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Vlaknima ojačani polimeri
II. dio: Utjecaj na mehanička svojstva

Fibre Reinforced Polymers
Part II: Effect on Mechanical Properties

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Sažetak

U članku su opisani različiti utjecaji na mehanička svojstva vlaknima ojačanih polimera, kao što su smjer i količina vlakana, njihova impregnacija polimernom osnovom te adhezija između vlakana i polimerne osnove. Smjer vlakana može biti jednosmjeran (okomit na smjer opterećenja) te dvosmjeran ili višesmjeran (pod različitim kutovima na smjer opterećenja), ili pak nasumce raspoređen. Količina vlakana povećava i čvrstoću kompozita, no ojačanja vlaknima mogu biti učinkovita samo ako se opterećenje prenosi s osnove na vlakna. To zahtijeva dobru impregnaciju vlakana polimernom osnovom, a ona ovisi o vrsti i viskozitetu polimerne osnove (prije polimerizacije) te mogućnosti dobrog ovlaživanja svakog vlakna. Kako bi se poboljšala adhezija polimerne osnove i staklenih vlakana, koriste se vezni posrednici, osobito silani. Oni se siloksanskim mostovima vežu s površinom stakla, a kopolimerizacijom iniciranom slobodnim radikalima vežu se s polimernom osnovom poboljšavajući tako adheziju između vlakana i polimerne osnove. Ta dobra povezanost važna je ne samo za mehanička svojsta nego i za smanjenje nepovoljnog utjecaja vode na graničnu površinu vlakno-osnova.

Uvod

Vlakna se mogu ojačavati polimerima na dva načina. Prvi je kada se cijela protezna baza ili polimerni fiksnoprotetski rad ojačava vlaknima, a drugi kada se njima ojačava slabo mjesto protetskoga rada. Zato ta dva ojačanja možemo nazvati potpunim ojačanjima vlaknima (POV-om), odnosno djelomičnim ojačanjem vlaknima (DOV-om) (1).

Čimbenici koji utječu na čvrstoću vlaknima ojačanih kompozita (VOK-a) su:

1. smjer vlakana,
2. količina vlakana,
3. impregnacija vlakana polimernom osnovom,
4. adhezija između vlakana i polimerne osnove.

Introduction

The fibre reinforcements of polymers can be performed in two ways. First, when the whole denture base or polymer fixed-prosthetic appliance is reinforced with fibres, and second, when fibres are used to reinforce a weak place in the prosthetic appliance. Thus, such reinforcements can be referred to as complete fibre reinforcements (CFR), or partial fibre reinforcements (PFR) (1).

Factors which influence the strength of fibre reinforced composites (FRC) are:

1. Direction of fibres.
2. Amount of fibres.
3. Impregnation of fibres with the polymer matrix.
4. Adhesion between fibres and the polymer matrix.

Smjer vlakana

Istosmjerna vlakna mogu biti u obliku vrpca ili užadi koja se sastoje od 1.000 do 200.000 pojedinačnih vlakana. Neprekinuta istosmjerna vlakna daju najveću čvrstoću i krutost novostvorenom kompozitu (2), ali samo u jednom smjeru, tj. u smjeru vlakna (3). Zato kažemo da je ojačavanje istosmjernim vlaknima anizotropno te je posebice pogodno za uporabu kada se zna smjer najvećega opterećenja. Primjeri u kojima se koristi ta vrsta vlakana su ojačavanja tijela polimernih mostova, ojačanja djelomičnih polimernih proteza te periodontalnih splintova izrađenih direktnom metodom (1,4).

Ako su vlakna mrežasto postavljena u dva međusobno okomita smjera, tada ojačavaju konstrukciju u oba smjera, a novostvoreni kompozit ima ortotropna mehanička svojstva (5) i zato su takva ojačanja osobito korisna ako ne znamo točan smjer djelovanja najvećega opterećenja. Ta mrežasta ojačavanja imaju oblik tkanja i mogu biti različitih tekstilnih struktura (kao različite vrste platna).

Pravilno postavljanje kontinuiranih jednosmjernih vlakna teško je postići, jer su ona obično raširena i/ili pomaknuta lateralno u kalupu tijekom prešanja akrilata (6,7).

Iako ojačavanja mrežasto pletenim vlaknima znatno slabije ojačavaju kompozit kad je riječ o čvrstoći na savijanje, njihova je uporaba znatno povećala naprezanje kod loma za sve polimere. To je klinički vrlo važno, jer je kod nekih oblika proteza poželjna upravo žilavost. Tako su, na primjer, kod pokrovnih proteza često tanka područja oko pričvrstaka, zato žilavost materijala tog područja može smanjiti opasnost od loma ili perforacije toga dijela proteze. I rubovi kompozitnih krunica, ako su žilavi, mogu smanjiti moguće defekte u tom vrlo važnom području tijekom laboratorijskih i kliničkih postupaka (5). Kliničke su indikacije za uporabu dvosmjernih ojačavanja vlaknima i površinski retinirane periodontne udlage (4).

Kako je već spomenuto, tkana vlakna ojačavaju polimer u dva smjera, no vrijednosti svojstava savijanja tkanih (pletenih) vlakana usmjerenih pod kutom od 45º prema dužinskoj osovini manje su u odnosu prema vrijednosti svojstava savijanja istosmjernih vlakna (5).

Može se reći da je učinkovitost dvosmjernih ojačavanja vlaknima, kada su obavljena pod kutom od 45 stupnjeva prema opterećenju, 50 posto u odnosu prema istosmjernim ojačavanjima vlaknima kod kojih se ojačavanje računa kao 100 postotno, ako je postavljeno pod kutom od 90 stupnjeva prema opte-

Direction of fibres

Unidirectional fibres can have the form of rovings or cords consisting of 1,000 to 200,000 individual fibres. Continuous unidirectional fibres provide the greatest strength and stiffness of the newly formed composite (2), although only in one direction, i.e. direction of the fibres (3). Consequently, it can be said that reinforcements with unidirectional fibres have anisotropy character and are particularly suitable for use when the direction of the greatest loading is known. Examples of the use of these types of fibres are reinforcements of the structure of polymer bridges, reinforcements of partial polymer dentures, and reinforcements of periodontal splints fabricated by direct method (1,4).
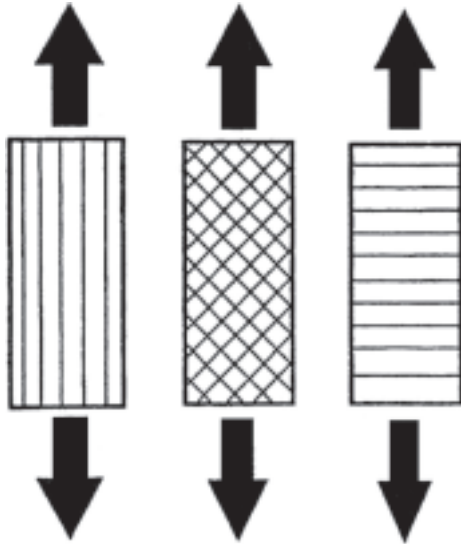
If the fibres are net-shaped, placed in two mutually vertical directions, then they reinforce the construction in both directions, and the newly-formed composite has orthotropic mechanical properties (5) and therefore such reinforcements are particularly useful when the precise direction of the effect of greatest loading is unknown. Such net-shaped reinforcements have woven form and can be of various textile structures (like various kinds of linen).

