

Površinske interakcije dentina i adheziva

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Sažetak

Novije generacije dentinskih adheziva ostvaruju s caklinom i dentinom osim mikromehaničkih sveza i kemijske sveze. Najnoviji sustavi koji imaju tzv. "self-etching primeres" (samojetkajuće primere) za caklinu i dentin pripadaju petoj generaciji dentinskih adheziva. Zajedničko je svojstvo tim sustavima što imaju hidrofilni monomer koji vlaži i prodire u dentin nakon kondicioniranja te imaju sposobnost potpune polimerizacije i stvaranja visokog umreženja kolagenih vlakana. Ti sustavi otopljeni su u otapalu kao što su alkohol ili aceton kako bi monomerom potpuno zamijenili vodu iz kolagene mreže. Novi dentinski adhezivi rabe se za povezivanje kompozitnog materijala sa zubnim strukturalama, prekrivanje pulpe, prevenciju postoperativne boli, za zaštitu preosjetljivih zubnih vratova, za stabilizaciju kaviteta i ostataka zubne strukture.

Ključne riječi: zaostatni sloj, hidrofilni monomer, voda, aceton, hibridni sloj.

Acta Stomatol Croat
1998; 459—466

PREGLEDNI RAD
Primljeno: 27. studenog 1997.

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Uvod

Kompozitne smole (KS) zbog visoke viskoznosti nemaju izraženiju sposobnost prijanjanja za zubne strukture. Posredujuća sredstva koja omogućuju da se kompozitni materijali (KM) povezuju na caklinu i dentin nazivaju se zajedničkim imenom "dentinski adhezivi" (DA).

Sveza adheziva s caklinom i dentinom može biti ostvarena na organskom (kolagen) ili anorganskom dijelu (kristali hidroksilapatita (HA), ili pak na oba (1).

Prijašnji adhezijski sustavi svezivali su se za dentin preko zaostatnoga sloja ("smear layer") (ZS) koji je prethodno bio pretvoren, ili izravno na dentinsku strukturu s koje odstranjuju ZS.

Novija su istraživanja pokazala da se u sustavima koji odstranjuju ZS jetkanjem i demineralizacijom površinskog dentina ostvaruje samo mikromehanička sveza (2,3).

Svezivanje (bonding) rezultira umreženjem ekspaniranih kolagenih vlakana hidrofilnim monomerom u površinskom dentinu stvarajući pritom hibridni sloj (HS) smola-dentin. Taj je sloj smješten između nedemineraliziranoga dentina i KM (4,5,6).

Dentinska propusnost i dentinska adhezija

Dentin je dinamičan sustav koji pokazuje različit stupanj propusnosti u blizini pulpe od udaljenijih slojeva. Uzrok je tomu u broju dentinskih tubu-

lusa (DT), kojih ima više uz pulpu a manje na caklinsko-dentinskom spojištu. Takav raspored DT uvjetuje veću propusnost dentina koji je bliže pulpi, a time i veću vlažnost površine dentina. Osim toga dublji slojevi dentina imaju manje minerala i intertubulusnog dentina (7).

Novije generacije DA imaju izrazito hidrofilna svojstva što omogućuje čvrstu svezu i u dubljim slojevima dentina (8).

Suvremeni DA imaju u sebi kisele kondicionirajuće dodatke ili primere za odstranjivanje ili pretvorbu ZS na površini dentina (9). Ta sredstva osim što čiste površinu zbog niskog pH ili kelacijom Ca, demineraliziraju peritubulusni i intertubulusni dentin, povećavaju hrapavost intertubulusnoga prostora, ekspaniraju mrežu kolagenih vlakana, te modificiraju vlažnost i propusnost dentina. Tako kondicionirana dentinska površina pokazuje manje ortofosfornih i karbonatnih skupina te porast amida, promjenu strukture i denaturaciju kolagena (10).

Prosječna dubina demineralizacije iznosi od 3 do 7 mikrometara (1,11). Kiselina primera penetrira uzduž tubulusa. Nakon završene demineralizacije dentina kolagen je destabiliziran i podložan enzimskoj degradaciji. Nazočnost kristala HA može kolagen stabilizirati i spriječiti njegovu denaturaciju i kolaps. Zarobljeni kristali HA su nakon demineralizacije u tijesnome doticaju s kolagenim vlaknima, a interfibrilarni kristali većinom su otopljeni.

Pojedina sredstva za jetkanje sadrže ione Ca, Fe i Al, koji mogu također stabilizirati kolagen i smanjiti dubinu demineralizacije dentina (12).

Za razliku od cakline, jetkanom dentinu ne raste površinska energija nužna za bolje vlaženje smolom. Umjesto toga dentiniski kondicioneri i primeri podižu površinsku napetost primera i adheziva do površinske energije vlažnog ili suhog dentina ovisno o tehnici svezivanja (1,12).

Primeri u DA sastoje se od smolastoga monomera (HEMA, 4-META, NPG-GMA, PMDM) i poliakrilne kiseline u vodenoj otopini ili u organskom otapalu (acetone, alkohol) (13,14). Imaju hidrofilne i hidrofobne skupine koje omogućuju s jedne strane veću površinsku napetost, te s druge strane bolje vlaženje hidrofobne smole, a time kemijsko i mikromehaničko svezivanje (15,16). Pošto ga se postavi, dentinski primer se ne polimerizira nego ga se lagano ispuhne zrakom zbog sadržaja vode (15).

Neki primeri sadrže glutaraldehid koji ima sposobnost da učvršćuje kolagena vlakna fiksiranjem bjelanjčevina, ima antibakterijski učinak te povećava permeabilnost dentina (17,18). Monomer TEGDMA (triethylene-glycol-dimethacrylate) je zajednička sastavnica spojne smole i KS. Udio mu je 30-50% u spojnoj smoli, te 15-25% u KS, a reducira viskoznost poboljšavajući time manipulativne sposobnosti (19).

