers did not increase the bond strength of their respective resin cements to base alloys
Matsumura et al. (1997)[27]	Stainless steel Dimension: 10 mm Ø × 2.5 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 10s	1. 4-AET, 2. 10-MDP, 3. MEPS 4. MAC-10 5. 4-META BSA: 5 mm Ø	AC repair resin containing PMMA + MMA-4-META/TBB or PMMA + MMA-TBB (6 mm Ø × 2 mm thick)	*n* = 8 TC: 4°C and 60°C DT: 1 min No. of cycles: 20,000 Standards: ISO/TR 11405 shear testing jig CHS: 0.5 mm/min	10-MDP was effective in bonding AC repair resin to the stainless steel alloy
Yanagida et al. (2004)[28]	Ti-Al-Nb Dimension: 10 mm Ø × 2.5 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 15 s	1. 4-AET 2. BPDM (adduct of 2-hydroxyethyl methacrylate and 3,4,4′,5′-biphenyl tetracarboxylic anhydride) 3. VBATDT + 10-MDP 4. 10-MDP 5. 4-META 6. MEPS 7. MAC-10 8. 4-META BSA: 5 mm Ø	AC acrylic resin based on 1. PMMA + MMA/BPO-amine 2. PMMA + MMA/4-META-TBB 3. Polyethyl methacrylate (PEMA)-β-methacrylate oxyethyl propionate (MAOP)/BPO-amine (6 mm Ø × 2 mm thick)	*n* = 16 TC: 4°C and 60°C DT: 1 min No. of cycles: 20,000 Standards: Not specified CHS: 0.5 mm/min	VBATDT + 10-MDP, 10-MDP, and MEPS exhibited greater SBS with the alloy when bonded with luting resin containing 4-META

(Contd...)

Table 2: *(Contd...)*

Authors (Year)	*Alloy adherends*, dimensions & surface treatments (ST)*	*Alloy primers and bonding surface area (BSA)*	*Superjacent adherends and dimensions*	*Number of specimens per group/ condition (n), sample treatment, standards, and crosshead speed (CHS)*	*Results and Conclusion*
Bulbul and Kesim (2010)[29]	1. Co-Cr 2. Au-Ag-Pt Dimension: 10 mm Ø × 2 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 10 s For noble alloy, 110 µm Al_2O_3 for 10 s	1. VBATDT + 10 MDP 2. 4-META 3. 10-MDP BSA: 8 mm Ø	AC repair, HC, and microwave resins (8 mm Ø × 2 mm thick)	*n* = 12 TC: 5˚C and 55˚C DT: 30 s No. of cycles: 5000 Standards: Not specified CHS: 0.5 mm/min	SBS of base and noble alloy-to-acrylic resins were improved by 10-MDP primer application
Imai et al. (2014)[30]	Ag-Pd-Cu-Au Dimension: 10 mm Ø × 2.5 mm thick ST: #600 SiC paper, SB with 50-70 µm Al_2O_3 for 10 s	1. VBATDT + 10-MDP 2. 10-MDP 3. 10-MDDT + 6-MHPA 4. 4-AET 5. MTU-6 6. MTU-6 + γ-MPTS + MAC-10 7. γ-MPTS + 10-MDP + VBATDT 8. VBATDT. BSA: 19.63 mm^2	LC indirect composite resin (6 mm Ø × 2 mm thick)	*n* = 11 TC: 5˚C and 55˚C DT: 1 min No. of cycles: 20,000 Standards: Not specified CHS: 0.5 mm/min	10-MDDT + 6-MHPA, and MTU-6 showed the greatest SBS
Matsumura et al. (1996)[31]	Co-Cr Dimension: 10 mm Ø × 2.5 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 10 s	1. 4-AET 2. 10-MDP 3. MEPS 4. MAC-10 5. 4-META BSA: 5 mm Ø	8 mm Ø × 2.5 mm thick alloys luted with self-adhesive luting agent containing 1. PMMA + MMA-4-META/TBB 2. 10-MDP + PMMA + MMA-4META/TBB PMMA + MMA-TBB	*n* = 8 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 100,000 Standards: ISO/TR 11405 shear testing jig CHS: 0.5 mm/min	Co-Cr alloy is more consistently bonded with a combination of a 10-MDP primer and 4-META/MMA-TBB luting resin
Yoshida et al. (1993)[32]	1. Co-Cr 2. Ag-Pd-Cu-Au Dimension: 10 mm Ø × 2 mm thick ST: #400 SiC paper, SB with 50 µm Al_2O_3 for 15 s. Some of the Ag-Pd-Cu-Au alloy specimens were also heated at 400°C for 3 min in an electric furnace	1. 4-META 2. VBATDT 3.10-MDP BSA: 5 mm Ø	LC opaque resin + veneering resin. (6 mm Ø × 2 mm thick)	*n* = 15 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 5000, 10,000, 20,000 Standards: Not specified CHS: 0.5 mm/min	10-MDP was effective in strongly bonding light-cured veneering resin to Co-Cr alloy. VBATDT primer considerably improved the bond between composite resin and Ag-Pd-Cu-Au alloy
Yoshida et al. (1999)[33]	Co-Cr Dimension: 10 mm Ø × 2 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 15 s	1. 4-AET 2. 10-MDP 3. 4-META 4. MEPS 5. MAC-10 BSA: 5 mm Ø	AC acrylic resin. (6 mm Ø × 2 mm thick)	*n* = 10 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 50,000 Standards: ISO/TR 11405 shear testing jig CHS: 0.5 mm/min	10-MDP and MEPS are effective hydrophobic primers for bonding resin to Co-Cr alloy

Suzuki et al. (2005)[34]	1. Ti-Al-Nb 2. Co-Cr Dimension: 10 mm Ø × 2 mm thick ST: #600 SiC paper, SB with 80 µm Al_2O_3 for 15 s	1. MEPS 2. MAC-10 3. 10-MDDT (10-methacryloyloxy decyl-6, 8-dithiooctanoate) + 6-MHPA (6-methacryloyloxy hexyl phosphono acetate) 4. 4-META BSA: 4 mm Ø	HC PMMA + MMA/ 4-META. (6 mm Ø × 6 mm thick)	*n* = 25 TC: 5°C and 55°C DT: 1 min No. of cycles: 10,000 Standards: Not specified CHS: 1 mm/min	MEPS and 4-META groups showed significantly higher SBS
Sanohkan et al. (2012)[35]	Co-Cr Dimension: 10 × 10 × 2.5 mm^3 ST: #240 to #600 SiC papers, SB with 50 µm Al_2O_3 for 10 s	1. γ-MPTS 2. 4-META 3. 6-MHPA 4. VBATDT + 10-MDP 5. Phosphonic acid acrylate in *tert*-butyl alcohol 6. γ-MPTS + 10-MDP + VBATDT BSA: 5 mm Ø	AC acrylic resin (5 mm Ø × 5 mm height)	*n* = 5 TC: Not performed Standards: Not specified CHS: 0.5 mm/min	γ-MPTS and 4-META were effective to bond autopolymerizing acrylic resin to Co-Cr alloy
Ishikawa et al. (2005)[36]	Stainless steel Dimension: 10 mm Ø × 2.5 mm thick ST: #1500 SiC paper	1.4-AETA (4-acryloyloxyethyl trimellitate anhydride) + 2-HEMA (2-hydroxy ethyl methacrylate) 2. 10-MDP 3. MP (meth-acrylate-phosphate) 4. 10-MDDT + 6-MHPA 5. 4-META BSA: 5 mm Ø	8 mm Ø × 2 mm thick alloy luted with AC resin cement using PMMA + MMA/TBB	*n* = 16 TC: 5°C and 55°C DT: 1 min No. of cycles: 20,000 Standards: ISO/TR 11405 CHS: 0.5 mm/min	Specimens primed with the 10-MDP material recorded the greatest bond strength for the alloys
Koizumi et al. (2012)[37]	Ti-Al-Nb Dimension: 10 mm Ø × 2.5 mm thick ST: #800, #1000, #1500 SiC papers	1. 4-AETA + 2-HEMA 2. VBATDT + 10-MDP 3. BPDM 4. 10-MDP 5. 10-MDDT + 6-MHPA 6. MAC-10 7. 4-META BSA: 5 mm Ø	8 mm Ø × 2 mm thick alloy disk was luted with AC with acrylic resin containing PMMA + MMA/TBB	*n* = 18 TC: 5°C and 55°C DT: 1 min No. of cycles: 20,000 Standards: ISO/TR 11405 CHS: 0.5 mm/min	10-MDP is more effective for bonding Ti-Al-Nb with AC resin

(Contd...)

