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REVIEW

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Vlaknima ojačani polimeri
Prvi dio: osnove i problematika izgradnje

Fiber-Reinforced Polymers
Part I: Basics and Construction Problems

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Sažetak
U članku je predstavljena problematika lomova polimernih materijala, posebice za izradu pomičnih proteza te potreba da se pojačaju. Dan je povijesni razvoj različitih pokušaja ojačanja polimera, već od ojačanja uporabom vlakana. Za to su pogodna ugljična, aramidska, polietilenska i staklena vlakna koja se danas i najviše rabe te tako dobivamo kompozitne materijale poboljšanih svojstava. Glavna zadaća vlakana u kompozitima je veća krutost i čvrstoća, a osnovni materijal (matriks) štiti vlakna i održava ih u položaju koji omogućuje najbolja svojstva kompozitnom materijalu. Problematična je granična površina između vlakna i osnove na kojoj se javljaju mikropukotine, što je posljedica uključevina zraka ili onečišćenja tijekom izrade kompozita, koje slabe mehanička svojstva kompozita. Zato se kvaliteta granične površine poboljšava tretiranjem površine vlakana adhezivnim sredstvima, osobito silanima, kako bi se povećala čvrstoća prianjanja između vlakna i polimerne osnove.

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Uvod

Polimetilmetakrilat se od ranih četrdesetih godina prošlog stoljeća najčešće koristi kao materijal za protezne baze i to zbog izvrsnog izgleda, jednostavne tehnologije primjene i lakoće kojom se može popravljati. No, veliki je nedostatak toga materijala mogućnost loma tijekom funkcije (1). Tako su lomovi polimernoga materijala proteznih baza jedan od najčešćih (64%) razloga za popravak pomičnih proteza (2-5). No, ipak je polimetilmetakrilat (PMMA) jedan od najrasprostranjenijih materijala koji se danas rabe u stomatološkoj protetici. Polimeri za protezne baze obično se sastoje od praška polimera i tekućine monomera koji pomiješani stvaraju tijekom procesa polimerizacije višefazni polimer.

Introduction

Polymethylmethacrylate has since the early 1940s become the most widely used material for the denture base, thanks to its acceptable esthetics, simple production technology and simplicity in repair. However, its main drawback is fracture in function (1). Polymer material fractures are one of the most frequent (64%) causes of removable prosthesis repair (2-5). Still, polymethylmetacrylate (PMMA) is one of the most widely used materials in modern prosthodontics. Polymers are usually composed of the powdered polymer and liquid monomer that, when mixed, during a number of phases of the polymerization, become a multiphasic polymer. Although it does not meet all the necessary require-

Iako - kako je istaknuto - ne zadovoljava u cijelosti sve uvjete, PMMA je u širokoj uporabi zbog jednostavne primjene i dobre estetike (6). Osobito je problematična niska čvrstoća i otpornost na zamor toga materijala, što uzrokuje prerane lomove. Smith (7) je opisao utjecaj zamora materijala na čvrstoću na savijanje i istaknuo ga kao razlog za lomove pomičnih proteza. Vallittuova (8) studija karakteristika lomnih površina pomičnih proteza potvrđuje da je zamor materijala glavni uzrok lomova proteza (9). Za razliku od gornje totalne proteze, kod donje proteze zamor materijala nije glavni uzrok lomova, nego su to u oko 80% slučajeva lomovi zbog udara ako padnu na tvrdu površinu (3). Kada donja totalna proteza padne na tvrdu površinu, najveći se stres događa u lingvalnom i labijalnom području drugog premolara (10) i nezavisan je od položaja proteze u trenutku udara, što je pak različito od nalaza da se većina lomova javlja u središnjem području proteze (3, 10).

Tijekom povijesti bilo je mnogo pokušaja kako bi se ojačali takvi polimeri i to uporabom različitih postupaka. Nastojanja da se ojačaju proteze izrađene od akrilata uključivala su ili modificiranje sastava gradivnoga materijala ili pak ugrađivanje ojačanja u sam polimer (1).

