MATERIAL ASPECTS OF EXPLOITATION OF DENTAL COMPOSITES BASED ON DIMETHACRYLATE RESINS

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Introduction

The enormous progress of medicine over the centuries must have resulted from the direct link between science and human life and health. The reason is that no motivation is as powerful as the improvement of the quality of our life.

The problem of reconstruction of damaged parts of human body, including teeth, has always been one of the most important issues in medicine. Nowadays the research on the tooth tissue replacement by artificial materials is among the fastest growing branches of dentistry.

When it comes to materials traditionally used in dental fillings, amalgams have many advantages, their excellent mechanical properties being the main one, but they became demonized as being suspected of releasing toxic mercury. However, this was not the reason for which they have been withdrawn from the market, as the currently used polymeric fillings may also be toxic due to possible release of unreacted monomers, of which ordinary patients are not informed. The real reason was that the aesthetic lobby prevailed.

The idea of contemporary restorative dentistry is keeping pace with nature by creating a "chameleon", which would be similar to natural tooth tissues – both visually and physically. Over the past several decades dental materials used as cavity fillings have evolved to reach a truly satisfactory form. They allow the damaged tooth tissue to be precisely reproduced, however, several important problems are still there to be finally solved. The most important of them seem to be [1]:

1. Reducing the "polymerization" shrinkage, resulting in improved marginal adaptation of the fillings.
2. Improving the mechanical properties of fillings, resulting in longer lifetime of composites.
3. Providing bactericidal function to composites – this will prevent the accumulation of dental plaque and secondary caries formation.

These three issues are the most serious challenges for dental composite engineering. Due to the great importance of these problems, I have decided to make them the main topics of this literature review.
1. “Polymerization” shrinkage of the composites based on dimethacrylate resins

Polymerization shrinkage of dental composites is a result of conversion of dimethacrylate oligomers (matrix) in the polymer network. During this process, the original van der Waals interactions disappear, together with forming covalent bonds between macromolecules. The result is the reduction of the initial distance between the chains (3–4 Å) to the distance of a single covalent bond ~ 1.5 Å. This means that regardless of the way of polymerization initiation process, all dental composites, both chemo- and light-cured, will reduce their volume. The average magnitude of the linear shrinkage, measured in vitro, is 0.2–2 % and volume contraction may be even several times higher and reach 7 % [2]. The vast majority of commercial composites reduces its volume on the average by 2–3 % [3–5].

The consequence of shrinkage, occurring during the composite cross-linking is the occurrence of stresses (2–6 MPa) [6] which determine the quality of the connection between the composite material and the hard tissues of the tooth. They can lead to various postoperative complications, such as the cohesive micro-cracks which weaken the internal structure of the material and may affect the deterioration of mechanical properties. But the most common complication is the leakage at the gingival edge of caries, localized in the dentine or root cement. These sites are preferred due to the fact that the adhesion strength of the composite material to dentine or cementum is lower than to the enamel. This marginal gap is quickly filled with fluid coming from the oral cavity and tubules, thus, is an ideal place for settlement by the caries bacteria. It was proved that regardless of the type of caries and filling material, the most common reason of filling replacement is clinically diagnosed secondary caries (70-90 % of cases), located just around the gingival area [7].
1.1 The magnitude of matrix shrinkage. The vectors of contraction.

The volumetric shrinkage during polymerization depends mainly on the molecular weight of the oligomer and the number of double bonds in the molecule. It is suggested that through a direct relationship with the marginal adaptation, the volumetric shrinkage and the associated contraction stress coming from the bonding of composite material with cavity walls, are among the key factors determining the clinical durability of fillings [8–10].

The polymerization shrinkage is represented by the so-called “vectors of contraction”. These vectors show the amount and direction of movement of the composite in the cavity during irradiation. The direction of contraction vectors is dependent on many factors, including the size and shape of the cavity, the adhesion strength of the material to the tooth walls, and the local conversion rate and degree of the composite. Above all, it depends however on the number of tooth surfaces, which are in contact with the composite material.

Thus, we can distinguish [11]:

- free shrinkage – observed for composite samples not connected with tooth surface; contraction vectors are directed concentrically, to the central part of the material;
- shrinkage of composite connected with one wall – directed to the wall;
- composite shrinkage connected with more than one wall – initially, the volume reduction is compensated by moving the material from the unconnected surface to the walls; volume reduction continues until the strength of polymerization shrinkage exceeds the strength of composite-tooth binding – the tensions inside the filling tear them away from the cavity wall and the marginal gap is formed.

Assuming that the cavity walls are rigid (and excluding the cohesive destruction), reduction of the internal stresses in the material can occur only through the elastic deformation and flow (movement) of the free, unattached part of the material. In the initial stage of polymerization, when the Young's modulus is low, such laminar flow is achieved without damaging the internal structure of the material, and without weakening the adhesion forces. It has been shown that by proper fitting of the geometry of cavity filling, it is possible to direct the flow of material, which in effect leads to stress compensation [12].

However, the chemical interference in the composite formula, aiming to reduce shrinkage and accompanying stresses, definitely brings more possibilities than adjusting the shape of the filling.
1.2 Polymerization shrinkage vs. Chemical composition of the organic phase

1.2.1 Matrix “Yesterday and Today”

Some of the first (1941) "aesthetic" polymer dental fillings were based on methacrylate monomers – methyl polymethacrylates dissolved in methyl methacrylate. Tertiary amines were used as a radical polymerization initiator system, in combination with benzoyl peroxide. Thanks to this combination of activator (amine) and initiator (peroxide), the cross-linking reaction could be carried out at mouth temperature and finished within a few minutes. However, these materials exhibited significant polymerization shrinkage (20–25 %), susceptibility to discoloration, reduced stiffness, high thermal expansion and poor adhesion to the tooth surface.

In 1957 Bowen patented a new type of resin which combined the advantages of methacrylates (fast polymerization) and epoxy resins (better adhesion to the tooth surface and higher mechanical strength). The new resin, known as "Bis-GMA" (Fig. 1), produced in the reaction of bisphenol-A with glycidyl methacrylate, became a breakthrough in this field and is still used as an essential component of dental composite matrix.

The advantage of Bis-GMA resin is a rigid aromatic structure and low water sorption. This second aspect is very important because water in the composite can act as a plasticizer, facilitating translational movement of the polymer chains, thereby reducing the mechanical strength of the polymer matrix.

![Bis-GMA resin](image)

Fig. 1 Bis-GMA resin, i.e. 2,2-bis-[4,4-(2'-hydroxy-3'-methacryloxypropoxy)phenyl]propane.

The three-dimensional spatial structure of bis-GMA, formed during polymerization, is characterized by high degree of entanglement of macromolecular chains, which are additionally linked by secondary van der Waals bonds. This results in the higher glass transition temperature and melting point of bis-GMA. Additionally, due to its higher molecular weight and the rigidifying function of the aromatic ring, the bis-GMA shrinkage value is reduced to about 5 %, while the mechanical strength of the matrix is significantly increased [2, 13].
Bowen’s "invention" has contributed to the rapid replacement of dental cements and acrylic resins by the dimethacrylate composites. However, as the increased molecular weight of the main component resulted in a significantly higher matrix viscosity, it was necessary to find an appropriate reactive diluent – a substance that would reduce the viscosity of Bis-GMA resin, at the same time actively participating in the polymerization reaction and facilitating the introduction of mineral filler.

The most common diluent used nowadays is triethylene glycol dimethacrylate (TEGDMA) (Fig. 2). It changes the viscosity of the system (Tab.1) and improves the flexibility of the final composite [14, 15].

![Fig. 2 TEGDMA resin, i.e. triethylene glycol dimethacrylate.](image)

TEGDMA resin structure is similar to that of bis-GMA, i.e. it has reactive double bonds in the methacrylate groups located at both ends of the molecule. However, the whole molecule is shorter, and as it does not contain aromatic rings, it has lower rigidity than bis-GMA, resulting in several orders lower viscosity [16].

<table>
<thead>
<tr>
<th>Bis-GMA/TEGDMA [wt. % /wt. %]</th>
<th>Viscosity [cP]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>1.2 x 10^6</td>
</tr>
<tr>
<td>76.2/23.8</td>
<td>5240</td>
</tr>
<tr>
<td>50/50</td>
<td>282</td>
</tr>
<tr>
<td>33.3/66.7</td>
<td>245</td>
</tr>
<tr>
<td>0/100</td>
<td>15</td>
</tr>
</tbody>
</table>

The smaller molecular weight of triethylene glycol dimethacrylate is responsible for significant shrinkage (approximately 13 %) during polymerization [13]. If we look at the problem only through the prism of shrinkage, we should conclude that the addition of TEGDMA to the matrix is disadvantageous. On the other hand however, it is practically impossible to introduce the filler into the matrix without reducing the viscosity of Bis-GMA resin.

In 1974 Foster and Walker patented a new type of bifunctional urethane dimethacrylate resin (UDMA) [17]. This type of oligomer is formed by the reaction of oligo(ethylene) glycol monomethacrylates containing one to four oxyethylene units
(e.g. HEMA – ethylene glycol monomethacrylate) with different diisocyanates (such as HMDI – hexamethylene diisocyanate) [18].

Urethane dimethacrylate resins are characterized by lower water absorption and viscosity in comparison with the bis-GMA, which makes the dilution of UDMA monomers unnecessary. Unfortunately, UDMA resins are also harder and brittler and their shrinkage is quite high (5–9%). In addition, this type of resin is sometimes less resistant to light and may be prone to discoloration [19, 20].

![UDMA resin](image)

**Fig. 3** UDMA resin, i.e. 1,6-bis(methacryloxy-2-ethoxycarbonyl amino)-2,2,4-trimethyl hexane.

Despite the time passed and the progress of science, the above-mentioned Bis-GMA, UDMA and TEGDMA oligomers, while imperfect, remain essential components of most commercial dental composites. However, the possibility of modifying the matrix resin in the context of polymerization shrinkage reduction is still among the most heavily researched issues in dentistry.

### 1.2.2 Current methods of resin matrix modification

#### 1.2.2.1 Cyclopolymerizable monomers and trifunctional methacrylates

Early attempts to reduce the polymerization shrinkage were focused on monomers which can cyclize during polymerization – oxybismethacrylates. It turned out that these compounds could be the basis for the development of new monomers which would provide a higher degree of matrix conversion [4, 5, 21].

Currently, much attention is paid to monomers, which would rather increase its volume during polymerization, than shrink [1]. In the 70's Bailey patented ring-opening polymerization of polycyclic monomers: spiroorthocarbons, spiroesters or bicyclic orthoesters. Thus, he contributed to the research on the possibility of using such monomers in restorative dentistry as well.

The popularity of spiro-ortho compounds stems from the fact that they can expand during polymerization. Their expansion is a consequence of ring opening with the breaking
of some covalent bonds. Therein, atomic bonds are replaced by secondary van der Waals bonds, which is the reverse situation than during the free-radical addition polymerization.

Expansion of spiro-ortho compounds during the polymerization is probably also associated with the presence of significant amounts of monomers in the crystalline form, which are not involved in the binding reactions [22–24].

Numerous studies [25–29] have indicated that replacement of traditional dimethacrylate resin by spiroorthocarbons or other spiroorthocompounds allowed to obtain materials with lower shrinkage and, additionally, with better adhesion to etched enamel, obtained by eliminating the stress in the "matrix tags" penetrating the etched enamel of the tooth [25]. Unfortunately, the volume contraction observed for cyclic monomer-based materials is still not satisfactory. In addition, spiroorthocarbons are sensitive to UV radiation, which limits the possibility of their commercial application [1].

Studies on the possibility of the combination of spiroorthocarbons with epoxy resins [22, 26] or bisphenol A [27, 29] have shown that such a matrix exhibits much smaller polymerization shrinkage, lower water absorption and is characterized by high resistance to dynamic strains. Trifunctional methacrylates (Fig. 5) exhibit similar properties. Additionally, they are characterized by good solubility in standard dimethacrylate oligomers, and thus they were considered an effective replacement for the classic matrix, ultimately however, they have never found a commercial application [30–32].

**Fig. 4** Spiroorthocarbons (SOC) – examples.

**Fig. 5** THMPE, i.e. 1,1,1-tri[4-(2’-hydroxy-3’-methacryloxypropyl phenyl]ethane.

1.2.2.2 Dendritic and liquid crystalline methacrylates

Liquid crystalline methacrylates were patented in 1999 [33]. They exhibit a high degree of conversion and low polymerization shrinkage, but the usage of such compounds has no economic justification, due to the costly synthesis. The fact that the polymer network
formed by crosslinking liquid crystalline methacrylates is very flexible, which can ultimately lead to deterioration of mechanical properties of composites, also raises some doubts [1].

Dendritic methacrylates are also an interesting group of compounds [34]. However, the high matrix flexibility is quite questionable also in this case. Although the use of dendritic monomers significantly reduces the volumetric shrinkage, too high flexibility of the matrix makes the mechanical properties of dendritic methacrylate-based composites much worse than in the case of commercial composites. However, they are still an interesting alternative for dimethacrylate resins, therefore studies on their improvement are still a subject of studies [35].

1.2.2.3 Thiol-ene oligomers (TATATO)

Besides the architecture modification studies of (meth)acrylate compounds, research on the use of monomers of completely different chemical nature than dimethacrylates, like thiol-ene oligomers (eg TATATO of PETMP) (Fig. 6a, b), is still carried out.

![TATATO](image1)

![PETMP](image2)

**Fig. 6 a)** TATATO – triallyl-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione.  
**b)** PETMP – pentaerythritol tetra(3-mercaptopropionate).

In contrast to the mechanism of free-radical chain growth polymerization (like in the case of dimethacrylate resins), polymerization of thiol-ene systems runs through the step-growth addition mechanism and their formation is facilitated by a rapid, highly efficient free-radical chain transfer reaction. Thus, crosslinked thiol-ene polymerizations proceed very rapidly, but will not reach the gel point until a relatively high functional group conversion is reached. This is important because if the composite reaches the point of gelation later, less shrinkage and shrinkage stress will appear in the material after crosslinking [36]. The TATATO/PETMP system is characterized also by higher curing depth and its polymerization is not inhibited by the presence of oxygen, as in the case of classical dimethacrylates [37].
1.2.2.4 Polyhedral Oligomeric Silsesquioxanes (POSS)

In the context of reducing shrinkage, considerable enthusiasm has been raised by the possibility of using polyhedral oligomeric silsesquioxane (POSS). The POSS skeleton is a compact cage structure, surrounded by symmetrically distributed functional groups. Its unique hybrid nature allows to obtain covalent organic-inorganic connections in nanoscale, which can find a variety of applications, depending on the type of organic substituents [38]. Due to the specific structure and chemical functionality, silsesquioxanes can be used together with other mineral fillers (e.g., SiO\textsubscript{2}, TiO\textsubscript{2}) and can be modified in the manner similar to siloranes [38, 39].

In recent years, POSS with methacrylate substituents has been synthesized (Fig. 7), which is compatible with the dimethacrylate resins. Thereby, the real opportunity to use polyhedric silsesquioxanes in the dental composite matrix was created.

![Schematic structure of POSS with methacrylate substituents.]

The first experiments on matrices with the addition of POSS showed that they are characterized by lower polymerization shrinkage and better mechanical properties than a standard matrix [40, 41]. The light-cured composites with the addition of POSS also exhibit good mechanical properties and the change of their volume during irradiation is lower than for standard matrix-based materials [42].
1.2.2.5 Siloranes

Siloranes (Fig. 8) represent a completely different concept of matrix development. Among all of the above compounds, only this group has found some real application in dental composite matrix.

The name "siloranes" comes from the name of two bricks of silorane molecule, i.e. the siloxane main chain which provides hydrophobic properties, and cycloaliphatic oxirane molecules which ensure low polymerization shrinkage.

![Fig. 8 Silorane.](image)

Studies have shown that silorane-based materials exhibit lower shrinkage (1 %), accompanied by smaller shrinkage stress, than most commercially available dental composites [43–46]. In terms of chemical structure, siloranes are completely different from all previously proposed materials. It entails far-reaching consequences: the new photoinitiation system (besides camphorquinone, including also an iodonium salt and an electron donor), cationic polymerization and the epoxy-based functional groups. These differences make siloranes totally incompatible with all existing dentin-composite binding systems. Thereby, successful application of them in dentistry practice requires much knowledge and individual treatment.

Silorane materials found their real place on the commercial market beside the dimethacrylates and have been offered for sale since the autumn of 2007 [46].
1.3 Fillers vs. Polymerization shrinkage

Inorganic phase is, alongside the organic one, an integral constituent of the composites. In dental materials, the inorganic phase is a filler, usually added in amounts of 75–90 % wt. (about 35–60 % vol.) [47]. The usage of such a large proportion of filler is primarily (but not exclusively) the result of efforts to minimize the volumetric shrinkage of the resin. It is well known that a high degree of filler content and a good dispersion of inorganic phase in the resin matrix decrease the size of volumetric shrinkage. In the case of commercial composites containing 60–70 vol. % filler, volumetric shrinkage is approximately 2 %, while the composites filled to a lesser extent (47 % vol.) can change its volume during the polymerization of up to 3.5 % [48].

It should be remembered however, that the correct assessment of a specific property of a composite material always requires a careful analysis of this parameter in the context of its possible impact on other properties. While desirable in the context of polymerization shrinkage, the high filler volume can cause an increase in the shrinkage stress, which is undesirable from the mechanical point of view. Fillers have much higher modulus than a polymer matrix. If the inorganic phase content increases, higher shrinkage strain is generated in the composite [49].