Table 2: *(Contd...)*

Authors (Year)	*Alloy adherends*, dimensions and surface treatments (ST)*	*Alloy primers and bonding surface area (BSA)*	*Superjacent adherends and dimensions*	*Number of specimens per group/ condition (n), sample treatment, standards, and crosshead speed (CHS)*	*Results and Conclusion*
Hiraba et al. (2019)[38]	Au-Cu-Ag-Pt-Pd Dimension: 10 mm Ø × 3 mm thick ST: #800, #1000, #1500 SiC papers	1. MTU-6 + γ-MPTS + MAC-10 2. MTU-6 3. VBATDT + 10-MDP 4. VBATDT 5. 10-MDP 6. γ-MPTS + 10-MDP + VBATDT 7. 10-MDDT + 6-MHPA 8. 4-AETA + 2-HEMA 9. 4-META BSA: 5 mm Ø	AC acrylic resin containing PMMA + MMA/TBB and TBBO (partially oxidized) (6 mm Ø × 1 mm thick)	*n* = 22 TC: Not performed Standards: Not specified CHS: 0.5 mm/min	10-MDDT + 6-MHPA was an effective primer for noble alloys
Nima et al. (2017)[39]	Ni-Cr Dimension: 8 × 10 × 2 mm^3 ST: #180 SiC paper, SB with 50 µm Al_2O_3 for 10 s	1. γ-MPTS 2. VBATDT + 10-MDP 3. MAC-10 + Phosphoric acid monomer BSA: 1 mm Ø	Adhesive + LC composite resin (1 mm Ø × 1 mm thick)	*n* = 10 TC: 5˚C and 55˚C DT: 30 s No. of cycles: 5000 Standards: Not specified CHS: 0.5 mm/min	The high SBS between alloy and composite resin was obtained for VBATDT + 10- MDP and 10-MAC primers
Matsumura et al. (1999)[44]	1. Au-Cu-Ag-Pt-Pd 2. Au-Pt-Pd 3. Pd-Ga-Co 4. Ag-Pd-Cu-Au 5. Ag-In-Zn-Pd Dimension: 10 mm Ø × 2.5 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 10 s	VBATDT BSA: 5 mm Ø	8 mm Ø × 2.5 mm thick discs luted with AC resin containing PMMA + MMA-4-META/TBB	*n* = 16 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 100,000 Standards: ISO/TR 11405 shear testing jig CHS: 0.5 mm/min	VBATDT is much more effective as a bonding promoter for noble metals. No statistical difference among the noble alloys in SBS primed with VBATDT
Okuya et al. (2010)[45]	1. Au-Pt-Pd-Ag 2. Pd-Au-In-Ag 3. Ag-Pd-Cu-Au Dimension: 10 mm Ø × 2.5 mm thick ST: #600 SiC paper	1. VBATDT 2. MTU-6 3. 10-MDDT + 6-MHPA BSA: 5 mm Ø	AC luting cement PMMA + MMA-TBB (6 mm Ø × 2.5 mm thick)	*n* = 5 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 2000 Standards: Not specified CHS: 1 mm/min	10-MDDT + 6-MHPA showed promising results with high Au alloys
Minami et al. (2011)[46]	1. Au-Pt-Pd-Ag 2. Au-Pt 3. Pd-Au-Ag 4. Ag-Pd-Cu-Au Dimension: 10 mm Ø × 2.5 mm thick ST: #240, #400, #600 SiC papers, SB with 50 µm Al_2O_3 for 5 s	1. MEPS 2. VBATDT 3. MTU-6 4. 10-MDDT BSA: 5 mm Ø	8 mm Ø × 2.5 mm thick alloy disc luted with adhesive resin cement PMMA + MMA-4-META/TBB.	*n* = 7 TC: 5 ± 1˚C and 55 ± 1˚C DT: 1 min No. of cycles: 20,000, 50,000 Standards: Not specified CHS: 1 mm/min	The 10-MDDT showed the highest SBS values

Watanabe et al. (1995)[47]	1. Au-Cu-Ag-Pt-Pd 2. Au-Cu-Ga-Ir Dimension: 8 mm Ø × 2 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 10 s	1. VBATDT 2. MEPS BSA: 5 mm Ø	6 mm Ø × 2 mm thick alloys luted with AC opaque resin PMMA + MMA-4-META/TBB	*n* = 5 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 5000, 10,000, 20,000 Standards: Not specified CHS: 0.5 mm/min	MEPS and VBATDT enhanced the bond strength of PMMA + MMA-4-META/TBB to both alloys
Yoshida and Atsuta (1997)[48]	1. Ag-Pd-Cu-Au 2. Au-Cu-Ag-Pt-Pd Dimension: 10 mm Ø × 2 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 15 s	1. MEPS 2. VBATDT BSA: 5 mm Ø	6 mm Ø × 2 mm thick alloys luted with resin cement: 1. 4-AET 2. 10-MDP 3. PMMA + MMA-4-META/TBB	*n* = 15 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 50,000, 100,000 Standards: Not specified CHS: 0.5 mm/min	The specimens primed with MEPS/VBATDT showed higher bond strengths
Matsumura et al. (1999)[49]	Ag-Pd-Cu-Au Dimension: 10 mm Ø × 2.5 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 10 s	1. MEPS 2. MTU-6 3. VBATDT 4. VBATDT + 10-MDP BSA: 5 mm Ø	LC composite resin (6 mm Ø × 2 mm thick)	*n* = 16 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 20,000 Standards: Not specified CHS: 0.5 mm/min	MEPS exhibited the greatest bond strength
Taira and Kamada (2008)[50]	Au-Cu-Ag-Pd-Pt Dimension: 10 mm Ø × 2.5 mm thick ST: #320, #600 SiC paper, SB with 50 µm Al_2O_3 for 5 s	1. MTU-6 2. 10-MDP 3. VBATDT 4. VBATDT + 10-MDP 5. MTU-6 + 10-MDP BSA: 5 mm Ø	8 mm Ø × 5 mm thick acrylic rod luted with AC based on PMMA + MMA-TBB resin	*n* = 12 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 5000 Standards: Not specified CHS: 0.5 mm/min	The combined use of VBATDT with MDP is advantageous to bonding durability compared with the use of only VBATDT or 10-MDP
Lee et al. (2015)[51]	1. Au-Pd-Pt 2. Au-Pd-Ag 3. Pd-Ag Dimension:10 × 10 × 1 mm^3 ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 5 s	1. VBATDT 2. MEPS 3. 10-MDDT 4. γ-MPTS + 3-mercapto propyl trimethoxy silane (SPS) BSA: 4.45 mm^2	DC resin cements (2.38 mm Ø)	*n* = 9 TC: 5˚C and 55˚C DT: 30 s No. of cycles: 5000 Standards: Not specified CHS: 1 mm/min	γ-MPTS + SPS are promising alternatives to VBATDT for improving resin bonding to dental noble alloys
Yoshida (2017)[52]	Au-Cu-Ag-Pt-Pd Dimension: 8.0 mm Ø × 2.0 mm thick ST: #1000 SiC paper	1. VBATDT 2. MTU-6 3. VBATDT + 10-MDP 4. 10-MDDT + 6-MHPA 5. 10-MDTP (10-methacryloyloxydecyl dihydrogen thiophosphate) + 10-MDP 6.10-MDTP BSA: 4 mm Ø	AC resin (5 mm Ø × 2 mm thick)	*n* = 10 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 2000 Standards: Not specified CHS: 0.5 mm/min	VBATDT significantly enhanced the bond strength

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Table 2: *(Contd...)*

Authors (Year)	*Alloy adherends*, dimensions and surface treatments (ST)*	*Alloy primers and bonding surface area (BSA)*	*Superjacent adherends and dimensions*	*Number of specimens per group/ condition (n), sample treatment, standards, and crosshead speed (CHS)*	*Results and Conclusion*
Yoshida and Atsuta (1999)[53]	Ag-Pd-Cu-Au Dimension: 10 mm Ø × 2 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 15 s	1. VBATDT 2. MEPS BSA: 5 mm Ø	AC PMMA + MMA-TBB, BPO-amine, and camphorquinone – amine complex. (6 mm Ø × 2 mm thick)	*n* = 10 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 20,000 Standards: ISO/TR 11405 shear testing jig CHS: 0.5 mm/min	MEPS had higher SBS than VBATDT
Taira et al. (2008)[54]	Ag-Pd-Cu-Au Dimension: 10 mm Ø × 2.5 mm thick ST: #320, #600 SiC paper, SB with 50 µm Al_2O_3 for 5 s	1. MTU-6 2. 10-MDP 3. Acid phosphoxyethyl methacrylate (PM) + MMA 4. Acid phosphoxy polyoxyethylene glycol methacrylate (PE) + MMA 5. Acid phosphoxy polyoxypropylene glycol methacrylate (PP) + MMA 6. VBATDT 7. VBATDT + 10-MDP 8. MEPS 9. MTU-6 + 10-MDP 10. MTU-6 + PM 11. MTU-6 + PE 12. MTU-6 + PP BSA: 5 mm Ø	8 mm Ø × 5 mm thick acrylic rod luted with AC based on PMMA + MMA-TBB resin	*n* = 6 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 5000 Standards: Not specified CHS: 0.5 mm/min	MTU-6 was superior to VBATDT as an adhesion-promoting monomer for Ag-Pd-Au-Cu alloy
Yoshida et al. (1996)[55]	1. Ag-Pd-Cu-Au 2. Co-Cr Dimension: 10 mm Ø × 2 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 15 s	1. MEPS 2. VBATDT 3. 10-MDP BSA: 5 mm Ø	6 mm Ø × 2 mm thick alloys luted with resin cements based on 1. 4-acryloyloxy ethyl trimellitate (4-AET) 2. 10-MDP 3. PMMA + MMA-4-META/TBB	*n* = 15 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 20,000, 50,000 Standards: Not specified CHS: 0.5 mm/min	MEPS improved the SBS between each of the three resin cements and Ag-Pd-Cu-Au alloy. The use of MEPS conferred high shear bond strengths of adhesive luting cements to noble metals
Imamura et al. (2018)[56]	Ag-Zn-Sn-In Dimension: 10 mm Ø × 2.5 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 15 s	1. VBATDT 2. 10-MDP 3. VBATDT + 10-MDP BSA: 5 mm Ø	AC PMMA + MMA/4-META-TBB (5 mm Ø, thickness not mentioned)	*n* = 10 TC: 5˚C and 55˚C DT: 1 min No. of cycles: 50,000 Standards: Not specified CHS: 0.5 mm/min	The bond strengths of 10-MDP were significantly high