Prvo važno pojačanje čvrstoće polimernoga materijala za protezne baze postignuto je dodavanjem sredstava za umreženje, zapravo polifunkcijskog monomera, na primjer polietilenglicoldimetakrilata (11). Drugo ojačanje postignuto je uporabom metalnih ojačanja u obliku žica, to jest mrežica kojima su se željeli ojačati polimeri za protezne baze i polimeri za privremene mostove (12-20), što je rezultiralo većom čvrstoćom na savijanje i na udarac (12, 18, 21), no utjecaj na zamornu čvrstoću na savijanje bio je neznatan (22). Bio je loš i estetski izgled gotova protetskoga rada (11).

Jedna od metoda bila je i ugradnja gumene faze u perlice polimera, kako bi se povećala udarna čvrstoća. Iako je taj način dobro poznat u tehnologiji plastičnih masa, vrlo je skup. Ugrađeni kopolimeri gumena metakrilata proizvedeni kemijskim modifikacijama su smole visoke otpornosti na udarac (19).

Sljedeći pristup ojačanju akrilatnih proteza jest ugradnja vlakana. Zato su se različite vrste vlakana dodavale akrilatnim protezama kako bi poboljšala njihova fizikalna i mehanička svojstva (20, 23-36). Tako su se koristila ugljična (grafitna) vlakna za ojačanje baza pomičnih proteza, pa i mostova na implantatima (24, 25, 37-40), a uporabljena su i za intraradikularno ojačanje kompozitnih nadogradnji na endodontski dobro tretiranim korijenima

ments, PMMA is widely known due to its simplicity in use and acceptable esthetics (6). Low rigidity and poor strength are main drawbacks of this material, leading to early fractures. Smith (7) has described the influence of material fatigue on flexural strength, presenting this as a cause for removable prosthesis fracture. Vallittu study (8) of the characteristics of the fracture surfaces of the removable prostheses has confirmed fatigue as the main cause of denture base fracture (9). In lower jaw, fatigue is not the main cause of fracture, but in around 80% the denture fractures when it hits a hard surface (3), the greatest stress being in lingual and labial areas of the second premolar (10). This stress is independent of the position of the denture during the fall. This is somewhat different from the fact that most of the denture fractures occur in the central portion of the denture (3, 10).

There were many attempts to strengthen such polymers, using different procedures, such as modification of the matrix, or incorporating some strengtheners in the polymer (1).

First significant enhancement of the strength of the denture base was accomplished by adding netting agents, i.e. polyfunctional monomers such as polyethyleneglycoldimetacrylate (11). Different strength enhancers were metallic strengtheners such as wires or nets that were aimed to enhance polymers for denture bases and temporary bridges polymers (12-20), that has lead to enhancement of flexural strength and resistance to fracture when dropped (12, 18, 21), but the influence on the fatigue was minimal (22), with poor esthetic outcome of the finished restoration (11).

One of the attempts used even gum phase in polymer pearls in order to enhance the resistance to fracture when dropped. Although well known in the technology of plastic materials, it is very financially burdensome. Incorporated polymers of the gum-methacylate, produced by chemical modifications, are resins with high resistance to fracture (19).

Further approach to enhance acrylic dentures was the incorporation of fibers. Different types of fibers were incorporated into the acrylic denture base in order to enhance their physical and mechanical properties (20, 23-26). Various carbonated (graphite) fibers were used in order to enhance the denture base, as well as implant-borne bridges (24, 25, 37-40), as well as for intraradicular core and post build-up to strengthen composite abutments on endodontically treated roots (41-44). Organic fibers, such as aramidic (45, 46) and polyzuba (41-44). Također su se istraživala i organska vlakna, kao što su aramidska (45, 46) i polietilenska vrlo visoke molekularne težine (26-29, 47-53) te staklena vlakna za ojačanje polimernih materijala (20, 22-25, 32, 36, 54-57) kako bi se povećala udarna čvrstoća i čvrstoća na savijanje. Ugljična vlakna su elastična tijekom manipulacije i estetski loša. Aramidska vlakna su također estetski loša i čine poteškoće tijekom poliranja polimera, a polietilenska imaju slabu adheziju polimera na ta vlakna i to zbog njihove glatke površine i nedostatka reaktivnih mjesta za kemijsko povezivanje (58, 59).

