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Impact of PVM/MA Copolymer on Dentin Bond Durability

Utjecaj kopolimera PVM/MA na trajnost adhezije na dentin

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Abstract
Objectives: This study investigated the effect of Polymethyl vinyl ether-co-maleic anhydride (PVM/MA) copolymer incorporation and aging with thermocycling on the shear bond strength (SBS) of an etch-and-rinse adhesive (Adper Single Bond Plus-ASB) and two different self-etch adhesive systems (Clearfil SE Bond-CSE and Fluorobond II-FLB) to dentin. **Materials and Methods:** Adhesive systems were applied to 240 dentin sections randomly selected from the occlusal surfaces of 60 extracted molar teeth. The test groups were as follows (n=20): (G1) Pure Clearfil SE (CSE) Bond; (G2) CSE with copolymer (50 mg/ml PVM/MA); (G3) Pure FL II Bond (FLB); (G4) FLB with copolymer (50 mg/ml PVM/MA); (G5) Pure Adper Single Bond (ASB); and (G6) ASB with copolymer (50 mg/ml PVM/MA). A resin composite (Clearfil Majesty Posterior) was applied to the dentin surfaces and light-cured. Half of the specimens from each group were tested immediately after preparation (IM) and the other half was tested after exposure to 20,000 thermal cycles (TC; 5-55 °C). SBS values were measured at a crosshead speed of 0.5 mm/min. Data were analyzed with ANOVA and Tukey's HSD. **Results:** The PVM/MA copolymer incorporation improved the performance of CSE in the IM group and ASB in the TC group, however, it showed no influence in the other adhesive groups. The self-etch adhesive CSE with the PVM/MA copolymer showed the highest bond strength to dentin surfaces in the IM group (22.0±1.7 MPa). However, copolymer corporation did not increase bonding performance of Fluor containing bonding agent FLB. Thermocycling of test specimens significantly decreased bond strengths in all test groups except for ASB resin adhesive with PVM/MA copolymer. **Conclusion:** Incorporating PVM/MA into ethanol-based, hydrophilic all-in-one bonding agents may offer a valuable strategy to improve the long-term stability of adhesive systems.

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Introduction

The primary objective of adhesive dentistry is to establish a durable bond with dental tissues. While modern adhesives achieve high initial resin-dentin bond strengths, these values deteriorate progressively over time (1-3), with reductions of approximately 30 % to 40 % reported within 6 to 12 months (4). Therefore, maintaining bond durability is crucial for the longevity of esthetic restorations, as a compromised adhesive interface can lead to gap formation between the tooth and the restoration (5, 6). The average service life of tooth-colored restorations is limited to approximately 5.7 years (4), and replacement of these defective restorations' costs about $5 billion annually in the United States alone

Uvod

Primarni cilj adhezivne dentalne medicine jest uspostaviti trajnu vezu sa zubnim tkivima. Iako suvremeni adhezivi postižu visoke početne vrijednosti čvrstoće veze uz dentin, one se progresivno smanjuju tijekom vremena (1 – 3) približno od 30 % do 40 % unutar 6 do 12 mjeseci (4). Zato je održavanje trajnosti adhezije ključno za dugotrajnost estetskih restauracija jer kompromitirani adhezijski spoj može potaknuti stvaranje pukotina između zuba i restauracije (5, 6). Prosječni vijek trajanja kompozitnih restauracija ograničen je približno na 5,7 godina (4), a zamjena neodgovarajućih restauracija u Sjedinjenim Američkim Državama trošak je od oko 5 milijardi dolara na godinu (7). Izravne restauracije kompo-

(7). Direct composite resin restorations demonstrate higher five-year failure rates compared to other direct restoration options, with failures predominantly attributed to marginal fractures and recurrent caries (8-10).

Marginal breakdown originates from weak adhesive bonding at the dentin-composite interface, which is further compromised by secondary caries (11). Bond degradation occurs through water sorption, hydrolysis of methacrylate ester linkages, and activation of endogenous dentin matrix metalloproteinases (12, 13). Biomodification of demineralized collagen with exogenous cross-linking agents significantly enhances dentin's biomechanical properties (10, 14-16). By strengthening collagen fibrils, these agents reduce enzymatic degradation and improve both hybrid layer stability and restoration longevity (8, 17, 18). Polymethyl vinyl ether-co-maleic anhydride (PVM/MA), a biodegradable polyanhydride commonly used in pharmaceutical formulations, demonstrates excellent bioadhesive and mucoadhesive properties in nanoparticulate delivery systems (19-21). Given these characteristics, PVM/MA shows considerable promise for dental applications, including adhesive systems, desensitizing agents, and remineralization protocols.

The bioadhesive properties of PVM/MA copolymer are primarily attributed to hydrolytic conversion of polyanhydride residues into carboxylic groups, enabling interaction with biological substrates. These functional groups facilitate adhesion through multiple mechanisms, including mechanical interpenetration and weak chemical bonding with glycoproteins. Importantly, PVM/MA demonstrates strong affinity for type I collagen, the predominant organic component of dentin (22, 23). It has also been reported that the PVM/MA copolymer plays a key role in reducing plaque retention by inhibiting the initial adhesion of bacteria to enamel surfaces via electrostatic repulsion and sequestration of calcium ions at the surface (24, 25).

Application of the PVM/MA which possesses therapeutic antibacterial properties into modern adhesive bonding agents would be of significant benefit to the advancement of conservative restorative dentistry (19). However, there is no information on its effect on bond strength and durability of adhesive systems to dentin surfaces. Its affinity for moist substrates and capacity to form stable interactions with collagen fibrils may enhance resin infiltration and hybrid layer integrity, potentially improving bond durability. Furthermore, the copolymer's biodegradability and interface stabilizing properties suggest promising applications for dealing with resin/dentin bond degradation, a significant challenge in adhesive restorations.

This study investigated the effects of the PVM/MA copolymer and aging with thermocycling on the shear bond strength (SBS) of an etch-and-rinse adhesive (Adper Single Bond Plus-ASB) and two different self-etch adhesive systems (Clearfil SE Bond-CSE and Fluorobond II-FLB) to dentin. The null hypothesis of the study was that the PVM/MA copolymer incorporation into the adhesive systems did not affect the SBS of dentin adhesives to dentin surfaces with (w) and without (w/o) aging with thermocycling.

zitnim materijalom pokazuju višu stopu neuspjeha tijekom pet godina u usporedbi s drugim izravnim restaurativnim opcijama, pri čemu se neuspjesi uglavnom pripisuju marginalnim frakturama i sekundarnom karijesu (8 – 10).

Marginalna degradacija potječe od slaboga adhezivnog vezivanja na spoju dentin – kompozitni materijal koje je dodatno kompromitirano sekundarnim karijesom (11). Razgradnja veze nastaje zbog apsorpcije vode, hidrolize metakrilatnih esterskih veza te aktivacije endogenih dentinskih matriksnih metaloproteinaza (12, 13). Biomodifikacija demineraliziranoga kolagena egzogenim umrežavajućim agensima značajno poboljšava biomehanička svojstva dentina (10, 14 – 16). Ojačavanjem kolagenih fibrila ti agensi smanjuju enzimsku razgradnju te poboljšavaju stabilnost hibridnog sloja i dugotrajnost restauracija (8, 17, 18). Kopolimer PVM/MA (kopolimer polimetil vinil eter-ko-maleinskog anhidrida), biorazgradivi polianhidrid koji se često koristi u farmaceutskim formulacijama, pokazuje izvrsna bioadhezivna i mukoadhezivna svojstva u nanopartikuliranim sustavima (19 – 21). S obzirom na ta svojstva, PVM/MA pokazuje značajan potencijal za dentalne primjene, uključujući adhezivne sustave, sredstva za desenzibilizaciju i protokole remineralizacije.