Correct placement of continuous unidirectional fibres is difficult to achieve, because the fibres are usually spread and/or displaced laterally in the mould while the acrylate is being pressed (6,7).

Although reinforcements with net-shaped woven fibres reinforce the composite to a far lesser degree with regard to the flexure strength, their use considerably increases resistance to fracture for all polymers. This is very important from the clinical point of view, because in the case of some forms of dentures, stiffness is a desirable property. For example, in the case of cover dentures, the area around the attachments is often thin and therefore the resilience of the material in this area can decrease the danger of fracture or perforation of this area of the denture. Furthermore, the marginal edges of composite crowns, if stiff, can decrease the possibility of defects in this very important area during laboratory and clinical procedures (5). Clinical indications for the use of bidirectional fibre reinforcements are also surface retained periodontal splints (4).

As previously mentioned woven fibres reinforce polymer in two directions. However, the values of the flexural properties of woven fibres directed under an angle of 45 degrees against the longitudinal axis are lower in relation to the values of the flexural properties of unidirectional fibres (5).

rečenju (Slika 1.) (8). Učinkovitost ojačavanja vlaknima naziva se Krenchelov čimbenik i koristi se kod teorijskih procjena čvrstoće vlaknima ojačanih kompozita.

Slika 1. Učinak ojačavanja (Krenchelov čimbenik) jednosmjernih vlakana u smjeru opterećenja (lijevo), dvosmjernih vlakana (sredina) i jednosmjernih vlakana okomitih na smjer opterećenja (desno).

Figure 1 Effect of reinforcement (Krenchel's factor) of unidirectional fibres in the direction of loading (left), bidirectional fibres (middle) and unidirectional fibres vertical in the direction of loading (right)

It can be said that the efficiency of bidirectional fibre reinforcements, when the reinforcements are under an angle of 45 degrees against the loading, is 50% compared to unidirectional fibre reinforcements, in which reinforcement is estimated as 100%, when placed under an angle of 90 degrees against the loading (Fig. 1) (8). Efficiency of fibre reinforcements is known as Krenchel's factor and is used in all theoretical estimations of strength of the fibre reinforced composites.

Ojačavanje vlaknima uporabom neprekinutih vlakana u nasumičnom rasporedu naziva se mat, a ojačavanja s nasumično usmjerenim kratkim vlaknima naziva se nasjeckani mat. Ta ojačavanja daju ista mehanička svojstva u svim smjerovima, tj. izotropna mehanička svojstva vlaknima ojačanim kompozitima. Ta vrsta ojačanja nije toliko zanimljiva i zasad se ne koristi za protetske konstrukcije, jer kod tih vrsta ojačavanja vlakna mogu izvirivati iz polimerne osnove te tako iritirati okolnu sluznicu (9), a i povećati kumulaciju plaka.

Vlakna za ojačavanje učinkovita su samo ako se stres može prenijeti s polimerne osnove na sama vlakna (10,11). To se može postići ako vlakna imaju duljinu jednaku ili veću od kritične dužine vlakana (11). Ona, pak, ovisi o mnogim čimbenicima, kao što su čvrstoća međusobne povezanosti (vlakna i osnove), smična čvrstoća osnove i vlačna čvrstoća samoga vlakana (11). Slaba adhezija vlakana povećava potrebnu duljinu vlakana, jer mehaničko trenje na spojnoj površini vlakno-matriks mora zamijeniti silu adhezije, pa se i preporučuje uporaba dugih neprekinutih vlakana (11).

Kod vlaknima ojačanih kompozita smjer vlakana, osim mehaničkih, određuju i termička svojstva. Tako se, na primjer, toplinski koeficijent rastezanja mijenja ovisno o smjeru vlakana za ojačavanje (12,13). To, pak, može imati važan klinički učinak, na primjer, kod adhezije vlaknima ojačanih kompo-

Fibre reinforcement by the use of continuous fibres in random order is known as mat, while reinforcement with randomly oriented short fibres is known as chopped mat. Such reinforcements provide the same mechanical properties in all directions, i.e. isotropic mechanical properties of fibre reinforced composites. This type of reinforcement is not of great interest and currently is not used for the purpose of reinforcing prosthetic appliances, because in such types of reinforcements fibres can protrude from the polymer matrix and irritate the surrounding mucus membrane (9), and also increase accumulation of plaque.

Fibres for reinforcements are only efficient when the stress can be transferred from the polymer matrix to the fibres themselves (10,11). This can be achieved when the fibres have the same or greater length than the critical fibre length (11). This depends on several factors such as the strength of the mutual bonding (fibre and matrix), sharing strength of the matrix and tensile strength of the fibre itself (11). Poor adhesion of the fibres increases the necessary fibre length because mechanical friction on the bonded surface, fibre-matrix must replace the adhesive force, and for this reason use of long continuous fibres is recommended (11).

In fibre reinforced composites apart from mechanical properties the direction of fibres also determines thermal properties. Thus, for example the

zitnih materijala za fasetiranje na metalnu konstrukciju protetičkoga rada, ili kod adhezije vlaknima ojačanog kompozita na zubna tkiva (14).

Linearni koeficijent toplinskog rastezanja vlaknima ojačanih kompozita znatno se razlikuje ovisno o smjeru vlakana za ojačavanje. Tako kompoziti ojačani jednosmjernim neprekinutim vlaknima imaju dva koeficijenta toplinskog rastezanja – jedan, u smjeru vlakana, mali je zbog mehaničkih ograničenja uvjetovanih vlaknima, a drugi, okomit na smjer vlakana, pokazuje visoke vrijednosti kao i sama polimerna osnova. Razlog visokim vrijednostima linearnoga koeficijenta toplinskoga rastezanja u smjeru poprečnom na smjer vlakana jest to što kruta vlakna u najvećoj mjeri sprječavaju širenje osnove u uzdužnom smjeru, pa je osnova prisiljena na širenje čak i veće od normalnoga, poprečno na smjer vlakana. Kao rezultat anizotropne prirode kompozita ojačanih jednosmjernim kontinuiranim vlaknima mogu se pojaviti toplinski inducirani stresovi unutar osnove, a između lamela kod križnih ili drugih vrsta laminata (11).

Sa stajališta kliničke stomatologije ti toplinski inducirani stresovi mogu igrati važnu ulogu u vezi s dugotrajnošću stomatoloških radova. Tako se, na primjer, fasete mogu odvojiti od podloge zbog nepodudarnosti toplinskih koeficijenata dvaju materijala. Pravilna usmjerenost vlakana za ojačavanje svakako može pridonijeti i pomoći u prevladavanju takvih problema (15).

Količina vlakana

Neka su istraživanja pokazala da povećanje količine vlakana u polimernoj osnovi povećava transverzalnu čvrstoću i čvrstoću na udarac kod ispitanih uzoraka izrađenih od polimera koji se rabe za izradbu baza proteza (7,16). Sama količina vlakana može se izraziti ili kao težinski ili kao volumni postotak. Kako količina vlakana u polimernoj osnovi utječe na mehanička svojstva vlaknima ojačanih kompozita, to je pravilnije količinu vlakana izražavati kao volumni postotak. Naime, uglljično-grafitna vlakna, te ona aramidna i polietilenska imaju nižu gustoću od staklenih, što kod iznošenja podataka u obliku težinskog postotka udjela vlakna može dovesti do pogrešnih zaključaka o omjeru

thermal coefficient of expansion changes depending on the direction of the fibres for reinforcement (12,13). This can have a significant clinical effect, e.g. in adhesion of the fibre-reinforced composite materials for veneering to the metal construction of the prosthetic appliance, or in adhesion of the fibre-reinforced composite to the dental tissue (14).