Zato je potreban vrlo zahtjevan postupak površinske obrade vlakana (predimpregniranje) kako bi se postigla bolja povezanost s polimernom osnovom - matriksom (51-53). Zato se danas najčešće koriste staklena vlakna - zbog dobre estetike (22, 23, 54-57) i dobre veze s polimerima preko silanskih veznih posrednika (60-62).

Postoje različiti tipovi staklenih vlakana: E-staklena vlakna, S-staklena vlakna, R-staklena vlakna, V- i Cemfil vlakna (63). E-vlakna imaju visok udio aluminija i nizak alkalija i borsilikata, a pokazuju najveće vrijednosti čvrstoće na savijanje u odnosu prema drugim navedenim vlaknima (23). Zato se ona i najčešće koriste u vlaknima ojačanim kompozitima (64). Osobito su prikladna za ojačanje svjetlosnopolimerizirajućih polimera, zbog izvrsne transparencije u odnosu prema drugim vlaknima što pridonosi širenju svjetlosti potrebne za polimerizaciju i u dublje slojeve, a lako se i režu škaricama na potreban oblik i duljinu (65).

Zato je posljednjih godina sve veće zanimanje za ojačanje polimera, jer je ustanovljeno kako dodatak raznih vlakana može imati veliki utjecaj na njihova mehanička svojstva (66).

Vlaknima ojačani kompozitni materijali

Kada se međusobno kombiniraju dva ili više različitih materijala dobiva se kompozitni (složeni) materijal. Njegova svojstva nema ni jedna od komponenti kompozitnoga materijala, nego su ta svojstva negdje između svojstava komponenti, obično u skladu sa zakonom miješanja (67). No, neka svojstva, posebice čvrstoća, mogu se znatno poboljšati u odnosu prema vrijednostima koje imaju pojedine komponente kompozitnoga materijala. Tako se kombinacijom volumnog udjela i položaja komponenti u kompozitu mogu stvarati materijali željenih, poboljšanih svojstava.

Moderni kompozitni materijali su i razvijeni sa zadaćom da zadovolje što više zahtjeva koji se po-

ethylene fibers with high molecular weight (26-29, 47-53) were used, as well as glass fibers (20, 22-25, 32, 36, 54-57), in order to enhance the flexural and collision resistance. Carbonated fiber are esthetically unacceptable and cause problems in polishing of the polymer, and polyethylene fibers show low adhesion of polymer due to smooth surface and lack of reactive places for chemical bonding (58, 59).

It requires a demanding procedure of fiber preparation (pre-impregnation) in order to establish a better bonding with the polymer base (matrix, 51,52,53). Most commonly used fibers today are glass fibers, due to acceptable esthetics (22, 23, 54-57) and good bonding with polymers via silane coupling agents (60-62).

There are different types of glass fibers: E-glass fibers, S-glass fibers, R-glass fibers, V-glass fibers and Cemfil fibers (63). E-fibers have a high percentage of aluminum and low percentage of alkalis and bore-silicates, and demonstrate greatest torsional resistance when compared to other fibers (23). E-fibers are also the most frequently used glass fibers in fiber-reinforced composites (64). These fibers are especially adequate for strengthening light-cured polymers due to their excellent transparency that, when compared to other fibers, contributes to light penetration needed for polymerization of the deeper layers. Additionally, they can easily be adapted to the required shape and length (65).

Based on these premises, in the last years the interest for polymer reinforcement has been increasing momentum, since it has been established that addition of different fibers can significantly contribute to polymer's mechanical properties (66).

Fiber-reinforced composite materials

When two or more different materials are combined, the product is a composed (composite) material. Its properties are different to properties of different materials that have been combined; these properties are somewhere in between the properties of the components, usually according to the mixing principle (67). Some properties, more notably strength, can be significantly enhanced when compared to values of the components of the composite material. The combination of the volume and location of components can result in materials with enhanced properties.

Modern composite materials have been developed with the aim to satisfy the demands that have been set in mechanics, shipbuilding, aerospace industry, construction, medicine etc. It must stavljaju u tehnici, brodogradnji, zrakoplovnoj industriji, graditeljstvu, medicini itd. No, valja istaknuti kako je upravo priroda ta koja je izgradila prve kompozite - i to biološke, kao na primjer mišiće, kosti, dentin, itd. Tako je kost prirodni kompozitni materijal u kojemu kolagena vlakna obavljaju zadaću vlaknastih ojačanja i s hidroksiapatitom čine vrlo složeni kompozit komplicirane strukturalne građe (68).