Bioadhezivna svojstva kopolimera PVM/MA primarno se pripisuju hidrolitičkoj konverziji polianhidridnih ostataka u karboksilne skupine, što omogućuje interakciju s biološkim supstratima. Te funkcionalne skupine omogućuju adheziju putem više mehanizama, uključujući mehaničku interpenetraciju i slabe kemijske veze s glikoproteinima. Važno je istaknuti da PVM/MA pokazuje visoki afinitet prema kolagenu tip I. koji je dominantna organska komponenta dentina (22, 23). Također je pokazano da je kopolimer PVM/MA ključan u smanjenju retencije plaka inhibicijom početne adhezije bakterija na površinu cakline putem elektrostatskog odbijanja i sekvestracije kalcijevih iona na površini (24, 25).

Primjena kopolimera PVM/MA, koji posjeduje terapijska antibakterijska svojstva, u suvremenim adhezivnim sustavima mogla bi znatno pridonijeti napretku konzervativne restaurativne stomatologije (19). No nema podataka o njegovu učinku na čvrstoću veze i trajnost adhezivnih sustava na dentinskim površinama. Njegov afinitet prema vlažnim supstratima i svojstvo stvaranja stabilnih interakcija s kolagenim fibrilima mogu poboljšati infiltraciju smole i integritet hibridnoga sloja, čime se potencijalno povećava trajnost adhezije. Nadalje, biorazgradivost kopolimera i njegova stabilizacija adhezivnoga spoja upućuju na obećavajuću primjenu u rješavanju degradacije veze adheziv – dentin, koja je značajan izazov u adhezivnim restauracijama.

U ovoj studiji istraživani su učinci kopolimera PVM/MA i starenja termocikliranjem na smičnu čvrstoću veze (SBS) jetkajuće-ispirućeg adheziva (Adper Single Bond Plus – ASB) i dvaju različitih samojetkajućih adhezivnih sustava (Clearfil SE Bond – CSE i Fluorobond II – FLB) na dentin. Nulta hipoteza studije bila je da ugradnja kopolimera PVM/MA u adhezivne sustave ne utječe na SBS dentinskih adheziva na dentinskim površinama sa starenjem termocikliranjem (w) i bez toga postupka (w/o).

Materials and Methods

The schematic drawing of the study setup is shown in Figure 1.

Sample preparation

Sixty extracted permanent human third molars free of caries, restoration, cracks, or other structural defects were collected from Oral Surgery Department of Penn Dental Medicine. All subjects were informed and consented to the use of their teeth for research and educational purposes. The teeth were polished with paste, rinsed thoroughly with water, and examined with a stereomicroscope for defects in enamel after removal of the residual tissues using scaling instruments. Until the time of the study, the teeth were stored in a 1 % chloramines T solution.

The occlusal surfaces of sixty extracted molar teeth were abraded just below the cusps to expose flat occlusal areas of dentin. The human molars were then sectioned mesio-distally below the dentin-enamel junction perpendicular to the long axis of the tooth, with a water-cooled low-speed diamond-coated separating disc to obtain thick slabs of coronal dentin. All dentin slabs were then sectioned mesio-distally and bucco-lingually to obtain four slices with the thickness of 3 mm. from each slab. Each test group was comprised of 10 teeth and 40 dentin sections yielding a total of 240 sections as the sample size. From each group, 20 dentin sections were randomly selected for bond tests of study groups. Individual specimens were embedded in acrylic resin, exposing only the occlusal dentin surface, which was then wet-polished with 600-grit silicon carbide (SiC) paper to standardize the smear layer.

Luting procedures

For three of the six test groups (G2, G4, and G6), prior to the application to the dentin surface 50 mg/ml PVM/MA copolymer powder (Lot #=03000256934, Gantrez S97BF, ISP Technologies, Wayne, NJ 07470) were added to the corresponding bonding agent and mixed thoroughly using fine micro brush tips (26). Adhesive systems were then applied to the dentin surfaces strictly, following the specified protocols by a single experienced operator (Table 1).

Materijali i metode

Shematski prikaz eksperimentalnog postava vidi na slici 1.

Priprema uzoraka

Prikupljeno je šezdeset ekstrahiranih trajnih humanih trećih kutnjaka bez karijesa, restauracija, pukotina ili drugih strukturnih oštećenja dobivenih od Zavoda za oralnu kirurgiju Penn Dental Medicine. Svi ispitanici bili su informirani i dali su pristanak za korištenje svojih zuba u istraživačke i obrazovne svrhe. Zubi su polirani pastom, temeljito isprani vodom te pregledani stereomikroskopom radi utvrđivanja oštećenja cakline nakon uklanjanja zaostalih tkiva instrumentima za čišćenje kamenca. Do početka istraživanja zubi su bili pohranjeni u 1-postotnoj otopini kloramina T.

Okluzalne plohe šezdeset ekstrahiranih kutnjaka abradirane su do razine neposredno ispod kvržica kako bi se izložile ravne okluzalne površine dentina. Humani kutnjaci zatim su prerezani mezio-distalno ispod caklinsko-dentinskoga spojišta, okomito na uzdužnu os zuba, uz upotrebu vodom hlađenoga niskobrzinskoga dijamantnoga diska za rezanje da bi se dobile debele pločice koronarnoga dentina. Sve dentinske pločice zatim su dodatno prerezane meziodistalno i bukolingvalno da bi se iz svake dobila četiri uzorka debljine 3 mm. Svaka ispitna skupina sastojala se od 10 zuba i 40 dentinskih uzoraka, što je ukupno 240 uzoraka. Iz svake skupine nasumično je odabrano 20 dentinskih uzoraka za ispitivanje čvrstoće veze. Pojedinačni uzorci ugrađeni su u akrilatnu smolu tako da je bila izložena samo okluzalna površina dentina koja je nakon toga mokro polirana silicijevim karbidnim (SiC) papirom granulacije 600 zbog standardizacije zaostatnoga sloja.