Yoshida et al. (2001)[57]	Ag-Pd-Cu-Au Dimension: 10 mm Ø × 2 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 15 s	1. VBATDT + 10-MDP 2. MEPS 3. MTU-6 BSA: 5 mm Ø	6 mm Ø × 2 mm thick alloy bonded with three resin cements based on 1.MAC-10 2.10-MDP and 3. PMMA + MMA/4-META-TBB	*n* = 10 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 100,000 Standards: ISO/TR 11405 shear testing jig CHS: 0.5 mm/min	Specimens primed with VBATDT + 10-MDP showed significantly greater bond strength
Piva et al. (2015)[58]	1. Ni--Cr 2. Ag-Pd 3. Ag-Au Dimension:10 mm Ø × 3 mm thick ST: #320, #400, #600, and #1200 SiC papers.	1. VBATDT + 10-MDP 2. HEMA-P (methacryloyloxy ethyl dihydrogen phosphate monomer) 3. ETMA (2,3-Epithiopropyl methacrylate) 4. HEMA-P + ETMA BSA: 1 mm Ø	LC resin cement (1 mm Ø × 1.5 mm thick)	*n* = 12 TC: Not performed Standards: Not specified CHS: 0.5 mm/min	VBATDT can increase the bond strength of precious metals, especially Ag-Pd alloys. The experimental formulation yielded less SBS with both base and noble alloys
Shimoe et al. (2010)[59]	Ag-Pd-Cu-Au Dimension: 10 mm Ø × 2.5 mm thick ST: #600 SiC paper, SB with 50-70 µm Al_2O_3 for 5 s	1. VBATDT + 10-MDP 2. PETP (pentaerythritol tetrakis (3-mercaptopropionate) 3. MEPS 4. MTU-6 5. 10-MDDT + 6-MHPA BSA: 5 mm Ø	Indirect composite veneering materials (6 mm Ø × 2 mm thick)	*n* = 10 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 20,000 Standards: ISO/TR 11405 shear testing jig CHS: 0.5 mm/min	PETP does not contain a radically polymerizable functional group and exhibited the least SBS
Ikemura et al. (2011)[60]	1. Au-Cu-Ag-Pt-Pd 2. Ag-Zn-In-Cu 3. Ag-Pd-Cu-Au 4. Ni-Cr Dimension: 6 mm Ø × 6 mm height ST: #600 SiC paper, SB with 40-50 µm Al_2O_3	1. 10-MDDT + 6-MHPA 2. 6-MHDT (6-methacryloyloxy hexyl-6,8-dithio octanoate) + 6-MHPP (6-methacryloyloxy hexyl-3-phosphono propionate) 3. 10-MDDT 4. 6-MHPA BSA: 5 mm Ø	LC micro-hybrid resin (5 mm Ø × 2 mm thick)	*n* = 6 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 5000 Standards: Not specified CHS: 1.0 mm/min	Combined primer application consisting of 6-MHDT + 6-MHPP provided efficacious bonding to precious and non-precious alloys
Ishii et al. (2008)[62]	1. Au-Pt-Pd 2. Ti-Al-Nb Dimension: 10 mm Ø × 2.5 mm thick ST: #800 SiC paper	1. VBATDT + 10-MDP 2. 10-MDP 3. VBATDT BSA: 5 mm Ø	8 mm Ø × 2.5 mm thick alloy luted with AC resin containing PMMA + MMA-TBB	*n* = 16 TC: 5˚C and 55˚C DT: 1 min No. of cycles: 20,000 Standards: ISO/TR 11405 CHS: 0.5 mm/min	10-MDP monomer was effective for bonding Ti-Al-Nb alloy

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Table 2: *(Contd...)*

Authors (Year)	*Alloy adherends*, dimensions and surface treatments (ST)*	*Alloy primers and bonding surface area (BSA)*	*Superjacent adherends and dimensions*	*Number of specimens per group/ condition (n), sample treatment, standards, and crosshead speed (CHS)*	*Results and Conclusion*
Kapoor et al. (2017)[63]	Ni-Cr Dimension: 7.0 mm Ø × 5 mm thick ST: 1. Oxidation at 600 °C – 980°C to simulate alloy surface for PFM 2. Some samples were SB with Al_2O_3	10-MDP BSA: 7 mm Ø	Self-adhesive resin cement, resin-modified GIC Alloys attached to dentin	*n* = 10 TC: 5˚C and 55˚C DT: 30 s No. of cycles: 550 Standards: ISO/TR 11405 shear testing jig CHS: Not mentioned	Phosphoric acid methacrylates in the self-adhesive resin cement provided a strong chemical reaction with the 10-MDP component of the alloy primer
Miyahara et al. (2020)[64]	Ag-Pd-Cu-Au Dimension: 11 mm Ø × 3 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 20 s	10-MDP BSA: 5 mm Ø	AC luting agent PMMA + MMA/TBB (5 mm Ø, thickness not mentioned)	*n* = 10 TC: 5˚C and 55˚C DT: 1 min No. of cycles: 20,000 Standards: Not specified CHS: 1 mm/min	The SBS between the alloy and the MMA-TBB resin cement using the 10-MDP was improved
Koizumi et al. (2006)[69]	Ti-Al-Nb Dimension: 10 mm Ø × 2.5 mm thick ST: #600 SiC paper, SB with 50-70 µm Al_2O_3 for 15 s	1. VBATDT + 10-MDP 2. 10-MDDT + 6-MHPA BSA: 5 mm Ø	Resin cements based on 1. PMMA + MMA-4-META/TBB 2. MAC-10, PMMA + MMA/BPO. (6 mm Ø × 2 mm thick)	*n* = 16 TC: 4˚C and 60˚C DT: 1 min No. of cycles: 20,000 Standards: Not specified CHS: 0.5 mm/min	10-MDP and 6-MHPA enhanced the SBS of resin containing MAC-10 to the titanium alloy
Kurahashi et al. (2019)[70]	Co-Cr Dimension: 15 mm Ø × 3 mm thick ST: #600 SiC paper Some samples were silicoated	1. 10-MDTP + 10-MDP 2. 10- MDP + Silane monomer BSA: 5 mm Ø	AC resin (5 mm Ø × 5 mm height)	*n* = Not mentioned TC: Not performed Standards: Not specified CHS: 1 mm/min	Silica coating combined with MDTP + 10-MDP yielded high SBS with Co-Cr alloy
Yilmaz et al. (2011)[72]	Co-Cr Dimension: 10 mm Ø × 10 mm height ST: SB with 110 µm Al_2O_3 for 30 s. Nd:YAG laser irradiation	VBATDT + 10-MDP BSA: 19.6 mm^2	HC denture base resin (5 mm Ø × 1 mm thick)	*n* = 30 TC: 4˚C and 56˚C DT: 20 s No. of cycles: 2000 Standards: Not specified CHS: 1 mm/min	SBSs were highest when the sandblasted surfaces were laser irradiated and treated with the primer
Kalra et al. (2015)[73]	Co-Cr Dimension: 10 mm Ø × 2 mm thick ST: 110 µm Al_2O_3 for 14 s	VBATDT + 10-MDP BSA: 5 mm Ø	HC acrylic denture base resin (5 mm Ø × 2 mm thick)	*n* = 10 TC: Not performed Standards: Not specified CHS: 0.5 mm/min	VBATDT + 10-MDP along with sandblasting significantly improved the bonding of heat-cured denture base resin with the Co-Cr alloy
Korkmaz et al. (2019)[75]	1. Ni-Cr 2. Ti-Al-V Dimension: 10 × 10 × 2 mm^3 ST: #240, #400, #600 SiC papers, 30 µm Al_2O_3	VBATDT + 10-MDP BSA: 5 mm Ø	Bonding agent containing 10-MDP + 4-META + Light-cure composite resin. (5 mm Ø × 3 mm thick)	*n* = 11 TC: 5˚C and 55˚C DT: 30 s No. of cycles: 5000 Standards: Not specified CHS: 0.5 mm/min	VBATDT + 10-MDP demonstrated the highest SBS with the alloys

*Ag, silver; Al, aluminium; Au, gold; Co, cobalt; Cr, chromium; Cu, copper; Ga, gallium; In, indium; Ir, iridium; Mo, molybdenum; Nb, niobium; Ni, nickel; Pd, palladium; Pt, platinum; Sn, tin; Ti, titanium; V, vanadium; Zn, zinc

Table 3: Descriptive data of the included studies (n = 15) concerning tensile bond strength (TBS)