HEMA (2-hydroxyethylmethacrylate) dodaje se spojnoj smoli u 30-50% kako bi se povećala snaga i stabilnost sveze za dentin. HEMA snizuje viskoznost smole, penetrira u ZS te ostvaruje mikromehaničku i kemijsku svezu s dentinom, kopolimerizirajući pritom s adhezivskom smolom (15,19,20,21). HEMA omogućuje da se kristali HA zarobe u dentinu. Zbog hidrofilnosti lako difundira u vlažna kolagena vlakna (14,22,23). Nakon polimerizacije HEMA je čvrsto svezana sa zubnim tkivom (24).

Samokondicionirajući primeri sadržavaju osim monomera i maleičnu kiselinu (0,8-4%). Maleična kiselina ne demineralizira dostatno duboko te to ograničuje penetraciju monomera čiji smolasti zupci ("resin tags") zbog polimerizacijske kontrakcije mogu biti izvučeni iz DT, što slabi svezu i uzrok je njihovu pucanju. To pak dovodi u pitanje učinkovitost jednokomponentnih dentinskih adhezivskih sustava (11,17).

Jetkanjem ortofosfornom kiselinom omogućuje se istodobni tretman cakline i dentina ali s opasnosti povećane demineralizacije i denaturacije kolagena te jake propustljivosti dentina. Ortofosforna kiselina također denaturira kolagena vlakna tijekom otklanjanja ZS. To uzrokuje kolaps kolagenoga matriksa i smanjuje prostor za infiltraciju smole i otežano se stvara HS. Kolagena vlakna koja nisu obložena monomerom brže hidroliziraju (25). Aplikacijom HEMA, 4-META + acetone primera može se spriječiti kolaps kolagena i omogućiti penetraciju monomera i impregnacija supstrata.

Neki adhezivi ostvaruju bolju svezu za vlažan nego za suh dentin. To se objašnjava time da voda sprječava jači kolaps kolagenih vlakana i olakšava penetraciju hidrofilnog monomera (17).

Da bi se stvorila dobra sveza i premostio dentin smola mora infiltrirati i intratubulusni i peritubulusni dentin kako bi stvorila smolaste zupce i jedinstveni HS. Intratubulusna infiltracija smole stvorit će smolaste zupce koji će, vežući se sa stijenkama tu-

bulusa, oblažući je, prevenirati nastanak mikropukotine, blokirati osjetljivost i pojačavati retenciju smole. Idealna bi infiltracija bila kada bi smola mogla potpuno zamijeniti vodu oko kolagenih vlakana, maksimalno ih podižući, infiltrirajući ih do dubine demineralizacije, pojačavajući njihove fizičke mogućnosti i sprječavajući njihovu hidrolizu. Kako adhezijski sustavi postaju sve više hidrofilni, stvaranje smolastih zubaca teoretski raste što je preparirani dentin bliže pulpi. Smola može doseći DT i intertubulusni dentin samo ako se odstrani ZS jetkanjem kiselinom ili ako može difundirati kroz ZS. Djelotvornost svezivanja nekog adhezijskog sustava mjeri se adekvatnošću sveze i premošćenjem dentinske površine. Kako struktura dentina nije homogena, tako će i o tome ovisiti snaga sveze i kapacitet premošćenja.

Tzv. "self-etching/self-priming" sustavi koriste se kiselim otopinom primera koja može penetrirati kroz vodom ispunjene kanaliće između čestica ZS u dentin. Kako se ova vrsta primera ne ispire s površine, demineralizirani ZS je ugrađen u HS. I intertubulusna i intratubulusna permeabilnost kritične su za ostvarenje optimalne snage sveze i premošćenja dentinske površine. Sposobnost smole da prožima DT i intertubulusni dentin ovisi o više čimbenika. U površnom dentinu, koji ima manje tubulusa nego duboki, prodiranje smole u intertubulusni dentin odgovarat će za većinu snage sveze. U vrlo dubokom dentinu veći je broj DT pa će intratubulusna prodornost smole biti odgovorna za retenciju i premošćenje. Teži stupanj infiltracije smole u DT (intratubulusna permeabilnost) obično je povezan s dentinskim fluidom pod pulpnim tlakom i s česticama minerala u sklerotičnom dentinu. Infiltracija smole u intertubulusni dentin jako je ovisna o površinskoj poroznosti nakon jetkanja. Ako kolageni matriks demineraliziranoga dentina kolabira zbog presušenosti, smanjit će se permeabilnost demineralizirane zone (1).

Stvaranje i uloga hibridnoga sloja

HS je mješavina polimerizirane smole, smolom obloženih kolagenih vlakana i zarobljenih kristala HA (12). Otporan je na djelovanje kiselina. Impregnacija i oblaganje kolagenih vlakana zbiva se na molekularnoj razini, a novostvoreni HS ujedinjuje dentinski supstrat s priležecim restorativnim materijalom.

Za stvaranje hibridnoga sloja ključna su dva čimbenika:

- odgovarajuće pripremljen supstrat uklonjenjem ZS i demineralizacijom dentina,
- odgovarajuća mješavina monomera koja difundira u dentin i impregnira ga stabilizirajući demineralizirani dentinski matriks (23).

Stvaranje HS traži prikladno pripremljenu dentinsku površinu kiselim primerom/kondicionerom te difuziju i penetraciju monomera smole. HS je tanji na lateralnim stijenkama gdje su DT usporedni s površinom kaviteta (4). Debljina HS je indikator dubine dekalifikacije dentina. Kao "elastični odbojnik" HS može apsorbirati stres koji se događa tijekom polimerizacije KS i time prevenirati nastanak pukotine zbog polimerizacijske kontrakcije u kavitetu (26).

Uloga vode i acetona

Voda je usko povezana s procesom svezivanja za dentin. U tome procesu voda dolazi iz nekoliko izvora: iz dentinske tekućine (fluid), iz atmosfere (ovisno o relativnoj vlažnosti), iz procesa ispiranja, te iz otopine adheziva. Prije se voda smatrala kontaminatom koji ometa svezivanje. Prijašnji DA bili su hidrofobni i time nedjelotvorni u nazočnosti vode. Današnji DA su hidrofilni što povećava snagu sveze za dentin. Prevelika količina vode može pak biti uzrokom slabije sveze s dentinom (1,6).