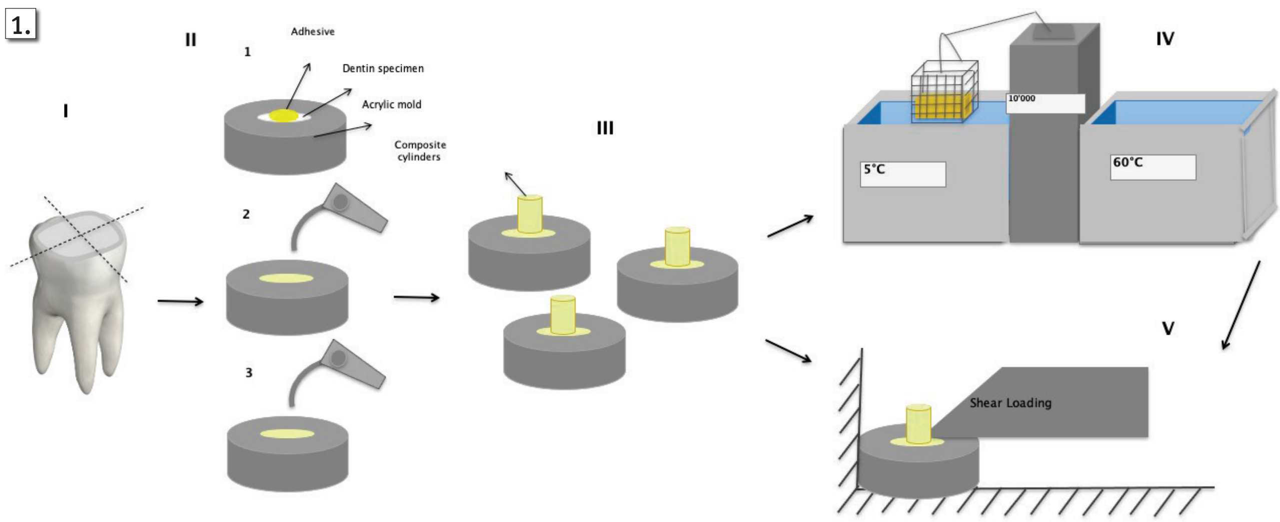
Postupci cementiranja

Za tri od šest ispitnih skupina (G2, G4 i G6), prije nanošenja na dentinsku površinu dodano je 50 mg/mL praha kopolimera PVM/MA (Lot #=03000256934, Gantrez S97BF, ISP Technologies, Wayne, NJ 07470) u odgovarajući adheziv te je smjesa temeljito homogenizirana s pomoću finih mikročetkica (26). Adhezivne sustave zatim je jedan iskusni operater primijenio na dentinske površine strogo slijedeći propisane protokole (tablica 1.).

Table 1. Description of the three adhesives used in this study, including their composition and application procedures
Tablica 1. Opis triju adheziva korištenih u ovoj studiji, uključujući njihov sastav i postupke primjene

Category	Dental adhesive	Chemical composition	Directions
2-step etch-and-rinse	ASB (3M ESPE, St. Paul, MN, USA)	Etchant: 35% H_3PO_4 Adhesive: BisGMA, HEMA, dimethacrylates, ethanol, water, polyacrylic and polyitaconic acids, silica	Apply the etchant for 15 s, rinse and blot excess water using a cotton pellet. Apply the bond for 5 s, and light-cure for 10 s.
2-step self-etch	FLB (Shofu, Kyoto, Japan)	Primer: Water, ethanol, carboxylic acid monomer, phosphoric acid monomer. Adhesive: S-PRG filler, UDMA, TEGDMA, 2-HEMA	Apply the primer for 5 s and wait for 10 s, dry with strong air for 5 s. Apply the bond for 5 s, and light-cure for 10 s.
	CSE (Kuraray, Co, Ltd. Tokyo, Japan)	Primer: 10-MDP, HEMA, hydrophilic dimethacrylate, camphorquinone, N,N-diethanol-p-toluidine, water Adhesive: 10-MDP, HEMA, bis-GMA, dimethacrylate, camphorquinone, N-diathanol-p-toluidine, silica	Apply the primer for 5 s and wait for 10 s, dry with strong air for 5 sec. Apply the bond for 5 s, and light-cure for 10 s.

1.



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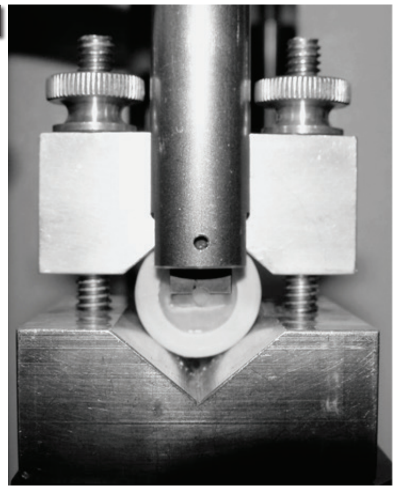

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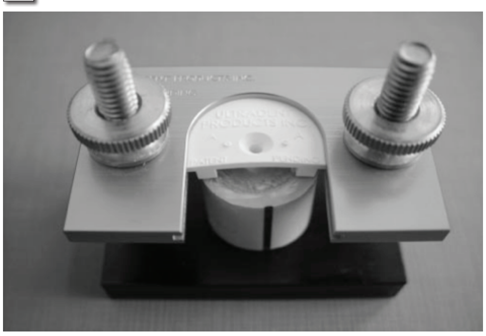


Figure 1. Experimental setup of the study
Slika 1. Eksperimentalni postav istraživanja
Figure 2. Application apparatus of composite on the dentin surface.
Slika 2. Aplikacijski uređaj za nanošenje kompozitnog materijala na dentinsku površinu
Figure 3. Application of force on composite block by the stub-shaped apparatus.
Slika 3. Primjena sile na kompozitni blok s pomoću nastavka u obliku klina

The test groups were the following: (G1) Pure CSE; (G2) CSE with Copolymer (50 mg/ml PVM/MA); (G3) Pure FLB; (G4) FLB with Copolymer (50 mg/ml PVM/MA); (G5) Pure ASB; and (G6) ASB with Copolymer (50 mg/ml PVM/MA). After bonding applications, resin composite (Clearfil Majesty Posterior, Kuraray, Japan) cylinders were built on the dentin surfaces in cylindrical-shaped plastic matrices with an internal diameter of 2.1 mm and height of 3 mm (Figure 2). The excess composite was carefully removed with a scalpel blade. The composite cylinders were then light-cured (Optilux 500, Kerr/Demetron, Danbury, CT, USA) according to the manufacturer's instructions.

SBS test

The specimens were stored at 37° C in water for 24 h. For the IM groups, half of the specimens from each group were tested immediately after water storage. The remaining half of the specimens were however tested after exposure to 20,000 thermal cycles for TC groups. (THE-1100, SD Mechatronik, Feldkirchen-Westerham, Germany) between 5° C and 55° C with a dwell time of 60 s in the cold and hot tanks with a transfer time of 3 s. After the TC protocol, the specimens were individually transferred to the specifically designed for shear bond strength testing machine (Bisco Shearforce Test

Ispitne skupine bile su sljedeće: (G1) čisti CSE; (G2) CSE s kopolimerom (50 mg/mL PVM/MA-e); (G3) čisti FLB; (G4) FLB s kopolimerom (50 mg/mL PVM/MA-e); (G5) čisti ASB i (G6) ASB s kopolimerom (50 mg/mLl PVM/MA-e). Nakon adhezivnog postupka cilindri kompozitnoga materijala (Clearfil Majesty Posterior, Kuraray, Japan) izrađeni su na dentinskim površinama u cilindričnim plastičnim matricama unutarnjeg promjera 2,1 mm i visine 3 mm (slika 2.). Višak kompozitnoga materijala pažljivo je uklonjen skalpelom. Cilindri kompozitnoga materijala nakon toga svjetlosno su polimerizirani (Optilux 500, Kerr/Demetron, Danbury, CT, SAD) prema uputama proizvođača.