Linear coefficient of thermal expansion of the fibre reinforced composites differs greatly with regard to dependence on the direction of the fibres for reinforcement. Such composites, reinforced with unidirectional continuous fibres, possess two coefficients of thermal expansion. One, in the direction of the fibres, is small due to mechanical limitations conditioned by the fibres, and the other, vertical on the direction of the fibres, displays high values, as well as the polymer matrix. The reason for the high values of the linear coefficient of thermal expansion in transverse direction on the direction of fibres, is due to the fact that the hard fibres to a large degree prevent expansion of the matrix in the longitudinal direction, and thus the matrix is forced to expand, even more than normal, in the direction transverse on the direction of the fibres. As a result of the anisotropic nature of the composites reinforced by unidirectional continuous fibres, thermally induced stresses within the matrix itself can occur between the lamellas in crossed or other types of laminates (11).

From the perspective of clinical dentistry these thermally induced stresses can play an important role in the durability of dental appliances. Thus, for example, the veneers can detach from the base due to disparity of the thermal coefficients of the two materials. Correct orientation of the fibres for reinforcement can definitely contribute and help in overcoming such problems (15).

Amount of fibres

Some investigations showed that an increased amount of fibres in the polymer matrix increases the transverse strength and impact strength of the tested samples, fabricated from polymers used for the production of denture bases (7,16). The amount of fibres can be expressed either as a weight percentage, or volume percentage. As the amount of fibres in the polymer base effects the mechanical properties of fibre reinforced composites, it is more correct to express the amount of fibres as a volume percentage. Namely, carbon-graphite fibres, aramide and polyethylene fibres have lower density than glass fibres, which, when presenting data in the form of weight percentage of the fibre share, can lead to false conclu-

udjela vlakana i čvrstoće vlaknima ojačanih kompozita (17).

Ledizesky i suradnici (18), istražujući čvrstoću na udarac kod protezne baze ojačane istosmjernim polietilenskim vlaknima, pronašli su kako koncentracija od 13,4 volumna postotka daje čvrstoću na udarac od 44 kJ/m^2, dok je čvrstoća neojačanog PMMA samo 10 kJ/m^2. Kada su uporabili nasjeckana polietilenska vlakna, za istu čvrstoću na udarac valjalo je uporabiti čak 37 vol% vlakana (19). Vallittu (16) je uporabom istosmjernih staklenih vlakana koncentracije 13 vol%, tj. 25 tež.% za ojačavanje protezne baze, postigao istu čvrstoću na udarac kao i s ispjeskarenom čeličnom žicom promjera 1 mm.

Vallittu i suradnici (10) navode kako udjel staklenih vlakana od čak 58 tež.% povećava čvrstoću na savijanje za čak 146 %. No, isto tako ističu da je teško postići povećanje koncentracije vlakana u polimernoj osnovi, što kao posljedicu ima povećanje čvrstoće na savijanje, i to iz triju razloga: 1. lateralnog pomaka vlakana kada se akrilatno tijesto preša u kivetu; 2. slabe mogućnosti vlaženja vlakana polimernim materijalom, što stvara neujednačen sloj polimera koji okružuje pojedina vlakna unutar niti (vrpce); 3. polimerizacijske kontrakcije PMMA uništava homogenost strukture sloja polimera na površini vlakana i tako slabi vezu između vlakana i polimera (smanjuje se uporabom predimpregnacije) (10).

Ladizesky i suradnici (18), pak, kažu da udjel polietilenskih vlakana u njihovim protezama od 26 do 39 vol.%, uz jako dobru penetraciju akrilatne smole između vlakana, učinkovito ojačava.

No, veći udjel vlakana ne znači nužno i veću čvrstoću na savijanje. Čimbenici kao što su dobra impregnacija vlakana polimernom osnovom, adhezija polimerne osnove na vlakana za ojačavanje i/ili svojstva samih vlakana prema svojstvima polimerne osnove, utječu na čvrstoću na savijanje i mogu objasniti zašto ispitivani uzorci s većim udjelom vlakana nemaju uvijek i bolja mehanička svojstva (17).

Neki autori navode kako postotni udjeli vlakana za ojačavanje trebaju biti niski. Tako se Gutteridge (20) koristio ojačavanjima polietilenskim vlaknima ultra visoke molekulske težine s udjelom od 1 do 3 tež.% i zaključio kako uporaba udjela vlakana s više od 4 tež. % otežava njihovu ugradnju i manipulaciju te je preporučio vlakna od 1 tež.%.

Clarke i suradnici (21) su, pak, preporučili udjel vlakana od 2 %, a rezultati Karacaera i njegovih suradnika (22) upućuju na to kako udjel vlakana ne utječe na čvrstoću na savijanje, ali povećanjem

sions with regard to the ratio between the fibre share and strength of fibre reinforced composites (17).

Ledizesky et al, while investigating impact strength in denture bases reinforced with unidirectional polyethylene fibres, found that a concentration of 13.4 volume percentage provides impact strength of 44 kJ/m^2, while the strength of non-reinforced PMMA amounts to only 10 kJ/m^2. In order to achieve the same impact strength when chopped polyethylene fibres are used, it was necessary to use as much as 37 vol% fibres (19). Vallittu (16) achieved the same impact strength as sandblasted steel wire of 1mm in diameter by using unidirectional glass fibres in a concentration of 13 vol%, i.e. 25 weight% for reinforcement of a denture base.

Valittu et al. (10) reports that a share of glass fibres of as much as 58 weight% increases flexural strength by as much as 146 %. Furthermore, they report that it is difficult to achieve an increase in concentration of fibres in the polymer matrix, which results in increased flexural strength, for the following three reasons: 1) Lateral shifting of fibres when the acrylic mass is pressed in the flask, 2) Poor possibility of wetting the fibres by polymer material, which leads to the formation of an uneven layer of polymer, which surrounds individual fibres within the thread (strip), 3) Polymer contraction of PMMA destroys the homogenous structure of the polymer layer on the surface of the fibres and in this way weakens the bond between the fibres and polymers (decreases with use of pre-impregnation) (10).

Ladyzesky et al (18) report that the share of polyethylene fibres in their dentures of 26-39 vol. %, with excellent penetration of acrylic resin between the fibres, lead to more efficient reinforcement.

However, a greater share of fibres does not necessarily mean greater flexural strength. Factors, such as good impregnation of fibres with the polymer matrix, adhesion of the polymer matrix to fibres for reinforcement and/or characteristics of the fibres themselves contra the characteristics of the polymer matrix, influence flexural strength and can explain why tested samples with a greater share of fibres do not always have better mechanical properties (17).

Some authors report that the percent shares of fibres for reinforcement should be low. Gutteridge (20) used reinforcements with polyethylene fibres of ultra high molecular weight with a share of 1 to 3 weight% and concluded that use of a share of fibres of more than 4 weight% inhibits their incorporation and manipulation, and he recommended a fibre share of 1 weight%.

udjela povisuje se udarna čvrstoća. Slični su rezultati i u studiji Behra i suradnika (17) u kojoj se ističe kako nema ovisnosti između volumnoga udjela vlakana i vrijednosti čvrstoće na savijanje.