Voda može interferirati s fizičkim i kemijskim procesom bondinga. Uz nazočnost ZS debljina dentina nema utjecaja na dentinsku vlažnost. Odmah nakon jetkanja smanjena debljina dentina utjecat će na dentinsku vlažnost. Porast lokalne koncentracije vode ispunja površinske i potpovršinske poroznosti s vodom što otežava zamjenu vode hidrofilnim monomerom. Voda može također razrijediti koncentraciju hidrofilnog monomera (27). Ti problemi površinske vlažnosti mogu se izbjeći uporabom samokondicionirajućih svezujućih sustava postavljenih izravno na razmjerno suh ZS.

Nakon jetkanja i ispiranja vodom, približno 70% volumena demineraliziranog dentina (ili 50% intertubulusnoga dentina) okupirano je vodom u zamjenu za minerale otklonjene jetkanjem. Ta je voda prijeko potrebna da bi se kolagena mreža održala u napetom stanju, zadržavajući poroznost potrebnu za in-

terdentinsku penetraciju smole. Ako je dentin presušen, voda koja je pridržavala kolagenu mrežu hlapiti i uzrokuje njihov kolaps zbog površinskih tlačnih sila (28). Prostor između kolabirane kolagene mreže je smanjen, a to snižava permeabilnost intertubulusnog dentina za adhezijsku smolu (29). Uzrok je kolapsa kolagene mreže dehidracija zrakom, što povećava modul elastičnosti kolagena. To nastaje zbog stvaranja sekundarnih sveza između peptidnih lanaca u kolagenom triplet heliksu koji je spriječen u nazočnosti vode. Ako kolagen nije ponovno ovlažen vodom i ako je apliciran primer bez vodene baze, kolagena mreža ne može reekspandirati i može ostati stisnuta u kolabiranome stanju. Osušeni, kolabirani kolagen treba vodu kako bi dovoljno snizio modul elastičnosti i mogao reekspandirati. Postavi li se primer bez vodene baze, može se očekivati vrlo mala infiltracija smole u demineraliziranu zonu. Umjesto toga smola premošćuje kolabirani zgusnuti kolagen s vrlo malom penetracijom u reduciranu poroznost oko kolagenih vlakana intertubulusnog dentina. Rezultat niske retencije smole vjerojatno je rezultat površinske adhezije za hrapavu površinu (30).

Primeri koji sadržavaju vodu mogu također dobro djelovati na dentin, jer će voda sadržana u primeru plastificirati kolabirani kolagen dopuštajući mu reekspanziju, što povećava veličinu prostora između kolagenih vlakana.

Kada se primer koji sadržava vodu aplicira na suhi dentin, postoje dvije mogućnosti ishoda: ako je koncentracija vode u primeru preniska, vodom siromašni monomer smole i/ili organsko otapalo obložiti će kolagena vlakna brže nego što voda može plastificirati kolagen i neće biti posve reekspandiran. Ako je dovoljno vode za plastificirati kolagen brže nego što ih smola/otapalo može obložiti, kolagena mreža stupnjevito ekspandira u isto vrijeme infiltracije monomera. U tome je slučaju moguće da veća količina monomera smole ispuni ekspandiranu demineraliziranu zonu. Previše vode brzo će reekspandirati kolagenu mrežu, ali će razrijediti koncentraciju monomera. To može objasniti vezu između snage sveze i koncentracije HEMA u primeru. Više koncentracije HEMA (rezultat manje koncentracije vode) aplicirano na suhi, kolabirani demineralizirani dentin neće dopustiti njegovu reekspanziju, što smanjuje snagu sveze (31,32).

Ako dentin nije isušeno nego je još uvijek vlažan, adhezivni agens mora fizički zamijeniti vodu da bi infiltrirao u prostor između eksponiranih kolagenih vlakana (intertubulusna dentinska permeabilnost). Jedan način da se izbjegne presušenost dentina jest uporaba organskoga otapala pomiješanog s vodom koji kemijski odstranjuje vodu u demineraliziranoj zoni difuzijom.

Kada se primer koji sadrži aceton aplicira na vlažan demineralizirani dentin, voda difundira od vlažnog dentina u aceton, a aceton (koji je u većoj količini nego voda) difundira u demineralizirani dentinski matriks.

Monomer otopljen u acetonu također difundira u prostor već ispunjen vodom. Ta kemijska dehidracija kolagene mreže uzrokovana supstitucijom vode acetonom također povećava modul elastičnosti kolagena. U ovom slučaju voda se postupno gubi kao otapalo i monomeri zauzimaju prostor oko kolagenih vlakana. Time je manje skupljanje ili kolaps kolagene mreže. Kako organsko otapalo hlapiti, kolaps kolagene mreže je spriječen, jer kolagena vlakna ostaju zaglavljena u "spongioznom" ekspandirajućem stanju. Uz to, aceton i alkohol imaju veći stupanj hlapljenja nego voda. Drži se da oni kako hlapiti prave manju tenzijsku površinsku silu na kolagenu mrežu nego vodeni primeri. Prostor između kolagenih vlakana ispuni se smolastim monomerom kada otapalo ishlapi (33). Ako tijekom toga procesa voda prođe iz DT putem transdentinalne permeabilnosti, kolagen može biti previše navlažen i omekšan.

Samokondicionirajući primeri postavljaju se na dentin prekriven ZS koji je suši nego jetkani dentin. Ti svezujući sustavi ne sadržavaju posebne otopine kiselih kondicionera. Umjesto toga oni se apliciraju izravno na ZS. Kako su nazočni ZS i zupci smole, transdentinalna je permeabilnost smanjena i nema znatnije vlažnosti na dentinskoj površini. Inicijalna penetracija toga agensa u ZS usporena je zbog manjka razrijeđenosti površinskom vodom (34).