It should be realized that the amount of filler "possible" to introduce into the dimethacrylate matrix, is limited to a large extent by the requirements of the composite paste rheology. This means that the composite intended for commercial use should have the proper consistency... But what does "proper" mean?

The word "proper", although a relative term, is used deliberately, because the answer will depend on who provides it. For dentists, the proper consistency is the consistency of plasticine – tensile but without sticking to the tools. From the viewpoint of specialists from materials engineering, composite paste must have a sufficient density and a uniform, homogeneous structure. It is impossible to describe "proper consistency" by specific numerical values, identical for each filler type. In fact, achieving the desired consistency is highly dependent on what kind of particles are introduced – what is their size, shape, surface area, method of surface modification, etc.

Thus, it is known that e.g. a filler in the form of submicron, pyrolytic amorphous silica of average particle size less than 0.1 micron, limits the possibility of achieving a higher degree of filling than 40–50 % by weight. It is primarily connected with the large surface area
of such silica \(120 \text{ m}^2/\text{g}\) [50]. This also means that much serious problems may be associated with attempts to introduce large quantities of fillers with smaller particles and much higher surface areas (so-called nanofillers).

However, the question remains whether the introduction of large amounts of nanofillers to the matrix, is really reasonable. It is well known on the other hand, that during the dispersion of a nanofiller in the matrix, the polymer macromolecules are immobilized on the particle surface and such system exhibits a larger surface of interaction. Generally, it creates a matrix-filler connection of higher quality in the composite. Although with a smaller filler weight content, nanofiller-matrix composites are sometimes much better than conventional ones. In the case of the nanofiller, it is the most important (and most difficult at the same time) to achieve a good dispersion of inorganic phase in the resin matrix, rather than to attempt to pack a larger amount of nanofillers in there.

1.3.1 Fillers – today

Inorganic phase in commercial dental composites is usually a powder of particles with different sizes and shapes, inert with respect to the copolymers (for this reason it is generally subjected to modification – see next Section). Generally, the solid phases in dental composites consist of different silicon compounds: dioxide (amorphous silica, quartz), borosilicate, Li-Sr-Ba-Al glass, and oxides: zirconia and alumina. Due to the different structure and chemical nature, each of these compounds can play a slightly different function in the restorations. Probably for this reason, usually more than one type of filler are used in the commercial composites.

Quartz is the hardest filler. Its hardness is greater than of most glasses, and therefore, its presence in a composite results in an increased resistance to abrasion. Additionally, due to the appropriate refractive index, quartz allows to obtain highly aesthetic fillings. Most of glass fillers behave similarly. Their addition results in the so-called "chameleon effect" – the fillings conformed to the shade of surrounding tissues.

The introduction of elements with high atomic weight (barium, zirconium, strontium, tantalum) to dental composites makes it possible to obtain a good contrast in the radiographs, which facilitates the correct diagnosis of fillings [21, 51, 52]. However, studies have shown that Ba-containing composites have a tendency to barium leaching, which can deteriorate mechanical strength of the fillings and increase the degree of abrasive wear [53].
1.3.1.1 Modification of the surface of filler

The hydrophilic nature of the surface of siliceous fillers cause that they are poorly dispersible in hydrocarbon matrix. At the same time however, they belong to the group of fillers which are the easiest to modify. Modification of the filler particles must be done in a way which allows to sustain the chemical properties of resin matrix. The main reason of surface modification is to improve the mechanical properties of dental composites, by increasing the compatibility of the inorganic filler and dimethacrylates.

One of the most popular ways of surface modification is silane treatment of fillers. Modification of the filler surface by a silane bonding agent increases the silica dispersibility in dimethacrylate resins by weakening the filler-filler interactions. At the same time, due to physico-chemical binding, the filler-matrix interaction increases. Reducing the tendency of silica particles to agglomerate and improving its wettability by the resin, we increase the filler content in the dimethacrylate matrix. Additionally, the mixture viscosity is reduced and thus the processing properties are also improved [54–57]. For the composites in which the silanized filler is used, we also observe the improvement of mechanical properties of filling: its tensile strength, compressive strength, toughness and wear resistance [55].

From the chemical point of view, the silanization takes place by the attachment of silane adhesion promoters (Fig. 9) to the substrate (e.g. silica). This reaction is only possible when hydroxyl groups are present on the surface of a substrate. Only then they react with silanes to form relatively stable Si–O bonds [54].

Silane adhesion promoters have generally two types of functional groups: the "X" type – such as methoxy (–OCH\(_3\)), ethoxy (–OCH\(_2\)CH\(_3\)) or acetoxy (–COCH\(_3\)) – capable of hydrolysis, and the "R" type groups, which can be reactive or unreactive chemically with regard to the polymer matrix.

![Fig. 9 General chemical formula of silane adhesion promoters.](image)

Reactive (organofunctional) groups are capable of reacting with a suitable polymer to form covalent bonds between the filler and the polymer matrix [58]. Depending on the type of organofunctional substituent, we can distinguish the following groups of silane adhesion
promoters: vinyl, amine, mercaptan, epoxy, methacrylate, isocyanate, sulfides, and many other of minor technical meaning [54, 56]. In practice, it is the organofunctional group that determines the choice of a particular silane as a bonding agent to a specific polymer.

In the case of dental composites, fillers placed in dimethacrylate resins are generally modified by $\gamma$-methacryloxypropyltrimethoxysilane (Fig. 10). The amount of silane used for modification depends mainly on the number of isolated –OH groups on the filler surface.

![Fig. 10](attachment://silane_A-174.png)

**Fig. 10** Silane A-174 ($\gamma$-methacryloxypropyltrimethoxysilane) – the most popular in dental composite technology.

The process of silanization of filler containing hydroxyl groups, in the presence of water (the most common environment), can be divided into four stages:

1) Hydrolysis of the silane alkoxy groups to form silanetriol.

![Silanetriol](attachment://silanetriol.png)

2) Condensation of silane to form oligomers with –OH groups directed toward the substrate (e.g. silica); close monitoring of pH and concentration of the solution is required at this stage, because these two factors have a decisive influence on the condensation of silanetriols.

![Silane oligomers](attachment://silane_oligomers.png)

3) The reaction of previously formed oligomers with the surface of the substrate (to form hydrogen bonds), with simultaneous condensation of unreacted hydroxyl groups of oligomeric silane (in an ideal case, the monolayer is formed on the substrate...
surface). Such reactions are possible due to the electrophilic nature of the hydrogen of silanetriol hydroxyl groups – as a result of the small electronegativity of silicon compared to carbon [59]:

4) Drying of the modified silica (at 110 °C), causing dehydration and the replacement of hydrogen bonds by covalent Si–O bonds.

Silanization depends mainly on its first phase – the prehydrolysis of silane adhesion promoter. This process is designed to generate the hydroxyl form of silane (silanol, silanetriol) as the oligomeric form, which is achieved by the proper selection of reaction parameters: pH, temperature and silane concentration. Badly chosen parameters can cause the silanol groups to react with each other (to form siloxane polymers) rather than with the filler.

The theoretical concentration of silane (expressed in wt. %) which is needed to cover the filler surface with a monolayer, can be calculated based on the surface area of the filler and the so-called coverage area of silane [54]. Optimal properties of composites are generally obtained when a slightly smaller amount of silane adhesion promoter is used than it would appear from equation (1).

\[
\text{[\% wt.] = \frac{\text{surface area of filler \left[ m^2/g \right]} \times \text{coverage area of silane \left[ m^2/g \right]} \times 100 \%} \]

(1)
The silane coverage depends primarily on the size of their molecules, which means that it is in a direct relation to their molar mass. For most of silane adhesion promoters, surface coverage area decreases linearly with increasing molar mass. Thus, the coverage area of the "small" methyltrimethoxysilane (136 g/mol) equals 572 m$^2$/g, whereas 1 g of γ-methacyryloxypropyltrimethoxysilane (248 g/mol) used in dental composites technology, is able to cover only 314 m$^2$ of a filler [54].

The pH of the silanization bath is commonly regulated with acetic acid, because it is easily removable from the post-reaction environment. Silanetriols (or silanols) are the most stable at pH 3–6, and their rapid condensation is observed at pH 7–9 [60]. The condensation of silanetriols leads initially to the creation of dimers, trimers, tetramers, and ultimately – low-reactive polymers with three-dimensional structure. This situation happens not only in the case of incorrectly chosen pH, but also when not enough substrate or no substrate at all is present in the reaction environment [56].

In fact, more than a monolayer of silane may be formed on the filler surface after silanization. This phenomenon is undesirable in the case of composites, because it reduces the share of covalent bonds in filler-matrix interphase, thereby reducing the stress-transferring ability of the final composite [61].

Adsorption of silanes on the substrate surface can be varied. It depends mainly on the surface roughness of the filler and the molecular weight of the silane. Generally, when the specific area of filler is high (e.g. for silica), a few monomolecular layers of silane are adsorbed, whereas the smooth surface of glass fibers is usually covered by many layers of silane. Thickness of silane layers adsorbed on a glass fiber grows until the so-called initial concentration of association will be achieved. This is the moment when the hydrolised silane molecules begin to form hydrogen bonds only between themselves, thus inhibiting the growth of layers on the substrate [62].

1.3.2 Fillers – recent developments

1.3.2.1 Fibrous fillers: whiskers and glass fibers

The studies on improving the inorganic phase in dental composites are currently focused on fiber fillers: single crystal fibers (whiskers) [63–67] or fine glass fibers [68–71]. The number of papers that appeared in the last decade indicates that fibers are still an interesting alternative to round-shaped particles. The fiber form appears to be more
beneficial than the fine form, as it provides better energy absorption by the filler and thus reduces internal stresses in the material and usually results in an increased mechanical strength of the composites and diminished susceptibility to abrasion [65, 69].

Specially crafted whisker fillers – single crystals of an elongated shape and small size (0.1–1 \(\mu m\)), are characterized by particularly high strengthening potential. The application of whiskers leads to even twofold higher flexural strength than in commercial composites. Other mechanical properties, like resistance to scratch, abrasion or formation and propagation of microcracks, are also improved [63].

Unfortunately, their non-aesthetic appearance and small (and rather negative) impact on the value of shrinkage, cause that fillings containing fibrous fillers could not find place on the commercial market [70].

1.3.2.2 **Nanofillers in dental composites**

Nowadays there is a real propensity for the "nano". The achievements of modern technology and science allow the production of smaller and smaller particles. The widespread misuse of the prefix "nano", meets with a great deal of mistrust and skepticism. But the truth is that the development of nanotechnology, which gains great importance in this century, allows not only to change but also to model the features of materials.

The transition from microparticles to nanoparticles causes a significant increase of specific surface area of materials and thus dramatically changes their output characteristics – physical, chemical and optical properties [72]. In spite of the considerable difficulties associated with the introduction of larger amounts of nanofiller to the matrix and not fully examined toxicity of nanoparticles, the possibility of their use in dental materials still arouses enthusiasm.

The mechanical properties of composites containing nano-sized fillers are closely associated with the solid-phase dispersion in the polymer matrix. That, in turn, depends primarily on good wetting of the nanofiller surface by the polymer. Due to their very small size, nanoparticles tend to form secondary structures – aggregates and agglomerates, mainly connected by van der Waals bonds. A problem thus appears with wetting and evenly distributing the resin on the surface of individual particles. The essence of the wetting mechanism has not been fully understood. It seems advantageous however, that the step of distributing the filler in the matrix should be preceded by infiltration, i.e. the penetration of resin macromolecules to the aggregates and agglomerates. This process depends largely on the viscosity of the wetting medium – matrix. Both too low and too high viscosity
may render the macromolecules unable to penetrate the compact structure of the agglomerates.

The tendency to agglomerate and the difficulty in ensuring the adequate level of wettability, make the process of preparation of nanoparticles-containing composites difficult. Optimization of the composition formula is therefore a complex matter and should be preceded by a thorough analysis.

Studies have shown that the introduction of TiO$_2$ nanoparticles modified by organofunctional silane increases the microhardness of composites and their resistance to bending [73]. An improvement of mechanical properties has also been reported in the case of composites containing nano-Al$_2$O$_3$ [74].

At the moment, apart from the composites filled with silica and zirconia nanoparticles (Filtek Supreme composite, available on the market since 2002), which are highly aesthetically thanks to the increased transparency of fillings [75, 76], other nanocomposites are actually absent at the dental market. It seems that the huge potential of nanotechnology development has not yet been fully and effectively used by restorative dentistry.

### 1.3.3 Other mineral fillers – potential application in dental composites

The attempts of usage hydroxyapatite (HA) in dental composites are the natural consequence of the high content of this compound in the human enamel (see Chapter 2, p. 24). This inept imitation of nature has yielded some results, e.g. the increased surface hardness of hydroxyapatite-containing samples, but the influence of HA on the Young's modulus or bending resistance of composites is quite ambiguous [77, 78]. There is also a problem with large water sorption of hydroxyapatite-containing composites, which effectively excludes their clinical use [79, 80].

Besides, the presence of hydroxyapatite in the light-cured dental composites deteriorates their optical properties. Due to their high refractive index and tendency to scatter light, the HA-containing materials have neither gained general acceptance nor appeared on the commercial market.

Other potentially interesting fillers, like montmorillonite (MMT), shared the fate of hydroxyapatite. Montmorillonite nanofillers aroused special interest because of their layered (lamellar) structure and high aspect ratio. They are composed of silicate sheets
separated by spaces (galleries) of the same height and, currently, are commonly used in various engineering nanocomposites of enhanced mechanical strength and high hardness. According to the literature, the addition of small amounts of MMT results in a vast improvement in mechanical, thermal and barrier properties [81].

Efficiency of MMT reinforcement, just like in the case of other nanofillers, is closely linked with the necessity to provide a high degree of filler dispersion in the matrix, as well as its appropriate compatibilization. A special feature of all montmorillonites is that the binding forces between layers of silicate are quite weak, so the molecules of water or other polar solvents can easily penetrate between the galleries.

Preparation of nanocomposites containing layered fillers includes two options: intercalation – the penetration of polymer macromolecules between the silicate layers and pushing them apart without destroying the layered structure, and exfoliation – the destruction of ordered structure by breaking the filler interlayer interactions (layer separation). From the standpoint of improving the mechanical properties of composites, the MMT exfoliation process seems to be more desirable because it provides a stronger filler-matrix interaction, and the composite produced is more homogeneous [82].

The attempts to introduce MMT to methacrylate resins are still conducted. The studies have indicated that PMMA/MMT composites exhibit a significant reduction of polymerization shrinkage [83]. Organofilization of montomorillonite manages to produce intercalated composites with varying degree of filling [84], but, like in the case of hydroxyapatite, their high refractive index and high water sorption raise some doubts.
2. Mechanical properties of dental composites – can we catch up with nature?

In the time when the dentistry seeks new, better solutions, one of the key factors determining the practical possibilities of using a composite material as a tooth filling is its mechanical strength. To achieve such mechanical parameters as the "nature" – tooth enamel, the hardest human tissue (Tab. 2) – still remains a dream only.

Tab. 2 Mechanical properties of human enamel [84].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>compressive strength [MPa]</td>
<td>95–140</td>
</tr>
<tr>
<td>shear strength [MPa]</td>
<td>90</td>
</tr>
<tr>
<td>tensile strength [MPa]</td>
<td>8–35</td>
</tr>
<tr>
<td>Young modulus [GPa]</td>
<td>9–90</td>
</tr>
<tr>
<td>microhardness [GPa]</td>
<td>3,2–4,4</td>
</tr>
<tr>
<td>nanohardness [GPa]</td>
<td>3,1–3,4</td>
</tr>
</tbody>
</table>

The hardness of the enamel is mainly associated with its chemical composition. The crystalline hydroxyapatite prisms constitute the basic framework structure of enamel (94–96 % wt.), therefore the enamel is considered a natural, biological ceramic material [51, 86]. However, hydroxyapatite crystals are bonded by organic compounds (glycoproteins) and their specific mutual orientation gives the enamel properties more similar to metals than to ceramics, i.e. high viscoelasticity and fracture toughness [86]. In this context, the application of amalgams to fill tooth cavities seemed reasonable, especially that numerous clinical studies have confirmed their good mechanical resistance – much higher than that of dimethacrylate-based dental composites [87–92].

The materials used in dentistry today are the resultant of the desires to make the most accurate and at the same time the most aesthetic "reconstruction" of damaged tooth tissue. Therefore, amalgam fillings, although much more durable, definitely lose the competition with polymer composites.
The filling aesthetics and the ability to accurately reproduce the damaged tooth tissues are of course not all requirements for dental composites. The requirements collected in the PN-EN ISO 4049 standard [93] are definitely much more demanding and impose the necessity to test a broad spectrum of properties, before the materials reach the market. The standard includes tests of biocompatibility, cure depth, color, transparency (translucency), sensitivity to light and color stability after irradiation, water sorption and water solubility. The lack of requirements for mechanical properties of dental materials is really surprising. The standard [93] takes into account only the static test of three-point bending, which seems to be "non-representative" for dental fillings, which are subjected to high loads and stresses, working every day in a dynamic short-circuit contact. Lack of normative studies on the mechanical and tribological properties of dental composites seems to exclude the possibility of their full and comprehensive evaluation.