Authors (Year)	*Alloy adherends*, dimension & surface treatment (ST)*	*Alloy primers and bonding surface area (BSA)*	*Superjacent adherends and dimensions*	*Number of specimens per group/ condition (n), Sample treatment, standards, and crosshead speed (CHS)*	*Results and Conclusion*
Ikemura et al. (2011)[40]	1. Au-Cu-Ag-Pt-Pd 2. Ag-Zn-In-Cu 3. Ag-Pd-Cu-Au alloy Dimension: 7.0 mm Ø × 6.5 mm height ST: #1000, #2000, #4000 SiC papers	1. 2-MEDT (2-methacryloyloxyethyl-6, 8-dithiooctanoate) 2. 6-MHDT 3. 10-MDDT 4. BMEDS (*bis* (2- Methacryloyloxy ethyl) disulfide) 5. BMPDS (*bis* (5- Methacryloyloxy pentyl) disulfide, 6. BMDDS (*bis* (10- Methacryloy-loxy decyl) disulfide) 7. 4-META 8. VBATDT 9. MPMA (N-(4-mercaptophenyl) methacrylamide) BSA: 5 mm Ø	5 mm Ø × 50 mm high stainless steel rod luted with AC PMMA + MMA/ BPO-DEPT redox	n = 5 TC: 4°C and 60°C DT: 1 min No. of cycles: 2000 Standards: Not specified CHS: 2 mm/min	On bonding to Au alloy, the bond strengths of 2-MEDT, 6-MHDT, and 10-MDDT were significantly higher than other primers
Banerjee et al. (2009)[41]	1. Co-Cr 2. Ni-Cr Dimension: Not mentioned ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 10 s	1. 10-MAC 2. 4-META 3. VBATDT + 10-MDP BSA: 3 mm Ø	Inverted cone (5 mm Ø at the top; 3 mm Ø at bonding end) AC acrylic resin	n = 8 TC: Not performed Standards: Not specified CHS: 0.05 cm/min	Both Co-Cr and Ni-Cr alloys treated with VBATDT + 10-MDP had significantly higher TBS than without primers
Kadoma (2002)[42]	1. Au-Cu-Ag-Pt-Pd 2. Ag-Pd-Cu-Au 3. Ag-Zn-In-Cu 4. Stainless steel 5. Co-Cr 6. Ni-Cr Dimension: 5 mm Ø × 4 mm thick ST: #1000, #2000, and #4000 SiC papers	1. 10-MDP 2. EP3MA (4,5-epithiopentyl methacrylate) 3. EP8MA (9,10- epithiodecyl methacrylate) BSA: 5 mm Ø	5 mm Ø × 4 mm thick alloy luted with AC resin containing PMMA + MMA-TBBO PMMA + MMA/ BPO-DEPT (N,N-*bis* (2-hydroxyethyl)-p-toluidine)	n = 5 TC: 4°C and 60°C DT: 1 min No. of cycles: 2000 Standards: Not specified CHS: 2 mm/min	The TBS obtained by the combined use of EP3MA and 10-MDP was generally higher for PMMA + MMA-TBBO. The values obtained by the combined use of EP8MA and 10-MDP were conversely higher for redox resin
Kadoma (2003)[43]	1. Au-Cu-Ag-Pt-Pd 2. Ag-Pd-Cu-Au 3. Ag-Zn-In-Cu 4. Stainless steel 5. Co-Cr 6. Ni-Cr Dimension: 5 mm Ø × 4 mm thick ST: #1,000, #2,000, and #4,000 SiC papers	1. 5VS (5-(4-vinylbenyl)-2-thiobarbituric acid) 2. VBATDT 3. EP8MA BSA: 5 mm Ø	5 mm Ø × 4 mm thick alloy luted with AC resin containing 1. PMMA + MMA-TBBO 2. PMMA + MMA/ BPO-DEPT redox	n = 5 TC: 4°C and 60°C DT: 1 min No. of cycles: 2000 Standards: Not specified CHS: 2 mm/min	The TBS to precious alloys generally increased in the order of 5VS < VBATDT < EP8MA

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Table 3: *(Contd...)*

Authors (Year)	*Alloy adherends*, dimension & surface treatment (ST)*	*Alloy primers and bonding surface area (BSA)*	*Superjacent adherends and dimensions.*	*Number of specimens per group/ condition (n), Sample treatment, standards, and crosshead speed (CHS)*	*Results and Conclusion*
Ikemura et al. (2011)[61]	1. Au-Cu-Ag-Pt-Pd 2. Ag-Zn-In-Cu 3. Ag-Pd-Cu-Au Dimensions: 7.0 mm Ø × 6.5 mm height ST: #1000, #2000, #4000 SiC papers	1. 2-MEDT 2. 6-MHDT 3. 10-MDDT 4. 12-MDDDT (12-Methacryloyloxydodecyl-6,8-dithiooctanoate) 5. 2-AEDT (2-Acryloyloxyethyl-6,8-dithiooctanoate) 6. MAEDT (1-Methyl-2-acryloyloxyethyl-6,8-dithiooctanoate) 7. EMEDT (1-Ethyl-2-methacryloyloxyethyl-6,8-dithiooctanoate) 8. BMMMDT (*Bis*(methacryloyloxymethyl)methyl-6,8-dithiooctanoate) BSA: 5 mm Ø	7.0 mm Ø × 6.5 mm high alloy were luted with adhesive resin containing PMMA + MMA/TBBO	*n* = 5 TC: 4°C and 60°C DT: 1 min No. of cycles: 2000 Standards: Not specified CHS: 2 mm/min	12-MDDDT achieved high TBS to Au-Cu-Ag-Pt-Pd, MEADT with Au-Ag-Pd, and 6-MHDA with Ag-Zn-In-Cu
Kapoor et al. (2017)[63]	Ni-Cr Dimension: 7.0 mm Ø × 5 mm thick ST: 1. Oxidation treatment at 600°C – 980°C to simulate alloy surface for PFM Some samples with SB with Al_2O_3	10-MDP BSA: 7 mm Ø	Alloys attached to dentin with self-adhesive resin-modified glass ionomer cement	*n* = 10 TC: 5°C and 55°C DT: 30 s No. of cycles: 550 Standards: ISO/TR 11405 CHS: Not mentioned	Methacrylates in the self-adhesive resin cement provided a strong chemical reaction with the 10-MDP component of the alloy primer
Taira and Imai (1995)[65]	1. Au-Cu-Ag-Pt-Pd 2. Ag-Pd-Cu-Au 3. Co-Cr Dimension: 10 mm Ø × 2 mm thick ST: #200 to #600 SiC papers	1. S - thiophosphoric methacrylate 2. DP-10-methacryloyloxy decyl phosphate 3. EP- di(2-methacryloyloxy ethyl) phosphate BSA: 5 mm Ø	8 mm Ø × 30 mm length acrylic rod luted with luting resin consisting of PMMA + MMA-TBB	*n* = 5 TC: 4°C and 60°C DT: 1 min No. of cycles: 2000 Standards: Not specified CHS: 2 mm/min	TBS was good for the primers containing DP and EP
Jamel et al. (2019)[66]	Ni-Cr Dimensions: 9 mm Ø × 3 mm thick ST: #400, #600 SiC paper, oxidation at 980°C for 5 min, SB with 125 µm Al_2O_3	1. 10-MDP 2. MEPS BSA: Not mentioned	Self-adhesive DC cement (4 mm Ø × 4 mm thick)	*n* = 5 TC: 5°C and 55°C DT: 30 s No. of cycles: 300 Standards: Not specified CHS: 0.5 mm/min	Both 10-MDP or MEPS primers showed similar behavior on TBS
Jung et al. (2019)[67]	Co-Cr alloy Dimension: 6 × 1 × 1 mm^3 ST: SB with 125 µm Al_2O_3 for 5 s	1. MTU-6 2. MEPS 3. VBATDT + 10-MDP 4. Phosphonic acid methacrylate monomer BSA: 1 mm^2	Resin cements (6 × 1 × 1 mm^3)	*n* = 15 TC: Not performed Standards: Not specified CHS: 1.0 mm/min	The VBATDT + 10-MDP showed higher chemical bonding with Co-Cr alloy

Ikemura et al. (2011)[68]	1. Au-Cu-Ag-Pt-Pd 2. Ag-Zn-In-Cu 3. Ag-Pd-Cu-Au 4. Co-Cr 5. Ni-Cr Dimension: Not mentioned ST: #1000, #2000, #4000 SiC paper	1. 10-MDDT + 10-MDPP (10- Methacryloyloxy decyl-3-phosphono propionate) 2. 10-MDDT + 6-MHPP 3. 10-MDDT + 6-MHPA 4. 10-MDDT + 10-MDP 5. 10-MDDT + 4-ACP (4-acryloyloxy ethoxy carbonyl phthalic acid) 6. 10-MDDT + 4-MCP (4-methacryloyloxy ethoxy carbonyl phthalic acid) 7. 6-MHPA 8. 10-MDDT BSA: 5 mm Ø	Adhesive resin PMMA + MMA-TBBO resin.	*n* = 5 TC: 4°C and 60°C DT: 1 min No. of cycles: 2000 cycles Standards: Not specified CHS: 2 mm/min	10-MDDT + 6-MHPA had good TBS to the alloys
Antoniadou et al. (2000)[71]	1. Au-Pt-Pd-Ag-In 2. Au-Ag-Cu-Pt Dimension: 6.4 mm Ø × 3.4 mm thick ST: #320, #500, and #800 SiC papers, SB with 50 µm Al_2O_3 for 14 s	1. VBATDT + 10-MDP 2. 10-MDP + 2-HEMA + N-methacryloyl 5- aminosalicylic (5-NMSA) BSA: 3.3 mm Ø	AC composite resin with/ without 10-MDP (3.3 mm Ø × 15 mm height)	*n* = 10 TC: 5°C and 55°C DT: 30 s No. of cycles: 100,000 Standards: Not specified CHS: 2 mm/min	Combinations of both primers yielded high TBS with the noble alloys
Lee et al. (2010)[74]	Co-Cr Dimension: Not specified ST: SB with 250 µm Al_2O_3	MEPS BSA: Not specified	HC denture base resin.	*n* = 10 TC: Not performed Standards: Not specified CHS: 25 mm/min	The bead retention showed significantly higher mean separation forces than a smooth alloy plate
Azimian et al. (2012)[76]	Au-Pd-In-Ga Pd-Ag-Sn-In Dimension: 8 mm Ø × 3.4 mm thick ST: #600 SiC paper, SB with 50 µm Al_2O_3 for 15 s	1. γ-MPTS + 10-MDP + VBATDT 2. γ-MPTS + 10-MDP 3. VBATDT + 10-MDP BSA: 3.2 mm Ø	3.2 mm Ø DC composite resin (height not mentioned)	*n* = 8 TC: 5°C and 55°C DT: 30 s No. of cycles: 37,500 Standards: Not specified CHS: 2 mm/min	10-MDP-containing primers showed higher TBS alternatives to using other primers
Ikemura et al. (2011)[77]	Au-Cu-Ag-Pt-Pd Dimensions: 15 × 15 × 2 mm^3 ST: #240, #600 SiC papers, SB with 50 µm Al_2O_3	1. 3-methacryloyl oxypropyl triethoxy silane (3-MPTES) + 6-MHPA + 10-MDDT 2. 3-MPTES + 10-MDDT BSA: 5 mm Ø	5 mm Ø × 10 mm height stainless Co-Cr alloy luted with a DC resin cement	*n* = 7 TC: Not performed Standards: Not specified CHS: 1 mm/min	A ternary combination of 3-MPTES, 6-MHPA, and 10-MDDT contributed to increasing the TBS to Au-Cu-Ag-Pt-Pd

(Contd...)