Kada kiseli primer infiltrira kroz ZS/čepove ZS, zbog povećane koncentracije vode može razrijediti smolu (9). Ako je aplicirana ograničena količina primera, voda se gubi iz primera hlapljenjem. Kiselo-st primera brzo neutralizira ZS ostavljajući manje kiseline potrebne za jetkanje mineraliziranoga denti-

na. To može objasniti zašto samojetkajući primeri pokazuju tanji HS u usporedbi sa sustavima koji se koriste kiselim kondicionerima prije aplikacije primera. Kako je voda stalno nazočna zbog transdentalne permeabilnosti, bit će potrebno nanijeti nekoliko slojeva primera da bi se postigla adekvatna infiltracija u demineraliziranu zonu i DT.

Voda je u usporedbi s acetonom slabije otapalo za HEMA-temeljeni dentinski primer i daje manju snagu sveze te duže vrijeme aplikacije primera od acetona. Moguće objašnjenje toga je sposobnost vode da interferira s polimerizacijom smolastoga sustava.

Individualni monomeri ili mješavina monomera proizvode jaču snagu sveze za caklinu i dentin ako su sadržani u otapalu kao što je aceton. Aceton kao izvanredan nosač monomera uspostavlja doticaj s caklinom i dentinom. Osim toga, on odstranjuje vodu zaostalu u kolagenskoj mreži te pridonosi vlaženju s hidrofilnim monomerom (35). Hlapljenje acetona sprječava prodor zraka u smolu i time smanjuje kontaminaciju kisikom koji inhibira polimerizaciju (36).

Djelotvornost acetona u odstranjivanju vode vrlo je velika, jer voda sprječava proces polimerizacije. Druga je prednost acetona što, navlačeći vodu, omogućuje bolju penetraciju i vlaženje kolagene mreže monomerom i njegovu gustoću. Pošto otopina aceton/HEMA infiltrira vlažnu kolagenu mrežu, aceton i HEMA se pomiješaju s vodom zaglavljenu u kolagenoj mreži. Aceton/voda faza tada hlapi, ostavljajući HEMA molekule manje više same u kolagenoj mreži. Ako je aceton otapalo, HEMA vrlo brzo prožima i zasićuje kolagenu mrežu. Ako je voda otapalo, HEMA molekule neće tako brzo zasititi kolagenu mrežu jer voda neće tako lako hlapiti. Kod vodene otopine HEMA u kolagenoj je mreži sadržano više vode, što smanjuje stupanj polimerizacije a time i kakvoću, tj. jakost sveze. Aplicirano spojno sredstvo sada penetrira u demineraliziranu površinu i kopolimerizira s HEMA molekulama iz primera (37).

Sve kisele otopine koje se rabe kao dentinski kondicioneri postoje u vodenom otapalu. Voda ionizira kiselinu i otapa minerale otklonjene s dentinske površine tijekom jetkanja. Ispiranjem nakon jetkanja voda otklanja otopljene minerale i ostavlja demineraliziranu dentinsku površinu pokrivenu vodom. Konačna koncentracija smole u deminerali-

ranoj zoni i u DT bit će rezultat toga kako je smola uspjele zamijeniti zaostalu vodu. Teoretski, za očekivati je da će monomer u vodenoj otopini difundirati u jetkane DT, a koncentracija će mu biti reducirana s većom udaljenošću.

“Self-etching” primeri moraju biti ne samo dovoljno kiseli, da bi prevladali “odbojni kapacitet” ZS i dentina, nego također imati i dovoljnu koncentraciju monomera kako bi uspješno konkurirali vodi kada difundira kroz ZS u dentin. U tom slučaju voda je nužna za inicijalnu ionizaciju kisele sastavnice već nazočne u otopini. Voda iz DT podržat će ionizaciju kiseline i pomoći postići pH potreban za demineralizaciju dentinske površine i otopiti njezine reakcijske produkte.

Demineralizirani dentin sadrži vezanu vodu u kolagenu. Iako se voda između vlakana može potpuno zamijeniti monomerom, dio vode iz vlakana difundira van i stvara sloj oko kolagenih vlakana koji sprječava oblaganje vlakana monomerom. Ta voda može interferirati sa stupnjem polimerizacije smole i HS. Kritična količina vode nužna je za fizičku infiltraciju smole i kemijsku interakciju sa sastavnicama demineralizirane zone (plastificirajući učinak vode na kolagen, ubrzanje HEMA polimerizacije). Kolagen koji nije zaštićen smolom može s vremenom oslabiti (1,38).

Pulpna podnošljivost

Izravna oštećenost pulpe primjenom kiselina nije dokazana. Jetkanje dentina drži se sigurnim i neštetnim za pulpu ako mu je debljina veća od 0,5 mm (13). Veća propusnost dentina odstranjenjem ZS ne omogućuje samo povećani izlazak dentinskoga likvora nego je olakšan i prodor toksičnih supstancija prema pulpi. Difuzija sastavnica DA olakšana je strujom dentinskoga likvora. Na sklerotičnom dentinu djelovanjem kiseline slabo se povećava permeabilnost. Kod njega i peritubulusni i intertubulusni dentin sadrže više minerala otpornih na kiseline, a ZS takvoga dentina manje je topljiv nego ZS normalna dentina (17,39).

U kulturi stanica DA pokazuju citotoksični učinak u obliku inhibicije rasta stanica, inaktivnost mitohondrija i DNA-sinteze. Oštećenost pulpe nije toliko izražena zbog toksičnosti koliko zbog nedostatne rubne zatvorenosti i začepljenosti tubulusa te pro-

dora bakterija u njih. Glutaraldehyd kao sastavnica primera pokazuje veću citotoksičnost u kulturi stanica nego HEMA (17).

Indikacije za uporabu adheziva

DA su indicirani kada je debljina zaostatnog dentina veća od 0,5 mm. Ako je debljina manja, tretman može biti još siguran pod uvjetom da vrijeme jetkanja ne prelazi 15 sekundi. DA mogu se upotrebljavati kao rutinski tretman ekspaniranoga dentina umjesto uobičajenih kavitetnih lakova i premaza temeljenih na $\text{Ca}(\text{OH})_2$. Prednost im je što povećavaju napetost površine supstrata, premošćuju i začepuju tubulus sprječavajući time bakterijsku invaziju, te čine tvorbu prilično netopljive barijere. Sve češće se rabe i za redukciju postoperativne preosjetljivosti.