2.1 Factors affecting the mechanical properties of dental composites

Mechanical properties of a material are closely linked with its response to deformation or loading. It is commonly believed that external stresses acting on dental composites are transferred from the continuous phase (polymer matrix), through the binding phase (silane), to the dispersed phase – the filler particles. Therefore, the final properties of composites will largely depend on the quality of interphase connections, the geometry of the filler, the surface area of filler, the ability to create so-called "structure" and the dispersion and distribution of the filler in the polymer matrix [94]. In fact, these factors have also their physical "extension" – in the form of the output characteristics of the matrix and fillers – such as viscosity, or polarity. Additionally, if we take into account the specific, variable oral cavity environment, it is easy to understand why the process of predicting and modeling the mechanical properties of a dental composite is such a complex and multifaceted matter.

Common knowledge indicates that the strengthening effect of a filler in composites is observed only to a certain particle size limit (of its aggregates and agglomerates). Above this limit, instead of the expected improvement, a deterioration of mechanical properties of composites is often observed. The dimensional limit is not clearly defined however, and may depend on the nature of both the continuous and dispersed phase.
An appropriate dispersion of the filler in the resin matrix is essential for the macroscopic homogeneity of the composite, as well as for the efficiency of the filler strengthening action. From this point of view, the structure of not only the primary particles but also their aggregates and agglomerates should be taken into account. The other properties, like surface area, degree of loading and energetic characteristics of the filler, will determine the ability of the filler to interact with the matrix and to create its own reinforcing network – the "structure".

Until recently, agglomerates had been described as particles larger than typical primary particles for a particular type of filler (typically 10–100 microns), without going into details of their internal structure [95]. However, later research revealed that the structure so significantly affects the properties of a material [96], that the structure of any filler should be subjected to additional analysis. For similar reasons, each matrix–filler system requires a separate, individual consideration.
2.2 Selected mechanical properties of dental composites

2.2.1 Bending strength – the only test of mechanical properties included in the PN-EN ISO 4049 standard.

The three-point bending test is the only mechanical test included in the standard for dental materials [93]. Flexural strength (σₜ) can be calculated based on equation (2):

\[
\sigma_t \ [MPa] = \frac{3Fl}{2bh^2},
\]

where:
F – the load at the center of the beam [N], l – support span [mm], b – width of the specimen [mm], h – thickness of the specimen [mm].

Static three-point bending test requires the preparation of relatively large samples (25 mm x 2 mm x 2 mm), differing greatly in size from the diameter of a dental lamp optical fiber. A disadvantage of this method is that such a long sample requires repeated irradiation, which may result in overlapping of irradiated areas. The reaction between the activator and the photoinitiator, within the overlapping zones of radiation, generates a greater number of radicals, resulting in a higher degree of crosslinking in comparison to neighboring areas and the sample becomes non-homogeneous. Such heterogeneity may lead to different stress distribution in the material, which is reflected in the varied values of flexural strength. It should also be noted that preparation of such long samples is difficult from the technical point of view and, actually, completely "clinically" unfounded, because the real dental fillings are several times smaller [97, 98].

It seems that the three-point bending test, more than for dental composites, is reasonable for determining the flexural strength of fixed partial dentures, which have similar size like the samples tested. Also, the loads applied in three-point bending tests are similar to those which occur during chewing [51].
2.2.2 Hardness

Due to the fact that hardness correlates well with other mechanical properties, such as the Young's modulus, and the measurements of hardness are relatively easy to conduct, these tests are commonly used to assess the mechanical strength of dental composites. But it should be remembered that hardness is not a material constant which can be clearly defined, but rather a complex property, which strongly depends on the method and conditions of measurement.

In the physical sense, hardness measurements quantify the resistance of a material to plastic deformation. Hardness can be determined based on the simple equation (3):

\[ H = \frac{P}{A_{\text{proj.}}} \]  

where:

- \( H \) – hardness [Pa],
- \( P \) – load [N],
- \( A_{\text{proj.}} \) – surface area of indent [m\(^2\)].

### 2.2.2.1 Microhardness measurements

In the context of mechanical properties of light-cured dental composites, hardness measurements are used most frequently to assess the degree of crosslinking. This assessment can be done by measuring the hardness of a material at certain depths [99–101].

Due to the small size of dental fillings, the hardness measurements of dental composites should be made with small indenters and relatively small loads. For this kind of methods, dentistry uses the term "microhardness" measurements [102].

In the case of microhardness measurement of dental composites, Knoop or Vickers indenters are used the most commonly (Fig. 11) [51, 99, 101–107].
During these tests, a small diamond pyramid is pressed into the sample under loads. An applied load ranging from 10 g to 1000 g is used. This low amount of load creates a small indent that must be measured under a microscope (by measuring the diagonals of the indent).

The difference between the Vickers and Knoop tests is simply the shape of the diamond pyramid indenter. The Vickers test uses a square pyramidal indenter which is prone to crack brittle materials. Consequently, the Knoop test using a rhombic-based pyramidal indenter was developed which produces longer but shallower indentations. Both methods provide high accuracy and allow the use of one scale for the entire range of hardness [108].

Microhardness measurements are troublesome and have some limitations, mainly due to the significant influence of human (operator) factors on the obtained numerical values. It seems that accuracy, precision and reproducibility of results obtained from microhardness measurements is dependent, in a meaningful way, on the experience of the "operator" [109].

### 2.2.2.2 Nanoindentation

Hardness may be an indicator of ease of "finishing" (grinding, polishing) of the surface filling and its resistance to scratches during the use. This is important not only for aesthetic reasons, but also for durability, as lower scratch resistance increases the risk of micro-cracks propagation and can lead to deterioration of mechanical properties of tooth fillings [51]. In this context, it seems reasonable to focus attention primarily on the surface
layer, in which the tribological and ageing processes are initiated. It seems that it is the quality of this layer which determines the quality of the dental filling. Nanoindentation is a fast and reliable technique for evaluating local mechanical properties, such as hardness and elastic modulus, of very small volumes of the material. During nanoindentation, a precisely defined three sided diamond pyramid with an equilateral triangle as the base area is brought into contact with the sample surface. The applied load and the displacement into the specimen are recorded simultaneously. The load-displacement curves obtained during an indentation experiment are essential to calculate the hardness and elastic modulus of the test material.

Nanoindentation is probably the only one technique, which allows to precisely define the mechanical properties of the surface layer [110]. This technique allows to obtain information that would not be provided by volumetric experiments. Probably because of that, this method has gained special importance and popularity in the studies of mechanical properties of hard tissues (including teeth) and biomaterials [111–116].

Nanoindentation is noninvasive and allows to avoid operator errors, because the whole process is controlled by an automated measuring system. Application of small forces (0.5–5 mN) allows to explore the surface layer of a material also in the elastic deformation range. The latter differs nanoindentation from microhardness measurements, which concern only the plastic deformations of materials.

In a commercial apparatus, the displacement of indenter is typically monitored by capacitance or inductance (the indenter is mounted directly onto the middle plate of the capacitor), whereas force actuation is provided through electrostatic force generation, magnetic coils, or expansion of a piezoelectric element [111]. The interaction between the tip and the sample during a nanoindentation experiment is illustrated in Fig. 12 [111]. Load and displacement are monitored continuously during the experiment, resulting in a load-displacement curve, as shown in Fig. 13.

**Fig. 12** Scheme of the indentation process. $P_{\text{max}}$ – maximum load applied, $h_{\text{max}}$ – penetration depth, $h_c$ – contact depth (height of the contact between the tip and the sample), $h_f$ – final depth.
The analytical model proposed by Oliver and Pharr [101], where unloading curve is subjected to analysis, allows to determine both the hardness\(^1\) and the Young’s modulus. Taking into account the dimensions of filler particles in dental composites, and dimension of a tooth filling, it should be noticed that nanoindentation is an ideal technique to evaluate mechanical properties of dental composites [117–120].

According to the literature [117], reduced modulus\(^2\) of dimethacrylate-based dental composite is located generally in the range of 15–45 GPa, with nanohardness about 1–2 GPa. For comparison, the nanohardness of human tooth enamel may be twice higher (3.5–4 GPa) with significantly higher reduced modulus – about 75–80 GPa [112, 113]. When we move toward the dentin (the deeper parts of the tooth), the enamel nanohardness decreases to about 3 GPa, and the modulus to about 60 GPa [117], but still these values are several times higher than for composite materials.

Due to the extremely diverse morphology of dental composites and the usage of light curing technique which may result in a crosslinking gradient, it should be considered whether it is appropriate to describe the mechanical properties by a single, specific numerical value. If we assume that due to the gradient of crosslinking, the top layer of filling is characterized by increased hardness (in comparison to the interior part of the material), any generalizations which describe the hardness of a dental material by a specific numerical value, become a major misstatement.

\(^1\) During nanoindentation, yield point of material is not always exceeded, therefore using the term “nanohardness” will be more reasonable.

\(^2\) The measured modulus is a function of “contact” created by the indenter (usually diamond)–tested material pair. For this reason, the more precise term is “reduced modulus”.

---

**Fig. 13** Scheme of a typical load-displacement curve.
2.2.3 Tribological properties – wear

Wear of materials is a natural process which always occurs when one surface moves in relation to the other, under load. This process is generally considered as negative, because of the mass loss and changes of the initial size of materials.

The key factor which determines the amount of wear is the time during which the surfaces are in motion [121]. Healthy enamel of human teeth is durable and it does not generally require any medical intervention for many years. In a sense, the same is expected of dental materials used for the reconstruction of occlusal surfaces of teeth. However, in order to design materials with desired properties, the nature of wear mechanisms of teeth and fillings should be explored first.

2.2.3.1 Estimation of wear resistance – is it possible?

Mechanical strength and, above all, wear resistance, are the main factors determining the possibility of effective use of a composite material as a tooth filling. These performance parameters are important mainly because of the generally poor mechanical condition of polymer materials. To some extent, they are also responsible for the health of the patient, his physical and psychical comfort, which is however mentioned less often.

The complexity and multiplicity of mathematical formulas concerning the wear process indicates that estimation of wear resistance is an extremely complex and troublesome matter. Meng and Ludema have counted of about 300 various "models" of wear [122]. Despite this large number, most of them seem to be completely useless. Introduction of experimental data to one of the existing mathematical models is very difficult, mainly because the process of wear is very complicated in itself – its character can vary dramatically even during a single experiment. An additional difficulty is that friction usually leads to the modification of materials by generating changes in the structure of their surface layer both in the micro- and nanoscale (related to the "response" of the sample to the presence of a counterface and to the working conditions). Such changes are often difficult to notice, especially for composite materials, which have a complex structure and morphology [123].
2.2.3.2 Mechanisms of wear of dental composites

It is difficult to define the wear in one sentence, but it may be said that wear is "the ultimate consequence of interaction between surfaces, which is manifested in gradual removal of material". In general, dentistry distinguishes four main types of wear processes, which occur in the oral environment [121]:

1) **Abrasive wear** – is probably the most common type of wear; it occurs when hard asperities plough into softer surfaces, resulting in plastic deformation. Microcutting is a dominating mechanism.

In dentistry, when asperities are an integral part of materials (e.g. filler particles protruding from dental composite) this process is named "two-body abrasion". If they are separate particles enmeshed between the surfaces (such as particles of food) we speak of "three-body abrasion". If such particles are carried by a stream of gas or liquid, they have some kinetic energy and cause erosion.

2) **Adhesive wear** – occurs when surfaces slide against each other. The effects of friction cause the asperities on one surface cold welded to another surface. The sequence of events is as follows: deformation of asperities in contact → removal of surface impurities → adhesive connection → shearing of adhesive connection → formation of wear debris. The formation of adhesive connections and their shearing is a stochastic process. It is accompanied by mass transfer from one surface to another. The volume of material transferred is proportional to the real area of contact and the sliding distance.

3) **Fatigue wear** – occurs when one surface slides over another; two zones are formed then: the zone of compression in the material ahead of the motion, and the tensile zone behind the motion, caused by plastic deformation of the material. Cracks initiate in the subsurface and propagate as a result of repeated cycles at a depth regulated by the material properties. Eventually, the cracks propagate to the surface and the material that was surrounded by the cracks is lost. This displaced material may itself form wear debris, which cause three-body abrasion.
4) **Tribochemical wear** – occurs as a result of chemical interaction between surfaces; causes the formation of a layer whose chemical structure and mechanical properties are different from the working surfaces. Such a modified layer is subsequently removed and a "fresh" layer of material is unveiled, which may again react and change its chemical composition. It should be noticed that such a chemically modified surface layer can also reduce the wear volume, because some substances act as lubricants.

In fact, the division proposed by Mair *et al.* [121] is nothing new and is entirely matched to the classical approach [124]. However, the full spectrum of dental composite wear processes requires a supplementation by two other types of wear as well:

5) **Attrition** – a specific type of wear, characteristic of the oral environment. It is a physiological process, progressive with age, manifested by the loss of enamel due to mechanical forces from opposing teeth. As a result of physiological attrition processes, enamel can reduce its thickness by 20–30 µm per year [125].

6) **Fretting** – the phenomenon of surface layer destruction, occurring at the contact area between two materials under load, subjected to minute relative motions by vibration or other factors, like cyclic load, temperature changes or corrosive environment [124, 126, 127].

We may distinguish four basic types of fretting, depending on the direction of the relative movement of surfaces against each other: tangential, radial, rotational and torsional (Fig. 14). The characteristic geometry of teeth suggests that during chewing, radial fretting occurs the most frequently [127].

![Fig. 14 Scheme of four basic fretting modes, according to [126]: a) tangential fretting, b) radial fretting, c) rotational fretting, d) torsional fretting.](image)

---

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The fretting phenomenon is described sporadically in the literature devoted to dental prosthetics [127], but not included in estimations of wear of dental composites.

The phenomenon of wear of dental composites is the result of a variety of processes occurring in the oral cavity, in particular – abrasion (including erosion) and attrition. The presence of radial fretting is not without significance either. In fact, all these processes can occur simultaneously or sequentially, in various configurations and different ways.

### 2.2.3.3 Abrasive wear of composites

Mathematical models of abrasive wear of multiphase materials are based on several simple assumptions. The Zum-Gahr equation (4) is among the most widespread ones [128].

\[
W_c = V_1 \cdot W_1 + V_2 \cdot W_2
\]

where: \(W\) – wear volume, \(V\) – phase content; \(C, 1, 2\) indexes – composite, continuous phase, dispersed phase, respectively.

This equation is based on the assumption that all components of the composite material are worn to the same extent, as if they were separate components. Following this reasoning, the contribution of each component in the abrasion resistance of a composite material depends only on the content of this component and its wear rate. Thus, this model completely omits other key factors responsible for the resistance to abrasive wear of a composite, i.e. particle size and distribution of the filler in the polymer matrix, properties of the filler-matrix interphase, geometry and mechanical properties of the filler agglomerates.

Wear "models", proposed over the years, are much more complicated. For this reason, they appear to be more accurate, and to illustrate the complexity of the wear process fuller and better. However, most of them concern one particular friction pair and specific external and internal factors accompanying the friction. It is therefore easy to conclude that none of the equations can be regarded as a universal model. Only a few of them seem to have a more general dimension, and could find practical application (Table 3). However, due to the dynamic, changeable oral cavity environment, it seems impossible to choose a single model which would correspond to the expectations of dental materials engineering, even if we assume that we are working with the same friction pair in the physico-chemical sense.
The reason is that the surface layer is of different nature than the bulk of the material, and it can repeatedly and unpredictably change its chemical composition in contact with external environment, which significantly impedes the formulation of any general equations or models.

### Tab. 3 Selected abrasive wear models of polymers/composites (W – wear volume) [123, 129]

<table>
<thead>
<tr>
<th>Model</th>
<th>Formula</th>
<th>Description</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratner et al. (1964)</td>
<td>$W = \frac{\mu P}{H \sigma e}$</td>
<td>$\mu$ – friction coefficient, $P$ – normal load, $H$ – hardness, $\sigma$ – stress and strain rupture</td>
<td></td>
</tr>
<tr>
<td>Giltrow (1970)</td>
<td>$W \sim \frac{1}{C^{0.5}}$</td>
<td>$C$ – cohesive energy</td>
<td></td>
</tr>
<tr>
<td>Czichos (1983)</td>
<td>$W = \frac{P s (1 + 4 \mu^2)^{0.5}}{\sigma_y}$</td>
<td>$P$ – normal load, $s$ – sliding distance, $\mu$ – friction coefficient, $\sigma_y$ – stress and strain rupture of polymer</td>
<td></td>
</tr>
<tr>
<td>Friedrich et al. (1985)</td>
<td>$W = \Omega \cdot \frac{H^{0.5}}{G_{ic}}$</td>
<td>$\Omega$ – probability factor of microcracking, $H$ – hardness of composite, $G_{ic}$ – fracture energy</td>
<td></td>
</tr>
<tr>
<td>Vaziri et al. (1988)</td>
<td>$W = \frac{K \mu_p}{H \sigma e}$</td>
<td>$K$ – constant, $\mu_p$ – ploughing contribution to the friction coefficient, $H$ – hardness, $\sigma$ – stress and strain rupture</td>
<td></td>
</tr>
<tr>
<td>Yamaguchi (1990)</td>
<td>$W = \beta NP_s$</td>
<td>$\beta$ – abrasive wear factor, $N$ – scratching efficiency factor, $P$ – normal load, $s$ – sliding distance</td>
<td></td>
</tr>
<tr>
<td>Viswanath (1995)</td>
<td>$W \sim \frac{P v t \alpha}{\gamma}$</td>
<td>$P$ – normal load, $v$ – sliding velocity, $t$ – time, $\alpha$ – roughness, $\gamma$ – surface energy</td>
<td></td>
</tr>
</tbody>
</table>

Abrasive wear results in the removal of the surface layer of material. The mechanism of wear depends therefore primarily on the mechanical properties of this layer. In soft and ductile solids, the primary wear mechanism is associated with plastic deformation – correspondingly, the hardness of the material is a key factor in governing the wear rate. On the other hand, the dominant mechanism in brittle solids depends on the surface fractures, and therefore the key property is fracture toughness of the material.