SBS test

Uzorci su pohranjeni u vodi na temperaturi od 37 °C tijekom 24 sata. Za IM skupine, polovina uzoraka iz svake skupine ispitana je odmah nakon pohrane u vodi. Preostala polovina ispitana je nakon izlaganja djelovanju 20 000 toplinskih ciklusa za TC skupine (THE-1100, SD Mechatronik, Feldkirchen-Westerham, Njemačka), između 5 °C i 55 °C, s vremenom zadržavanja od 60 sekundi u hladnom i toplom spremniku te vremenom prijenosa od 3 sekunde. Nakon protokola termocikliranja, uzorci su pojedinačno postavljeni u uređaj posebno dizajniran za ispitivanje smične

Machine, Bisco Inc, Schaumburg, IL, USA), and then the specimens were secured in the jaw of the machine so that the luted cylindrical composite sample bases were parallel to the shear force direction. The specimens were stressed in a horizontal direction at a crosshead speed of 0.5 mm/min with a semi-circular rod (Figure 3). The maximum load necessary to fracture was recorded in Newton (N) and then converted into Megapascal (MPa) values using the formula dividing the peak load by the bonding area. Shear bond strength (SBS) is then calculated with the formula below:

$$\text{SBS (MPa)} = \frac{\text{Force at failure (N)}}{\text{Bonded area (mm}^2\text{)}}$$

Scanning Electron Microscopic (SEM) evaluations

Twelve human molar teeth were used for SEM analysis of resin /dentin interfaces. Teeth were assigned to the same experimental groups and treated in the same manner as described above for bond strength testing. Resin composite build-ups were constructed in two increments of approximately 1.5 mm and light activated for 40 s each. Then, each tooth was longitudinally sectioned into two halves using a low-speed diamond saw under a water spray coolant.

All samples then were embedded in a self-curing epoxy resin for 1 day. Samples were ground with a series of increasingly finer SiC abrasive papers (400-1200 grits), highly polished with diamond powder down to 0.05 µm particle size. They were cleaned ultrasonically at each step for 10 minutes. The polished specimens were immersed into 10 % phosphoric acid solution for 15 s. After rinsing with water for 15 s, the specimens were treated with 10 % sodium hypochlorite (NaOCl) solution for 30 s, rinsed thoroughly with water, and fixed in 2 % glutaraldehyde solution (pH=7.4) for 2 hours. Then, they were dehydrated through ascending series of ethanol (50-100%) until critical point of dry. Specimens were sputter coated with 15 nm of gold and observed with a SEM (Jeol JSM T330A, Jeol, Inc., Peabody, MA, USA).

Failure mode analysis

After the SBS tests, the failed specimens were examined under a light stereomicroscope (Olympus ZS 61, Olympus Corp., Tokyo, Japan) at x 4.0 magnification in an attempt to identify the failure patterns. Failure modes were classified as adhesive failure (AF) when between the bonding agent and dentin, cohesive failure (CF) when in the composite resin or dentin, or mixed failure (MF) when within the bonding agent and/or dentin.

Statistical analysis

Statistical analyses were performed with commercially available software (SigmaPlot 12, Systat Software, Inc., San Jose, CA, USA). The effect of the incorporation of the PVM/MA copolymer to the bonding agent and thermal aging on the SBS was analyzed with the two-way analysis of variance (ANOVA). Post hoc comparisons were performed with Tukey HSD tests. Significance was evaluated at $p<0.05$ level.

čvrstoće veze (Bisco Shearforce Test Machine, Bisco Inc, Schaumburg, IL, SAD), te su učvršćeni u stezaljku uređaja tako da su baze cementiranih cilindričnih kompozitnih uzoraka bile paralelne sa smjerom djelovanja smične sile. Uzorci su opterećeni u horizontalnom smjeru pri brzini pomaka glave od 0,5 mm/min s pomoću polukružnog utora (slika 3.). Maksimalno opterećenje potrebno za lom zabilježeno je u njutnima (N), a zatim pretvoreno u megapaskale (MPa) dijeljenjem maksimalnoga opterećenja s površinom adhezije. Smična čvrstoća veze (SBS) zatim je izračunata prema sljedećoj formuli:

$$\text{SBS (MPa)} = \frac{\text{Force at failure (N)}}{\text{Bonded area (mm}^2\text{)}}$$

Skenirajuća elektronska mikroskopija (SEM)

Za SEM analizu spoja adheziv – dentin korišteno je dvanaest humanih kutnjaka. Zubi su raspoređeni u iste eksperimentalne skupine i obrađeni jednako kao što je opisano za ispitivanje čvrstoće veze. Nadogradnje kompozitnoga materijala izrađene su u dvama inkrementima debljine približno 1,5 mm i svjetlosno polimerizirane po 40 sekundi za svaki sloj. Svaki zub zatim je uzdužno prerezan na dvije polovine niskobrzinskom dijamantnom pilom uz hlađenje vodenim sprejom.

Svi uzorci zatim su jedan dan uklopljeni u samopolimerizirajuću epoksidnu smolu. Uzorci su brušeni serijom SiC abrazivnih papira sve finije granulacije (400 – 1200), a zatim visoko polirani dijamantnim prahom do veličine čestica od 0,05 µm. Nakon svakog koraka ultrazvučno su čišćeni 10 minuta. Polirani uzorci uronjeni su u 10-postotnu otopinu fosforne kiseline tijekom 15 sekundi. Nakon ispiranja vodom 15 sekundi, uzorci su 30 sekundi tretirani 10-postotnom otopinom natrijeva hipoklorita (NaOCl), temeljito isprani vodom te fiksirani u 2-postotnoj otopini glutaraldehida (pH = 7,4) tijekom 2 sata. Zatim su dehidrirani u rastućoj koncentraciji etanola (50 – 100 %) do kritične točke sušenja. Uzorci su presvučeni slojem zlata debljine 15 µm postupkom raspršivanja i promatrani SEM-om (Jeol JSM T330A, Jeol, Inc., Peabody, MA, SAD).

Analiza načina loma

Nakon SBS ispitivanja, slomljeni uzorci analizirani su svjetlosnim stereomikroskopom (Olympus ZS 61, Olympus Corp., Tokio, Japan) pri povećanju × 4,0 radi određivanja tipa loma. Načini loma klasificirani su kao adhezivni lom (AF) između adheziva i dentina, kohezivni lom (CF) unutar kompozitnoga materijala ili dentina, ili mješoviti lom (MF) unutar adheziva i/ili dentina.

Statistička analiza

Statističke analize obavljene u komercijalno dostupnom softveru (SigmaPlot 12, Systat Software, Inc., San Jose, CA, SAD). Učinak ugradnje kopolimera PVM/MA u adheziv i toplinskoga starenja na SBS analiziran je dvofaktorskom analizom varijance (ANOVA). Post hoc usporedbe provedene su Tukeyjevim HSD testom. Razina značajnosti postavljena je na $p < 0,05$.

Results

Shear bond strength test

The means and standard deviations of the test groups are presented in Table 2. The results of the two-way ANOVA of the SBS data are given in Figure 4. The statistical results of the two-way ANOVA showed that there was an interaction between the copolymer application and TC (Df=5, F=18.46 and P<0.0001). Two-way ANOVA revealed that the copolymer application influenced the SBS of adhesive systems to dentin (Df=5, F=123.4 and P<0.0001). Meanwhile, two-way ANOVA analysis showed that TC significantly affected the SBS values of all the groups (Df =1, F=200.7 and P<0.0001).