Preporučuje se uporaba DA kao zaštitni premaz nakon poliranja ispuna. Naime, poliranjem zbog zagrijavanja i trenja nastaje mogućnost da pukne stanjeni rub KM ili mogućnost mikrofrakture cakline te nastanak mikropukotine koji je uz to potenciran i polimerizacijskom kontrakcijom. Da bi se to izbjeglo potrebno je nakon završene obrade i poliranja jetkati rubove ispuna te ih premazati niskoviskoznom smolom. Potrebno je da adheziv bude hidrofilan, jer mikropukotina i pošto se ispere i osuši često sadrži ostatke vode (13).

Snaga svezivanja za dentin

Dentinska sveza rezultira iz smolaste infiltracije demineralizirane dentinske površine. Snaga sveze razlikuje se u površinskom i središnjem dijelu dentina, što je uvjetovano različitim udjelom intertubulusnog i peritubulusnog dentina te brojem i orijentacijom DT (4,40). Snaga sveze za dentin određena je:

- strukturom dentina
- dubinom stvorenih mikropora
- vrstom monomera i otapala
- količinom monomera koji je zamijenio vodu u kolagenoj mreži
- snagom zubaca smole ("resin tags") u tubulusima

- stvaranjem HS
- površinskom adhezijom (1,22,35,41,42).

Što je jača sveza KS i dentina to je veći udio kohezijskih fraktura (17).

Snaga sveze za dentin sa sačuvanim ZS iznosi 10 MPa, a ako se ZS odstrani 18-20 MPa (1,27). Najveća snaga sveze je kod jetkanog dentina i iznosi 32 MPa, a rezultat je oblikovanju HS u intertubulusnom dentinu s uklještenošću zubaca smole na otvoru DT s mogućom hibridizacijom stijenke DT zbog odstranjenja peritubulusnog dentina.

U idealnim uvjetima HS je glavni svezujući mehanizam u površinskom dentinu. Nakon jetkanja vrlo je porozan i sposoban za dobru infiltraciju smolom. U dubljemu dijelu dentina veći utjecaj na čvrstoću sveze imaju smolasti zupci nego HS zbog ograničene količine intertubulusnog dentina jer tubulusi postaju veći i bliži.

Kohezijska snaga mineraliziranoga dentina iznosi 54-138 MPa. Kod snage sveze 15-20 MPa povećava se postotak kohezijskih fraktura u dentinu ili kompozitu. Frakture pri nižim snagama sveze (ispod 15-20 MPa) smatraju se uzrokom abnormalne distribucije stresa. Kohezijske snage nekih najčešće rabljenih adhezijskih sustava u rasponu su od 60-85 MPa (1).

Za kompenzaciju polimerizacijske kontrakcije potrebno je da snaga sveze bude barem 17-20 MPa (43).

Zaključak

Noviji adhezijski sustavi sadrže nekoliko aktivnih sastavnica u jednoj bočici i sigurno su napredak u jednostavnijoj primjeni.

Prevenција mikropukotine i postoperativne preosjetljivosti ovisi o stupnju integriteta između KS i zuba. Odstranjivanje ZS omogućuje bolju snagu sveze za nove DA. Snaga sveze između dentina i spojnog sredstva, kao i između spojnoga sredstva i KS, treba biti veća od snage polimerizacijske kontrakcije.

Nije dokazano na koji način primjena više sastavnica u zajedničkoj otopini utječe na stabilnost i trajnost sveze s dentinom.

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Surface Interactions of Dentine and Adhesives

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Summary

Modern dentine adhesive systems are supposed to work on a micromechanical and chemical attachment principal. Dentine adhesive systems which possess so-called self-etching primers for enamel and dentine belong to five generations of resin-bonding agents. The basic compositional concept realized in these adhesive systems is to use monomers with hydrophilic properties for wetting of and penetration into the dentin collagen web, exposed by acid conditioning, capable of good polymerization and formation of a highly cross-linked network. These dentine adhesive systems are dissolved in solvents such as ethanol or acetone which completely enable exchange of water trapped in the collagen network with monomers, and are used for adhesion of composite resins with tooth tissue, for pulp capping, prevention of postoperative sensitivity, cervical desensibilization and stabilization of the cavity and rest of the tooth structure.

Key words: smear layer, hydrophilic monomer, water, acetone, hybrid layer

Acta Stomatol Croat
1998; 467—473

REVIEW

Received: November 27, 1997

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Introduction

Due to high viscosity composite resins do not have the ability to bond to the tooth structure. Bonding agents which afford the bonding of composite resins to enamel and dentine are called "dentine adhesives".

Bonding with enamel and dentine can be accomplished on its organic component (collagen), its mineral component (hydroxyapatite) or both (1).

Adhesive systems for dentine bonding have been developed to adhere to dentine either via a smear layer, or by modifying or totally removing it.

Recent studies strongly suggest the nature of the bond to be micromechanical for adhesive systems

that a by removing the smear layer by acid etching and demineralizing the superficial dentine (2,3).

In this case bonding may result in entanglement of the exposed collagen fibrils by hydrophilic adhesive resin monomers in superficial dentine, thereby forming a resin-dentine hybrid layer located between solid dentine and the covering restorative material (4,5,6).

Dentine permeability and dentine adhesion

Dentine is a dynamic substrate which shows a different degree of permeability close to the pulp and far away from it. This is because of the diffe-

rent size of the dentine tubules which are more dense near the pulp than on the enamel-dentine junction. Furthermore, deeper dentine has less minerals and intertubular dentine (7).

The latest generation of dentine adhesives have hydrophilic characteristics which afford hard bonding, even in deeper dentine layers (8).