Table 3: *(Contd..)*

Authors (Year)	*Alloy adherends*, dimension & surface treatment (ST)*	*Alloy primers & bonding surface area (BSA)*	*Superjacent adherends and dimensions.*	*Number of specimens per group/ condition (n), Sample treatment, standards, and crosshead speed (CHS)*	*Results and Conclusion*
Petrie et al. (2001)[78]	1. Au-Pd-In-Ga: Sn plated 2. Ni-Cr-Be: Acid etched Dimension: 3.5 mm Ø × 5 mm thick ST: #240, #320, #400 SiC papers, SB with 50 µm Al_2O_3 for 10 s	VBATDT + 10-MDP For non-Sn plated Au-Pd-In-Ga BSA: 9.62 mm^2	Alloys were cemented to enamel by resin cement	*n* = 21 TC: Not performed Standards: Not specified CHS: 0.5 mm/min	The air-abraded Au-Pd-In-Ga treated with VBATDT + 10-MDP exhibited the highest TBS

*Ag, silver; Al, aluminum; Au, gold; Be, beryllium; Co, cobalt; Cr, -chromium; Cu, copper; Ga, gallium; In, indium; Ir, iridium; Mo, molybdenum; Nb, niobium; Ni, nickel; Pd, palladium; Pt, platinum; Sn, tin; Ti, titanium; V, vanadium; Zn, zinc

luted with AC resin cement,[17,22,31,36,37,42–44,46–48,55,57,61,62] heat-cure (HC) resin,[2,18,19,29,34,72–74] light-cure (LC) resin,[8,24,30,32,39,49,58–60,67,75] dual-cure (DC) resin,[23,51,53,66,76] stainless steel (SS) alloys with AC/DC resins,[40,77] and corresponding alloys luted with dentin/enamel by self-adhesive resin cement/resin-modified glass ionomer.[63,78] The alloys included in this review were 16 noble (Au-Pt, Au-Pt-Pd, Au-Pt-Pd-Ag, Au-Pt-Pd-Ag-In, Au-Cu-Ag-Pt-Pd, Au-Cu-Ga-Ir, Au-Ag-Cu-Pd, Au-Ag-Cu-Pt, Au-Ag-Pt, Au-Pd-Ag, Au-Pd-In-Ga, Pd-Au-Ag, Pd-Au-In-Ag, Pd-Ag-Sn-In, Pd-Ga-Co, Ag-Pd-Cu-Au) and 9 predominantly base (Co-Cr-Mo, Ni-Cr-Be, Ni-Cr, Ag-Zn-Sn-In, Ag-Zn-In-Cu, Ag-In-Zn-Pd, stainless steel, Ti-Al-V, Ti-Al-Nb) alloys at various compositional proportions. The commonly used noble alloys in the admitted studies were Au-Cu-Ag-Pt-Pd and Ag-Pd-Cu-Au. The commonly used base alloys were Co-Cr and Ti-Al-Nb. None of the studies had discussed the effect of alloy composition on the primers' bond strength. Out of 62 included studies, 14 studies had not mentioned or executed thermocycling (TC).[2,18,22,23,35,38,41,58,67,70,73,74,77,78] Therefore, the application of alloy primers not only enhanced the SBS but also the TBS of the superjacent resins; however, thermocycling compromised the bonding efficacy to a lesser extent when compared with bond strength on unprimed alloy surfaces.

Risk of Bias

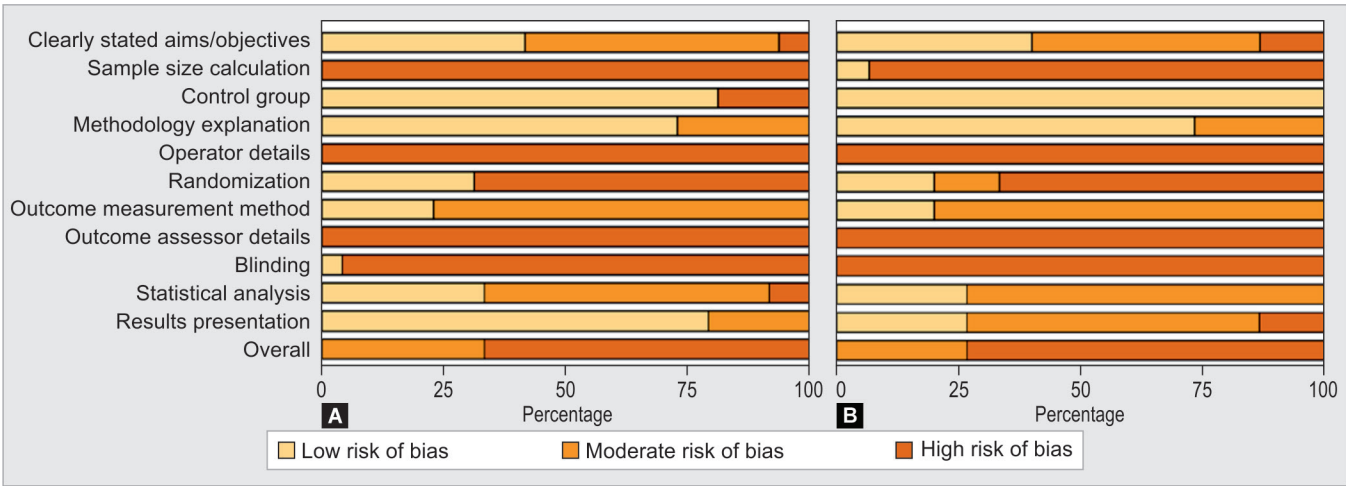
The 48 studies concerning SBS admitted in the systematic review showed 33.4% moderate RoB and 66.6% high RoB overall (Fig. 1A). Two[46,72] out of 48 studies explained the blinding procedures. None of the included studies in the SBS category elicited sample size calculation, operator, and outcome assessor details. The 15 studies concerning TBS admitted in the systematic review showed 26.8% moderate RoB and 73.2% high RoB overall (Fig. 1B). One study[78] out of 15 described the sample size calculation. None of the included studies in the TBS category elicited blinding protocol, operator, and outcome assessor details. No studies were found with low RoB.

Meta-analyses

Concerning SBS, 4 primers (for noble: VBATDT + 10-MDP and MTU-6; for base: 10-MDP, MEPS, and VBATDT + 10-MDP) and 4 alloys (Noble: Au-Cu-Ag-Pt-Pd and Ag-Pd-Cu-Au; Base: Co-Cr and Ti-Al-Nb) were included in the quantitative synthesis (Fig. 2). A significant difference in the SBS between the experimental (with primer) and control (without primer) groups was observed using VBATDT + 10-MDP ($Z = 3.51$; $p = 0.0005$) and MTU-6 ($Z = 7.48$; $p < 0.00001$) on Ag-Pd-Cu-Au. Concerning Ti-Al-Nb, there was a significant difference between the groups using VBATDT + 10-MDP ($Z = 5.67$; $p < 0.00001$) and 10-MDP ($Z = 7.84$; $p < 0.00001$). Concerning Au-Cu-Ag-Pt-Pd, there was a significant difference between the groups using VBATDT + 10-MDP ($Z = 2.20$; $p = 0.03$). However, no difference was observed while using MTU-6 ($Z = 1.86$; $p = 0.06$). Regarding Co-Cr, there was a significant difference between the groups using 10-MDP ($Z = 2.43$; $p = 0.02$). However, no difference was observed while using MEPS ($Z = 0.98$; $p = 0.33$). Irrespective of the primers' type or alloys, priming the alloy surface had a positive impact on the SBS values, as the overall differences were significant between experimental (with primer) and control (without primer) groups ($Z = 7.04$, $p < 0.00001$). The overall data were not homogeneous ($I^2 = 100\%$; χ^2 $p < 0.00001$). Also, there was no significant homogeneity in the subgroup meta-analyses ($I^2 = 99\%$; χ^2 $p < 0.00001$ and $I^2 = 96\%$; χ^2 $p < 0.00001$ for VBATDT + 10-MDP and MTU-6, respectively, concerning Ag-Pd-Cu-Au; $I^2 = 100\%$;

Table 4: Classification of dental alloy primers

Classification	*Alloy primers*
Neat primers: Single monomer with a reactive functional group	
Carboxylic acid-based/anhydrides	4-META, 4-AET, 4-AETA, MAC-10, BPDM
Sulfur-containing/thiol-thione based	VBATDT, MTU-6, EP3MA, EP8MA, PETP, 10-MDDT, ETMA, 2-MEDT, 6-MHDT, BMEDS, BMPDS, BMDDS, MPMA, 2-AEDT, 12-MDDDT, MAEDT, EMEDT, BMMMDT
Silane-based	γ-MPTS.
Phosphoric acid-based	10-MDP, HEMA-P, PM, PE, PP, DP, EP, S
Phosphonic acid ester-based	6-MHPA
Binary primers: Two monomers with different reactive functional groups	
Thio + phosphoric	VBATDT + 10-MDP, MTU-6 + 10-MDP, HEMA-P + ETMA, MTU-6 + PM, MTU-6 + PE, MTU-6 + PP, 10-MDDT + 10-MDP
Thio + phosphonic	10-MDDT + 6-MHPA, 6-MHDT + 6-MHPP, 10-MDDT + 10-MDPP, 10-MDDT + 6-MHPP
Thio + silicic	3-MPTES + 10-MDDT
Thio + carboxylic	10-MDDT + 4-ACP
Phospho + silicic	γ-MPTS + 10-MDP
Ternary primers: Three monomers with different reactive functional groups	
Thio + phosphor + silicic	γ-MPTS + 10-MDP + VBATDT
Thio + carboxylic + silicic	MTU-6 + γ-MPTS + MAC-10
Thio + phosphonic + silicic	3-MPTES + 6-MHPA + 10-MDDT
Hybrid primers: Structurally altered single monomer containing two reactive functional groups	
Thiophosphoric	MEPS, 10-MDTP
Thiosilicic	SPS
Thiocarboxylic	5-VS



Figs 1A and B: Summary of RoB concerning A. SBS; B. TBS

χ^2 $p < 0.00001$ for both the primers concerning Au-Cu-Ag-Pt-Pd; $I^2 = 99\%$; χ^2 $p < 0.00001$ and $I^2 = 100\%$; χ^2 $p < 0.00001$ for 10-MDP and MEPS, respectively, concerning Co-Cr; $I^2 = 99\%$; χ^2 $p < 0.00001$ for both VBATDT + 10-MDP and 10-MDP concerning Ti-Al-Nb).