Bez obzira na različite preporuke u količini vlakana za ojačavanje, dokazano je i laboratorijski i klinički, da i mala količina pravilno smještenih vlakana znatno povećava čvrstoću protetskoga rada (1,23).

Impregnacija vlakana polimernom osnovom

Jedan od glavnih problema tijekom uporabe vlaknastih ojačanja jest njihova slaba impregnacija polimernim materijalom osnove te nejednako raspoređivanje (24-27). Slaba impregnacija vlakana potiče mnoštvo problema pri uporabi vlaknima ojačanih kompozita. Tako su, na primjer, slabo impregnirana vlakna mjesta gdje se povećano upija voda, što može rezultirati štetnim hidrolitičkim djelovanjem vode i tako smanjiti mehanička svojstva vlaknima ojačanih kompozita (28). Vrlo važan problem kod slabe impregnacije vlakana jest i diskoloracija područja ojačavanja, zbog ulaska mikroorganizama u pukotinu nastalu između slabo impregniranih vlakna i polimerne osnove (5). Te su pukotine istodobno i spremišta kisika, što omogućuje da on inhibira polimerizaciju unutar vlaknima ojačanog kompozita. To, pak, može povećati koncentraciju ostatnoga monomera i smanjiti čvrstoću vlaknima ojačanog kompozita (29).

Zato je potreban djelotvoran postupak impregnacije kako bi se polimeru osnove omogućilo da dođe u kontakt sa svakim vlaknom zasebno. Iz industrije su poznati mnogi postupci impregnacije koji se mogu primijeniti i u stomatologiji, no oni potpuno ne zadovoljavaju sve zahtjeve. Stupanj impregnacije vlakana može se, na primjer, odrediti i brojenjem pojedinih neimpregniranih vlakana pod mikroskopom (30).

Tako se stupanj impregnacije može definirati kao broj impregniranih vlakana podijeljen s ukupnim brojem vlakana (30). Tako se numerička vrijednost stupnja impregnacije kreće od 0 za potpuno neimpregnirana vlakna, do 1 za potpuno impregnirana vlakna. Pod pojmom impregniranog vlakna smatramo vlakno za ojačavanje potpuno uronjeno (inkapsulirano) u polimernu osnovu. Značenje vrijednosti stupnja impregnacije osobito dolazi do izražaja

Clarke et al (21), however, recommended fibre share of 2%, while the results of Karacaer et al (22) indicate that the share of fibres has no influence on flexural strength, although by increasing the share impact strength is increased. Similar results were obtained in a study by Behr et al (17) which showed that there is no dependence between the volume share of fibres and values of flexural strength.

Regardless of the different recommendations on the amount of fibres for reinforcement, it has been proved both in the laboratory and clinically, that even a small amount of correctly oriented fibres significantly increases the strength of the prosthetic appliance (1,23).

Impregnation of fibres with the polymer matrix

One of the major problems in the use of fibre reinforcements is poor impregnation of fibres with the polymer material of the base and uneven distribution of fibres (24-27). Poor impregnation of fibres causes numerous problems in the use of fibre reinforced composites. Thus, for example, poorly impregnated fibres are areas where increased water sorption occurs, which can lead to the harmful hydrolitic effect of water, and consequently reduce the mechanical properties of fibre reinforced composites (28). A very important problem with regard to poor impregnation of fibres is also discoloration of the reinforced areas due to the entrance of micro-organisms into the gap which appear between the poorly impregnated fibres and the polymer matrix (5). These gaps are also reservoirs of oxygen, which enable oxygen to inhibit polymerisation within the fibre reinforced composite. This can increase the concentration of residual monomer and decrease the strength of the fibre reinforced composite (29).

Consequently an effective method of impregnation is necessary in order to enable the polymer base to come into contact with each fibre separately. In industry there are many known methods of impregnation, which can also be applied in dental medicine. However, they do not entirely satisfy all requirements. The degree of fibre impregnation can, for example, be determined by counting individual non-impregnated fibres under the microscope. (30).

Thus the degree of impregnation can be defined as the number of impregnated fibres divided by the total number of fibres (30). Such numerical value of the degree of impregnation ranges from 0 for completely non-impregnated fibres to 1 for completely impregnated fibres. An impregnated fibre is considered to be a fibre for reinforcement which is completely immersed (encapsulated) in the polymer

kod malih konstrukcija kao što su i protetski radovi, jer tada utjecaj dobro impregniranih vlakana ističe sposobnost ojačavanja konstrukcije uporabom vlakana.

Kako je već dobro poznato, tijekom polimerizacije volumno skvrčavanje monomera (metilmetakrilat s dimetakrilatom za umreženje) iznosi teorijskih 21 % (31). Kako bi se postigao ravnomjeran sloj polimerne osnove na površini skupine vlakana, iznimno je važno da skvrčavanje unutar skupine vlakana, tj. između njih, bude što manje. Zato čisti monomer nije pogodan za impregnaciju vlakana. Razmjerno znatno skvrčavanje monomera može se smanjiti dodavanjem praha PMMA u monomernu tekućinu. Zato se pokušala obaviti impregnacija potapanjem vlakna u niskoviskoznu mješavinu polimernog praha i monomerne tekućine (26,32). No, unatoč uporabe te niskoviskozne mješavine, učinak impregnacije vlakana bio je daleko od optimalnog (26,27).

Utvrđeno je kako postoje dva osnovna razloga zbog kojih nema dobre impregnacije: 1) nepravilno ovlaživanje skupina vlakana mješavinom polimernog praha i monomerne tekućine, 2) skvrčavanje polimernog materijala tijekom polimerizacije između vlakana za ojačavanje. To znači da to polimerizacijsko skvrčavanje može smanjiti čvrstoću vlaknima ojačanih kompozita (24). No, veza između staklenoga vlakna i polimerne osnove također ovisi o mehaničkoj retenciji koja se javlja upravo zbog polimerizacijske kontrakcije polimerne osnove i površinske hrapavosti (uzdužne i poprečne brazde) vlakana. Tako nastaje sila trenja (frikcije) između staklenoga vlakna i polimerne osnove (33).

Vallittuovo istraživanje (27) na kompozitu ojačanom staklenim E-vlaknima pokazalo je da su vrijednosti vlačne čvrstoće i modula elasticiteta dobivene istraživanjem, bile znatno niže od istih teorijskih vrijednosti. Nakon obrade SEM-om utvrđeno je kako su postojala područja u kojima staklena vlakna uopće nisu bila obložena polimernom osnovom, što je očito utjecalo na smanjenje vrijednosti mehaničkih svojstava vlaknima ojačanih kompozita.

Za razumijevanje problematike impregnacije vlakana za ojačanje potrebno je nešto reći o strukturi višefaznog polimera za izradu proteznih baza tj. osnove. Taj polimer polimerizira se iz polimetilmetakrilatnog (PMMA) praha u obliku sitnih perlica i metil-metakrilatne (MMA) tekućine koja sadržava i male količine sredstva za umreženje kao što je etilenglikoldimetakrilat (EGDMA) ili butandioldimetakrilat (BDMA) (34). Tijekom miješanja monomera

matrix. Significance of the value of the degree of impregnation is particularly important in the case of small constructions, such as prosthetic appliances, because in this case the influence of well-impregnated fibres emphasises the capability of the reinforcement of the construction by the use of fibres.