Lee et al. [130] introduced another model of wear of composite materials, which is mainly based on the three mechanisms: ploughing, cracking and particle removal. It employs the simplified two-dimensional geometry in which triangular abrasive medium particles act on a composite containing ideally rectangular filler particles (Fig. 15).
The penetration depth $x$ of the abrasive medium depends on its geometry, the applied normal load, and the mechanical properties of the composite material and the abrasive medium (5).

$$L = \frac{1}{2} (2w b H_c) \quad \text{and} \quad \frac{x}{w} = \tan \theta, \quad \text{stąd} \quad x = L/(bH_c) \cdot \tan \theta$$

where $b$ – thickness of the substrate and the abrasive medium, $H_c$ – hardness of the composite, $x$ – penetration depth, $\theta$ – abrasion angle, $2w$ – tip angle of the asperity, $L$ – normal load.

The abrasive medium will alternately plough the matrix and the reinforcement, and thus experience different ploughing loads for the different phases. The ploughing load for each phase can be described by the equation (6):

$$F_p = xbH_i,$$

where $H_i$ – hardness of either the matrix or the reinforcement.

In composites consisting of a soft (ductile) matrix and hard (brittle) reinforcement, maximum load is applied on the material when the abrasive medium ploughs the hard phase. Its magnitude depends on the depth of penetration, the average distance between abrasive particles and the hardness of the filler. If the values of these parameters are very small compared to the size of filler particles, ploughing is the dominant abrasion mechanism. When their values are comparable or larger than that of the reinforcement, the material will be removed due to the cracking at the matrix/filler interface or in the filler phase. The crack trajectory depends on whether the interfacial bonding or the filler particles are stronger.
When the ratio of the fracture toughness of the interface, $G_{lf}$, and the reinforcement, $G_R$, is less than 0.25 (Fig. 16a), ploughing by the abrasive medium may lead to the crack propagation in the weak interface. If the interfacial bonding between matrix and reinforcement is strong ($G_{lf}/G_R > \frac{1}{4}$), the crack will not propagate in the interface, but into the reinforcing phase (Fig. 16b) [130].

![Fig. 16](image-url)

**Fig. 16** Routes of cracking, depending on the strength of inter-phase interactions: a) weak interactions, b) strong interaction.

### 2.3 Morphology vs. Mechanical properties of dental composites

Durability of dental composites is dependent on a number of factors, which can be divided into two main groups: the 1st – concerning the chemical composition and the 2nd – associated with the morphology of the composite. The second group seems to be the most important, because the solid particles introduced into the polymer matrix generally act as a reinforcing agent, so their volume, geometry, dispersion and distribution in the matrix resin play a major role in the development of overall strength of dental composites [131–133].

The papers that appeared over the years, both empirical and theoretical ones, clearly confirm the crucial influence of composite morphology on the mechanical properties of dimethacrylate-based materials. Most studies have concerned the impact of filler particle size on wear rate. However, only few of them noticed that the contribution of individual fractions of particles of different sizes is more important than average particle size. The largest fraction of particles determines the tribological behavior of dental materials. Suzuki *et al.* [134] demonstrated that composites containing small spherical filler particles (~0.2 µm) exhibit the highest mechanical strength and the lowest wear rate. Venhoven *et al.* [135] additionally postulated the existence of a critical particle size (1.3–1.5 µm), below which food particles (the erosive medium) are unable to penetrate the intermolecular space, which results in increasing the mechanical strength of a composite.
In addition to particle size, geometry and distribution of filler in the matrix (mainly the distance between particles) are also essential factors. Jørgensen et al. [136] showed that improvement in wear resistance can be achieved by decreasing the size of filler particles and the distance between them and increasing the filler content in the material. They explained it by the possibility of better packing of the hard particles in the soft matrix, which acts as a protection against abrasion of polymer phase. Turssi et al. [137] investigated the use of composites with the same content of filler but of differently shaped particles. They observed that the presence of spherical-shaped filler particles is less favorable than the addition of a filler with irregular particle shapes. The highest abrasion resistance is exhibited by materials with irregularly shaped and sized particles, while the highest abrasion was observed for materials containing large filler particles of the same shape.

Both the research of Turssi [137] and in vitro studies of Lambrechts [132] confirmed that the reduction of filler particle size (to about 0.1–0.2 µm) results in the improvement of wear resistance of dental composites. It was explained not by the higher packing density, but rather by the fact that small particles have a lesser impact on the curing process (smaller particles are a lower barrier to radiation than larger particles) [137].

The results of my research [138–140] have also shown that it is very important whether the particle size changes gradually – from very large, through medium, to very small particles, or filler particles have a bimodal distribution, lacking the intermediate size. The latter situation seems to be more favorable. The material containing bimodal filler (two-sized particles only: <1 µm, and ~10 µm) exhibited higher abrasion resistance and fracture toughness, while the composite containing a fine, spherical filler particles was the least resistant to wear. It stands in opposition to earlier experiments of Lambrechts [132] and Jørgensen [136].

In addition to the geometry and packing density of filler particles in the resin matrix, the ability of composites to transfer stresses from the matrix to the solid phase, provided by silanization of the filler surface, is also a very important issue [141, 142]. The application of silane adhesion promoter allows the filler-matrix chemical bonding and protects against hydrolytic degradation [143, 144]. In hybrid composites containing different fillers, the wear resistance decreases linearly with decreasing amount of silanated silica, as the chemical bonding between matrix and filler protects the matrix against the abrasive medium. However, if the filler is weakly associated with the resin or is not chemically bonded, the wear rate may be higher due to the chipping of filler particles [143].
Undoubtedly, there is a close connection between the morphology of dimethacrylate dental composites and their mechanical strength. However, there are still a lot of discrepancies about what is the best and the most desirable morphology and probably because of that, a wide range of various composites is still available on the dental market.

In the context of mechanical properties of dental composites however, the term "the best" requires a holistic treatment of the subject. We should remember that improving one property often leads to dramatic deterioration of another, e.g. the attempts to improve the hardness usually result in increasing of the fragility of composites.

(*like in the Heisenberg’s uncertainty principle – just as we are unable to measure two complementary variables simultaneously and with the same accuracy, just so, we cannot arbitrarily affect the mechanical properties which result from each other*)
3. Cariogenic oral bacteria – is there a way to deal with them?

3.1 „Residents” of the oral cavity. Dental plaque.

Bacterial flora of the oral cavity is one of the most diverse communities of bacteria that can be found in the human body. This is related primarily to the construction of oral cavity, forming a complex, multi-element space in which each surface (teeth, tongue, palate etc.) becomes a habitat for characteristic microflora. Oral bacteria are sometimes called "opportunistic amphibions" because in relation to the host organism (human) they may behave in two ways: in some situations being harmless symbionts, and playing a pathogenic role in others. Some microorganisms are responsible for oral cavity diseases, e.g.: dental caries or periodontal disease, but some of them may lead to systemic diseases such as bacterial endocarditis, pneumonia, osteomyelitis in children, low birth weight of premature babies, or diseases of circulatory system [145, 146].

The gingival plaque, which is a type of microbial biofilm, is the main factor responsible for oral diseases. Two types of this plaque may form on the tooth surface: supragingival and sub-gingival. The former type – the biofilm associated with the tooth surface at gingival margin – is the main cause of dental caries [147].

Colonization of tooth surfaces by microorganisms is a repetitive and multi-stage process. Microorganisms themselves are not able to colonize a cleaned tooth surface. At the early stage of dental plaque formation, when the cleaned teeth have contact with saliva, the thin film (organic pellicle) of glycoproteins from saliva is formed on the tooth surface. This thin layer is the source of specific receptors which allow the attachment of bacteria.

Colonization begins with the adherence of salivary organisms to the acquired pellicle. This adhesion has a specific character – particular bacterial strains colonize specific areas of the mouth, such as Streptococcus salivarius colonizes the tongue, while Streptococcus mutans has an affinity to the surface of teeth. The next step is self-aggregation of bacteria and their growth [147, 148].

Dental caries develops under a bacterial biofilm (dental plaque), producing acids from extracellular and intracellular polysaccharides which are responsible for demineralization of the tooth surface (causing the etching of calcium phosphates and carbonates). In the early stages this process is reversible and fluorine is the catalyst of remineralization –
the incorporation of calcium and phosphates in the crystalline structure of enamel. Whether caries can develop or is inhibited, is decided by the balance between protective factors contained in the saliva (phosphates, calcium, fluoride) and antibacterial ingredients coming from the outside, and on the other hand pathological factors such as presence of cariogenic bacteria, frequent consumption of saccharides and glandular salivary dysfunction.

The processes of de- and remineralization occur several times during the day. If the balance is maintained, the saliva, acting as a natural buffer solution, copes well with the lowering of the biofilm pH. If the balance is unsettled and the pH remains low for a long time, the dental plaque microorganisms (mainly Streptococcus mutans and Lactobacillus acidophilus) multiply rapidly, producing large amounts of lactic, formic and acetic acid. When the biofilm pH drops below the critical value (5.0–5.5), the demineralization of hydroxyapatite crystals occurs and a cavity is formed [149, 150].

### 3.2 Secondary caries vs. Type of dental filling

The term "secondary caries" refers to dental caries forming at the tooth–filling border or under the filling. In the dental practice, secondary dental caries is a very widespread problem and the reason of exchanging of about 60% of all fillings [151, 152]. Bacterial flora of dental plaque, which plays a significant role in the formation of primary caries, also contributes to the secondary caries development [153, 154]. The presence of Streptococcus mutans in all samples of dental plaque indicates that this strain of bacteria is the main etiological factor of dental caries [155].

The studies of Lindquist and Emilson [155] have shown that the necessity of reconstruction of the tooth surface using restorative materials, as a consequence of dental caries, generally results in faster growth of bacteria than on untreated tooth surface. It means that filling surfaces, regardless of their nature, are much more likely to become inhabited by cariogenic bacteria, than the surfaces of teeth (except for the occlusal surfaces) [155].

However, the accumulation of dental plaque and rate of the secondary caries formation, strongly depends on the type and properties of filling. Numerous in vivo and in vitro studies of commercially available restorative materials: amalgams, glass ionomer
cements, chemo- and light-cured composites, have shown that bacteria colonize the surface of light-cured fillings the most readily [151, 153, 155–158] – particularly those located at the side of tongue and cheeks [155]. The literature indicates that the main reason of this situation is the difference in roughness of various dental materials. Bollen et al. [159] suggest that there is a certain limit value of surface roughness (0.2 µm), below which this parameter does not play any role in the accumulation of dental plaque. However, taking into account the differences in finishing procedures like polishing or grinding, each restorative material requires an individual approach.

Favored retention of bacteria on the surface of resin composites is difficult to explain only by the differences in roughness of dimethacrylate materials compared to enamel or amalgams [160]. The possibility of leaching of certain components from the fillings seems to be an interesting hypothesis. Those components, e.g. TEGDMA resin in dimethacrylate composites, would be involved in the biofilm formation and the *Streptococcus mutans* growth. Studies [161] have shown, that this resin increases the activity of glucosyltransferase – the enzyme supervising the synthesis of sticky disaccharides (glucans), which readily bind to saliva-coated enamel and contribute to the mass increase of dental plaque [161].

The reason for increased bacterial "interest" in dimethacrylate fillings is also the absence of any active ingredients inhibiting the bacteria proliferation. In case of the composite shrinkage during curing, the lack of antimicrobial additives gives bacteria an opportunity to penetrate the gap formed on the tooth-filling border and the development of secondary caries. Probably this is the main reason why the presence of fluorine (enamel, glass ionomer cements), or silver in materials (glass ionomer cements, amalgams) makes the bacteria reluctant to colonize non-polymeric restorations [151].

### 3.3 Antibacterial additives in dimethacrylate composites

An ideal solution of the problem of dental plaque and secondary caries formation would be a material characterized by low *Streptococcus mutans* adhesion, and which would inhibit the growth and proliferation of bacteria at a very early stage [162]. In theory there are two possibilities to achieve this aim: the introduction of bioactive factors to the resin matrix or modification of the inorganic phase of dental composites [163].
3.3.1 Matrix modifications

The most natural and obvious way of modifying the resin matrix to ensure the antibacterial properties, seemed to be the introduction of fluorinated analogues of bis-GMA to the matrix [164, 165]. Studies have shown that fluorine-containing oligomers are characterized by lower water sorption and higher hardness than the Bis-GMA resin, which results in higher mechanical strength of the composite during long-term use [166, 167]. However, there is no certainty that fluorine in the light-cured composites acts as an antibacterial or bacteriostatic agent [164]. In principle, the influence of fluorine addition is reflected only in the increase in hydrophobicity of the materials [168, 169], which makes the adhesion of the biofilm to the filling surface difficult.

In some other studies, modification of resin matrix by the introduction of soluble antibacterial additives, such as chlorhexidine (1,6-di-(4-chlorofenylobiguanido)-hexane, CHX), was also applied.

CHX is widely used in mouth rinses, gels and toothpastes [170, 171]. The mechanism of action of this popular antiseptic is based on its high positive charge. This charge makes for its strong affinity to the negatively polarized cell membrane of bacteria, thanks to which CHX easily penetrates into the cytoplasm and produces insoluble antigen-antibody complexes with phosphorus-containing nucleic acids and ATP. The result of these reactions is the inhibition of bacteria growth or destruction of their cells [172, 173].

Examinations by Kirby-Bauer method, which involves the diffusion of the active substance (antibiotic) from the disc-shaped sample to the agar substrate, showed that addition of only 1% CHX to the resin matrix causes the formation of a bacterial growth inhibition zone around the sample. However, the problem is that the chlorhexidine release is short-lasting, initially being very high and diminishing with time. The concentration of antiseptic is significantly reduced after several days of incubation, and dramatic decrease in the effectiveness of its action is then observed [174].

The influence of chlorhexidine addition on the mechanical properties of composites also raises some doubts. Jędrychowski et al. [170] have found that the addition of 1% chlorhexidine gluconate to the dimethacrylate matrix, results in lower compressive strength and tensile strength of composites. The interference in bonding of filler and matrix, or changes in the conditions of composite curing, may be the main reason for this phenomenon. The CHX elution, leading to the gradual porosity increase and weakening
of the composite microstructure, also seems to influence the mechanical properties of a composite [163].

In addition to the introduction of a leachable antimicrobial component into the matrix resin, there is also the possibility of “immobilization” of antimicrobial agents by copolymerization of an antibacterial monomer (e.g. methacryloyloxydodecylpyridinium bromide, MDPB) with other components of the matrix. In this case, during the use of the filling, the active ingredients are not being released to the oral environment, because the antibacterial monomer is covalently bound in the polymer network.

Such an antibacterial monomer, MDPB, is a compound of the antibacterial agent quaternary ammonium dodecylpyridinium bromide, and the methacryloyl group, –O–C(O)–C(CH₃)=CH₂, and acts as an inhibitor of bacteria adhesion [174]. Imazato et al. [163] have confirmed that the addition of 0.2 % MDPB inhibits the dental plaque formation, even after 3 months storage of samples in water. For obvious reasons, the inhibition zones around the samples were not observed in Kirby-Bauer tests, but *Streptococcus mutans* did not multiply under the tested samples. Subsequent studies have shown that, in contrast to chlorhexidine, the presence of antibacterial monomer does not deteriorate the mechanical properties of composites [175], does not affect the cross-linking process [176] and has little effect on color stability and water sorption [177].

Beyth et al. [178] have found that an effect similar to MDPB can be achieved with quaternary ammonium polyethylenimine (PEI) nanoparticles embedded at 1 % w/w in a clinically used bonding. These results indicate that quaternary ammonium PEI nanoparticles immobilized in resin-based materials have a strong antibacterial activity upon contact, without leaching of the nanoparticles and without compromising the mechanical properties of cured composites.

Despite certain benefits, it should be noticed that materials containing an antibacterial agent immobilized in bonding, only act against bacteria that are in direct contact with them. This contact is often worsened by natural protein adsorption on the filling surface. Additionally, in contrast to antibiotics, MDPB cannot penetrate through the walls and membrane cells of bacteria, and thus acts rather as a bacteriostatic agent and its real effectiveness is low. Probably those restrictions cause that none of these antimicrobial additives has become a component of commercial dental restoratives yet [163].
3.3.2 Addition of silver to the solid phase

A large volume of filler (75–90 % wt.) in dental materials based on dimethacrylate resins suggests theoretically that the filler, rather than matrix, will more strongly influence the final properties of the composite. It seems, therefore, that attempts to provide bactericidal function to dental composites by modifying the solid phase will be easier to perform and more effective than matrix modification.

The impressive history of the antibacterial action of silver [179–182], and its widespread usage in medicine [183], reaching back several centuries, completely justifies the attempts to introduce Ag to dental composites as well. The effective action of silver compounds in relation to oral pathogens has been confirmed [162, 184–186].