Svojstva vlaknima ojačanih kompozita ne mijenjaju se samo u ovisnosti o svojstvima građevnih komponenti, nego i njihova geometrijskog položaja u kompozitu. No, glavna zadaća vlakana u kompozitima jest povećati krutost i čvrstoću. Osnovni materijal – matriks štiti vlakna i održava ih u određenom položaju koji daje najbolja svojstva kompozitnom materijalu. Pri tome spojno područje između tih dvaju materijala ima važnu zadaću u prijenosu opterećenja s matriksa na vlaknasta ojačanja (69). Ako su vlaknasta ojačanja slabo povezana s matriksom, tada se na njih može prenijeti samo mali dio opterećenja. Nepravilna impregnacija vlakana polimernom osnovom uzrokuje smanjenje čvrstoće novostvorenoga kompozita, a manjak adsorbiranog monomera na površini vlakna prije polimerizacije uzrokuje nastanak šupljina unutar kompozita (70). Ta “slaba mjesta” spojnog područja prema svojoj smanjenoj čvrstoći odgovaraju područjima na kojima se pojavljuju šupljine u polimernoj osnovi (matriksu), tj. nepravilnosti u građi samog materijala koji valja ojačati.

Granična površina između vlakna i osnove

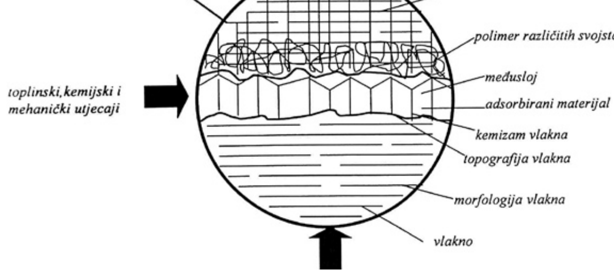
Granična površina između vlakna i osnove nastaje kao rezultat vezivanja vlakna i osnove (matriksa), a od njih se razlikuje morfologijom i kemizmom te predstavlja kritično područje kod vlaknima ojačanih kompozita (Slika 1) (72).

be stressed that the nature itself composed the first composite materials – biological ones – muscles, bone, dentine, etc. Bone is a natural composite material in which the collagen fibers play the role of fiber reinforcement, that, in combination with hydroxiapatite represent a complex composite with complex structural architecture (68).

The properties of fiber-reinforced composites do not differ only depending on the properties of the components, but depending on their geometrical position in the composite. The main aim of the fibers in composites is the enhancement of strength and rigidity. The matrix protects the fibers and maintains their position that gives the best properties to the composite material. The connection between these two materials plays an important role in load transmission from the matrix to the fiber material (69). If the fiber reinforcements are not tightly connected with the matrix, only small amount of the load can be transferred on them. Irregular impregnation of the fibers with the polymer base causes diminished strength of the newly formed composite, while lack of adsorbed monomer on the surface of the fiber before polymerization causes air-trappings in the composite (70). These “weak spots” of the connection resemble air-trappings in the polymer base (matrix), i.e. irregularities in the material architecture that need to be strengthened.

Border surface between the fiber and matrix

The border surface between the fiber and the matrix is a result of the linking of the fiber and the matrix; it has its own morphology and chemistry and represents the critical area in fiber-reinforced composites (Fig. 1) (72).



Slika 1. Shematski prikaz međusloja (granične površine) u vlaknima ojačanom polimernom (72)
Figure 1. Schematic view of the layer (border surface) in the fiber-reinforced composite (72)

Na graničnoj površini, tj. između vlakna i polimerne osnove, postoje barem tri vrste veza: kemijske, mehaničke i električne. No, neovisno o prirodi i vrsti veza na graničnoj površini, prijenos opterećenja preko nje isključivo je mehanički. Tako granična površina ima zadatak prenositi opterećenja s polimerne osnove na vlakna za ojačanje (73).