As is well known, the volume contraction of monomer during polymerisation (methylmethacrylate with dymethacrylate for cross-linking) amounts to theoretical 21% (31). In order to achieve an even layer of the polymer matrix on the surface of a group of fibres it is particularly important that contraction within the group of fibres, i.e. between them, is minimal. For this reason pure monomer is unsuitable for fibre impregnation. By adding PMMA powder to the monomer liquid relatively significant contraction of monomer can be decreased. Impregnation was therefore attempted by immersing fibres in a low viscosity mixture of polymer powder and monomer liquid (26,32). In spite of the use of this low viscosity mixture, the effect of fibre impregnation was far from optimal (26,27).

Two basic reasons have been determined because of which good impregnation does not occur: 1) Incorrect wetting of the groups of fibres with a mixture of polymer powder and monomer liquid, 2) Contraction of the polymer material during polymerisation between the fibres for reinforcement. Thus, polymeric contraction can decrease the strength of the fibre reinforced composite (24). However, the bond between the glass fibre and polymer base also depends on mechanical retention, which occurs due to the polymer contraction of the polymer base and surface roughness (longitudinal and transverse grooves) of the fibres. In this way friction force occurs between the glass fibre and polymer matrix (33).

Vallittu (27) carried out an investigation on composite reinforced with glass E-glass fibres, and showed that the values of tensile strength and module of elasticity obtained, were significantly lower than the same values obtained theoretically. Following SEM analysis it was determined that areas existed in which E-glass fibres were not coated at all with polymer matrix l, which obviously influenced the decrease in values of the mechanical properties of the fibre reinforced composites.

In order to understand the problems of fibre impregnation for reinforcement it is necessary to reflect on the structure of the multi-phase polymer for fabrication of denture bases, i.e. the matrix. This polymer is polymerised from polymethylmethacrylate (PMMA) powder, in the form of tiny beads

i polimera i razdoblja tjestaste konzistencije, monomer otapa i bubrenjem povećava površinu PMMA perlica, no monomer ne otapa potpuno zrnca PMMA (27). Zato mješavina PMMA-MMA sastavljena od perlica praha i tekućine monomera, tvori vrlo viskoznu tjestastu fazu sa slabom mogućnošću ovlaživanja (15,35). Tako ne samo da teško impregnira niti (vrpce) staklenih vlakana, nego se zbog visokog viskoziteta teško aplicira u područja između vlakana (27). Čak i u područjima u kojima su vlakna dobro impregnirana, zrnca PMMA postavljaju se između vlakana i razmiču ih, uzrokujući tako podebljanje snopa vlakana. Tako mješavina zrnaca polimera i tekućine monomera ne otežava samo impregnaciju vlakana, nego njihovim razmicanjem smanjuje količinu vlakana po jedinici volumena. Problem se javlja više kod tlačno-toplinsko polimerizirajućih, negoli kod autopolimerizirajućih polimera (5), iako je tjestasto razdoblje mješavine tlačno-toplinsko polimerizirajućeg polimera trebalo omogućiti perlicama PMMA da budu u većoj mjeri otopljene, odnosno da njihova površina nabubri, nego što je to kod autopolimerizirajućih polimera (27).

Studija Vallittua i suradnika (35) također je pokazala kako je impregnacija vlakana bolja kod uporabe autopolimerizirajućih materijala u odnosu prema tlačno-toplinskim polimerizirajućim materijalima, iako je i kod prvospomenutih u materijalu bilo područja sa šupljinama i porozitetima.

Teorijski bi se bolja impregnacija staklenih vlakana polimerom mogla postići manjim viskozitetom PMMA-MMA mješavine, što se jednostavno dobiva mijenjanjem omjera praha i tekućine. No, tada je problem povećana polimerizacijska kontrakcija što, kako je već rečeno, izaziva stvaranje pukotina i šupljina između vlakana i polimernog matriksa (15). Druga poteškoća koju se mora istaknuti kod povećane polimerizacijske kontrakcije zbog previše monomerne tekućine jest distorzija (iskrivljenje) tako izrađene proteze ili njezina ojačavanja (36). Još se može reći da je stupanj polimerizacije autopolimerizirajućih vrlo rijetko viskozno zamiješanih polimera niži od stupnja polimerizacije viskoznije zamiješanih polimera. No, to se može djelomice kompenzirati prilagodbom sastava mješavine PMMA-MMA (37).

and methylmethacrylate (MMA) liquid, which also contains small amounts of media for cross-linging, such as ethylenglycoldimethacrylate (EGDMA), or butanedyoldimethacrylate (BDMA) (34). During the mixing of monomer and polymer and the period of paste-like consistency, monomer dilutes and increases the surface of the PMMA beads by swelling. However, monomer does not completely dilute the PMMA granules (27). Therefore, the PMMA-MMA mixture, composed of beads of powder and monomer liquid, forms a high-viscosity dough-like phase with poor wetting capability (15,35). Thus, not only does it have difficulty impregnating the threads (strips) of glass fibres, but also, due to high viscosity, applies with difficulty in the areas between the fibres (27). Even in areas where the fibres are well impregnated, PMM granules position themselves between the fibres and shift them apart, causing thickening of the fibre bundle. Thus, the mixture of polymer granules and monomer liquid not only hinders impregnation of fibres, but also by their shifting apart decreases the amount of fibres per volume unit. The problem occurs more often in pressure and heat polymerising, than in autopolymerising polymers (5), although the dough-like period of the mixture of pressure and heat polymerising polymer should allow the PMMA beads to be diluted to a greater amount and their surface swells, than is the case in autopolymerising polymer (27).

A study by Vallittu et al (35) also showed that fibre impregnation is better when autopolymerising materials are used compared to pressure and heat polymerising materials. Although in the case of the former, areas were found with voids and porosity within the material.

Theoretically, better impregnation of glass fibres with polymer could be realised by lower viscosity of the PMMA-MMA mixture, which can be obtained by simply changing the ratio between powder and liquid. However, in that case appears the problem of increased polymer contraction, which, as already mentioned, results in the formation of crevices and gaps between the fibres and polymer matrix (15). Another problem, which can occur due to increased polymer contraction because of excessive monomer liquid, is distortion of such a fabricated denture or its reinforcement (36). In addition, it can be said that the degree of polymerisation of autopolymerising very low viscosity mixed polymers, is lower than the degree of polymerisation of higher viscosity mixed polymers. However, this can be partly compensated by modification of the composition of the PMMMA-MMA mixture (37).

Adhezija između vlakana i polimerne osnove (matriksa)

Kako bi se poboljšala adhezija između polimerne osnove (matriksa) i staklenih vlakana, koriste se različita vezivna sredstva. Ona najčešća su silani koji kemijski reagiraju s površinom staklenoga vlakna i polimernim materijalom osnove i tako znatno poboljšavaju mehanička svojstva vlaknima ojačanog kompozita (38,39). Svakako da kemijsko povezivanje vlakana s polimernom osnovom utječe i na veću čvrstoću na savijanje, što su ustanovili i Shimozato i suradnici (40) u istraživanju s ugljičnim vlaknima.