While comparing VBATDT + 10-MDP and MTU-6 when used on noble alloys (Fig. 3), there were no overall significant differences in the SBS between the primers ($Z = 0.57$, $p = 0.57$) with the overall data heterogeneity ($I^2 = 97\%$; χ^2 $p < 0.00001$). No significant difference was observed between the primers on both the noble alloys with heterogeneous data in the subgroup meta-analysis (Ag-Pd-Cu-Au: $Z = 0.27$, $p = 0.79$; $I^2 = 97\%$; χ^2 $p < 0.00001$; Au-Cu-Ag-Pt-Pd: $Z = 0.44$, $p = 0.66$; $I^2 = 98\%$; χ^2 $p < 0.00001$). The comparison, 10-MDP vs MEPS on Co-Cr showed no difference in SBS (Fig. 4) between the primers with heterogeneous data ($Z = 1.52$, $p = 0.13$; $I^2 = 99\%$; χ^2 $p < 0.00001$). Likewise, there was no significant SBS difference between 10-MDP and VBATDT + 10-MDP on Ti-Al-Nb (Fig. 4) with data heterogeneity ($Z = 0.15$, $p = 0.88$; $I^2 = 83\%$; χ^2 $p = 0.003$).

Regarding the TBS, two primers (6-MHDT and 10-MDDT) and two alloys (Au-Cu-Ag-Pt-Pd and Ag-Pd-Cu-Au) were included in the quantitative synthesis. Upon comparing the 6-MHDT and 10-MDDT (Fig. 5), there was no overall difference between the primers when used on the above noble alloys ($Z = 0.41$, $p = 0.69$) with overall heterogeneous data ($I^2 = 81\%$; χ^2 $p = 0.001$). In the subgroup meta-analysis, no significant difference was observed between the primers on both the noble alloys with heterogeneous

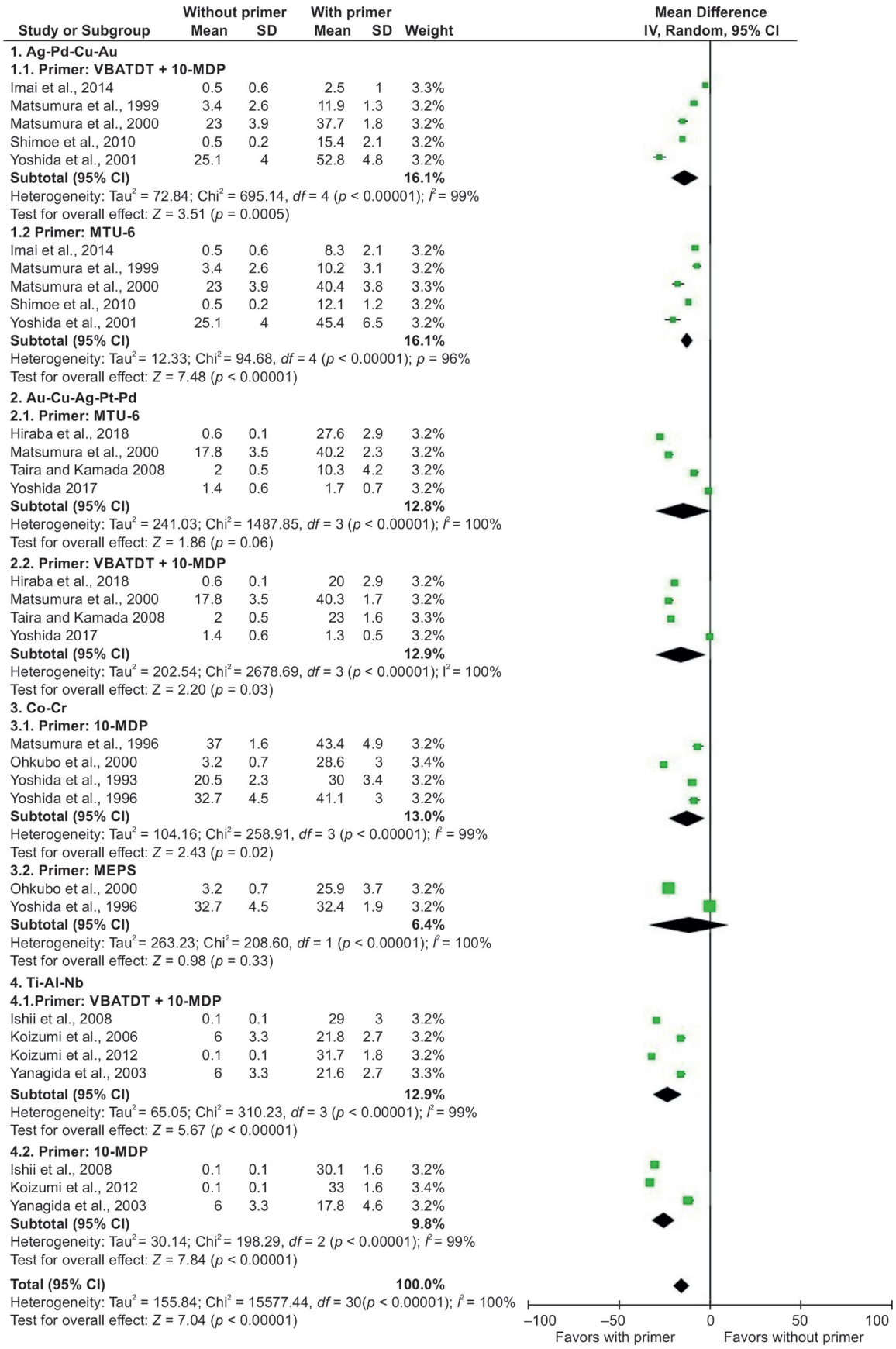


Fig. 2: Results of SBS meta-analyses with and without primer application, using a random-effects model

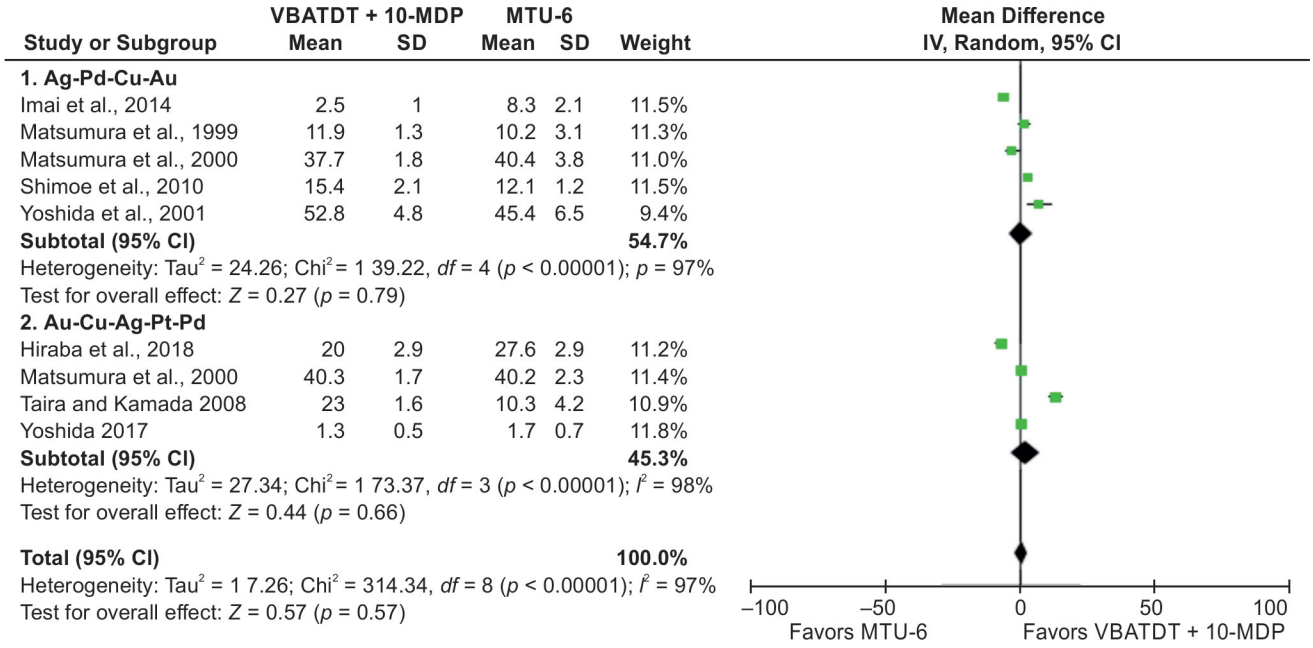


Fig. 3: Results of SBS meta-analyses concerning VBATDT + 10-MDP vs MTU-6 primed noble alloys, using a random-effects model