Može se reći da je granična površina područje u kojemu se svojstva vlakna mijenjaju do svojstava polimerne osnove, i obrnuto. Zna se da reakcije koje nastaju između polimerne osnove i površine vlakna nisu određene vezom u samo jednoj plohi, nego se to područje međusobnog djelovanja širi u obliku prijelaznoga područja - jednog međusloja čija debljina može varirati od 5 do 100 nm. Pretpostavlja se da je taj međusloj trodimenzijsko područje koje okružuje cijelo vlakno i čija su svojstva drugačija od svojstava osnove, ali postupno konvergiraju prema njima porastom udaljenosti od vlakna.

Struktura i priroda toga prijelaznog područja ili međusloja znatno utječe na karakteristike i svojstva vlaknima ojačanih kompozita, a osobito na mehaničku čvrstoću, otpornost na zamor te na kemijsku i toplinsku postojanost.

Značenje nastanka mikropukotina na graničnoj površini

Ponašanje vlaknima ojačanih kompozita tijekom njihove uporabe izravno ovisi o učestalosti mikropukotina na graničnoj površini vlakno-osnova, to jest u nastalom međusloju. Tih mikropukotina gotovo uvijek ima, a nastaju zbog uključivanja mjehurića zraka i raznih onečišćenja tijekom izrade vlaknima ojačanih kompozita (74).

Na pojavu i učestalost mikropukotina u graničnom području utječu karakteristike same osnove, kao što je njezin kemijski sastav, sposobnost ovlaživanja, sporedni produkti koji nastaju tijekom polimerizacije osnove itd., a također i karakteristike vlakna te sam postupak izradbe vlaknima ojačanih kompozita.

Zbog slabog ovlaživanja vlakana za ojačanje, samom polimernom osnovom granična površina između vlakna i osnove predstavlja kritično mjesto na kojemu se pojavljuju mikropukotine te je česta i pojava šupljina i uključevina zraka tijekom izrade vlaknima ojačanih kompozita, što na tim mjestima uzrokuje veliku koncentraciju naprezanja bez obzira na način i vrstu opterećenja. Ako su šupljine smještene tik uz vlakna mogu prouzročiti i njihov lom, ako su tlačno opterećena. Ako su pak šupljine i uključevine zraka

There are at least three types of links between the matrix and the fiber: chemical, mechanical, and electrical. Independently of the nature of the link, the transmission through it is strictly mechanical. One of the most important characteristics of the border surface is the transmission of the load from the polymer matrix to the fiber-reinforcements (73).

It can be said that the border represents the area where fiber characteristics are changed to the characteristics of the matrix, and vice versa. It is known that the reactions occurring between the matrix and the fibers are not determined by the link in only one surface. The area of interrelationship is widened to a so-called transitional area or one layer that can be 5 to 100 nm thick. One can assume that the internal layer represents a three-dimensional area that surrounds the fiber, and that its properties differ from the properties of the matrix, but that it converges to the matrix with the rise of the distance from the fiber.

The structure and the nature of this transitional area (internal layer) have significant influence on the characteristics and properties of the fiber-reinforced composites, especially on mechanical strength, fatigue resistance, and chemical and warmth integrity.

The importance of microfractures occurring on the surface

The properties of reinforced composites during use depend on the frequency of microfractures on the surface between the matrix and the fiber, i.e. in the layer between these two materials. These microfractures are ubiquitous, and occur as a result of air inclusion and various impurities during the process of reinforcement (74).

The incidence and frequency of microfractures are influenced by the properties of the matrix, possibilities of wetting, side-products occurring during the polymerization etc., as well as by the fiber's properties and the process of reinforcement itself.

Due to poor wetting of the fibers with the polymer matrix the borderline between these two materials is the critical point for microfractures, as well as for air inclusion during the process of reinforcement. These facts cause great concentration of stress regardless of the type and mode of the load. If the hollow areas are close to the fiber they can cause the fracture of the fiber if they are loaded. If the hollow areas and air inclusions are further in the polymer matrix and they do not include the fiber, their influence is weaker. A weak bond between the fiber and the matrix causes fractures, and in the end there is a potisnute u polimernu osnovu i ne dodiruju vlakna, tada imaju manji utjecaj na svojstva vlaknima ojačanih kompozita. Slaba veza između vlakna i osnove često uzrokuje napukline, a u konačnici i lom međusloja već pri malim opterećenjima zbog velike koncentracije naprezanja na tim mjestima (75).