Mogućnost primjene silana kao veznih posrednika u stomatologiji, istraživalo je posljednjih desetljeća mnogo znanstvenika (41-51). Dosad je postavljeno mnogo teorija o tome kako silani utječu na poboljšanje veze, a dokazano je da se odnos silanskih spojeva i stakla temelji na dvije vrste veza (52). Jedna od njih su siloksanski mostovi stvoreni kondenzacijskom reakcijom između silanolskih skupina i staklene površine. Istodobno s tom kondenzacijskom reakcijom, karbonilna skupina silanolske molekule stvara hidrogensku (vodikovu) vezu. Isto je tako važna i veza između veznoga posrednika i polimerne osnove, jer se stvara kopolimerizacijom (iniciranom slobodnim radikalima) između silana i polimerne osnove tijekom polimerizacije (53). Tako se postiže dobra adhezija između polimera i staklenih vlakana, a time i poboljšavaju mehanička svojstva vlaknima ojačanih kompozita (54).

Silanski vezni posrednici mogu se kondenzirati na površinu stakla, odnosno staklenih vlakana samo na temperaturama višima od sobne. Tako je zagrijavanje na 80ºC-110ºC tijekom nekoliko sati uporabljeno za polimerizaciju γ-metakriloksipropiltrimetoksisilana (γ-MPS) na površini E-staklenih vlakana (55,56). Takvo toplinsko djelovanje stvara višeslojni vezni posrednik na površini staklenih vlakana s kovalentnim i hidrogenskim svezama na spojnoj površini (52,56,57). Dakle, ako se rabe tlačno-toplinski polimerizirajući akrilati, tada temperatura polimerizacije akrilata također može polimerizirati i silanske vezne posrednike na površini staklenih vlakana što rezultira adekvatnom čvrstoćom adhezije (24). Kada se koristi samopolimerizirajući akrilat, temperatura polimerizacije je razmjerno niska. Čak ni vršne temperature postignute u radikalnim uvjetima polimerizacije samopolimerizirajućih akrilata, ne dosežu temperaturu nužnu za polimerizaciju γ-MPS-a, osobito ako se uzme u obzir i smanjenje vršnih temperatura polimerizacije zbog volu-

Adhesion between fibres and the polymer matrix

In order to improve adhesion between the polymer matrix and glass fibres various means of bonding are used. The most important means of bonding are silanes, which chemically react with the surface of the glass fibres and with the polymer material of the matrix, and in this way significantly improve the mechanical properties of fibre reinforced composites (38,39). Evidently, chemical bonding of fibres with the polymer base has an effect on increased flexural strength, which was also determined by Shimozato et al (40) in their investigation of carbon fibres.

The possibility of the application of silanes as bonding agents in dental medicine has been investigated by a number of authors over the last decades (41-51). So far many theories have been put forward on how silanes influence bonding improvement, and it has been demonstrated that the bonding of silane compounds and glass is based on two types of bonds agents (52). One type is siloxane bridges created by the condensation reaction between silanol groups and the glass surface. Simultaneously with this condensation reaction the carbonyl group of silanol molecules forms a hydrogen bond. Equally important is the connection between the bonding agent and polymer matrix, which is created by co-polymerisation (initiated by free radicals) between silane and the polymer matrix during polymerisation (53). Thus creating satisfactory adhesion between the polymer and glass fibres, which improves the mechanical properties of fibre reinforced composites (54).

Silane bonding agents can be condensed on the glass surface, namely glass fibres, only at temperatures higher than room temperature. Consequently, heating at 80-110°C for several hours is used for polymerisation of γ-methacryloxypropyltrimethoxysilane (γ-MPS) on the surface of E-glass fibres (55,56). Such thermal activity leads to the formation of a multi-layer bonding agent on the surface of the glass fibres with covalent and hydrogen bonds on the bonding surface (52,56,57). It follows that if pressure and heat polymerising acrylates are used, then the polymerisation temperature of acrylates can also polymerise silanic bonding agents on the surface of glass fibres, leading to adequate strength of the adhesion (24). When autopolymerising acrylate is used, the polymerisation temperature is relatively low. Even the peak temperatures reached in radical conditions of polymerisation of autopolymerising acrylates do not reach the temper-

mnog udjela vlakana u polimernoj osnovi (55,58). Kako bi se postigla kondenzacija γ-MPS-a na površinu staklenih vlakana, γ-MPS se može predpolimerizirati uporabom odgovarajuće topline, prije nego što se vlakna umeću u polimernu osnovu (53). Viša temperatura polimerizacije γ-MPS-a ne znači nužno i bolju adheziju. Tako je Vallittuaova studija (53) pokazala da tretiranje γ-MPS-a temperaturom od 100°C rezultira većom čvrstoćom na savijanje od tretiranja temperaturom od 150°C. To se može protumačiti tako što na temperaturi od 100°C nije u cijelosti završen tretman γ-MPS-a, pa je sloj toga veznog posrednika nabubrio pod utjecajem monomera zamiješanoga s polimernim perlica, i to prije polimerizacije samoga polimera. To je rezultiralo boljim prodiranjem polimerne smole u sloj veznoga posrednika te je tijekom polimerizacije ostvarena bolja veza (53). Na temperaturi od 150°C završen je tretman γ-MPS-a, te njegov sloj ne bubri pod utjecajem monomera, a ujedno sljepljuje pojedinačna staklena vlakna tvoreći skupinu niti. Na taj način otežava prodor polimeru osnove u prostor između niti i tako slabi međusobnu adheziju (53).

Taj drugi aspekt adhezije između polimerne osnove i staklenoga vlakna je veza koja se javlja na spojnoj površini polimera i silanskoga veznog posrednika, a stvara se kopolimerizacijom silanskog veznog posrednika i polimerne osnove tijekom polimerizacije potaknuta slobodnim radikalima. Zato valja pripaziti kako se biraju silanski spojevi da bi se odabrali oni čije su funkcionalne skupine istovrsne onima kod polimerne osnove.

Vrlo važan čimbenik kod uporabe silanskih veznih posrednika svakako je debljina polimeriziranog γ-MPS-a višeslojnog nanosa na staklenim vlaknima. Ta količina γ-MPS na staklenim vlaknima može se varirati uporabom različitih koncentracija otopine γ-MPS-a (56). Bilo je i istraživanja o uporabi tlačno-toplinsko polimerizirajućih polimera primijenjenih na E-staklenim vlaknima na koje je nanesena otopina γ-MPS-a koncentracije od 30 do 100 %. Koncentracija od 100 % rezultirala je dobrim vezivanjem, ali su se nažalost javili problemi u impregnaciji staklenih vlakana polimerom. Kondenzacijska polimerizacija silanskoga veznog posrednika povezala je međusobno staklena vlakna i na taj način omela impregnaciju staklenih vlakana polimernom osnovom (24). Ni uporaba 30 postotne otopine γ-MPS-a nije potpuno riješila taj problem. Općenito se može zaključiti da već i male koncentracije otopine γ-MPS-a, kao na primjer 0,01 postotna, poboljšavaju mehanička svojstva vlaknima oja-

ature necessary for polymerisation of γ-MPS, particularly when one also takes into account the decrease in peak temperatures of polymerisation due to volume share of the fibres in the polymer matrix (55,58). In order to achieve condensation of γ-MPS on the glass fibre surface, γ-MPS can be previously polymerised by the use of adequate heat before the fibres are placed in the polymer matrix (53). Higher temperature of polymerisation of γ-MPS does not necessarily mean better adhesion. Thus, a study by Vallittu (53) showed that treatment of γ-MPS with temperature of 100°C resulted in greater flexural strength than treatment with temperature of 150°C. This can be explained by the fact that at a temperature of 100°C treatment of γ-MPS was not complete and the layer of this bonding agent swelled under the influence of monomer mixed with polymer beads, prior to polymerisation of the polymer itself. This resulted in better penetration of polymer resin in the layer of the bonding agent, and during polymerisation a better bond was achieved (53). At a temperature of 150°C treatment of γ-MPS is complete and its layer does not swell under the influence of monomer, and at the same time bonds individual glass fibres forming a group of threads, hindering penetration of the polymer matrix in the area between the threads, consequently weakening mutual adhesion (53).