The highest SBS was obtained in the self-etch adhesive CSE with PVM/MA copolymer group (Group G2) w/o TC (22.0 ± 1.7 MPa), followed by CSE without PVM/MA copolymer in Group G1 w/o TC (19.2 ± 2.3 MPa). The results confirmed that PVM/MA in CSE significantly improved the initial bond strength, but after thermocycling it caused a marked reduction, indicating reduced thermal stability and greater susceptibility to degradation.

The lowest bond strength was obtained in the FLB without PVM/MA copolymer group (Group G3) w TC (5.6 ±

Rezultati

Ispitivanje smične čvrstoće veze

Srednje vrijednosti i standardne devijacije ispitnih skupina prikazane su u tablici 2.

Rezultati dvofaktorske analize varijance podataka o SBS-u nalaze se na slici 4. Statistički rezultati dvofaktorske analize varijance pokazali su interakciju između primjene kopolimera i termocikliranja (Df = 5, F = 18,46 i P < 0,0001). Dvofaktorska analiza varijance pokazala je da je primjena kopolimera utjecala na SBS adhezivnih sustava na dentin (Df = 5, F = 123,4 i P < 0,0001). Istodobno, analiza je pokazala da je termocikliranje značajno utjecalo na vrijednosti SBS-a u svim skupinama (Df = 1, F = 200,7 i P < 0,0001).

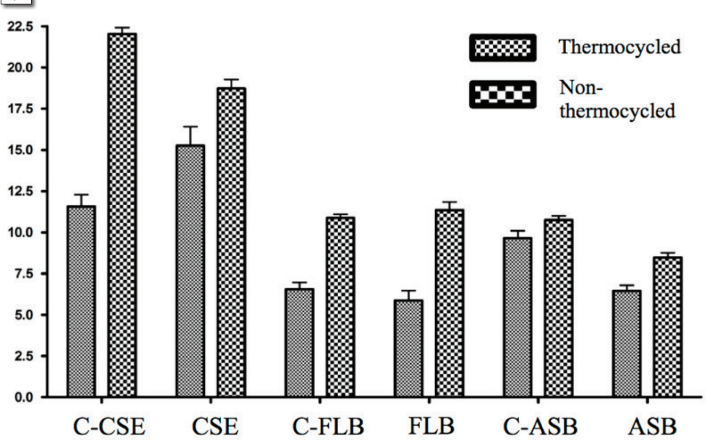
Najviša vrijednost SBS-a zabilježena je u skupini samojetkajućeg adheziva CSE s kopolimerom PVM/MA (skupina G2) bez termocikliranja (22,0 ± 1,7 MPa), nakon čega slijedi CSE bez kopolimera PVM/MA u skupini G1 bez termocikliranja (19,2 ± 2,3 MPa). Rezultati su potvrdili da je PVM/MA u CSE-u značajno poboljšao početnu čvrstoću veze, ali je nakon termocikliranja prouzročio izraženo smanjenje, što upućuje na smanjenu toplinsku stabilnost i veću podložnost degradaciji.

Table 2. Shear bond strength mean values in MPa
Tablica 2. Srednje vrijednosti smične čvrstoće veze izražene u MPa

Groups	Shear Bond Strength (MPa) ± SD	
	IM (without TC)	TC
G1 CSE	19.2±2.3[e]	15.1±5.2[d]
G2 PVM/MA-CSE	22.0±1.7[f]	11.6±3.1[c]
G3 FLB	10.9±2.2[c]	5.6±2.7[a]
G4 PVM/MA-FLB	10.3±1.0[c]	6.2±1.8[ab]
G5 ASB	8.5±1.2[bc]	6.4±1.6[ab]
G6 PVM/MA-ASB	10.7±1.1[c]	9.6±2.1[c]

*Means with same letter are not significantly different • *Srednje vrijednosti označene istim slovom nisu statistički značajno različite.

4.



5.

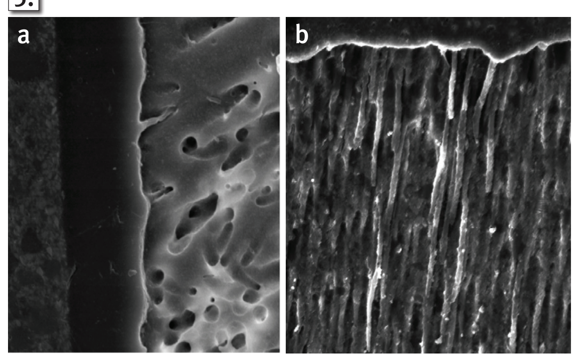


Figure 4. The self-etch adhesive CSE with PVM/MA copolymer showed the highest bond strength to dentinal surfaces without thermocycling. CSE without copolymer provided the strongest bond in the post-thermocycling group. Copolymer incorporation had varying effects on bond strengths; it improved performance of CSE in the immediate, and of ASB in the aged (TC) group and had no influence in the other groups. Thermocycling significantly decreased bond strengths in all test groups except for ASB.

Slika 4. Samojetkajući adheziv CSE s kopolimerom PVM/MA pokazao je najveću čvrstoću veze na dentinskim površinama bez termocikliranja; CSE bez kopolimera pokazao je najveću čvrstoću veze nakon termocikliranja; ugradnja kopolimera imala je različite učinke na čvrstoću veze; poboljšala je učinkovitost CSE u neposrednoj skupini i ASB u skupini nakon starenja (TC), a u ostalim skupinama nije imala utjecaja; termocikliranje je značajno smanjilo čvrstoću veze u svim ispitnim skupinama, osim u ASB skupini

Figure 5. SEM images for resin/dentin interfaces of ASB after thermocycling of the samples: a) ASB applied interface b) PVM/MA-ASB interface

Slika 5. SEM prikazi spoja adheziv – dentin za ASB nakon termocikliranja uzoraka: a) spoj nakon primjene ASB-a b) spoj PVM/MA–ASB

Table 3. Percentage of fracture modes of all experimental groups
Tablica 3. Postotna raspodjela tipova loma u svim eksperimentalnim skupinama

Experimental groups	Without TC (%)			With TC (%)		
	AF	CF	MF	AF	CF	MF
G1 CSE	100	X	X	80	10	10
G2 PVM/MA-CSE	90	X	10	90	X	10
G3 FLB	83	7	10	85	5	10
G4 PVM/MA-FLB	80	10	10	80	10	10
G5 ASB	95	X	5	90	X	10
G6 PVM/MA-ASB	90	10	X	90	10	X

2.7 MPa). However, PVM/MA incorporation into the FLB neither improved the initial bond strength nor effectively stabilized FLB against thermal stress.

For ASB, the effect of PVM/MA was most beneficial. While the addition of the polymer coating slightly increased initial values without statistical significance, a marked improvement was observed after thermocycling. PVM/MA–ASB achieved significantly higher bond strength (9.6 ± 2.1 MPa) than ASB alone (6.4 ± 1.6 MPa), demonstrating that PVM/MA effectively enhanced the thermal durability of the adhesive.