Many dentine bonding agents use acid conditioners or primers to remove or reduce the thickness of the smear layer on the dentine surface (9). These agents clean the surface because of the low pH or chelation with Ca. They demineralize peritubular and intertubular dentine, funnel dental tubules, expose collagen fibres and modify dentine permeability and wetness. Conditioned dentine surfaces show less orthophosphoric and carbonate groups and increase of amids, different structure and denatured collagen (10).

The degree of depth of dentine demineralisation is 3-7 micrometers (1,11). The primer acid penetrates through tubules. After dentine demineralisation collagen is destabilised and free for enzymatic degradation. The presence of hydroxyapatite crystals can stabilise collagen and prevent their collapse and denaturation. After demineralisation, encapsulated hydroxyapatite crystals are in close contact with collagenous fibres and the interfibrillar crystals mostly dissolve.

Some etching agents possess Ca, Fe, Al ions which can stabilise collagen and decrease the depth of dentine demineralisation (12).

In contrast to etching enamel, etching the dentine does not increase its surface energy which is necessary for better wetting with resin. Instead, dentine conditioners and primers increase the surface energy of primers and adhesives until the surface energy of dry or wet dentine dependent of the bonding technique (1,12).

Primers in dentine adhesive systems consist of monomer (HEMA, 4-META, NPG-GMA, PDMA) and polyacril acid in water or organic solvent (such as acetone or alcohol) (13,14). They possess hydrophobic and hydrophilic groups which afford increase of surface energy on the one hand and better wetting of hydrophilic resins on the other, and therefore satisfactory chemical and micromechanical bonding (15,16). After placement, dentine primer has to

be softly air dried without polymerising, because of the water content (15).

Some primers contain glutaraldehyd which have the ability of hardening collagenous fibres through the fixing protein, antibacterial effect and increasing dentine permeability (17,18). Monomer TEG-DMA (triethylene-glycol-dimethacrylate) is a common component of bonding resins and composite resins. It is present in 30-50% of bonding agents and 15-25% of composite resins, reducing viscosity and thus providing better manipulating ability (19).

HEMA (2-hydroxyethylmethacrylate) is added to bonding resins (30-50%) in order to increase bond strength and stability of bonding to dentine. HEMA decreases viscosity of resin, penetrates the smear layer and forms a micromechanical and chemical bond with dentine, copolymerising with adhesive resin (15,19,20,21). HEMA enables encapsulating of HA-crystals in dentine. Because of its hydrophilicity, it penetrates in wet collagenous fibres (14,22,23). After polymerisation HEMA is in a strong bond with tooth tissue (24).

Self-etching primers consist, apart from monomers, of maleic acid (0.8-4%). Maleic acid does not demineralize sufficiently, which limits monomer penetration which polymerise in resin tags and can be pulled and out from dentine tubules, decreasing the bond. That brings in questions effectively of one-component dentine adhesive systems (11,17).

Etching with orthophosphoric acid is possible in the treatment of enamel of and dentine at the same time with the danger of higher demineralisation and denaturation of collagen and higher dentine permeability. Orthophosphoric acid denature collagenous fibres during removing of smear layer. This leads to the collapse of the collagen matrix and increases the space for resin infiltration and difficult hybrid layer formation. Collagenous fibres which are not encapsulated with monomer hydrolyse more rapidly (25). Application of HEMA, 4-META + acetone primer could prevent collagen matrix collapse and afford monomer penetration and substrate impregnation.

Some adhesives make a better bond with wet than with dry dentine. Which can be explained by the fact that water prevents higher collagenous fibres collapse and facilitates hydrophilic monomer penetration (17).

To achieve good bonding and sealing of dentine, resins must infiltrate both intratubular and intertubular dentine to form resin tags and a uniform hybrid layer. Intratubular infiltration of resins will form resin tags that, assuming that they bond to the tubule walls, will seal the tubules, prevent microleakage, block sensitivity and provide resin retention. Ideal intertubular infiltration is accomplished when resins are able to completely replace the water around the collagen fibrils, enveloping them to the maximum extent, infiltrating to the depth of demineralisation, reinforcing their physical properties and protecting them from hydrolytic attack. As bonding systems become more hydrophilic, the contribution of resin tag formation to resin retention theoretically increases as dentine is prepared closer to the pulp. Resins can only reach dental tubules and intertubular dentine when the smear layer has been removed by the acid-etching or when they are able to diffuse through the smear layer.

The so-called self-etching/self-priming systems, utilise an acidic priming solution which can permeate through water-filled channels between the constituent particles of the smear layer, thereby enlarging them and penetrating into the top of the underlying solid dentine. Since this self-etching/self-priming solution is not rinsed from the surface, the demineralized smear layer is incorporated into the hybrid layer. Both intratubular and intertubular permeability is critical for achievement of optimal bond strength and sealing of dentine surfaces. The ability of resins to permeate both dental tubules and intertubular dentine is influenced by several variables. In superficial dentine, which contains fewer tubules than deep dentine, permeation of resins into intertubular dentine will be responsible for most of the bond strength. In a very deep dentine, dental tubules are more abundant and, therefore, intratubular permeability of resin will probably be responsible for a large fraction of the total retention and sealing. Difficulties regarding the infiltration of resins into the dental tubules (intratubular permeability) are usually related to the presence of the dental fluid under pulpal pressure and mineral casts in sclerotic dentine. Resin infiltration into intertubular dentine is highly dependent on the superficial porosity present after acid-etching. If the collagen fibril matrix of the demineralized dentine collapses due to air-drying, it may reduce the permeability of the demineralized zone (1).

Formation and role of the hybrid layer

The hybrid layer is composed of polymerised resin, which encapsulates collagenous fibres and encapsulated HA-crystals (12). It is resistant to acid act. Impregnation and collagenous fibres encapsulation achieved on molecular degree, and new formatted hybrid layer unite dentine substrate with overlaying restorative material.

For formation of the hybrid layer two factors are important:

- adequate preparation of the substrate by removing the smear layer and demineralisation of dentine
- adequate monomer mixture which defender in dentine and impregnate it stabilising therefore the demineralized dentine matrix (23).