Šupljine u vlaknima ojačanim kompozitima mogu se pojaviti u različitim oblicima i veličinama, a nastaju iz dva osnovna razloga:

- ulazak zraka u vlaknima ojačani kompozit tijekom njegove izradbe, pa nastaju uključevine zraka zbog kemijske reakcije tijekom polimerizacije osnove i/ili zbog slabog ovlaživanja vlakna polimernom osnovom;
- stvaranje vlačnih i tlačnih naprezanja u vlaknima ojačanom kompozitu zbog različitog ponašanja osnove i vlakana za očvršćivanje tijekom polimerizacije osnove.

Zaključak je da je kvaliteta granične površine vlakno-osnova ključna za dobra svojstva vlaknima ojačanih kompozita. Zato se ona može i mora poboljšati tretiranjem površine vlakana različitim adhezivnim sredstvima. Njihova je zadaća poboljšati i povećati čvrstoću prianjanja između vlakna i polimerne osnove, povećati savitljivost nastalog međusloja i omogućiti bolje ovlaživanje površine vlakana polimernom osnovom. Tako se smanjuje mogućnost nastanka šupljina i uključevina zraka u međusloj i znatno poboljšavaju mehanička svojstva vlaknima ojačanog kompozita.

Međuslojna smična čvrstoća

Mjera za kvalitetu granične površine, odnosno međusloja, jest međuslojna smična čvrstoća. Ona ovisi o čvrstoći prianjanja između vlakna za ojačanje i osnove te o veličini dodirnih površina vlakana i adhezije na tim površinama. Razumljivo je da je dobra adhezija potrebna duž cijele granične površine vlakana za ojačanje i osnove, upravo zato da bi se što veće opterećenje moglo prenijeti s polimerne osnove na vlakna za ojačanje.

Kad je riječ o anorganskim vlaknima (npr. staklenim) ojačanim kompozitima, adhezija se može podijeliti u tri segmenta (76):

- kemijska adhezija nastaje zbog kemijskih veza između površine vlakna i osnove. Takve veze mogu se postići u izravnoj reakciji između vlakna i osnove ili pak uporabom veznih posrednika koji stvaraju “kemijski most” između vlakana i osnove.

  Kako se staklena vlakna slabo vežu s polimernom osnovom, tretiraju se veznim posrednicima

total fracture of the layer, even with weak loading, due to the stress concentration in such places (75).

Air inclusions in fiber-reinforced polymers can appear in different types and sizes, but mainly have two causes:

- Inclusion of air in the reinforced composite during fabrication, which results in air inclusions due to the chemical reaction in polymerization and/or poor wetting of the fiber by the matrix
- Pressure and compression in the fiber-reinforced composite due to different properties of the matrix and the fiber during polymerization of the matrix

It can be implied that the quality of the border surface between the fiber and the matrix holds the key importance for the good properties of the fiber-reinforced composites. Their task is to enhance the grip between the fibers and the polymer matrix and enable better wetting of the fiber surface, in order to minimize the possibility of air inclusion, enhancing the mechanical properties of the fiber-reinforced composite.

Tensile strength between layers

Tensile strength measures the quality of the border surfaces and depends on the strength of adherence of fibers and matrix, on the size of the surfaces of the fibers, and adhesion on these surfaces. It is understandable that good adhesion is needed along the whole border between the fiber and matrix, since it enables the transfer of a greater load from the matrix to the fiber.

In composites reinforced with anorganic fibers (i.e. glass fibers), the adhesion can be divided in three segments (76):

- Chemical adhesion that is a result of chemical bonds between the surfaces of the fiber and matrix. Such bonds can be created in a direct reaction between the fibers and the matrix, or via agents that build a “chemical bridge” between the fiber and the matrix. Glass fibers that poorly bond with the matrix are treated with silanes. They bond to the fiber surface as well as to the matrix, and enhance flexural strength and hydrothermal resistance of the newly formed layer (77).
- Physical adhesion is a result of the downgrading of the free energy of the system when two surfaces with different surface tensions, γ_v i γ_o, are fused and a layer with surface tension γ_{vo} is formed. Adhesive workload W_a that can reversibly separate these two surfaces is defined as:

od kojih su najvažniji silani. Oni mogu kemijski reagirati i s površinom staklenoga vlakna i s polimernom osnovom te tako pojačavaju međuslojnu smičnu čvrstoću i hidrotermalnu otpornost novonastalog međusloja (77).