Failure type analysis

TC decreased bond strengths in all test groups. The failure type analysis revealed that the most common mode of failure in the test groups was adhesive (Table 3).

Scanning Electron Microscopic (SEM) evaluations

Representative SEM micrographs of the resin/dentin interfaces are shown in Figure 5. SEM images showed that resin/dentin interface of ASB group presented an irregular, porous interface with short, poorly defined resin tags, indicating limited resin infiltration.

In contrast, the samples with PVM/MA-ASB exhibited a dense and homogenous interface with long well-adapted resin tags, suggesting improved penetration and stronger bonding to dentin. Radiopaque areas were observed within some dentinal tubules and along the hiybrid layer, likely due to localized filler or mineral deposition. The resin tags showed rough surfaces, possibly from resin extensions into nano-sized openings after etching along the tubule walls, indicating variable infiltration and polymer distribution within the interface.

Discussion

This study investigated the effect of PVM/MA copolymer incorporation and aging with thermocycling on the shear bond strength of different adhesive bonding systems (Clearfil SE Bond, Adper Single Bond Plus, and Fluorobond II). The PVM/MA copolymer incorporation had varying effects on the bonding capacity and durability of different adhesive systems used in this study. The SBS results found that the null hypotheses of the study were partially rejected. This was due to the fact that significant differences in bond strength values were observed between the different bonding agents in both IM and TC Groups, except for all ASB groups.

Najniža čvrstoća veze zabilježena je u skupini FLB bez kopolimera PVM/MA (skupina G3) s termocikliranjem (5,6 ± 2,7 MPa). Međutim, ugradnja PVM/MA-e u FLB nije poboljšala početnu čvrstoću veze niti je učinkovito stabilizirala FLB pod utjecajem toplinskog opterećenja.

Za ASB, učinak PVM/MA-e bio je najpovoljniji. Iako je dodatak polimera blago povećao početne vrijednosti bez statističke značajnosti, nakon termocikliranja uočeno je značajno poboljšanje. PVM/MA-ASB postigao je značajno višu čvrstoću veze (9,6 ± 2,1 MPa) u usporedbi s ASB-om bez dodatka (6,4 ± 1,6 MPa), što pokazuje da je kopolimer PVM/MA učinkovito poboljšao toplinsku trajnost adheziva.

Analiza tipa loma

Termocikliranje je smanjilo čvrstoću veze u svim ispitnim skupinama. Analiza tipa loma pokazala je da je najčešći način u ispitnim skupinama bio adhezivni (tablica 3.).

Skenirajuća elektronska mikroskopija (SEM)

Reprezentativne SEM snimke spoja adheziv – dentin prikazane su na slici 5.

SEM snimke pokazale su da je taj spoj u skupini ASB bio nepravilan i porozan s kratkim i slabo definiranim smolastim nastavcima, što upućuje na ograničenu infiltraciju smole.

Nasuprot tomu, uzorci s PVM/MA-ASB-om pokazali su gusto i homogeno sučelje s dugim, dobro prilagođenim smolastim nastavcima, što upućuje na poboljšanu penetraciju i jače vezivanje za dentin. Radioopakna područja uočena su unutar pojedinih dentinskih tubula i duž hibridnoga sloja, vjerojatno kao posljedica lokaliziranog taloženja punila ili minerala. Smolasti nastavci imali su hrapave površine, vjerojatno zbog prodiranja smole u otvore nanometarskih dimenzija nastale nakon jetkanja duž stijenki tubula, što upućuje na varijabilnu infiltraciju i raspodjelu polimera unutar sučelja.

Rasprava

U ovoj studiji istraživan je učinak ugradnje kopolimera PVM/MA i starenja termocikliranjem na smičnu čvrstoću veze različitih adhezivnih sustava (Clearfil SE Bond, Adper Single Bond Plus i Fluorobond II). Ugradnja kopolimera PVM/MA različito je utjecala na svojstvo vezivanja i trajnost različitih adhezivnih sustava korištenih u ovom istraživanju. Rezultati SBS-a pokazali su da su nulte hipoteze studije djelomično odbačene. To je posljedica činjenice da su ustanovljene značajne razlike u vrijednostima čvrstoće veze između različitih adhezivnih sustava u IM i TC skupinama, osim za sve ASB skupine.

Thermocycling is widely used in dental research in order to recreate temperature variations existing under intraoral conditions by exposing samples to repetitive cycles of hot and cold alterations (27, 28). The difference in thermal expansion between the resin and tooth can trigger the occurrence of volumetric changes during temperature changes, resulting in fatigue of the adhesive/dentin interfaces (29, 30). The tooth/restoration interface usually degrades due to polymerization shrinkage stresses, cyclic fatigue, and wear actions, hence microgaps can be present at the tooth/restoration margins (5, 31). Consequently, oral bacteria and biofilms colonizing restoration margins and penetrating interfacial microgaps can directly contact the adhesive resin, triggering degradation of the resin-dentin interface (32). In the current study, statistically significant differences in SBS values were observed after thermocycling in CSE and FLB adhesive groups with or without PVM/MA incorporation. The ASB groups likewise showed numerical decreases following thermocycling, however they were not statistically significant.

The PVM/MA copolymer contains highly reactive anhydride residues capable of interacting with various mono and bifunctional reactants (33-35). These anhydride groups are also susceptible to hydrolytic degradation. Upon hydrolysis, each anhydride residue converts into two carboxylic acid side groups, imparting weak acidic character to the polymer. These carboxylic acid groups enhance hydrogen bonding capacity with polar molecules such as water and alcohols, thereby increasing interaction potential with biological substrates like collagen. Furthermore, PVM/MA chains can undergo cross-linking through multiple pathways: amidation with diamines, esterification with diols, or reactions with bis-epoxy compounds following anhydride hydrolysis via ring-opening and esterification mechanisms (33, 36, 37). This chemical versatility suggests that PVM/MA functions as a dynamic polymer capable of adapting its properties to the local environment and forming stabilizing networks within the adhesive interface.

In agreement with previous studies, the shear bond strength of groups G1, G3 and G5 without PVM/MA, which were also used as the control groups, was decreased after TC application (28, 38-40). CSE, being a self-etch adhesive, provided a superior and more predictable bond strength to dentin, resulting in overall higher bond strength values as compared to the etch-and-rinse adhesives included in this study. However, when comparing the results of the PVM/MA incorporated G2, G4 and G6 adhesive groups, the bonding agent ASB in G6 group showed distinctive results. The shear bond strength of ASB increased with the copolymer incorporation, and thermocycling did not significantly change the bond strengths of the material. This 'striking' finding highlights a unique synergy between PVM/MA and this specific ethanol-based etch-and-rinse system.