Due to the expanded, porous structure, and thus excellent sorption properties, SiO$_2$ – the most popular filler of dental composites, is an excellent base to various modifications [187]. Yamamoto et al. [188], Kawashita et al. [189] and Jeon et al. [190] have investigated various possibilities for the modification of silica by silver compounds. Actually, the mechanism of antibacterial action of Ag-modified fillers is similar to the action of antibiotics introduced into the matrix and depends on the releasing (leaching) of Ag$^+$ ions upon contact with moist oral environment. Silver blocks metabolic processes occurring in bacterial cells by reacting with –SH groups of enzymes, deactivating their catalytic action and distorting the metabolic processes. However, the antibacterial activity of Ag-modified silica is short-lasting, similarly to chlorhexidine.

The possibility of using zeolites as carriers of silver seems to be more promising. According to the theory, Ag$^+$ is released from the zeolite (exchanged) with rate controlled by the concentration of cations present in the environment. As the ionic strength of oral environment is not high, the modification of zeolites with silver would probably cause the desirable, slow release of silver ions. It potentially creates an opportunity to extend the time of effective antibacterial action. However, the silver zeolite application in dental composites requires further studies to confirm the efficacy of bactericidal action of this filler in the oral environment [191].

Yoshida et al. [192] have found that the antibacterial action of silver is not always caused by the release of Ag$^+$ ions to the environment. This situation was observed for example in the case of silver immobilized on silica gel, or zirconium phosphate – Zr$_2$(HPO$_4$)$_3$. It was suggested that, as a result of the catalytic action of silver, oxygen
is changed into active oxygen (including hydroxyl radicals) by the action of light energy and/or \( \text{H}_2\text{O} \) in the air or water only at polar surfaces, and that this active oxygen causes structural damage in bacteria.

Although silver exhibits a specific antibacterial potential, it is probably not an appropriate filler for light-cured dental composites. Silver-containing composites, besides the questionable antibacterial properties, have one major drawback – high susceptibility to discoloration, which is not acceptable for aesthetic reasons [163].

### 3.4 Polymerization shrinkage and bacteria

Suppose that...

...the tooth filling is a ball with a diameter of 2 mm (which gives a volume of approximately 4.188 mm\(^3\)) and shrinks, at the best case, 2% vol. "only" (so the filling reduces its volume by 0.084 mm\(^3\)). It means, hypothetically, that the diameter of the filling is reduced from 2 mm to 1.986 mm and the filling will move away from the cavity wall by about 7 µm. The average bacterial cell dimension is 1 µm. So...?

Whether we reduce the volumetric shrinkage from 2% to 1 or 0.5%, it is really unimportant for bacteria ... The limitation of shrinkage is not the solution. The answer is to completely eliminate shrinkage, which, at this moment, is probably a little unreal. Therefore, in the experimental part of my work I have omitted this aspect of research.
Polymeric dental fillings have revolutionized the approach to the restoration of occlusal surfaces of teeth. It turned out that it can be done not only quickly and precisely, but most of all – aesthetically. However, the total cost paid by patients using these "benefits" is much higher than the monetary price only. The truth is that dimethacrylate-based dental composites remain far behind the non-aesthetic amalgams, in relation to their polymerization shrinkage, mechanical properties and tendency to accumulate dental plaque. It results in the formation of secondary caries around the filling and, consequently, ends with a re-visit to a dental office and new expenses. The circle is vicious... although aesthetic...

The analysis of literature on dimethacrylate composites leads to a series of alarming conclusions. Lack of cooperation between dentistry and materials engineering is clearly visible. A number of different materials is produced which vary in quality and content of the inorganic phase, and therefore also in morphology. The varied morphology, in turn, results in differences in the "behavior" of composites during their use. However, there is no certainty about the real effect of size, shape and quantity of the filler on the mechanical properties of dental composites. Scientists often postulate mutually exclusive theses. Perhaps these discrepancies are linked to the fact that even different portions of the same composite paste can be highly non-homogeneous and require testing with several or even dozens of repetitions.
5. Purpose and scope of work

Analysis of the commercial materials by scanning electron microscopy (SEM) and a review of literature have revealed that dental composites based on dimethacrylate resins have a very diverse morphology. Those differences suggest that there is no knowledge about the optimal morphology which would provide the desired mechanical strength. Additionally, in the literature there is lack of information on the possible occurrence of composites with a gradient structure resulting from the use of photopolymerization to cure the samples.

The methods used to dental materials testing are also questionable, because they often require preparation of very large samples, inappropriate to the actual size of dental fillings. In addition, the research methodology does not take into account the fact, that the properties of surface layer of cured composites can be completely different than the volumetric properties which are measured in the bulk.

It seems that the production of antibacterial composites is not only possible, but also necessary. From the practical point of view, it may drastically reduce the risk of secondary caries formation around composite restorations. However, such antibacterial materials have not appeared on the dental market so far.

5.1 Aim of work

The aim of my study was an attempt to clarify how the morphology of dimethacrylate-based dental composites affects the properties of fillings made of them. I also undertook to prove the thesis that the surface layer has the greatest impact on the durability of composites and, for that reason, the current methodology of research of dental composites requires some modifications.

Due to the absence of dental composites with bactericidal function on the commercial market, I also undertook some attempts to develop my own materials, which would exhibit antibacterial activity.
5.2 Scope of work

Implementation of the aim required to take action in two directions:

1) Testing of commercially available dental composites – searching for a correlation between the size and shape of filler particles, their distribution in the resin matrix and the morphology of the surface layer of samples, and their mechanical properties: wear resistance, hardness, impact toughness and resistance to accelerated aging.

2) Based on the knowledge from the 1st stage of the researches, I have undertaken attempts to develop own dental composite based on a mixture of dimethacrylate resins: Bis-GMA and TEGDMA, with new fillers, which have not been applied before or the state of knowledge on the possibilities of their use is minimal. My attention was focused primarily on the possibility of introduction of bactericidal additives to the composites.
6. Materials and reagents

6.1 Commercial composites

Selected commercial dental composites have been studied. Summary information about these materials, obtained from the manufactures, is presented in Table 4.

Tab. 4 Commercial composites – manufacturer’s data.

<table>
<thead>
<tr>
<th>COMPOSITE</th>
<th>MANUFACTURER</th>
<th>MATRIX</th>
<th>THE TYPE OF COMPOSITE</th>
<th>TYPE OF FILLER</th>
<th>wt. % /vol. % of filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeramX</td>
<td>Dentsply DeTrey (Germany)</td>
<td>methacrylate modified</td>
<td>hybrid</td>
<td>Ba-Al-B-Si glass, nanoSiO₂</td>
<td>76/nd*</td>
</tr>
<tr>
<td></td>
<td><a href="http://www.dentsply.de">www.dentsply.de</a></td>
<td>polysiloxane</td>
<td>nanoceramic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Enamel Plus</td>
<td>Micerium spa (Italy)</td>
<td>Bis-GMA, UDMA</td>
<td>microhybrid</td>
<td>pyrogenic SiO₂ 0,04 µm, glass 0,7µm</td>
<td>75/53</td>
</tr>
<tr>
<td></td>
<td><a href="http://www.micerium.com">www.micerium.com</a></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Enamel</td>
<td>Micerium spa (Italy)</td>
<td>Bis-GMA, UDMA</td>
<td>microhybrid</td>
<td>pyrogenic SiO₂ 0,04 µm, glass 0,7µm</td>
<td>75/53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filtek P60</td>
<td>3M ESPE (USA)</td>
<td>Bis-GMA, UDMA,</td>
<td>microhybrid</td>
<td>SiO₂, ZrO₂</td>
<td>83/61</td>
</tr>
<tr>
<td></td>
<td><a href="http://www.3m.com/espe">www.3m.com/espe</a></td>
<td>Bis-EMA, TEGDMA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filtek Supreme</td>
<td>3M ESPE</td>
<td>Bis-GMA, UDMA,</td>
<td>nanofil</td>
<td>nanoSiO₂, ZrO₂/SiO₂ nanoclusters</td>
<td>78,5/nd</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bis-EMA, TEGDMA,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filtek Z250</td>
<td>3M ESPE</td>
<td>Bis-EMA, UDMA,</td>
<td>microhybrid</td>
<td>ZrO₂, SiO₂</td>
<td>80/60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bis-GMA, UDMA,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gradia Direct</td>
<td>GC (USA)</td>
<td>UDMA</td>
<td>microhybrid</td>
<td>prepolymerized SiO₂, F-Al-Si glass</td>
<td>77/65</td>
</tr>
<tr>
<td></td>
<td><a href="http://www.gcamerica.com">www.gcamerica.com</a></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>QuixFil</td>
<td>Dentsply DeTrey</td>
<td>UDMA, TEGDMA</td>
<td>microhybrid</td>
<td>Sr-Al glass, NaF</td>
<td>86/66</td>
</tr>
<tr>
<td>Tetric Ceram HB</td>
<td>Ivoclar Vivadent</td>
<td>Bis-GMA, UDMA,</td>
<td>microhybrid</td>
<td>Ba-Al-F-Si glass, YbF₃, SiO₂</td>
<td>79/58</td>
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<tr>
<td></td>
<td></td>
<td>TEGDMA</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Valux Plus</td>
<td>3M ESPE</td>
<td>Bis-GMA, UDMA,</td>
<td>microhybrid</td>
<td>ZrO₂/SiO₂</td>
<td>bd/66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TEGDMA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Admira</td>
<td>VOCO (Germany)</td>
<td>prepolymerized</td>
<td>Ormocer</td>
<td>sulfate apatite, quartz, SiO₂</td>
<td>78/nd</td>
</tr>
<tr>
<td></td>
<td><a href="http://www.voco.com">www.voco.com</a></td>
<td>polysiloxane, dimethacrylates</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*nd – no data
6.2 Homemade composites

6.2.1 Resin matrix

6.2.1.1 Reagents used in the matrix preparation

In addition to the commercial dental composites, homemade dental composites based on the mixture of dimethacrylate resins:

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Name</th>
<th>Manufacturer</th>
<th>wt. % in the matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis-GMA</td>
<td>2,2-bis-[4,4-(2-hydroxy-3-methacryloxypropoksy)phenyl] propane</td>
<td>Aldrich</td>
<td>60</td>
</tr>
<tr>
<td>TEGDMA</td>
<td>triethylene glycol dimethacrylate</td>
<td>Fluka</td>
<td>40</td>
</tr>
</tbody>
</table>

with some additional ingredients (total mass not exceeded 1.5 wt %):

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Name</th>
<th>Function</th>
<th>Manufacturer</th>
<th>wt. % in the matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>CQ</td>
<td>camphorquinone</td>
<td>photoinitiator</td>
<td>Aldrich</td>
<td>0,3–0,5</td>
</tr>
<tr>
<td>DMAEMA</td>
<td>2-(dimethylaminoethyl) methacrylate</td>
<td>co-initiator</td>
<td>Merck</td>
<td>0,8–1,0</td>
</tr>
<tr>
<td>BHT</td>
<td>2,6-di-t-butyl-p-crezol</td>
<td>inhibitor</td>
<td>Fluka</td>
<td>0,1</td>
</tr>
</tbody>
</table>

were also the objects of my study.

6.2.1.2 Preparation of the resin matrix

Bis-GMA resin (Bisphenol A glycerolate dimethacrylate, Aldrich) was poured into a crystallizer placed on a hot plate. After several minutes, lower viscosity monomer – triethylene glycol dimethacrylate (TEGDMA, Aldrich) was added in weight ratio of 4:6 and the mixture was stirred for half an hour using a magnetic stirrer. After that, appropriate quantities of camphorquinone (photoinitiator, Aldrich), BHT (2,6-di-t-butyl-p-crezol, Fluka) and DMAEMA (2-(Dimethylaminoethyl) methacrylate, Merck) were added and stirred for another 3 hrs until complete dissolution of all ingredients. Additional components were added to dimethacrylate resins in amounts not exceeding 1.6 wt. %.

For the preparation of the matrix containing nanosilver particles, the procedure was similar to that used in the case of standard matrix. Instead of classic TEGDMA resin (Aldrich), specially prepared dispersion of silver nanoparticles in TEGDMA resin (1000 ppm, Amebox Ltd., Poland) was used. The matrix was seasoned for 3 months before the use.
6.2.2 Inorganic phase

Various mineral substances were used as fillers in own dental composites. They had different sizes and shapes, and were introduced to the matrix in the form provided by the manufacturer or after surface modification (silanization).

6.2.2.1 Fillers

<table>
<thead>
<tr>
<th>Type of filler</th>
<th>Description / Chemical composition</th>
<th>Size of particles</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosil 380</td>
<td>SiO₂</td>
<td>~7 nm</td>
<td>Degussa</td>
</tr>
<tr>
<td>Arsil</td>
<td>SiO₂</td>
<td>50–100 µm</td>
<td>Z.Ch. Rudniki, Poland</td>
</tr>
<tr>
<td>5 % Si–doped hydroxyapatite (Si-HAp)</td>
<td>[Ca₅(OH)(PO₄)₃]ₓ–Si</td>
<td>&lt; 200 nm</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Nanomer² 90 L31PS</td>
<td>MMT modified with octadecylamine (15–35 wt.%) and 3-aminopropyltriethoxysilane (0.5–5 wt.%)</td>
<td>&lt;100 nm</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Nanofil SE3010</td>
<td>MMT – the basic surface treatment is a dimethyl, di(hydrogenated tallow)alkyl ammonium salt</td>
<td>&lt;10 µm</td>
<td>Southern Clay Products, Inc.</td>
</tr>
<tr>
<td>Dellite HPS</td>
<td>(Si,Al)₈(Al,Fe,Mg)₄O₂₀(OH)ₓ₋₂Xₙ·ₘ(H₂O)</td>
<td>nd</td>
<td>Laviosa</td>
</tr>
<tr>
<td>Nano-titanium dioxide</td>
<td>TiO₂</td>
<td>~21 nm</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Nano-zirconium dioxide</td>
<td>ZrO₂</td>
<td>&lt;100 nm</td>
<td>Aldrich</td>
</tr>
<tr>
<td>VST 283-600</td>
<td>Ca₃Si₃O₉ / CaO · SiO₂ surface modified</td>
<td>nd</td>
<td>Quarzwerke</td>
</tr>
<tr>
<td>Aerogel</td>
<td>SiO₂₂, [trimethylsilyloxy]–modified</td>
<td>nd</td>
<td>Cabot</td>
</tr>
<tr>
<td>Halloysite</td>
<td>Al₂Si₂O₅(OH)₄ · 2 H₂O</td>
<td>nd</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Expanded perlite</td>
<td>SiO₂, Al₂O₃, K₂O+Na₂O, MgO+CaO, Fe₂O₃</td>
<td>nd</td>
<td>ZGM Zebiec, Poland</td>
</tr>
<tr>
<td>Dibutyrylchitin</td>
<td><img src="image" alt="Dibutyrylchitin structure" /></td>
<td>nd</td>
<td>IMPiB Torun, Poland</td>
</tr>
</tbody>
</table>
6.2.2.2 Modification of filler surface (silanization process)

Selected fillers were surface modified using two silane bonding agents:

- γ-methacryloxypropyltrimethoxysilane (U–511, Unisil, Poland) 314 m²/g
- vinyltrimethoxysilane (U–611, Unisil, Poland) 527 m²/g

The suspension of nanosilver in the silane U-611 (1000 ppm, Ampeox, Poland) was also used to modify the silica surface.

The compositions of silanizing bath (No. 1÷3b) used in the modification of silica (Aerosil 380) are presented in Table 5 (the weights of particular ingredients are calculated for 10 g of filler). The amount of silane coupling agent, necessary to produce a silane monolayer on the surface of silica, was calculated based on the equation (1):

\[
\text{[%wt.]} = \frac{\text{surface area of filler [m}^2/\text{g]} \times 100 \%}{\text{coverage area of silane [m}^2/\text{g]}}
\]  

(1)

Following the literature reports about significant impact of the silanization procedure on the properties of the modified filler, I applied various silanizing baths. For example, the use of excess silane (silanizing bath 3a) resulted in an increased amount of filler in the resin matrix, but the mechanical properties of the composite were deteriorated.

According to Chen et al. [61], the introduction of an amine instead of acetic acid may enhance the hydrolytic resistance of a composite, compared with a material filled with silica silanized without an amine. Overview of the results of my studies is provided in Chapter 10.1.
Tab. 5 The compositions of silanizing baths (amounts calculated per 10 g of Aerosil 380).