- fizikalna adhezija nastaje zbog smanjenja slobodne energije sustava u slučaju kada se spoje dvije površine različitih površinskih napetosti γ_v i γ_o i čine međusloj s međuslojnom napetosti γ_{vo}. Adhezijski rad W_a koji je potrebno uložiti za reverzibilno razdvajanje tih dviju površina definiran je kao

$$W_a = \gamma_v + \gamma_o - \gamma_{vo}$$

pri čemu je:

W_a - adhezijski rad
γ_v - površinska napetost vlakna
γ_o - površinska napetost osnove
γ_{vo} - površinska napetost međusloja vlakno-osnova.

- mehanička adhezija nastaje zbog hrapavosti površine vlakna i sposobnosti ovlaživanja polimerne osnove. Poveća li se površinska hrapavost vlakna za ojačanje, povećat će se i njegova sposobnost da bude ovlaženo.

Istraživanje granične površine vlakno-osnova i međusloja između ta dva gradbena materijala vlaknima ojačanog kompozita, iznimno je važno za njihovo što čvršće povezivanje, a to izravno utječe na svojstva vlaknima ojačanih kompozita. Time se povećava mogućnost njihova mehaničkog opterećenja i novih konstrukcijskih rješenja u stomatološkoj praksi.

Oštećenja vlaknima ojačanih kompozita

Nastanak i razvoj oštećenja u kompozitnim materijalima vrlo je složena pojava, a može se razvrstati na osnovne vrste oštećenja: poprečni lom osnove (matriksa), odvajanje vlakana za ojačanje od osnove (izvlačenje), lom samih vlakana, popuštanje veze vlakno-osnova te raslojavanje ili delaminacija. Na nastanak oštećenja jako utječe vrsta uporabljenih vlakana za ojačanje, jer se znatno razlikuje kod staklenih, ugljičnih, polietilenskih i aramidskih vlakana (78, 79).

Suprotno metalima, početak loma kod kompozitnih materijala može se dogoditi već pri niskim naprezanjima zbog velikoga broja mikropukotina (obično nastalih tijekom izrade) koje rastu istodobno. Kako je istaknuto, one mogu biti u samoj osnovi, vlaknima, graničnoj površini između vlakna i matrice, to jest u međusloju kompozitnog materijala (80).

$$W_a = \gamma_v + \gamma_o - \gamma_{vo}$$

W_a - adhesive workload
γ_v - fiber surface tension
γ_o - matrix surface tension
γ_{vo} - surface tension of the layer between the fiber and the matrix

- Mechanical adhesion that is a result of the surface roughness and the capability to wet the polymer matrix. By enhancing the surface roughness of the fiber its capability to be wetted is enhanced as well.

The research of the layer between the fiber and the matrix is of utmost importance for enhancing their connections that directly influences the properties of the fiber-reinforced composites. Thus new solutions in the dental practice appear by enlarging the possibility of their loading.

Damaging the fiber-reinforced composites

Development of damage in composite materials is a complex phenomenon that can be divided into basic types of damage: cross fracture of the matrix, detachment of the fiber, fiber fractures, weakening of the fiber-matrix interface and delamination. There is significant difference between damage of glass, graphite, polyethylene and aramidic fibers (78, 79).

Contrary to metals, fracture initiation in composite materials occurs in low flexure due to a great number of microfractures (usually occurring during production process) that grow at the same time. They can appear in the matrix, the fibers, in the border surface or in the layer between the fiber and the matrix (80).