Current dentin adhesives are formulated with hydrophilic and hydrophobic monomers dissolved in solvents such as acetone, ethanol, or water (41-44). Solvent type influences adhesion quality: ethanol–water-based adhesives show slower interfacial degradation than acetone-based ones (41, 42). A systemic review of controlled clinical trials revealed that Class V restoration retention rates of an ethanol-based adhesive performed

Termocikliranje se često koristi u dentalnim istraživanjima kako bi se reproducirale temperaturne varijacije koje postoje u intraoralnim uvjetima izlaganjem uzoraka ponavljanim ciklusima izmjena toploga i hladnoga (27, 28). Razlika u toplinskom širenju između smole i zuba može potaknuti volumetrijske promjene tijekom temperaturnih promjena, što rezultira zamorom na spoju adheziv – dentin (29, 30). Spoj zub – restauracija obično degradira zbog naprezanja prouzročenih polimerizacijskim skupljanjem, cikličkoga zamora i trošenja, zbog čega se na rubovima restauracija mogu pojaviti mikropukotine (5, 31). Posljedično, oralne bakterije i biofilm koji koloniziraju rubove restauracija i prodiru u međupovršinske mikropukotine mogu izravno doći u doticaj s adhezivom, što potiče degradaciju spoja adheziv – dentin (32). U ovoj studiji utvrđene su statistički značajne razlike u vrijednostima SBS-a nakon termocikliranja u CSE i FLB skupinama, s ugradnjom PVM/MA-e ili bez te ugradnje. ASB skupine također su pokazale numeričko smanjenje nakon termocikliranja, ali bez statističke značajnosti.

Kopolimer PVM/MA sadržava visoko reaktivne anhidridne ostatke sposobne za interakciju s različitim monofunkcionalnim i bifunkcionalnim reaktantima (33 – 35). Ti anhidridni ostatci također su podložni hidrolitičkoj razgradnji. Tijekom hidrolize svaki anhidridni ostatak prelazi u dvije karboksilne skupine, pa se kod polimera pojavljuje slaba kiselost. Te karboksilne skupine povećavaju kapacitet stvaranja vodikovih veza s polarnim molekulama poput vode i alkohola, čime se povećava potencijal interakcije s biološkim supstratima kao što je kolagen. Nadalje, lanci PVM/MA-e mogu se umrežavati putem više mehanizama: amidacijom s diaminima, esterifikacijom s diolima ili reakcijama s bis-epoksidnim spojevima nakon hidrolize anhidrida putem mehanizama otvaranja prstena i esterifikacije (33, 36, 37). Ta kemijska svestranost upućuje na to da PVM/MA djeluje kao dinamičan polimer koji može prilagoditi svoja svojstva lokalnom okruženju i stvarati stabilizirajuće mreže unutar adhezivnoga spoja.

U skladu s dosadašnjim istraživanjima, smična čvrstoća veze skupina G1, G3 i G5 bez PVM/MA-e, koje su također korištene kao kontrolne skupine, smanjila se nakon primjene termocikliranja (28, 38 – 40). CSE, kao samojetkajući adheziv, osigurao je superiornu i predvidljiviju čvrstoću veze na dentin, što je rezultiralo općenito višim vrijednostima čvrstoće veze u usporedbi s jetkajuće-ispirućim adhezivima uključenima u ovu studiju. No pri usporedbi rezultata skupina G2, G4 i G6 s ugrađenim kopolimerima PVM/MA, adheziv ASB u skupini G6 pokazao je specifične rezultate. Smična čvrstoća veze ASB-a povećala se ugradnjom kopolimera, a termocikliranje nije značajno utjecalo na čvrstoću veze toga materijala. Taj nalaz pokazuje specifičnu sinergiju između PVM/MA-e i ovoga na etanolu temeljenoga jetkajuće-ispirućeg sustava.

Suvremeni dentinski adhezivi formulirani su s hidrofilnim i hidrofobnim monomerima otopljenima u otapalima poput acetona, etanola ili vode (41 – 44). Vrsta otapala utječe na kvalitetu adhezije: adhezivi na bazi etanola i vode pokazuju sporiju degradaciju spoja u usporedbi s acetonskim sustavima (41, 42). Sustavni pregled kontroliranih kliničkih better than those placed using an acetone-based adhesive after 36 months (43). Water sorption and material solubility have similarly been identified as key factors affecting long-term bond stability and biocompatibility (45), while surface physicochemical properties such as interfacial elemental composition and roughness also directly influence bond strength outcomes (46). ASB adhesive contains ethanol-based and phosphonate-based monomers, diols, and water. Each component can react with PVM/MA anhydride residues, forming a hydrophobic protective structure. These reactions promote cross-linking via condensation between carboxyl and bis-epoxy groups and radical polymerization of methacrylate, producing a densely interconnected polymer matrix incorporating methacrylate, silane, fillers, and PVM/MA chains (33, 37-43). This cross-linked architecture enhances bond durability by limiting water infiltration, improving mechanical strength, and resisting hydrolytic degradation. Ethanol saturation of etched dentin further improves bonding (47), consistent with the SEM images of ASB after thermocycling (Figure 5).

PVM/MA copolymer, upon hydrolysis of its anhydride groups, exhibits hydrophilic character and demonstrates good compatibility with HEMA. It can form cross-links with both methacrylate and HEMA components of the adhesive, contributing to a reinforced bonding structure (33, 34). While methacrylate in the adhesive interact with the calcium ions of hydroxyapatite in the tooth structure, they simultaneously participate in polymerization with PVM/MA. When PVM/MA is incorporated, the carboxylic acid groups (formed from anhydride hydrolysis) can undergo esterification reactions with hydroxyl-containing compounds, forming ester linkages (-COO-R) during polymerization. However, this esterification reduces the material's hydrophilicity by converting hydrophilic -COOH groups into more hydrophobic ester bonds (34). This property enables the system to develop hydrophobic character and maintain stability after polymerization, which may explain PVM/MA's strong adherence to the adhesive material and its enhanced resistance to thermocycling, particularly in the etch-and-rinse adhesive system (ASB)

The positive effect of PVM/MA observed with ASB suggests that this approach may also enhance the performance of both ethanol and HEMA based all in one adhesive particularly universal adhesive, which share similar hydrophilic and water-rich formulations. By providing a hydrophobic protective barrier, PVM/MA has the potential to reduce water sorption, protect functional monomers from hydrolysis, and stabilize the hybrid layer over time. Incorporating this strategy into universal adhesive systems could therefore improve their resistance to thermomechanical aging and extend the clinical longevity of adhesive restorations.

In this study, the PVM/MA copolymer incorporated bonding agents showed either the same or increased bond strength values. The predominant failure was adhesive between the bonding agent and dentin for all experimental groups, with or without thermocycling application. The weakest link seems to be the bonding interface of the dentin adhesive agent. The samples with cohesive failure were not included in the data.

studija pokazao je da retencija restauracija klase V., izvedenih adhezivom na temelju etanola, postiže bolje rezultate u odnosu prema onima izvedenim adhezivom na bazi acetona poslije 36 mjeseci (43). Apsorpcija vode i topljivost materijala također su ključni čimbenici koji utječu na dugoročnu stabilnost veze i biokompatibilnost (45), a površinska fizikalno-kemijska svojstva, poput elementarnog sastava sučelja i hrapavosti, također izravno utječu na rezultate čvrstoće veze (46). Adheziv ASB temeljen je na etanolu i sadržava fosfonatne monomere, diole i vodu. Svaka od tih komponenti može reagirati s anhidridnim ostatcima PVM/MA-e, tvoreći hidrofobnu zaštitnu strukturu. Te reakcije potiču umrežavanje kondenzacijom između karboksilnih i bis-epoksidnih skupina te radikalskom polimerizacijom metakrilata, čime nastaje gusto umrežena polimerna matrica koja uključuje metakrilat, silan, punila i PVM/MA lance (33, 37 – 43). Ta umrežena struktura povećava trajnost veze ograničavanjem infiltracije vode, poboljšanjem mehaničke čvrstoće i otpornosti na hidrolitičku razgradnju. Zasićenje jetkanoga dentina etanolom dodatno poboljšava vezivanje (47), što je u skladu sa SEM nalazima za ASB nakon termocikliranja (slika 5.).