This other aspect of adhesion between the polymer base and glass fibre is the bond which occurs on the bonding surface of the polymer and silane bonding agent, which is formed by copolymerisation of the silane bonding agent and polymer matrix during polymerisation induced by free radicals. Care should therefore be taken in the selection of silane compounds in order to select those whose functional groups are of the same type as those of the polymer matrix.

A very important factor in the use of silane bonding agents is without doubt the thickness of the polymerised γ-MPS multi-layer coating on the glass fibres. The amount of γ-MPS on the glass fibres can vary with the use of different concentrations of the γ-MPS solution (56).

Investigations have been carried out on the use of pressure and heat polymerising polymers applied on E-glass fibres, in which γ-MPS solution was coated in concentrations of 30-100%. A concentration of 100% resulted in good bonding, although problems appeared in impregnation of the glass fibres with polymer. Condensation polymerisation of the silane bonding agent bonded the glass fibres, and in

čanih kompozita u odnosu prema onima na kojima staklena vlakna nisu prije toga impregnirana otopinom γ-MPS-om (57). Pogodne koncentracije silana kreću se od 0,5 do 2,0 %, čime se eliminira međusobno povezivanje staklenih vlakana tijekom polimerizacije silanskoga veznog posrednika. Važno je istaknuti kako koncentracija silanske otopine za nanošenje na staklena vlakna samostalno ne određuje debljinu γ-MPS- sloja veznog posrednika na površini staklenih vlakana. Za to su zajednički odgovorni načini tretiranja (polimerizacije) sloja veznog posrednika i metoda aplikacije, te one određuju koja je količina γ-MPS-a zapravo adsorbirana na površinu staklenih vlakana (56).

Utjecaj vode na vlaknima ojačane kompozite

Polimeri koji se rabe u stomatologiji najčešće su višefazne akrilatne smole sastavljene od predpolimeriziranih perlica praha, pretežito polimetilmetakrilata, i tekućine monomera kao što je metil-metakrilat sa sredstvima za umrežavanje etilenglikoldimetakrilat (EGDMA) ili 1,4-butandioldimetakrilat (1,4-BDMA) (34,59-61). Apsorpcija vode takve višefazne akrilne smole iznosi oko 2 tež.% (28, 62-64). Takahashi i suradnici (65, 67) otkrili su da polimeri za izradu proteznih baza različitog monomernog sastava pokazuju i različitu otpornost na utjecaj vode. Važnu ulogu ima hidrofilnost same polimerne osnove. Tako je najveća apsorpcija vode izmjerena za hidrofilni hidroksietilmetakrilat (HEMA) monomer (od čak 8,3 tež.% tijekom imerzije u vodi od samo 7 dana), a najniža (0,9 tež.%) za polimere koji ne sadržavaju hidrofilne monomere (67). Apsorpcija vode ovisi i o sredstvu za umreženje koje sadržava polimer (68), no sredstvo za umreženje EGDMA (59,69) ima samo mali učinak na apsorpciju vode (68). Ulazak vode primarno je potaknut difuzijom, a dio apsorpcije nastaje zbog polarnosti molekula polimerne smole koja se javlja zbog nezasićenih veza unutar samih molekula i neuravnoteženih međumolekularnih sila (70). Molekule vode prodiru u prostore između polimernih lanaca i zadržavaju se u njima te razmiču polimerne lance. Molekule vode djeluju kao plastifikator i polimerni lanci postaju pokretljiviji, a posljedica je smanjena

this way hindered impregnation of the glass fibres with the polymer matrix (24). This problem was not completely eliminated even with the use of 30% solution of γ-MPS. It can generally be concluded that even small concentrations of γ-MPS solution, for example 0.01% , improve the mechanical properties of fibre reinforced composites, compared with those where the glass fibres were not previously impregnated with γ-MPS solution (57). Suitable concentrations of silane range from 0.5-2.0%, thereby eliminating mutual bonding of glass fibres during polymerisation of the silanic bonding agent. It is important to mention that the concentration of the silane solution for coating glass fibres does not determine alone the thickness of the γ-MPS layer of the bonding agent on the surface of the glass fibres. This is the joint responsibility of the method of treating (polymerisation) the layer of the bonding agent and also the method of application, and they determine which amount of γ-MPS is in fact adsorbed on the surface of the glass fibres (56).

Effect of water on fibre reinforced composites

Polymers used in dental medicine are most frequently multi-phase acrylic resins composed of pre-polymerised powder beads, mainly polymethylmethacrylates, and monomer liquid, such as methyl-methacrylate with cross-linking agents for reticulation ethyleneglycoldimethacrylates (EGDMA) or 1.4-butanedyoldimethacrylate (1.4-BDMA) (34, 59-61): Water absorption of such multi-phase acrylic resin amounts to approximately 2weight% (28, 62-64). Takahaski et al (65, 67) found that polymers for fabrication of denture bases of different monomer composition also show different resistance to the effect of water. An essential role is played by the hydrophilic quality of the polymer base itself. Thus, the greatest water sorption was measured for hydrophilic hydroxyethilmethacrylate (HEMA) monomer (of 8.3 weight% during immersion in water of only 7 days), and the lowest (0.9 weight%) for polymers which do not contain hydrophilic monomers (67). Water sorption also depends on the cross-linking which contain polymer (68), although EGDMA cross-linking (59,69) only has a minor effect on water sorption (68). The entrance of water is primarily caused by diffusion and some sorption occurs due to molecule polarity of the polymer resin, which occurs because of unsaturated bonds within the molecules themselves and because of unbalanced intermolecular forces (70). Water molecules penetrate into areas between the polymer chains and remain

čvrstoća na savijanje i modus elasticiteta (70). Apsorpcija vode općenito pogoršava mehanička svojstva polimera (68,71-73).

Uporaba staklenih vlakana, zato što ne upijaju vodu, teorijski bi trebala smanjiti količinu apsorbirane vode u kompozit (74), pa bi tako apsorpcija vode kod vlaknima ojačanih kompozita trebala biti manja nego kod čiste polimerne osnove. Ako se koristi veći udjel vlakana za ojačanje, tada se apsorpcija vode u polimer može smanjiti čak 25 % (75). No, vlaknima ojačani kompoziti u kojima vlakna nisu u cijelosti impregnirana polimernom osnovom nego postoje šupljine i poroziteti, mogu pokazivati povećanu apsorpciju vode (14,15,26,28,35,67,76-80), što utječe na dugotrajnost tako izrađenih protetskih radova u vlažnom mediju oralne šupljine. Može se reći da absorpcija vode ovisi o stupnju impregnacije vlakana za ojačanje unutar polimerne osnove, te lošije impregnirana područja vlakana s više šupljina i poroziteta jače upijaju vodu, pa se smanjuje čvrstoća na savijanje nakon imerzije u vodi (35).