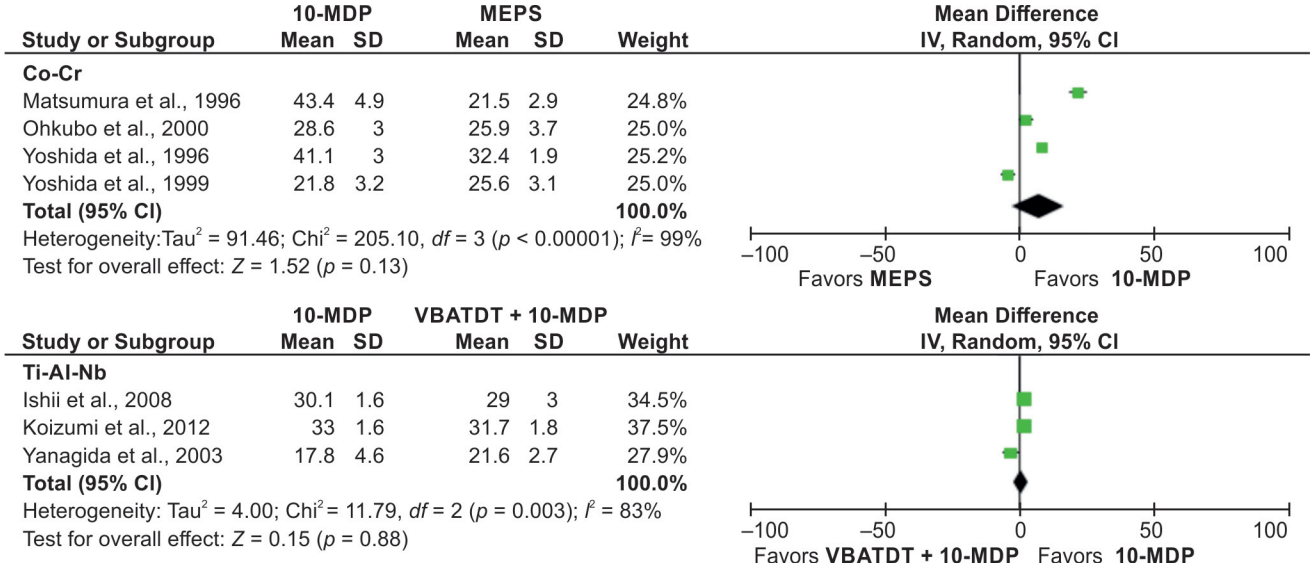


Fig. 4: Results of SBS meta-analyses concerning 10-MDP vs MEPS primed Co-Cr and 10-MDP vs MTU-6 primed Ti-Al-Nb, using a random-effects model

data (Ag-Pd-Cu-Au: $Z = 0.7$, $p = 0.48$; $I^2 = 91\%$; χ^2 $p = 0.001$; Au-Cu-Ag-Pt-Pd: $Z = 0.4$, $p = 0.69$; $I^2 = 65\%$; χ^2 $p = 0.09$).

Discussion

This review is the first of its kind to systemize and assimilate data concerning *in vitro* studies evaluating the effect of various alloy primers on the bond strength (SBS and TBS) of superjacent resins with alloys. Since myriad alloy primers (commercial and experimental) are available for a particular alloy, it is difficult to discern a proper inference concerning the utility of appropriate primers. The first null hypothesis was rejected because the application of primers significantly improved the bond strength of the resin irrespective of the alloys used. The second null hypothesis was accepted as no significant differences existed between the selected primers used on an alloy.

The sulfur-containing primers (VBATDT + 10-MDP and MTU-6) yielded high SBS with noble alloys (Au-Cu-Ag-Pt-Pd and Ag-Pd-Cu-Au). Carboxylic acid-based/anhydride, silane-based, and phosphoric acid-based primers are incapable of forming a strong durable bond with the noble alloys. Previously, the noble alloys containing Cu were heat-treated/annealed for the formation of a trilayered oxide layer for chemical bonding with 4-META/10-MDP.[79] The bond strength of 4-META/10-MDP with annealed noble alloys was significantly lower than the sulfur-containing primers with non-annealed alloys.[32] VBATDT with sulfur/thiol/mercapto units bonded successfully to the noble alloys. However, the thiol form undergoes a chain transfer reaction due to free mercapto units

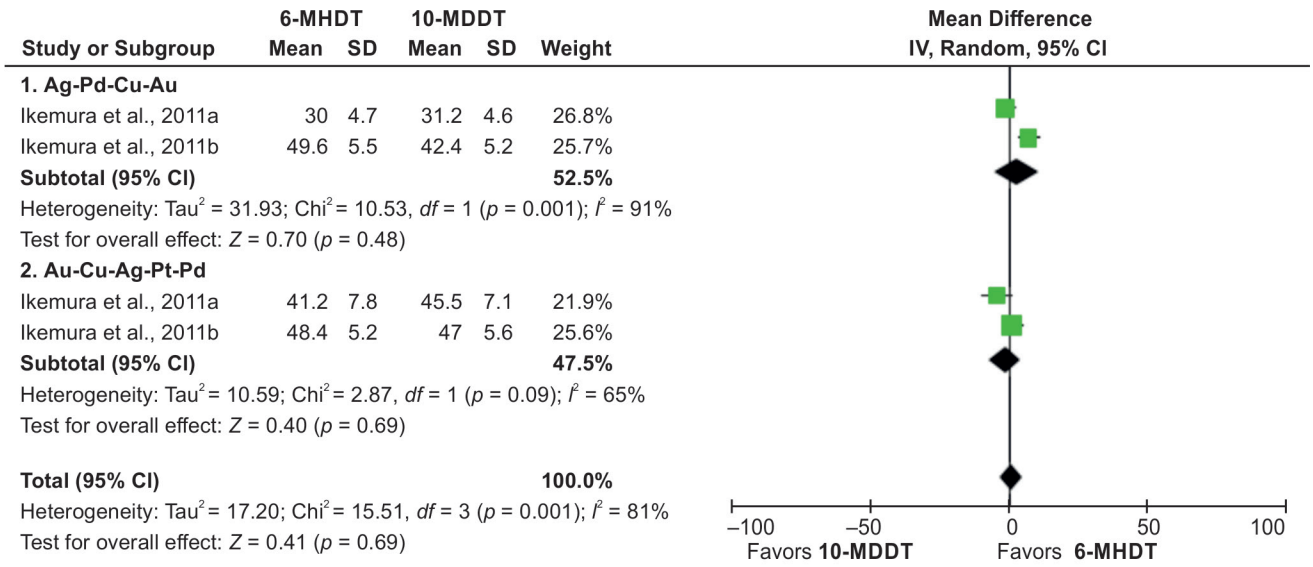


Fig. 5: Results of TBS meta-analyses concerning 6-MHDT vs 10-MDDT primed noble alloys, using a random-effects model

during the propagation of vinylic free radicals and deteriorates the polymerizing phenomenon of the superjacent dental resins.[14] Nevertheless, the free mercapto units or the thiol form react with its acryloyl-moiety causing premature gelation of the primer which adversely affects the primer's storage stability.[80] Hence, a successful attempt was made by recrystallizing the thiol form VBATDT in a concoction of diethyl ether and *n*-hexane that yielded its thione form without free mercapto units.[81] VBATDT bonds with the noble alloys by the conversion of thione [=N-C(=S)-] to thiol [-N=C(-SH)-] form which is followed by the thiol interaction through chemisorption with Pd and Cu to form chemical[80,82] and ionic[83] bonds, respectively. This complex bonding mechanism was extrapolated for MTU-6 as well.[50,54] The 10-MDP in VBATDT + 10-MDP synergistically enhances the bond strength by chemically interacting with the elemental Cu in noble alloys to form a chemical bond.[44] The results posed by the MTU-6 + 10-MDP combination is as the same as the former.[50] Hence, in this present review, the VBATDT + 10-MDP combination rather than the VBATDT alone and MTU-6 were selected for meta-analyses concerning noble alloys keeping the number of studies adhering to the inclusion criteria in consideration.

6-MHDT and 10-MDDT are the other two noble alloy sulfur-containing dithiooctonoate primers included in the meta-analysis in this review. The sulfur-containing primers were conveniently categorized into cyclic and non-cyclic disulfide primers of which the above primers are a cyclic type. Unlike the VBATDT, cyclic disulfides do not behave as a chain transfer agent and seldom exhibit premature polymerization with 2 months of storage stability at 50°C incubation. Therefore, the dithiooctonoate-based primers polymerize through ring-opening polymerization resulting in disulfide oligomers and LC polymerization of the methacryloyl moiety.[60] The disulfide bond (-S-S-) cleaved intramolecularly on the noble alloy surface resulting in -S·S- radicals which initiate the block-radical vinyl polymerization and subsequently lead to the formation of a chemisorbed stable Au-S monolayer on the alloy surface with instantaneity.[43,60,84,85] Finally, a cyclic disulfide priming monomer formed two chemical bonds with the alloy surface. With the non-cyclic disulfides, the bonding mechanism is as same as the former except for the formation of two independent molecules from a monomer due to the central -S-S- cleavage. Hence, the cyclic disulfides had higher bond strength than the non-cyclic disulfides and VBATDT.[46,51] The other experimental disulfides were 2-MEDT (2-Methacryloyloxyethyl-6,8-dithiooctanoate), 12-MDDDT (12-Methacryloyloxydodecyl-6,8-dithiooctanoate), 2-AEDT (2-Acryloyloxyethyl-6,8-dithiooctanoate), MAEDT (1-Methyl-2-acryloyloxyethyl-6,8-dithiooctanoate), EMEDT (1-Ethyl-2-methacryloyloxyethyl-6,8-dithiooctanoate), and BMMMDT (*Bis*(methacryloyloxymethyl)methyl-6,8-dithiooctanoate) which possessed lower TBS than the 6-MHDT and 10-MDDT with Au-Cu-Ag-Pt-Pd and Ag-Pd-Cu-Au.[61] For the above context, it is apparent that the structure of sulfur-containing primers should be considered while selecting the primer for the noble alloys.