Hybrid layer formation confirms adequately preparing the dentine surface with acid primer/conditioner and diffusion and penetration of resin monomer. The hybrid layer is thinner on the lateral walls where the dentine tubule are parallel with the cavity surface (4). The thickness of the hybrid layer shows how deep is the dentine is demineralised. The hybrid layer can absorb stress like an "elastic buffer", which occurs during composite resin polymerisation and therefore prevent the formation of microleakage, caused by polymerisation contraction in the cavity (26).

The role of water and acetone

Water is intimately involved in dentine bonding. The water present during bonding procedures comes from several sources such as dental fluid, atmospheric water, rinsing procedures and also from the adhesive solutions. In the past, water has always been considered as a contaminate which would compete against resin bonding. This concept originated because earlier dentine bonding agents were highly hydrophobic and therefore ineffective in the presence of water. Too much water may be the result of poorer bonding with dentine (1,6).

Water can to interfere with the chemical and physical process of bonding. In the presence of the smear layer the dentine thickness does not influence dentine wetness. After etching the decrease in dentine thickness will influence dentine wetness. In-

creased water on the surface makes hydrophilic monomer infiltration difficult. Water can also dilute monomer concentration (27). Such problems with surface wetness may be prevented by using self-etching bonding agents applied directly to the dry smear layer.

After etching and rinsing with water, approximately 70% volume of demineralised dentine (or 50% intertubular dentine) is occupied with water instead of minerals which are dissolved during etching. This water is necessary for keeping the collagen matrix extended. If the dentine is overdraw, the water which was keep collagen matrix extended evaporates, causing the collapse of collagenous fibres (28). The space between collagenous fibres is reduced what decreased permeability of intertubular dentine for adhesive resin (29). Dehydration in air also increases the modulus of elasticity of collagen. This is due to the formation of secondary bonding between peptide chains in the collagen triple helix that is prevented when water is present. If the collagen is not re-wet by water and non-aqueous primers are applied, the collagen network may not re-expand and may remain stiffened in a collapsed state. Dried, collapsed collagen needs water to lower the modulus of elasticity sufficiently so that it can re-expand. If no water is available and a non-aqueous resin primer is applied on the surface, little infiltration of the resin into the demineralized zone may be expected. Instead, the resin coats the surface of the collapsed, stiffened collagen network with little or only partial resin penetration into the reduced porosity around the collagen fibres of intertubular dentine. The resultant low resin retention will probably be the result of surface adhesion to a rough surface (30).

Water-containing primers may also work well on dry dentine because the water content of the primer will plasticize the collapsed collagen, allowing it to re-expand, which increases the size of the spaces between the collagen fibres.

When water containing primers are applied to air dried dentine, two events may occur: if the water concentration in the primer is too low, the water miscible resin monomer and/or the organic solvent will stiffen the collagen network faster than the water can plasticize the collagen and it will not completely re-expand. If there is enough water to plasticize the collagen faster than the resin/solvent can stiffen it, it may gradually expand at the same time as the re-

sin monomer is infiltrating. In this case, there is a possibility that greater amounts of resin monomers may fill the expanding demineralized zone. Too much water would rapidly re-expand the collagen network but would also dilute the monomer concentration. This may explain the relationship between bond strengths and HEMA concentration of primer systems that were placed on air dried dentine after etching. Higher concentrations of HEMA (resulting in lower water concentrations) applied to dry, collapsed demineralized dentine would not permit its re-expansion, leading to lower bond strengths (30,31).

If dentine is not air dried but is left wet, the adhesive agents still must physically replace the water to infiltrate into spaces between the exposed collagen fibrils (intertubular dentine permeability). One way to avoid air drying of dentine is to use water miscible organic solvents to chemically remove the water in the demineralized zone by diffusion.

Several primers contain acetone in association with resin monomers. When they are applied to moist demineralized dentine, the water diffuses from the wet dentine into the acetone, while the acetone (which is in great excess relative to the water) diffuses into the demineralized dentine matrix.

The primer monomers dissolved in acetone also diffuse into the spaces previously occupied by water. This chemical dehydration of the collagen network caused by substitution of water by acetone also increases the modulus of elasticity of collagen. In this case, the water is gradually lost as the solvents and resin monomers occupy the spaces around the collagen fibrils. Therefore, there is much less shrinkage or collapse of the collagen network. Should the organic solvent evaporate, collapse of the collagen network will be prevented because the collagen fibrils will be stiffened in the expanded state. Additionally, acetone and alcohol have much higher vapour pressures than water. Spaces between the collagen fibrils become filled with resin monomers as the primer solvent evaporates (33). If during this process, water is made available from the dental tubules through transdentinal permeability, the collagen may be rewet and softened.

Self-etching primers is applied to smear layer covered dentine which is considerably dryer than acid etched dentine. These bonding systems do not employ separate acidic conditioning solutions. Instead

they are applied directly to smear layers. Since the smear layer and the smear plugs are present, the transdental permeability is greatly reduced and no significant wetness is present on the dentine surface. The initial penetration of these agents into the smear layer is therefore facilitated because of lack of dilution by surface water (34).

As the acidic primer infiltrates through the smear layer/smear plug complex, increasing concentrations of water will be present and may begin to dilute the resin concentration (9). Since a limited amount of primer is applied, water in the primer begins to be lost by evaporation. The acidity of the primer is rapidly buffered by the smear layer leaving less acidity available to etch mineralised dentine. This may explain why self-etching primers show a much thinner hybrid layer formation when compared with systems that utilise an acidic conditioner prior to primer application. Since the presence of water is likely to be constantly renewed by transdental permeability, several layers of primer may be necessary to achieve proper infiltration into the demineralized zone and into the dental tubules.

Compared to acetone, water is inferior as a solvent for HEMA-based dentine primers, gives lower bond strength and requires longer priming time than acetone. A possible explanation of this is the ability of water to interfere with the polymerisation of the resin systems.