<table>
<thead>
<tr>
<th>Type of silane, [g]</th>
<th>Water [g]</th>
<th>Ethanol [g]</th>
<th>Acetone [g]</th>
<th>methylene chloride [g]</th>
<th>acetic acid [g]</th>
<th>diethylamine [g]</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 U-511 12</td>
<td>125</td>
<td>125</td>
<td>x</td>
<td>x</td>
<td>0,12</td>
<td>x</td>
<td>Silane and acetic acid were added to water/ethanol solution, intensively mixed and left for 1 hr to silane prehydrolysis. After that time, silica filler was introduced. The reaction mixture was intensively stirred for 1 hr and was dried in under vacuum (temp. 110 °C for 10 hrs). Cured sample had a very low mechanical strength – easy to crush it by hands.</td>
</tr>
<tr>
<td>1a U-511 12</td>
<td>125</td>
<td>125</td>
<td>x</td>
<td>x</td>
<td>0,12</td>
<td>x</td>
<td>Procedure the same as in the 1\textsuperscript{st} case, but the filler was washed out by solvent after the drying, to remove of unreacted polysiloxanes from the surface of silica. Cured samples do not break in hands (as opposed to procedure 1).</td>
</tr>
<tr>
<td>1b U-511 5</td>
<td>124</td>
<td>124</td>
<td>x</td>
<td>x</td>
<td>1,60</td>
<td>x</td>
<td>Procedure as in 1\textsuperscript{st}, except that the time of silane prehydrolysis was 10 min. The composition of the bath was slightly changed: smaller volume of silane, higher volume of acetic acid.</td>
</tr>
<tr>
<td>2 U-511 12</td>
<td>18</td>
<td>x</td>
<td>120</td>
<td>60</td>
<td>0,37</td>
<td>x</td>
<td>Silane was introduced to the mixture of acetone, methylene chloride and water and then, during intensive stirring, acetic acid was added. The mixture was left for 1 hr (prehydrolysis of silane). After this time, the silica was introduced and mixture was stirred for 4 hrs. Drying conditions: atmospheric pressure, 110 °C, 10 hrs.</td>
</tr>
<tr>
<td>2a U-611 7,2</td>
<td>10,5</td>
<td>x</td>
<td>72</td>
<td>36</td>
<td>0,20</td>
<td>x</td>
<td>Procedure as in 2\textsuperscript{nd} bath, but different adhesion promoter was used – vinyltrimethoxysilane.</td>
</tr>
<tr>
<td>3 U-511 12</td>
<td>23</td>
<td>x</td>
<td>205</td>
<td>x</td>
<td>x</td>
<td>5</td>
<td>Silane was introduced to the mixture of acetone, water and diethylamine. The mixture was left for 5 min. (prehydrolysis of silane). After this time, the silica was introduced and mixture was stirred for 1 hr. Silica was drained on the filter using a vacuum pump and washed twice with acetone. Drying conditions: atmospheric pressure, 110 °C, 10 hrs.</td>
</tr>
<tr>
<td>3a U-511 19</td>
<td>23</td>
<td>x</td>
<td>205</td>
<td>x</td>
<td>x</td>
<td>5</td>
<td>Procedure as in 3\textsuperscript{rd} bath. Increased amount of silane (about ~60% more than calculated) has allowed the introduction of a higher amount of silica to the matrix.</td>
</tr>
<tr>
<td>3b U-611 7,5</td>
<td>14</td>
<td>x</td>
<td>123</td>
<td>x</td>
<td>x</td>
<td>3</td>
<td>Procedure as in 3\textsuperscript{rd} bath, but different adhesion promoter was used – vinyltrimethoxysilane.</td>
</tr>
</tbody>
</table>
7. Preparation of samples

7.1 Preparation of homemade composites

All composites were made based on 2 g of resin mixture. Modified filler was added in small portions and carefully grinded in an agate mortar, until the desired consistency was obtained. Grinding of a batch of composite paste lasted 1–2 hours. The composite pastes were packed in special polypropylene syringes with piston.

The list of such prepared composites, including the filler used, the filler weight, and the procedure of filler modification, is presented in Table 6.

**Tab. 6 Homemade composites.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Matrix wt. %</th>
<th>Filler</th>
<th>wt. %</th>
<th>No. of silanizing bath (Tab. 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>standard 52</td>
<td>Aerosil 380</td>
<td>48</td>
<td>2a</td>
</tr>
<tr>
<td>2</td>
<td>standard 32,5</td>
<td>Aerosil 380</td>
<td>67,5</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>standard 47</td>
<td>Aerosil 380</td>
<td>53</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>standard 62</td>
<td>Aerosil 380</td>
<td>38</td>
<td>3b</td>
</tr>
<tr>
<td>5</td>
<td>standard 47</td>
<td>Aerosil 380</td>
<td>53</td>
<td>1a</td>
</tr>
<tr>
<td>6</td>
<td>standard 40</td>
<td>Aerosil 380</td>
<td>60</td>
<td>3a</td>
</tr>
<tr>
<td>7</td>
<td>standard 37</td>
<td>MMT, Cloisite Dellite HPS</td>
<td>63</td>
<td>without modification</td>
</tr>
<tr>
<td>8</td>
<td>standard 40,5</td>
<td>MMT, Nanomer® 1.31PS</td>
<td>59,5</td>
<td>without additional modification (as supplied)</td>
</tr>
<tr>
<td>9</td>
<td>standard 20</td>
<td>MMT, Nanofil SE3010</td>
<td>80</td>
<td>without additional modification</td>
</tr>
<tr>
<td>10</td>
<td>standard 42,5</td>
<td>Arsil</td>
<td>53,1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>nanoZrO₂</td>
<td>4,4</td>
<td>without modification</td>
</tr>
<tr>
<td>11</td>
<td>standard 32,5</td>
<td>Arsil</td>
<td>35,1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wollastonite (VST 283-600)</td>
<td>32,4</td>
<td>without additional modification</td>
</tr>
<tr>
<td>Table</td>
<td>Standard</td>
<td>Composition</td>
<td>Value</td>
<td>Application</td>
</tr>
<tr>
<td>-------</td>
<td>----------</td>
<td>-------------</td>
<td>-------</td>
<td>-------------</td>
</tr>
<tr>
<td>12</td>
<td>standard</td>
<td>Arsil</td>
<td>28</td>
<td>without additional modification</td>
</tr>
<tr>
<td>13</td>
<td>standard</td>
<td>Aerosil 380</td>
<td>40,3</td>
<td>3</td>
</tr>
<tr>
<td>14</td>
<td>standard</td>
<td>Halloysite</td>
<td>20,4</td>
<td>without modification</td>
</tr>
<tr>
<td>15</td>
<td>standard</td>
<td>Aerosil 380</td>
<td>45,2</td>
<td>3</td>
</tr>
<tr>
<td>16</td>
<td>standard</td>
<td>expanded perlite</td>
<td>17,4</td>
<td>without additional modification</td>
</tr>
<tr>
<td>17</td>
<td>standard</td>
<td>Si-doped hydroxyapatite</td>
<td>15</td>
<td>without modification</td>
</tr>
<tr>
<td>18</td>
<td>standard</td>
<td>Aerosil 380 + nanoAg</td>
<td>40,5</td>
<td>3</td>
</tr>
<tr>
<td>19</td>
<td>matrix + nanoAg ~ 100 ppm</td>
<td>Arsil</td>
<td>26</td>
<td>3</td>
</tr>
<tr>
<td>20</td>
<td>standard</td>
<td>Aerosil 380</td>
<td>26</td>
<td>3</td>
</tr>
<tr>
<td>21</td>
<td>standard</td>
<td>Arsil</td>
<td>54</td>
<td>3</td>
</tr>
<tr>
<td>22</td>
<td>standard</td>
<td>SiO₂ + nanoAg (IChP)</td>
<td>2,2</td>
<td>without modification</td>
</tr>
<tr>
<td>23</td>
<td>standard</td>
<td>Arsil</td>
<td>43,6</td>
<td>3</td>
</tr>
<tr>
<td>24</td>
<td>standard</td>
<td>Dibutyrylchitin</td>
<td>11,7</td>
<td>without modification</td>
</tr>
<tr>
<td>25</td>
<td>standard</td>
<td>nanoTiO₂</td>
<td>43,6</td>
<td>3</td>
</tr>
<tr>
<td>26</td>
<td>standard</td>
<td>TiO₂ + nanoAg (Amepon)</td>
<td>11,7</td>
<td>without modification</td>
</tr>
<tr>
<td>27</td>
<td>standard</td>
<td>nanoTiO₂ + nanoAg (Amepon)</td>
<td>11,7</td>
<td>without modification</td>
</tr>
<tr>
<td>28</td>
<td>standard</td>
<td>nanoTiO₂ + nanoAg (Amepon)</td>
<td>11,7</td>
<td>without modification</td>
</tr>
<tr>
<td>29</td>
<td>standard</td>
<td>nanoTiO₂ + nanoAg (Amepon)</td>
<td>11,7</td>
<td>without modification</td>
</tr>
<tr>
<td>30</td>
<td>standard</td>
<td>nanoTiO₂ + nanoAg (Amepon)</td>
<td>11,7</td>
<td>without modification</td>
</tr>
</tbody>
</table>
**7.2 Preparation of samples for experiments**

The materials have been extruded directly into a silicon (or polypropylene) mould and their surface secured with a microscope cover glass to minimize contact with air oxygen. Then, the top surface was photo-polymerized using a light-curing unit (SmartLite PS, Dentsply DeTrey, Germany) operating in a standard mode and emitting 450–490 nm radiation with the power density of 950 mW/cm\(^2\). During the photo-polymerization, the fiber tip was in contact with microscope cover glass. The temperature on its surface did not exceed a few dozens of °C.

Recommendations of materials’ producers were taken into account when selecting the exposure time for commercial composites. The own samples were photo-polymerized for \( t = 60 \) s (6x 10-second pulse).
8. Research methodology

8.1 Nanoindentation

Mechanical properties of the surface layer of dental composites were determined with a NanoTest 600 instrument (MicroMaterials Ltd., UK). A Berkovich diamond penetrated the surface layer of material with the loading/unloading rate of \( \frac{dP}{dt} = 0.1 \text{ mN/s} \) up to the max. force of 5 mN. All the experiments were run under controlled conditions of temperature (\( T = 20 \pm 2 \text{ °C} \)) and relative humidity (60\%\). The registered data were analyzed using the method proposed by Oliver and Pharr [110].

![Berkovich’s indenter (SEM image).](image-url)
8.2 Tribology

The friction of dental composites was determined with a block-on-ring T-05 tribometer (ITeE, Poland), with a carbide ring of 35 mm diameter, rotating against a flat block sample of dental composite material. The tribometer was equipped with a multi-channel electronic PC measurement unit – Spider 8 (HBM, Germany), for data acquisition. Measurements were carried out under the sliding speed of \( v = 12 \text{ cm/s} \) and the normal load of 100 N, at ambient temperature \((20 \pm 5) ^\circ \text{C}\) and relative humidity of \(60 \pm 5\) %. Friction experiments were run for six hrs. After every hour samples were removed from the instrument and weighed to determine the abrasion of the material. Density of the examined materials was determined by means of double weighing according to PN-EN ISO 1183-1:2004 (A).

8.3 Morphology

The size and distribution of filler particles in a polymer matrix and the degree of filling at different distances from the sample surface was carried out using AFM and SEM techniques.

8.3.1 AFM

Surface morphology of composites was studied with a Metrology Series 2000 instrument (Molecular Imaging, USA). Images were collected applying contact mode (LFC), taking advantage of the differences between mechanical and tribological properties between filler and matrix. The commercial silicon cantilevers CSC 37 (Mikro Masch, Estonia) with resonant frequency of 38 kHz and force constant 0.35 N/m, operating with height and friction scale, were used at scan frequency of 4 Hz.

8.3.2 SEM

The morphology of cross-section of composites was studied with scanning electron microscope AURIGA Crossbeam Workstation (Carl Zeiss, Germany). The secondary electrons signal (SE), detected at a voltage beam of 10 keV, was used.
8.4 Impact toughness

Impact toughness of composites was studied using an instrumented Resil 5.5 Charpy Hammer (CEAST, Italy), operating with mass of 0.238 kg and initial angle of 146°, what gives impact energy of 0.98 J and working range of 1.7 kN. 10 repetitions were performed for each material.

In order to avoid the necessity to prepare large-sized samples (standard measurements are performed for bars of 17 x 10 x 4 mm dimensions), the sample holder of the instrument had to be redesigned. Crushing impact was applied instead of conventional breaking, in order to better reflect the real use conditions in the oral cavity. It allowed to carry out the measurements on small cylinder-shaped samples (l = 5 mm, d = 2 mm), similar in size to dental fillings (Fig. 18).

Fig. 18 a) sample holder, b) polypropylene sample form, c) sample for the impact toughness measurements.

8.5 Positron Annihilation Lifetime Spectroscopy (PALS)

Positron annihilation lifetime spectroscopy (PALS) is a well established experimental technique for determination of free volume in multicomponent materials and for characterization of their nanoscale porosity.

It is a nondestructive, radioactive technique in which the anti-particles of electron (positrons) from a radioactive source are injected into the studied material. In the case
of polymers some of them are trapped in regions of low electron density, which are free volume holes of 0.2–0.6 nm radius. In this volume the bound state between positron and electron, called positronium (Ps), is formed. From two spin states of Ps only orto-positronium (o-Ps) lives in vacuum for a long time (142 ns), enabling its application in further analysis. o-Ps localized in a free volume hole annihilates with an electron from molecules of a wall in significantly shorter time (in the range of several ns). This process is called "pick-off annihilation" and is the main process of Ps annihilation in polymers.

The lifetime of Ps is related to the size of free volume, whereas the signal intensity is related to the number concentration of free volume sites. The lifetime might also depend to some extent, on the chemistry of functional groups in the polymer.

Analysis of the positron lifetime spectra of polymers gives usually three (sometimes four) components, attributed to para-Ps annihilation ($\tau_1$), free positron annihilation ($\tau_2$) and orto-Ps annihilation ($\tau_3$ and $\tau_4$). The third and the fourth components differentiate regions of various material packing density, which are very often present in semi-crystalline polymers or composites. The longest lifetimes come from annihilation of o-Ps in the amorphous phase, whereas in crystalline regions they usually do not exceed 1 ns. There is a correlation between the composition of material (filler content) and the intensity of the last two lifetime components. Generally, if the longest positron lifetime is related to the ortho-positronium annihilation in the polymer matrix, its intensity (associated with the probability of the formation of o-Ps) decreases with increasing filler volume fraction, as a result of the decreasing concentration of free volume in the composite [193–196]. The four components of PALS analysis of PTFE/silica composites indicates on the presence of two distinct distributions of free volumes, associated with filler concentration. Their intensities ($I_3$ and $I_4$) strongly depend on the concentration of silica. The value of $I_3$, representing the annihilation in the solid phase, increases, whereas the value of $I_4$, associated with the polymer matrix, decreases, with the increase of filler loading.

However, not only the concentration of filler may affect o-Ps lifetime. Shorter annihilation time of o-Ps in plastic/nanosilica composites in comparison to polymer filled with glass beads was explained by facilitated diffusion of positrons from the filler particles to the polymer matrix [196]. This was confirmed by the increase of intensity of the adequate lifetime component. Intensity of the component originated from the annihilation of o-Ps into the solid phase differ from linear behaviour, e.g. due to changes to morphology/organization of filler particles with concentration.
A conventional fast-fast spectrometer with BaF$_2$ scintillators was used for acquiring positron lifetime spectra. The time resolution (FWHM) of the system was 250 ps. The positron source – $^{22}$Na, of activity 30 µCi, enveloped in 7 µm Kapton foil, was sandwiched between two samples under investigation. A typical spectrum contained more than $10^6$ counts. The obtained spectra were analyzed using the LT routine [197].

The average time of positron annihilation ($\tau_m$) was calculated based on equation (7):

$$\tau_m = I_1\tau_1 + I_2\tau_2 + I_3\tau_3 + I_4\tau_4$$

where: $\tau_1, \tau_2, \tau_3, \tau_4$ – components of positron lifetime;
$I_1, I_2, I_3, I_4$ – intensities of the components.

8.6 Surface free energy

Surface free energy of samples was determined by measuring the contact angle. Droplets of liquids with different surface energy, i.e. diiodomethane (non-polar liquid) and water (bipolar liquid), were posed on samples of cured composites. Next, the images of droplets were made and the contact angle ($\theta$) was measured (Fig. 19) using a MultiScan v. 8.08 software (Computer Scanning System).

![Fig. 19 A droplet on the sample surface in the contact angle measurement.](image)

Surface free energy ($\gamma_s$) was calculated using the Owens-Wendt method. Under this method, the total surface free energy is the sum of two components: dispersive ($\gamma^d_s$) and non-dispersive interactions, mainly polar ($\gamma^p_s$) (8).

$$\gamma_s = \gamma^d_s + \gamma^p_s$$

(8)
The dispersive component can be determined based on the equation (9):

$$
\gamma_s^d = \left[ \frac{\sqrt{\gamma_1^p \cdot \gamma_2^p \cdot (\cos \theta_2 + 1)} - \sqrt{\gamma_2^p \cdot \gamma_1^p \cdot (\cos \theta_1 + 1)}}{2 \cdot (\sqrt{\gamma_2^d \cdot \gamma_1^d} - \sqrt{\gamma_2^p \cdot \gamma_1^d})} \right]^2
$$

(9)

The value of the polar component can be calculated from the equation (10):

$$
\gamma_s^p = \left[ \frac{\gamma_1 \cdot (\cos \theta_1 + 1) - 2 \cdot \sqrt{\gamma_2^d \cdot \gamma_1^d}}{\sqrt{\gamma_1^d}} \right]^2
$$

(10)

where:

\( \gamma_1^p, \gamma_1^d, \gamma_1 \) – respectively: the polar component, the dispersive component and their sum for the bipolar liquid;

\( \gamma_2^p, \gamma_2^d, \gamma_2 \) – respectively: the polar component, the dispersive component and their sum for the non-polar liquid;

\( \theta_1, \theta_2 \) – contact angles, respectively of: the bipolar liquid and the non-polar liquid.

Surface energy and its components for liquids, needed to Owens-Wendt calculations, are as follows [198]:

<table>
<thead>
<tr>
<th>LIQUID</th>
<th>( \gamma_L^{\text{L}} ) [mJ/m(^2)]</th>
<th>( \gamma_L^{\text{d}} ) [mJ/m(^2)]</th>
<th>( \gamma_L^{\text{p}} ) [mJ/m(^2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>72,6</td>
<td>21,6</td>
<td>51,0</td>
</tr>
<tr>
<td>diiodomethane</td>
<td>50,8</td>
<td>48,5</td>
<td>2,3</td>
</tr>
</tbody>
</table>
8.7 Tests of bactericidal properties

8.7.1 Disc diffusion test (inhibition zones)

Selected bacteria were used to the disc diffusion tests: *Escherichia coli* (Gram-) – ATCC 11229, *Bacillus subtilis* (Gram+) – PL LOCK 105, *Staphylococcus aureus* (Gram+) – ATTC 6538.