Kopolimer PVM/MA, nakon hidrolize anhidridnih skupina, pokazuje hidrofilnost i dobru kompatibilnost s HEMA-om. Može stvarati umrežene strukture s metakrilatnim i HEMA komponentama adheziva, čime pridonosi ojačanoj strukturi veze (33, 34). Uz interakciju metakrilata u adhezivu s kalcijevim ionima hidroksiapatita u strukturi zuba, metakrilati istodobno sudjeluju u polimerizaciji s kopolimerom PVM/MA. Dodatkom PVM/MA-e, karboksilne skupine (nastale hidrolizom anhidrida) mogu sudjelovati u esterifikacijskim reakcijama s hidroksilnim spojevima, stvarajući esterske veze (–COO–R) tijekom polimerizacije. No ta esterifikacija smanjuje hidrofilnost materijala pretvaranjem hidrofilnih –COOH skupina u hidrofobnije esterske veze (34). To svojstvo omogućuje sustavu hidrofobni razvoj i održavanje stabilnosti nakon polimerizacije, što može objasniti snažnu adheziju PVM/MA-e na adhezivni materijal i njegovu povećanu otpornost na termocikliranje, osobito u jetkajuće-ispirućem adhezivnom sustavu (ASB).

Pozitivan učinak PVM/MA-e uočen kod ASB-a upućuje na to da bi taj pristup mogao poboljšati učinkovitost adheziva u jednoj bočici na bazi etanola koji sadržavaju HEMA-u, osobito univerzalnih adheziva koji imaju slične hidrofilne formulacije bogate vodom. Stvaranjem hidrofobne zaštitne barijere, PVM/MA može tijekom vremena smanjiti apsorpciju vode, zaštititi funkcionalne monomere od hidrolize i stabilizirati hibridni sloj. Uvođenje te strategije u univerzalne adhezivne sustave moglo bi stoga poboljšati njihovu otpornost na termomehaničko starenje i produljiti kliničku dugotrajnost adhezivnih restauracija.

U ovoj studiji pokazali su adhezivni sustavi s ugrađenim kopolimerom PVM/MA jednake ili povećane vrijednosti čvrstoće veze. Prevladavajući tip loma bio je adhezivni između adheziva i dentina u svim eksperimentalnim skupinama, s primjenom termocikliranja ili bez toga postupka. Čini se da je najslabija karika upravo spoj dentinskog adheziva. Uzorci s kohezivnim lomom nisu bili uključeni u analizu.

Conclusions

The PVM/MA copolymer may offer a useful approach to improving dentin adhesive performance through its ability to interact with dental substrates and provide a hydrophobic barrier. Incorporating PVM/MA into ethanol-based, hydrophilic all-in-one bonding agents may offer a valuable strategy to improve the long-term stability of adhesive systems. The positive outcomes observed with ASB suggest that similar benefits could extend to other ethanol- and HEMA-based all-in-one adhesives, particularly universal adhesives with comparable hydrophilic formulations and high-water content. By limiting water sorption, protecting functional monomers from hydrolytic breakdown, and reinforcing the hybrid layer, PVM/MA has the potential to prolong the clinical durability of adhesive restorations. While further studies are needed, this strategy may represent a promising direction for the development of future adhesive materials.

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Zaključci

Kopolimer PVM/MA može poboljšati učinkovitost dentinskih adheziva zahvaljujući svojem svojstvu interakcije s dentalnim supstratima i stvaranju hidrofobne barijere. Ugradnja PVM/MA-e u etanolom temeljene, hidrofilne *sve-u-jednom* adhezive može biti učinkovita strategija za poboljšanje dugoročne stabilnosti adhezivnih sustava. Pozitivni rezultati uočeni kod ASB-a upućuju na moguću primjenu sličnoga pristupa i na druge adhezive u jednoj bočici temeljene na etanolu koji sadržavaju HEMA-u, osobito one univerzalne sa sličnim hidrofilnim formulacijama i visokim udjelom vode. Ograničavanjem apsorpcije vode, zaštitom funkcionalnih monomera od hidrolitičke razgradnje i ojačavanjem hibridnoga sloja, PVM/MA može produljiti kliničku trajnost adhezivnih restauracija. Iako su potrebna dodatna istraživanja, ovaj pristup može obećavati i odrediti smjer u razvoju budućih adhezivnih materijala.

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Sažetak

Ciljevi: Autori ove studije istraživali su učinak ugradnje kopolimera polimetil vinil eter-ko-maleinskog anhidrida i starenja termocikliranjem na smičnu čvrstoću veze (SBS) jetkajuće-ispirućih adheziva (Adper Single Bond Plus - ASB) te dvaju različitih samojetkajućih adhezivnih sustava (Clearfil SE Bond – CSE i Fluorobond II – FLB) na dentin. **Materijali i metode:** Adhezijski sustavi primijenjeni su na 240 dentinskih uzoraka nasumično odabranih s okluzalnih ploha 60 ekstrahiranih kutnjaka. Ispitne skupine bile su sljedeće (n = 20): (G1) čisti Clearfil SE (CSE) Bond; (G2) CSE s kopolimerom (50 mg/mL PVM/MA-e); (G3) čisti FL II Bond (FLB); (G4) FLB s kopolimerom (50 mg/mL PVM/MA-e); (G5) čisti Adper Single Bond (ASB); i (G6) ASB s kopolimerom (50 mg/mL PVM/MA-e). Kompozitni materijal (Clearfil Majesty Posterior) nanesen je na dentinske površine i svjetlosno polimeriziran. Polovina uzoraka iz svake skupine ispitana je odmah nakon pripreme (IM), a druga polovina nakon izlaganja djelovanju 20 000 toplinskih ciklusa (TC; 5 – 55 °C). Vrijednosti SBS-a mjerene su pri brzini pomaka ispitne glave od 0,5 mm/min. Podatci su analizirani jednofaktorskom ANOVA-om i Tukeyjevim HSD testom. **Rezultati:** Ugradnja kopolimera PVM/MA poboljšala je učinkovitost CSE-a u IM skupini i ASB-a u TC skupini, no nije pokazala utjecaj u ostalim adhezivnim skupinama. Samojetkajući adheziv CSE s kopolimerom PVM/MA pokazao je najveću čvrstoću veze na dentinskim površinama u IM skupini (22,0 ± 1,7 MPa). No ugradnja kopolimera nije povećala adhezivnu učinkovitost adheziva FLB koji sadržava fluor. Termocikliranje uzoraka značajno je smanjilo čvrstoću veze u svim ispitnim skupinama, osim za adheziv ASB s kopolimerom PVM/MA. **Zaključak:** Ugradnja kopolimera PVM/MA u hidrofilne adhezive u jednoj bočici temeljene na etanolu može biti korisna strategija za poboljšanje dugoročne stabilnosti adhezivnih sustava.

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