Phosphoric acid-based primers yield high and durable bond strength with the base alloys. These primers have the affinity to bond with the passive oxide layer formed on the alloy surfaces. Concerning Co-Cr alloy, the passive oxide is composed of chiefly hydrated chromium oxy-hydroxide [$CrO_x(OH)_{3-2}{\cdot}nH_2O$] and sparsely cobalt (II) oxide (CoO).[86] 10-MDP reacts with these oxides to form chemical bonds. This bond is more stable and durable when compared with 4-META.[32] MDP and MEPS were able to bond more chemically with the oxides of the Co-Cr alloy surface than the carboxylic acid-based primers.[33] Similarly, both the primers yielded strong durable chemical bond strength with Cp-Ti and Ti-Al-Nb by interacting with the surface oxides of Ti.[87] A hypothetical interaction between the niobium oxide (NbO_2) and the carbonyl (C=O) group of acrylates by chemisorption exists.[37] Co-Cr alloy is seldom thermally oxidized in any clinical or laboratory situations because thermal oxidation leads to the formation of thick cobalt (II, III) oxide (Co_3O_4) that would deteriorate the primer's adhesive bond strength.[86] 10-MDP yielded higher bond strength when compared with MEPS though both possessed reactive functional groups alike. However, the purity of the hydrophobic -O-P(=O)$(OH)_2$ of 10-MDP was higher than the impure -O-P(=S)A_{3-n} of MEPS with substituents, and therefore, this was the reason ascribed for the high bond strength by 10-MDP over MEPS.[16] Concerning Ti-Al-Nb, however, VBATDT + 10-MDP yielded higher bond strength than

MEPS for some unknown reasons.[88] This may be attributed to the presence of two carbonyl group bonding units in VBATDT + 10-MDP which is in contrast to a single carbonyl unit of MEPS. Hence, in the present review, 10-MDP, VBATDT + 10-MDP, and MEPS were admitted for meta-analyses concerning base alloys keeping the number of studies adhering to the inclusion criteria in consideration.

The bond strength at the ARI not only depends on the composition of the alloy and the primer but also on the type of superjacent material bonded (alloy/resin), the composition of the superjacent resin bonded, and thermocycling. Concerning the superjacent material's type, primed alloy-to-alloy adhesion with resin exhibited greater bond strength than the primed alloy-to-acrylic rod/cylinder adhesion[65,87] because the adhesive resin was interposed between the alloys in the former while thermocycling and suffered minimal mechanical stress at the ARI.[87] Tertiary amines have been added to the resinous luting agents either as an activator in AC resins or as a co-initiator in LC resins. The initiator system type also affects the primers' bond strength. A partially oxidized TBB system in superjacent resin is resistant to acid attacks by either intrinsic/inherent or extrinsic acidic primers. Therefore, butyloxy-radicals or butoxybutylborooxy radicals are formed without impediments either before or after powder liquid mixing.[69] As a contrariety, the BPO-amine redox initiator system in AC resins inevitably forms unenviable yellow amine salts (typically yellowish quaternary ammonium salts) of either phosphoric acid or carboxylic acid in the presence of corresponding intrinsic acidic monomers in the composition and thus, adversely affecting the bonding quality between the alloy and resin despite primer application.[69,87] Nevertheless, with the BPO-amine system, the polymerization shrinkage commences in an opposite direction from the superjacent adhesive resin–primer interface due to homogenous radical formation adversely affecting the bond strength. This is not the case with TBB initiation where the polymerization occurs from the adhesive resin–primer interface allowing durable bond formation.[55]

Phosphonic acid ester-based primers were also synthesized and studied individually and in combination with sulfur-containing primers regarding the bonding ability with the base alloys and noble alloys, respectively. Phosphonic acid primers were usually in the phosphonoacetate (6-MHPA) or phosphonopropionate (6-MHPP and 10-MDPP) ester forms. Also, other acetates and propionates are available with different alkyl spacers which were not included in this review as they have been used as enamel or dentin adhesives along with other base matrix monomers and not as alloy primers. In the beginning, vinyl phosphonic acid and vinylbenzyl phosphonic acid were introduced with low bonding capacity due to their low water solubility and rigid alkylene spacer group in the structures.[89] Progressively, the flexibility of the phosphonic acid ester-based primers was increased by incorporating six (C6; 6-MHPA/6-MHPP) and ten (C10; 10-MDPP) carbon methylene spacer chains which ultimately enhanced the bond strength with the base alloy adherends.[89,90] The hydrolytically stable acidic moiety of the phosphonic acid primers [R-P(=O)$(OH)_2$] has high interaction with the base alloy adherends with low polymerization activity due to the amine-based initiator system. New ternary amine-free initiator systems [I. BPO, *N*,*N*-di(hydroxyethyl)-p-toluidine (DEPT), 1-benzyl-5-phenyl barbituric acid (BPBA) (BPO-DEPT-BPBA system); II. 1-cyclohexyl-5-ethylbarbituric acid (CEBA), *p*-toluene sulfonate morphoride (*p*-TSMo), *tert*-butylperoxy maleic acid (*t*-BPMA) (CEBA-*p*-TSMo-*t*-BPMA)][91] were employed with the phosphonic acid primers to circumvent the formation of objectionable ammonium salts that impede the polymerization kinetics and thereby enhancing the cohesive forces between the primer and the base alloy adherends.[89] Phosphonic acid ester-based primers are categorized under ligand monomers which suffer rapid ionization in the presence of water to form oxygen anions -P(=O)$(O^-)_2$ which enables the primers to interact with the base alloys' oxide layer to attain the bonding potency.[89] The bonding mechanism of the 10-MDP is approximately the same as phosphonic primers; however, the definite difference between them in terms of polymerization kinetics and bond strength is yet to be highlighted. Therefore, from the initiator system's context, durable stable bonding may be impossible to achieve at the primed ARI when the polymerization kinetics of the superjacent adhesive resin is overseen.[88]

Thermocycling adversely deteriorated the bonding in all the studies included in this review at the ARI on both primed and unprimed alloys. The bond strength reduction rates for alloy-to-acrylic rod/cylinder adhesion and alloy-to-alloy adhesion were 94.0% and 22.4%, respectively. The sample assembly construction is responsible for this difference in bond strength. The alloy-to-acrylic rod/cylinder construction is for denture base resin directly bonded over a cast partial denture (CPD) alloy framework, whereas the alloy-to-alloy construction is propagated for a magnetic alloy bonded to an alloy framework. The bond strength reduction rate in the alloy-to-acrylic rod/cylinder adhesion is due to the mismatch in coefficients of thermal expansion (CTE) of superjacent resins (acrylic: 77.5 – 89.9 $\times 10^{-6}$/°C; composite: 37.1 $\times 10^{-6}$/°C) and the framework alloys (Ag-Pd-Cu-Au: 18.3 $\times 10^{-6}$/°C; stainless steel: 11 $\times 10^{-6}$/°C). This CTE mismatch is about 7–9-fold different between alloy and resin which makes the ARI vulnerable to thermal stress caused by thermocycling.[27] Nevertheless, the water uptake by the resin in the alloy-to-acrylic rod/cylinder design is higher during the thermal aging process than in the alloy-to-alloy adhesion design. Irrespective of the specimen assembly design, the debonding of the resin from the alloy surface was from the peripheries of the bonding area to the center. From the above context, it is apparent that the chemistry and bonding mechanism of the alloy primers and the specimen assembly design is critical to the success of a prosthesis involving alloy and resin. The stronger the ARI bonding by a primer, the slower the bond deterioration, and the lower the adhesive failure. Therefore, the alloy-to-alloy bonding with the adhesive resins is less affected upon thermocycling than the alloy-to-acrylic rod/cylinder bonding.[27] Other than thermal stress, the superjacent resins suffer mechanical stresses through occlusal loads, water sorption, salivary degradation at the ARI, and adherend's corrosion are the additional factors that affect the bonding durability in the oral environment.[92,93] Hence, the execution of thermocycling in the studies evaluating bond strength ought to be contemplated as an investigating parameter in assessing the primers. The *in situ* serviceability, bonding ability, or bond failure are impractical to forecast without clinical evaluation.[54]

This is probably the first literature review in the field of alloy primers and due to the heterogeneous parameters included in the quantitative syntheses, the results of this present review should be apportioned with caution. Furthermore, this review did not take into consideration other variables like the mode of bond failures. Nevertheless, the solvent's type, concentration, and solvent evaporation time were overseen in this review despite factors, such as vapor pressure, polarity, hydrophilicity, molecular weight, and solubility being critical when bonding between the primer and adherend is concerned.[94,95] Out of ethanol, acetone, MMA, and

isopropyl alcohol, acetone are the most commonly used solvent for alloy primers because of its high evaporative ability due to higher vapor pressure than ethanol. It also exhibits a "water-chasing" effect that keeps the moisture contamination of the adherend surface in check.[96] However, excessive acetone residues negatively affect the bond strength at the ARI. The perchance of publication bias is possible since this review considered only the studies written in English and did not consider the unpublished studies and conference proceedings. Databases, such as Google Scholar, EBSCOhost, and Scopus might have included in this review to have a more apparent view of the ARI. There are hardly any clinical trials performed in this field of bonding. Based on the observations of the literature concerning the primers' bond strength, an investigator/author is expected to provide an explicit explanation of sample size calculation, operator's details, techniques for randomization and blinding, and ISO guidelines adhered to.

Conclusions

In the light of variegated findings and the limitations of this review, it can be concluded that irrespective of the alloys employed, priming the alloy surface unanimously enhanced the bond strength. Cyclic disulfide primer, 10-MDDT, is best-suited for bonding noble alloys with superjacent resins when compared with VBATDT. Phosphoric acid- and phosphonic acid ester-based primers are best-suited for base alloys. Alloy primer hybridization leads to universal bonding systems for both noble and base alloys. The bond strength at the ARI is also dependent on the primers' structure including the functional moiety, primers' solvent, alloys' composition, resins' initiator system, acidic monomers in the resins, bonding surface area, and thermo-mechanical aging.

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