Amplified bacteria were mixed at the temperature of 40 °C with the growth medium solidified with agar, were poured on Petri dishes and allowed to solidify. After 30 min. The disc-shaped samples of the cured composite with 8 mm diameter were placed on the agar. The Petri dishes were placed in a thermostat at 37 °C for 24 hrs. After this time, the images of samples were made by an optical microscope and the results were measured – the bacterial growth inhibition zone around the tested samples.

8.7.2 Fluorescence method (viability of bacteria)

The surface of test samples was prepared according to the following procedure: a sterile area of samples was covered with a suspension of *Streptococcus mutans* bacteria (5 ml). After 10 min. incubation of the samples at 37 °C, the suspension of bacteria was collected and transferred to a microscope slide. Then, bacteria were stained using 5 µl solution of bis-benzidine (100 mg/ml) in 0.1 M phosphate buffer (pH 7.4). Subsequently, the surface was covered with 2 µl of propidine iodide solution (500 mg/ml in 70 % ethanol). The samples were incubated for another 2 hrs and observed under the fluorescent microscope Olympus GX71 equipped with a digital camera DP70. Image acquisition was carried out using the analySIS DOCU software, while bacteria were counted using Image J (with the "cell counter" addition). This procedure allowed to distinguish live (blue-white color) and dead cells (purple-red color).
PART A. COMMERCIAL COMPOSITES

9. Investigation results of commercial dental composites

The research of commercial dental composites was focused primarily on finding a correlation between the morphology of materials and their mechanical properties and abrasive wear. Particular attention was devoted to the surface layer of fillings. This layer seems to be the most important, because it has direct contact with the oral environment and the processes of aging are initiated there. Additionally, it should be noticed that the parameters of surface layer seem to be responsible for the overall mechanical strength of dental fillings.

The studies described in the present Chapter, were the starting point for further work related to the attempts of developing my own dental composites.

9.1 Mechanical properties and morphology of the surface layer

Analysis of the tribological test results makes it possible to see the differences in the resistance to abrasive wear of selected commercial dental composites (Tab. 7).

<table>
<thead>
<tr>
<th>Composite</th>
<th>Loss of volume (\text{[cm}^3\text{]})</th>
<th>Loss of volume [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valux Plus</td>
<td>4.64 (\times) (10^{-2})</td>
<td>8.2</td>
</tr>
<tr>
<td>Filtek Z250</td>
<td>4.40 (\times) (10^{-2})</td>
<td>8.0</td>
</tr>
<tr>
<td>Filtek P60</td>
<td>3.87 (\times) (10^{-2})</td>
<td>6.6</td>
</tr>
<tr>
<td>Filtek Supreme</td>
<td>3.52 (\times) (10^{-2})</td>
<td>6.2</td>
</tr>
<tr>
<td>CeramX Mono</td>
<td>4.69 (\times) (10^{-2})</td>
<td>7.7</td>
</tr>
<tr>
<td>Enamel Plus</td>
<td>4.91 (\times) (10^{-2})</td>
<td>8.8</td>
</tr>
<tr>
<td>Enamel</td>
<td>4.36 (\times) (10^{-2})</td>
<td>7.6</td>
</tr>
<tr>
<td>Tetric Ceram</td>
<td>3.34 (\times) (10^{-2})</td>
<td>5.4</td>
</tr>
<tr>
<td>QuixFil Universal</td>
<td>2.42 (\times) (10^{-2})</td>
<td>4.2</td>
</tr>
<tr>
<td>Gradia Direct</td>
<td>8.82 (\times) (10^{-3})</td>
<td>1.5</td>
</tr>
</tbody>
</table>
It is worth noting however, that the relative wear volume never exceeded 10% for any of the examined composites. It seems to be a very satisfactory result, considering the applied load and the fact that it was "dry" friction.

Analysis of the abrasive wear kinetics of commercial dental composites allows observing some regularity (Fig. 20). Three composites: Filtek Supreme, Valux Plus and Enamel, exhibit a relatively small material loss in the 1st hour of friction test. This may mean that their surface has a higher resistance to abrasion compared to the bulk of the material (so-called, "skin effect") [199].

![Fig. 20 Abrasion of commercial dental composites in time.](image)

Abrasion wear kinetics of the other composites has a strongly linear character. It suggests in turn, that the abrasiveness of these materials in subsequent hours of the tribological experiment was almost identical. These results indicate that the materials belonging to the first group exhibit a surface gradient of mechanical properties. It is probably a consequence of differences in their composition and morphology. Other composites are rather homogeneous.
Similar conclusions can be drawn by analyzing the median value of friction force during the 6-hour experiments. Friction characteristics of the dental composites studied are presented on Fig. 21. To make the figures more clear only the traces of friction force in first, third and sixth hours have been presented and compared. Tribological examinations evidenced that the friction force characteristics fall, in general, into three groups:

a) when friction force equilibrates slowly. The value of friction force increases from 20 N to approx. 40–45 N during the first hour
   – Composites: Filtek Supreme (Fig. 21a), Valux Plus (Fig. 21b);

b) when friction equilibrates more rapidly. The value of friction force stabilizes already after 20–25 minutes
   – Composites: QuixFil (Fig. 22a), Filtek Z250 (Fig. 22b);

c) friction presents generally a constant value during the whole experiment
   – the composites: Filtek P60 (Fig. 23a), Tetric Ceram (Fig. 23b).
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Fig. 21 Changes to the median of friction force in time for dental composites:

a) Filtek Supreme, b) Valux Plus (during the 1<sup>st</sup>, 3<sup>rd</sup> and 6<sup>th</sup> hour of experiment).

The slowest equilibration of friction force (Fig. 21) has resulted in a relatively small loss of volume in the 1<sup>st</sup> hour of friction (Fig. 20). This indicates the presence of the surface layer, which has a slightly different character than the bulk of the material. It results in increased resistance to abrasion of the composite at the initial phase of the tribological experiment. However, the highest overall resistance to abrasion was not observed for these samples, because, on the contrary – Valux Plus exhibits the highest total wear volume among all the materials tested.

The conditions of the tribological experiment are quite severe – 6 hours of dry friction under the normal load of 100 N. If we consider this issue only in terms of the total wear volume, we could conclude that the material most resistant to abrasion is Gradia Direct, or QuixFil.

However, we should consider what, in fact, is the more important and more "representative" parameter in the assessment of the abrasive properties: the total volume loss, or volume changes in the 1st hour of friction, which indicate the properties the surface layer? In my opinion, it is definitely the latter. The treatment of fillings like any other polymer composite, can lead to misleading conclusions. Conducting the research on relatively large samples (in relation to the actual dimensions of the filling) and the analysis of properties mainly in the bulk, does not allow for the formulation of realistic conclusions. Should not the experiments be designed so that their results would correspond to reality, after all?
Fig. 22 Changes to the median of friction force in time for dental composites: a) QuixFil, b) Filtek Z250 (during the 1st, 3rd and 6th hour of experiment).
The properties of the surface layer of the material determine the behavior of a dental filling in contact with external environment. Evaluation of these properties is not easy and requires the use of more sophisticated techniques, such as nanoindentation.

Comparing the results of nanohardness measurements (Fig. 24) with the wear volume values of the examined commercial composites (Tab. 8), I have noticed a correlation between these two parameters.
Fig. 24 Nanohardness of selected dental composites (measured at the depth of approx. 500 nm).

Tab. 8 Wear loss of commercial composites.

<table>
<thead>
<tr>
<th>COMPOSITE</th>
<th>WEAR LOSS (1\textsuperscript{st} hour) [mm(^3)]</th>
<th>TOTAL WEAR LOSS [mm(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valux Plus</td>
<td>2,4</td>
<td>46,4</td>
</tr>
<tr>
<td>Filtek Z250</td>
<td>8,7</td>
<td>44,0</td>
</tr>
<tr>
<td>Filtek P60</td>
<td>8,4</td>
<td>38,7</td>
</tr>
<tr>
<td>Filtek Supreme</td>
<td>1,4</td>
<td>35,2</td>
</tr>
<tr>
<td>CeramX Mono</td>
<td>8,9</td>
<td>46,9</td>
</tr>
<tr>
<td>Enamel Plus</td>
<td>6,4</td>
<td>49,1</td>
</tr>
<tr>
<td>Enamel</td>
<td>4,5</td>
<td>43,6</td>
</tr>
<tr>
<td>Tetric Ceram</td>
<td>5,5</td>
<td>33,4</td>
</tr>
<tr>
<td>QuixFil Universal</td>
<td>6,0</td>
<td>24,2</td>
</tr>
<tr>
<td>Gradia Direct</td>
<td>1,6</td>
<td>88,2</td>
</tr>
</tbody>
</table>

The total volume loss of composites studied turned out not to be related to the nanohardness of their surface layer – no correlation was observed. However, the nanoindentation technique allows for acquiring data from the top surface of samples only, so it seemed reasonable to check whether any correlation exists between nanohardness and volume loss after the 1st hour of tribological experiments.
It seems that there is a correlation between nanohardness and susceptibility to abrasion. The harder the surface layer, the higher is the loss of volume in the 1st hour of friction. The correlation coefficient for this relationship is relatively high, $R^2 = 0.90$ (Fig. 25).

![Fig. 25 Relationship between nanohardness and wear loss after 1st hour for the dental composites studied.](image)

In the group of composites studied, there are also some exceptions to this correlation (not included in the chart). Thus, in the case of Valux Plus and Filtek Supreme, where the kinetics of wear is not a straight line, I noticed the wear volume to be smaller than it appeared from the hardness of the surface layer. As I previously mentioned, the analysis of the friction curves seems to confirm the hypothesis that the top layer of these materials is different from their bulk. Perhaps, in these cases, a different mechanism of friction occurs or other factors come into play, such as e.g. the properties of the filler.

Filtek Supreme is the only representative of the so-called "nanofil"s" (a term borrowed from the dental nomenclature). Its inorganic phase consists of silica and zirconia nanoparticles (larger particles are not present), which perhaps affects the increased resistance to abrasion of the composite surface.

Analysis of the friction force curves of Filtek Supreme and Valux Plus indicates that the lapping process is not completed within 60 min., but it extends to the following hour. In this situation, the effectiveness of the abrasion process in the analyzed time interval
is lower than for other composites. Perhaps for this reason I have not observed any correlation between the nanohardness of their surface layer and the volume loss after the 1st hour of tribological experiment. Higher abrasion resistance of the surface layer of these materials is still quite astonishing. Therefore, perhaps the roughness of the samples should be checked.

In fact, even though the classical theories of friction emphasize the crucial value of hardness (as a parameter of wear rate), in the case of polymeric materials an important role is also played by Young’s modulus (E).

The nanoindentation technique allows to register the nanohardness of a sample in parallel with the so-called reduced modulus (E*) (Tab. 9). E* is closely linked with Young’s modulus (E), which can be calculated from the equation (11) [200]:

\[
E = (1 - \nu^2) \cdot \left[ \frac{1}{E*} - \frac{1 - \nu_i^2}{E_i} \right]^{-1}
\]  

(11)

where: \( \nu \) – Poisson’s ratio of the material, \( E* \) – reduced modulus, \( \nu_i \) – Poisson’s ratio of the indenter (for the Berkovich’s diamond, \( \nu_i = 0.07 \)), \( E_i \) – Young’s modulus of the indenter (\( E_i = 1140 \) GPa).

After substituting the constants, we obtain the equation (12):

\[
E = (1 - \nu^2) \cdot \left[ \frac{1}{E*} - 8.73 \cdot 10^{-4} \right]^{-1}
\]  

(12)

**Tab. 9** Average values of reduced modulus (E*) and H/E* ratio of dental composites.

<table>
<thead>
<tr>
<th>COMPOSITE</th>
<th>E* [GPa]</th>
<th>H/E*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valux Plus</td>
<td>12.5</td>
<td>13.4 \cdot 10^{-2}</td>
</tr>
<tr>
<td>Filtek Z250</td>
<td>18</td>
<td>20.7 \cdot 10^{-2}</td>
</tr>
<tr>
<td>Filtek P60</td>
<td>18</td>
<td>23.5 \cdot 10^{-2}</td>
</tr>
<tr>
<td>Filtek Supreme</td>
<td>10.5</td>
<td>19.3 \cdot 10^{-2}</td>
</tr>
<tr>
<td>CeramX Mono</td>
<td>10.1</td>
<td>29.9 \cdot 10^{-2}</td>
</tr>
<tr>
<td>Enamel Plus</td>
<td>8</td>
<td>17.1 \cdot 10^{-2}</td>
</tr>
<tr>
<td>Enamel</td>
<td>8.5</td>
<td>17.9 \cdot 10^{-2}</td>
</tr>
<tr>
<td>Tetric Ceram</td>
<td>10.5</td>
<td>14.5 \cdot 10^{-2}</td>
</tr>
<tr>
<td>QuixFil Universal</td>
<td>12.5</td>
<td>14.8 \cdot 10^{-2}</td>
</tr>
<tr>
<td>Gradia Direct</td>
<td>6</td>
<td>8.8 \cdot 10^{-2}</td>
</tr>
</tbody>
</table>
The values of Poisson's ratios of commercial dental composites range from $v = \frac{0.25}{0.45}$. For most commercial materials, the Poisson's ratio is about 0.33 (Filtek P60 – 0.31; Filtek Z250 – 0.33; Filtek Supreme – 0.35). If we substitute these values in equation (12), we will obtain the value of Young's modulus ($E$), lower by an average of 10% from the value of $E^*$. Unavailability of data for all samples make impossible the calculations for all materials.

The Poisson's ratio of a material (assuming, that it oscillates in the limit 0.3–0.4) does not significantly affect the calculated value of Young's modulus. It can be concluded, that $E^*$ is a parameter representative in the same way as $E$ (and directly proportional to it), so – the composites, tested under the same conditions, might be compared.

In the case of commercial dental composites, the correlation between the reduced modulus ($E^*$) and the wear volume of samples (both after the 1st hour of friction, and total), was not observed. However, according to Leyland and Matthews [201], I decided to look for a correlation between the wear volume and $H/E^*$ ratio. And indeed, such a correlation does occur (Fig. 26) – the higher the $H/E^*$ ratio, the larger is the wear volume during the 1st hour of tribological experiments.

![Fig. 26](image.png)

Fig. 26 Relationship between $H/E^*$ ratio and wear loss after 1st hour for the dental composites studied.

The authors [201] have rather suggested the occurrence of inversely proportional relationship, but in the case of commercial dental composites, the points on the chart are arranged in a manner indicating that the relationship is directly proportional. It probably
indicates a much higher importance of hardness than Young's modulus in the estimation of mechanical resistance of composites (which are brittle by nature).

I also wondered whether the morphology of dental materials can affect their tribological properties. Four samples of different wear volume have been chosen to the study: QuixFil, Filtek Supreme, Filtek P60 and Enamel Plus.

The SEM photographs taken (Fig. 27–30) show the morphology of cross sections of the samples at three depths – near the surface of the cured composites, and at 50 and 100 µm from the surface. I was interested in whether the analysis of SEM images makes it possible to capture the differences between the structure of the surface layer and the bulk (mass) of material.

First of all, the analysis of SEM images indicates the existence of significant differences in the size and shape of filler particles in the composites studied.

QuixFil composite is characterized by the most altered morphology (Fig. 27), among all materials tested. The presence of large, irregular glass particles of filler, between which the smaller particles are located, has been found.

Fig. 27 SEM morphology of the cross-section of QuixFil: a) 100 µm from the surface, b) 50 µm from the surface, c) of the top surface.
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Fig. 28 SEM morphology of the cross-section of Filtek Supreme:

a) 100 µm from the surface, b) 50 µm from the surface, c) of the top surface.

Fig. 29 SEM morphology of the cross-section of Filtek P60:

a) 100 µm from the surface, b) 50 µm from the surface, c) of the top surface.
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The resistance of QuixFil (Fig. 27) to abrasion wear is the highest. The filler particles in this material are significantly different from the others, not only because of their irregular shapes, but also in sizes. Particle size distribution in the composite QuixFil has a bimodal nature. I have observed the presence of two "fractions" of filler: first one – consisting of particle size of 10 µm, and the second one – of about 1 µm.

I have also observed the presence of a particle size gradient, when moving from the surface towards the deeper parts of the material. The largest particles can be observed in the bulk (Fig. 27a), while the smallest are found right near its surface (Fig. 27c).

For Filtek Supreme and Filtek P60, the particle size distribution of the solid phase is a statistical distribution, with the highest content of particles with a diameter smaller than 0.5 µm. Filler particles in these composites are spherical. In the case of Filtek Supreme, I have observed also the presence of a particle size gradient, in moving from the surface towards the deeper parts of the material (Fig. 28). However, in this case, the subsurface layer (Fig. 28b) is characterized by the higher content of large filler particles of an average size 2.5 µm, what was confirmed also by the atomic force microscope (AFM) (Fig. 31b). Filtek P60 is definitely more homogeneous (Fig. 29).

Fig. 30 SEM morphology of the cross-section of Enamel Plus:
a) 100 µm from the surface, b) 50 µm from the surface, c) of the top surface.
Among all the commercial materials tested, Enamel Plus exhibits the highest wear volume (Tab. 6). SEM images show that dimensions of filler particles in this composite are very small (average size about 0.7 µm). Additionally, Enamel Plus is the most homogenous (Fig. 30).