Individual monomers or monomer mixtures produced high bond strengths to enamel and dentine when applied in an acetone solution. Acetone is an excellent carrier for monomers and brings them in perfect contact with enamel and dentine. Furthermore, it eliminates small amounts of water from collagen network and brings better wetting with hydrophilic monomer (35). Acetone vapour prevent direct access of air to the resin and thereby reduced oxygen contamination which inhibits polymerisation (36).

Acetone is effective in removing the water, because the water would interfere with the polymerisation process. Another possibility is that evaporation of acetone/water, after the use of the acetone containing primer, increases the density of the hydrophilic monomer with the collagen mesh.

As the acetone/HEMA solution infiltrates the moist collagen mesh, acetone and HEMA mix with the water trapped inside the collagen mesh. The ace-

tone/water phase then evaporates, leaving the HEMA molecules more or less alone inside the collagen mesh. Because of this mechanism, HEMA infiltrates and saturates the collagen network quite fast when acetone is used as a solvent. However, when water is used as a solvent, the HEMA molecules will not saturate the collagen mesh as fast and efficiently because the water will not evaporate as easily and completely as in the case of the acetone/HEMA solvent (37).

All acidic solutions routinely used as dentine conditioners are presented in an aqueous solution. Water is necessary to ionise the acids and dissolve the solubilized minerals removed from the dentine surface during acid attaching. Post-etching rinsing with water removes the dissolved mineral and leaves a demineralized dentine surface covered with water. The final resin concentration in the demineralized zone and in the dental tubules will be a result of how well the resin competed with the residual water. Theoretically, one would expect that as water soluble primer monomers diffuse into the acid etched dental tubules, their concentration should be reduced with diffusion distance.

The self-etching primers should be acidic enough to overcome the buffer capacity of the smear layer and dentine. However, they must also have enough monomer concentration to successfully compete with water when they diffuse through the smear layer and into dentine. In the case of these systems, the water necessary for the initial ionisation of the acidic component is already present in the solution. Water from the dental tubules would enhance the ionisation of the acids and help to maintain the low pH necessary to demineralize the dentine surface and solubilize its reaction products.

Demineralized dentine contains bound water which is inside the collagen fibrils. Even if the water around the collagen fibrils can be completely removed and replaced by resin monomer, the water inside the collagen fibrils may osmotically be drawn out and form a layer of water around the fibres thus preventing direct contact of the fibres with the resin. This water may interfere with the degree of polymerisation of the resin within the hybrid layer. Critical amount of water is necessary for both physical resin infiltration and chemical interaction with the components of the demineralized zone (plasticizing effects of water on collagen, acceleration of HEMA polymerisation, etc.).

The collagen that is not protected by resin may become weaker in time (1,38).

Pulp damage

Damage of the pulp caused by etching has not been confirmed. Dentine etching is safe for pulp when its thickness is more than 0.5 mm (13). Higher dentine permeability after removing the smear layer make easily coming out of dentine liquor and toxic substances reaching the pulp. The diffusion of dentine adhesive components is simplified by current of dentine liquor. Etching of sclerotic dentine does not lead to higher permeability. Peritubular and intertubular dentine consist of minerals which are resistant to etching and the smear layer of such dentine is less soluble than the smear layer of normal dentine (17,39).

In cell-culture dentine adhesives shows cytotoxicity effect in the form of inhibition of cell growth, inactivity of mitochondria and DNA-syntheses. Pulp damage is mostly caused by inadequate marginal seal, dentine tubule seal and penetration of bacteria.

Glutaraldehyd as a primer component shows higher cytotoxicity in cell-culture as HEMA (17).

Indications for use of dentine adhesives

Dentine bonding agents are indicated if the remaining dentine thickness exceeds 0.5 mm. If the thickness is less than this, treatment may still be safe, as long as the etching time does not exceed 15 sec. Dentine bonding agents can be used as a routine treatment of exposed dentine instead of traditional cavity varnishes and Ca(OH)₂ based liners. The advantages of dentine bonding agents is that they increase the bondable surface, seal the tubules from bacterial invasion, and form a rather insoluble barrier. By using dentine bonding agents more extensively the protective coating could reduce postoperative sensitivity.

Stress induced during initial marginal adjustment and polishing could induce enamel fractures or composite fractures in areas where the material is thin. From this viewpoint it is important to mention the application of a low viscosity resin after polishing.

The resin placed around the margins should be hydrophilic, since the gap often retains water after the water rinse (13).

Bond strength to dentine

Dentine bonding is the result of resin infiltrating the demineralized dentine surface. Bond strength differs in the surface and central part of the dentine independent by of the amount of intertubular and peritubular dentine, number and orientation of dentine tubules (4,40). Bond strength is depends on:

- dentine structure
- demineralisation depth
- type of monomer and solvent
- amount of monomer which have placed water in collagen network
- strength of "resin tags" in dentine tubule
- hybrid layer formation
- surface adhesion (1,22,35,41,42).

Bond strength to dentine when the smear layer is present is 10 MPa, and when it is removed 18-20 MPa (1,27). The higher bond strength is with etched dentine - 32 MPa and is a result of a hybrid layer forming in the intertubular dentine and hybridisation of dentine tubules because of the removal of peritubular dentine.

The hybrid layer is the most important bonding mechanism in the surface dentine. After etching it is very porous and capable of resin infiltration. In the deeper part of the dentine resin tags are more responsible for the bond strength because the tubules are larger and closer together.

The cohesive strength of mineralised dentine is 54-138 MPa. The number of cohesive fractures is higher with bond strength of 15-20 MPa. Fractures with lower bond strength (less than 15-20 MPa) are caused by irregular stress distribution (1).

For compensation of polymerisation contraction bond strength needs to be at least 17-20 MPa (43).

Conclusion

The latest dentine adhesives are composed of several active components in one-bottle, simpler use which has greatly simplified.

Prevention of microleakage and postoperative sensitivity depends on the degree of integrity between the composite resin and the tooth. Removing the smear the layer causes better bond strength. Bond strength between the dentine and the bonding agent and between bonding agent and composite re-

sins must be higher than the polymerisation contraction strength.

It is yet not known how the use of several components in one bottle effects the stability and durability of bonding to dentine.