Zato kompozitni materijali obično apsorbiraju više vode od nepunjenih polimera, posebice kod viših temperatura kada je odvajanje vlakana od polimerne osnove veće i potiče lokalizirano upijanje vode (74). Količina apsorbirane vode uvjetovana je i kemijskom stabilnošću čestica punila prema vodi. Kod polimera punjenih česticama barijeva stakla, apsorpcija vode se povećava kako se smanjuje veličina čestica (81), a kod loše impregniranih vlakana s polimernom osnovom apsorpcija može biti razmjerno visoka (28,67).

Kako je već rečeno, dobro povezivanje staklenih vlakana i polimerne osnove može se postići uporabom silanskih veznih posrednika, no valja zapamtiti da je hidrolizi podložan i polimerizirani silanski vezni posrednik, tj. polisiloksanska mreža na površini staklenih vlakana (57). Hidroliza počinje kada voda difundira kroz polimernu osnovu i doseže spojno područje između staklenih vlakana i polimerne osnove. Tada se i smanjuju vrijednosti mehaničkih svojstava vlaknima ojačanih kompozita. Površina staklenih vlakana također je podložna hidrolizi, pa je za hidrolitičku stabilnost vrlo važan sastav površine staklenih vlakana, odnosno količina alkalija, zemljanih alkalnih iona i bornog oksida (B_2O_3) i to zato što su ti ioni isto kao i borni oksid reaktivni s vodom (51). Mehanizam hidrolitičke razgradnje temelji se na otapanju bornog oksida - spoja koji stvara staklo - površine staklenoga vlakna (17,80). Na taj se način rastvara potporna mreža stakla i voda smanjuje čvrstoću samoga vlakna te uništava spoj-

in these areas, as wen as separate polymer chains. Water molecules act as a plasticizer, and polymer chains become mobile with a consequent reduction in flexural strength and modus of elasticity (70). Water sorption generally worsens the mechanical properties of polymers (68,71-73).

As glass fibres do not absorb water their use should theoretically decrease the amount of absorbed water in the composite (74), and thus such water sorption in fibre reinforced composites should be less than in the pure polymer matrix. When a larger share of fibres for reinforcement is used, water sorption in the polymer can be reduced by as much as 25% (75). However, fibre reinforced composites, in which fibres are not entirely impregnated with the polymer matrix, and in which there are cavities and porosity, can show increased water sorption (14,15,26,28,35,67,76-80), which influences longevity of such fabricated prosthetics in the moist media of the oral cavity. It can be said that water sorption depends on the degree of impregnation of fibres for reinforcement within the polymer matrix and poorer impregnated areas of the fibres, with more voids and porosity, absorb water more and lead to a greater decrease in flexural strength after immersion in water (35).

For this reason the composite materials generally absorb more water than unfilled polymers, particularly at higher temperatures, when separation of fibres from the polymer matrix is more significant and stimulates localised water sorption (74). The amount of water sorption is also conditioned by chemical stability of the filler particles in proportion to water. In polymers filled with particles of barium glass water sorption increases when the size of the particles decreases (81), and in poorly impregnated fibres with the polymer matrix water sorption can be relatively high (28,67).

As previously mentioned, good bonding between the glass fibres and polymer matrix can be realised by using silane bonding agents. However, it should be kept in mind that the polymerised silane bonding agent, i.e. polysyloxane reticulation on the surface of the glass fibres, is liable to hydrolysis (57). Hydrolysis occurs when water difunds through the polymer base and reaches the bonding area between glass fibres and the polymer matrix, resulting in a decrease in the values of mechanical properties of the fibre reinforced composites. The surface of the glass fibres is also liable to hydrolysis, and consequently for hydralitic stability, the composition of the glass fibre surface is exceptionally important, namely, the

nu površinu staklenoga vlakna i polimera postignutu uporabom silanskoga veznog posrednika (2).

Istaknimo da će se pravilnom obradom staklenih vlakana smanjiti nastanak korozijskih procesa. U skladu s time staklena vlakna različitih proizvođača s različitim kemizmom površine, mogu se i različito ponašati prema utjecaju vode (18).

amount of alcalium, earth alkali ions and boric oxide (B_2O_3) due to the fact that these ions are, like boric acid, reactive to water (51). The mechanism of hydrolytic decomposition is based on the dilution of boric oxide, a compound which forms glass, from the surface of the glass fibre (17,80). In this way the support network of glass is decomposed and water decreases the strength of the fibre itself and destroys the bonding surface of the glass fibre and polymer, created by the use of a silane bonding agent (2).

It should be emphasised that correct treatment of glass fibres reduces the occurrence of corrosive processes. Consequently the glass fibres of different manufacturers, with different chemism of surfaces, can behave differently with regard to the effect of water (18).

Zaključak

Polimerni materijali zbog dobrih svojstava još će dugo biti među glavnim gradivnim materijalima u stomatologiji, a posebice u protetici. Pokušaji da se poboljšaju njihova mehanička svojstva doveli su do primjene ojačavanja vlaknima koja su dala pozitivne rezultate, ističući tako pozitivna svojstva polimera. Opisane poteškoće koje se još javljaju u izradbi i primjeni vlaknima ojačanih polimera, toliko su neznatne u odnosu prema višestrukoj koristi dobivenoj njihovom uporabom, da je neizbježan njihov daljnji razvoj te masovna uporaba u širokoj stomatološkoj praksi. To upućuje na to da je prijeko potrebna edukacija u radu s vlaknima ojačanim polimerima, kako bismo slijedili suvremena kretanja u svjetskoj stomatologiji.

Conclusion

Favourable properties of polymer materials confirm them as main structural materials in dental medicine, particularly in prosthetics. Attempts to improve their mechanical properties lead to the use of fibre reinforcements, yielding positive results and emphasising the positive characteristics of polymers. The described difficulties that still occur in the fabrication and application of fibre reinforced polymers are minor compared to the multiple benefits gained. Consequently, their further development and extensive use in dental medicine is inevitable, indicating the need for education in work with fibre reinforced polymers in order to follow current trends in dental medicine.

Abstract
The paper describes different effects on the mechanical properties of fibre reinforced polymers, such as direction and the amount of fibres, impregnation of fibres with the polymer matrix, and adhesion between fibres and the polymer matrix. Direction of the fibres can be unidirectional (vertical to the direction of loading), i.e. bidirectional or multidirectional (under different angles to the direction of loading), or even in random order. The amount of fibres also increases the strength of the composite, although reinforcement with fibres can only be efficient when loading is transferred from the matrix to the fibres. This requires good impregnation of the fibres with the polymer matrix, which depends on the type and viscosity of the polymer matrix (prior to polymerisation), and possibility of good wetting of each fibre. For improvement of adhesion between the polymer matrix and glass fibres bonding/ coupling agents are used, particularly silane. They bond to the surface of the glass by silane bridges and by co-polymerisation initiated by free radicals bond with the polymer matrix, thus improving adhesion between fibres and the polymer matrix. Apart from the mechanical properties, such good bonding is also important for reducing the unfavourable effect of water on the marginal surface of the fibre-base.

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