Although it is a complex phenomenon, there are two basic types of fractures of fiber-reinforced composite materials:

- *Fracture in a layer* – microfractures appear inside the matrix of fiber. They merge and spread along the fiber. If the fiber-reinforced material is multilayered, the polymer matrix can resist the flexural tension (flexural strength between the fibers, or fiber layers gives satisfactory resistance and rigidity vertically, against fiber reinforcements). If microfractures occur in fibers they are short and randomly arranged, leading to a fiber fracture that separates the fiber from the matrix.
- *Delamination* – this type of fracture starts at the edge of multilayered fiber-reinforced composites (laminates), in places with high tension and microfractures between layers. These fractures

Iako je, kao što je spomenuto, lom kompozitnih materijala složena pojava, dva su osnovna tipa loma vlaknima ojačanih kompozitnih materijala:

- *lom unutar sloja* – mikropukotine se nakupljaju unutar polimerne osnove ili vlakana te se spajaju i protežu duž vlakana za ojačanje. Ako se radi o višeslojnim vlaknima ojačanim kompozitnim materijalima, tada je polimerna osnova otporna na smična naprezanja - tzv. smična krutost između vlakana, odnosno slojeva vlakana - te daje zadovoljavajuću vlačnu i tlačnu čvrstoću i krutost u okomitom smjeru spram vlakana za ojačanje. Ako su pak mikropukotine u samim vlaknima, one su kratke i slučajno raspoređene te uzrokuju lom vlakna čime se prekida veza vlakno-osnova, tj. odvaja se vlakno od osnove;
- *lom između slojeva (raslojavanje ili delaminacija)* - takvi lomovi kreću s ruba višeslojnih vlaknima ojačanih kompozita (laminata) i to s mjesta velikih naprezanja na kojima se javljaju mikronapukline između slojeva. One se mogu proširiti kroz cijeli laminat i podijeliti ga na dva dijela (81). Nakon delaminacije najviše je smanjena tlačna čvrstoća u ravnini laminata (82, 83). Delaminacija je uvijek na spoju slojeva laminata kod loma osnove gornjega sloja (paralelan s vlaknima) prije pojave same delaminacije (84).

Lom polimerne osnove događa se iz dva razloga: zbog smicanja, pri čemu izravno ovisi o iznosu sile opterećenja te zbog savijanja, kada ovisi o krutosti na savijanje vlaknima ojačanog kompozita (84).

Zaključak

Razvoj polimernih materijala rezultirao je njihovom širokom primjenom u stomatološkoj praksi, ali se stalno nastoji poboljšati njihova mehanička svojstva. Za poboljšanje čvrstoće polimera osobito su se pogodnima pokazala ojačanja različitim vrstama vlakana. No, problematična je veza između vlakana za ojačanje i polimerne osnove, kako bi se omogućio prijenos opterećenja s polimerne osnove na vlakna. Poboljšanje adhezije između vlakana i polimerne osnove uporabom adhezivnih sredstava dovodi do veće čvrstoće međusobnog prianjanja, a time i do eventualnoga većeg opterećenja, omogućujući nova konstrukcijska rješenja u stomatološkoj praksi.

can spread along the laminate and divide it in two parts (81). After delamination, the flexural strength to tension in the laminate plane is low (82, 83). Delamination occurs always at layer connections where there is a fracture in the upper part matrix (parallel to the fibers); this fracture is followed by delamination (84).

Matrix fracture occurs for two reasons: due to transverse load that depends on the load force, and due to flexure depending on the rigidity of the fiber-reinforced composite (84).

Conclusion

The development of polymer materials has led to their wide use in dental practice, with a constant need for enhancement of their mechanical properties. Fiber reinforcement has been shown as a successful method for upgrading the rigidity of the polymers. The bond between the layer and the matrix remains problematic, since it does not give the opportunity for full transfer of the load from the matrix to the fiber. Perfecting adhesion between the fiber and the matrix by using adhesive agents results in a greater strength of the adhesion, as well as in greater loading capability, enabling new constructive solutions in dental practice.

Abstract

This article reviews the fracture problems of polymer materials for removable prostheses and the need for its reinforcement. The historical development of different attempts to strengthen the polymers all the way to the fiber-reinforcements is presented. Different materials can be used for polymer reinforcements: carbonated, aramidic, polyethylene and glass fibers, which are today most frequently used, creating composite materials with enhanced properties. Main features of the fibers in composites are greater rigidity and strength while the matrix provides the protection of the fibers as well as their position that gives the composite material the best properties. The border between the fiber and the matrix is somewhat dubious in a sense that there are often microfractures, caused by inclusion of air or impurities during the production process of composites that can weaken the mechanical properties of the material. Treating the fiber surface with adhesive agents, especially silanes, in order to enhance the grip between the fibers and polymer matrix, enhances the quality of the border.

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