Juxtaposition of the tribological results and the images of dental composites revealed that the composites in which filler particles are diverse in shapes and sizes exhibit the highest wear resistance. Bimodal morphology promotes better packing of solid particles in the matrix. Small particles come into the spaces between large particles, like a wedge. In this way, the relative movement of large filler particles is blocked. Small particles, highly packed and immobilized between large particles, do not "leak out" (to the friction zone). It seems to be a privileged situation, resulting in increased mechanical strength of dental composites (including their resistance to abrasion).
9.2 Impact toughness

Representative, previously selected samples of commercial dental composites (QuixFil, Filtek P60, Enamel Plus) were also subjected to impact toughness testing. I expected that the differences in morphology, leading to different behavior of these materials during the tribological test, will affect also the behavior of the composites during impact measurements.

Composite samples, having the form of 4 mm height and 2 mm of diameter rods, were polymerized through the thin microscopic slide using the standard procedure (see Chapter 8.2).

Impact toughness of the composites was studied using an instrumented Resil 5.5 Charpy Hammer (CEAST, Italy). In order to enable the analysis of small specimens, sample holder of the instrument had to be redesigned. Crushing impact was applied instead of conventional breaking, in order to better reflect the real use conditions in the oral cavity – Figure 32. Each time 10 samples were measured, out of which 6 with the closest results were taken for further analysis.

![Fig. 32 Scheme of the sample holder: 1 – horizontal frame, 2 – sample, 3 – vertical frame [140].](image)

Table 10 presents the parameters of impact toughness for the dental composites studied. Magnitude of the median was calculated for maximum dissipated force ($F_{\text{max}}$), time needed to reach $F_{\text{max}}$ ($t$), and energy absorption ($E$) during impact test. Figure 33 presents changes of force and energy vs. impact time, registered for the composites studied.
Tab. 10 Impact toughness parameters for the dental composites studied.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>t [ms]</th>
<th>( F_{\text{max}} ) [N]</th>
<th>( E ) [mJ]</th>
<th>Vol. % of filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>QuixFil</td>
<td>0.227</td>
<td>413.7</td>
<td>62.3</td>
<td>66</td>
</tr>
<tr>
<td>Filtek P60</td>
<td>0.248</td>
<td>389.7</td>
<td>56.7</td>
<td>61</td>
</tr>
<tr>
<td>Enamel Plus</td>
<td>0.257</td>
<td>368.9</td>
<td>55.5</td>
<td>53</td>
</tr>
</tbody>
</table>

Fig. 33 Force and energy vs. impact time curves for a) QuixFil, b) Filtek P60, c) Enamel Plus.
The significant scatter of experimental data set for dissipated force and absorbed energy, for the series of samples made of one material, generally confirm the heterogeneous nature of polymer dental composites.

An increase in the filler loading, together with non-uniform size distribution of its particles, make the energy absorbed by composite material higher, simultaneously shortening the time needed to reach the dissipated force maximum (see data for QuixFil Universal). The difference in energy absorbed by sample made of Filtek P60 and Enamel GE2 materials is insignificant. It can be the result of the same spherical shape and only a slight difference in the size distributions of their hard phase particles. Varying filler content does not seem to play any role in the energy-absorbing ability of the materials.

The implementation of ten repetitions for each material tested, showed the existence of considerable discrepancies in numerical values. Such a large diversity of the parameter values pointed out the highly heterogeneous nature of the dental composites (even those from one batch). Even more, it is worth considering the validity of preparation of such large samples (according to the standard [93]), made from more than one syringe of the composite. In fact, each batch of a commercial material may be completely different from others, so the preparation of samples from several batches seems to be completely pointless.

Although the standard for the impact testing of plastics does not include the possibility to perform the tests on samples other than rectangular bars, the solution proposed by me seems to be much more congruent with the nature and specificity of dental fillings. The experiments carried on smaller samples, i.e. with similar dimensions to the actual size of a filling, create the possibility of testing a huge number of samples from one batch of composite, without wasting large amounts of material. In my opinion, it is justified – not only practically but also economically.
9.3 Studies of ageing in lactic acid.

Despite the fact that the standard of dental composites for the reconstruction of occlusal surfaces of teeth [93] does not take the ageing test into account, it seemed reasonable to carry out such analysis.

The study was carried out to determine how (and whether) the oral environment affects the mechanical parameters of the fillings. The ageing tests are carried out for any other polymer materials, and indicate the important role of ageing factors in the changing (modification) of the mechanical resistance of materials during their use. From this point of view, it is also reasonable to perform-ageing experiments for dental composites.

In order to determine the influence of ageing on the properties of the commercial composites studied, I have prepared an aqueous solution of lactic acid of 1% concentration (pH 4.5–5). The selection of lactic acid as a medium for research was dictated by the fact that it is one of the main compounds formed in the oral cavity from carbohydrates by cariogenic bacteria. In extreme cases, like in disease states, pH of oral cavity may even fall down to 4.

Five randomly selected commercial composites have been tested: QuixFil, Filtek Z250, Filtek Supreme, Mono CeramX and Admira.

First, samples were placed in the 1% lactic acid for 7 days to check whether the ageing medium itself has any influence on the properties of composites – whether the storage of samples in the lactic acid causes the leaching of components from cured samples. Previous studies [202] have shown that dental materials are prone to detaching the filler particles from the matrix, as a result of ageing in different media (e.g. artificial saliva).

Thus, the samples were placed inside the solution of lactic acid (at 37 °C) and weighed after 72 hrs and after one week. The mass losses of the samples were converted on their volume losses (Tab.11).
As I supposed, ageing in lactic acid did not significantly influence the change in volume of dental composites. A small volume loss could be observed only for QuixFil. A 1 % solution of lactic acid is a rather non-aggressive medium and is not capable of swelling of dental composites.

Subsequently, the aged samples were subjected to the tribological tests. Figure 34 presents the total wear volume before and after 72 hours of ageing in lactic acid.
Samples subjected to aging in lactic acid exhibited a slightly different abrasiveness, than virgin samples (Fig. 34). In three cases: QuixFil, CeramX Mono and Admira, an improvement in the abrasion resistance of samples after storage in lactic acid was noticed. In one case (Filtek Supreme) I observed a slightly higher wear volume of the sample after aging, whereas for Filtek Z250 there was no change. It can be suspected that for the first four samples, the physical or chemical modification of their surface layer due to ageing has occurred. It resulted in a different behavior of materials during tribological tests. Perhaps, in some cases, these changes should be considered as "negligible", but the study of Admira composite showed a decrease in wear by up to 5 vol. %.

It seemed reasonable to compare the wear of composites during the first hour of tribological measurements with changes of nanohardness of surface layer, before and after ageing (Fig. 35). The relative % of changes was calculated based on equation (13):

\[
x = \frac{x_a - x}{x} \cdot 100\%
\]

where: \(x, x_a\) – values of the hardness/volume parameter for non-aged and aged samples, respectively.

![Fig. 35 Changes of wear volume (1st hour of friction) and changes of nanohardness – differences between virgin and aged samples.](image-url)
Negative values indicate a decrease in the hardness/abrasive wear of samples aged in lactic acid, whereas positive values indicate that the aged sample shows a higher hardness/abrasion, than the sample-stored under normal conditions.

Thus:

A) in two cases: Filtek Supreme and Filtek Z250, ageing in lactic acid caused a slight increasing of nanohardness and wear volume;

B) in the case of Admira and CeramX Mono composites I noticed a lower wear volume after ageing, together with the lowering of nanohardness of the surface layer.

These changes confirm my earlier hypothesis, that the higher the hardness of the surface layer, the higher is the volume loss of a material during the first hour of tribological experiments (see Fig. 25).

Additionally, the materials within each group (A or B, respectively) contain the same matrix. In the first case (group A), the matrix is a mixture of dimethacrylate resins: Bis-GMA, UDMA, Bis-EMA and TEGDMA, in the second case (group B) – methacrylate-modified polysiloxane. It suggests that the behavior of the material in the oral environment is not dictated by the nature and content of the inorganic phase, but rather by the chemical composition of the matrix.

And, to prove this hypothesis – the QuixFil composite (based on one another "set" of resins: UDMA and TEGDMA) behaves quite differently from the others. In this case, the increase of nanohardness of the surface layer is accompanied by the lower wear volume. In addition, QuixFil exhibits the highest volume loss during the storage in lactic acid (Tab. 11). Probably the most intense leaching of material components takes place here. Perhaps, in the matrix of QuixFil, the amount of TEGDMA resin is too large (non-stoichiometric) and unreacted oligomers are leached by lactic acid. Then, the large particles of glass filler are uncovered and the hardness of the surface layer increases. Simultaneously, the filler particles get closer to each other due to polymerization shrinkage and a coherent, "solid" layer of ceramic is created on the top surface. The presence of such a layer may be responsible for the reduction of wear volume. However, I have no sufficient evidence to confirm this hypothesis.
9.4 Conclusions of the investigation of commercial dental composites

Despite the continuous development of novel dental materials, the mechanical parameters of commercial dental composites are still worse than the properties of human enamel. In the mechanical sense, they are also a long way behind amalgams. The fact, that batches of commercial composite significantly differ between one another, is also quite surprising and makes it difficult to formulate general conclusions about the actual properties of dental materials. Scientists are trying rather to invent new compositions, instead of unifying the existing ones. This way each sample of dental filling is different and it cannot be assigned the general properties of a composite it is made of, as those are only determined by measurements "in bulk".

The next question is why the produced composites have such a diverse morphology? And, whether the manufacturers consider the influence of such a crucial factor as the internal structure of the material on the final mechanical strength of the composite?

It seems that certain types of morphology are privileged – like the presence of varied filler particles in the matrix (bimodal composite – small and large particles only, without the medium size). The obtained results suggest that we should look for the optimal morphology, i.e. which allows for efficient packing of the filler in the matrix space, resulting in improved mechanical resistance.

The top layer, treated somewhat offhandedly so far, should be an important aspect of research of dental composites. In practice, being in contact with the oral environment, it is largely responsible for the real behavior of the tooth filling. In the light of my research, the surface layer is often quite different in nature than the bulk composite. Such a gradient of cross-linking is most probably the result of the use of photo-polymerization technique for curing fillings [138].
PART B. HOMEMADE COMPOSITES

10. Results of the investigations of homemade dental composites

10.1 Silanization process. The influence of silanization on tribological properties.

Due to the hydrophilic nature of the surface of siliceous fillers, their homogeneous dispersion in the mass of polymer constitutes a significant problem. The method which overcomes this limitation is the modification of silica particles by organosilanes, which make the filler surface hydrophobic, and additionally – due to their bifunctional nature – provide the chemical bonding between the modified silica and the resin matrix.

During the silanization process, not only the choice of an appropriate type and amount of silane adhesion promoter, but also the procedure of modification is important: the silanizing bath composition (types of solvents, the presence of water or other additives catalyzing silane hydrolysis process in the reaction medium), the time of silane hydrolysis, and even the drying conditions of modified silica (pressure, temperature). It implies differences in the final properties of composite materials (mostly mechanical), but the most significant differences are visible at the initial stage of sample preparation – the grinding of the composite paste.

The filler behaves differently, depending on the type and amount of silane used and on the composition of the silanizing bath. Generally, in the case of modification of silica by vinyltrimethoxysilane (U-611) (Fig. 36), the compatibilization of the resin is difficult, due to the smaller affinity of silane functional groups for the dimethacrylate resins. Such modified silica is less "willingly" combined with a matrix. We do not observe the effect of the formation of a paste at the early stage of the composite grinding. The viscosity of the composite does not seem to change despite the increasing volume of the solid phase.
This effect disappears when more filler is added, but the final form and consistency of such a composite is slightly different than in the case of filler modification by 3-methacryloxypropyltrimethoxysilane (U-511). The composite give the impression of "inconsistency", and after exceeding of 40 % wt. of filler, it begins to stratify and crumble. It behaves similarly when confectioned longer than a few months, which makes it unsuitable for long storage.

When Aerosil 380 silica is modified with U-611, it is possible to introduce a smaller amount of filler to the resin matrix (Tab. 12) than in the case of modification with the standard silane bonding agent – 3-methacryloxypropyltrimethoxysilane (U-511). A single vinyl group at the end of the silane chain is not able to form stable chemical bonds with the resin molecules, resulting in the lack of matrix-filler interaction. It weakens the internal structure of the material. Maybe, the breaking of double bonds in the vinyl group during the exposure to light irradiation, which supports the process of linking, would be possible, but this effect is probably overridden by the "privileged" lack of matrix-filler connection, which reduces the filler content, and may consequently lead to lower mechanical strength of a dental composite.
More interestingly, the use of excess silane (Tab. 5, silanization 3b, 60% more silane in a mixture than the amount calculated) allows the introduction of higher amount of filler (Tab. 12, Composite 6), but the mechanical strength of the composite is deteriorated.

The application of bath 1 (Tab. 5) made the preparation of specimens for mechanical testing impossible. The mechanical strength of cured composite was too low and the prepared samples could be crushed in the hand. The composite containing silica modified according to the procedure 1b behaved similarly. Probably, too high acidity of the silanizing bath reduced the silanization process efficiency. Although I managed to prepare a composite paste containing 50 wt% of filler, it was impossible to prepare a satisfactory specimen for the tribological test.

Tab. 12 Silanizing bath and content of filler in homemade composites.

<table>
<thead>
<tr>
<th>Composite</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Enamel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content of filler [wt.%]</td>
<td>48</td>
<td>68</td>
<td>53</td>
<td>38</td>
<td>53</td>
<td>60</td>
<td>53</td>
</tr>
<tr>
<td>Type of silane</td>
<td>U-611</td>
<td>U-511</td>
<td>U-511</td>
<td>U-611</td>
<td>U-611</td>
<td>U-611</td>
<td>A-174 (U-511)</td>
</tr>
<tr>
<td>No. of silanizing bath</td>
<td>2a</td>
<td>2</td>
<td>3</td>
<td>3b</td>
<td>1a</td>
<td>3a</td>
<td>no data</td>
</tr>
</tbody>
</table>

The modification of silica by 3-methacryloxypropyltrimethoxysilane (U-511) looks quite different. There are at least three different possibilities to bind this silane with the surface of silica (Fig. 37): a) via hydrogen bonding between the silanol group of the U-511 silane and hydroxyl groups on silica surface (Fig. 37A), b) via additional hydrogen bonding of the carbonyl group with hydroxyl groups (Fig. 37B), or/and c) the formation of a multilayer silane structure of on the silica surface (Fig. 37C).

This silane adhesion promoter provides a strong chemical bonding of silica, via silane, with resin particles by the presence of functional methacryloxy group at the end of the silane chain.
Silica modified with U-511 exhibited a different behavior compared to dimethacrylate matrix than the filler modified with U-611, which was already clearly visible at the initial stage of preparation of composite pastes. In the first case, the filler merged with the resin matrix immediately, which was reflected in the formation of a homogeneous paste of gradually increasing viscosity. And finally, a highly uniform mixture of the desired viscosity was obtained. The final stage of grinding is the moment when the composite begins to separate from the walls of mortar and no longer stick to the tools. Manual grinding of the composite makes it possible to capture this moment, because the filler is added gradually in small portions (about 0.2 g) and each time it is thoroughly homogenized for several minutes. The higher the filler volume in the matrix, the longer is the time it should be homogenized. Only in this way it is possible to obtain the adequate dispersion of silica in the matrix.

The amount of filler that can be introduced into the matrix is obviously limited. My experience suggests that the tolerance is small – exceeding the "acceptable" amount of filler (required for the proper consistence of composite) by up to 1 % by weight can result in obtaining the cohesionless, "fragile" composite paste. On the other hand – too small amount of filler renders the composite sticky, which can be considerably troublesome in clinical practice.
According to the literature, commercial composites generally contain 70 and more wt. % of the inorganic phase. Such filler content was unreachable in own composites, even if silica was modified by U-511 silane. The probable reason of this situation is that I used the nanometer-sized silica of high surface area, which exhibits higher activity with respect to the matrix.

The introduction of filler modified by the silanizing procedure 3 (Tab. 5) to the matrix caused 15 wt. % lower filler content (Tab. 11, Composite 3) than the silanizing procedure 2 (Tab. 11, Composite 2). Such a big difference was quite surprising, because both silica and silane used for modification 2 and 3 were the same.

This difference naturally raises the question which of these procedures is better – the addition of acetic acid ("standard") and drying of silica under atmospheric pressure (procedure 2), or the addition of amine (as a catalyst of the silane prehydrolysis) and drying the filler under vacuum (procedure 3).

Chen et al. [61] have analyzed the IR spectra of silica modified with different silanizing baths. They found that the addition of 2 % n-propylamine to the silanizing bath significantly increased the coupling effectiveness of 3-methacryloxypropyltrimethoxysilane. The free silanol absorption peak at 3740 cm\(^{-1}\) disappeared, which means that the free silanol band has been eliminated (silane-silica bonding is practically 100 %). The application of amine, instead of "standard" acetic acid, as a silanization promoter, should be then considered.

The effectiveness of amines depends on their basicity, as well as their spatial structure. Aromatic amines are poor promoters because of their low basicity (pK\(_A\) = 5) compared to aliphatic amines (pK\(_A\) = 10–11). Primary amines, especially n-propylamine, are the most efficient in the silanization reaction, probably because of the absence of steric hindrance. Thus, diisopropylamine and diisobutylamine containing bulky side chains attached to the nitrogen atom are much less efficient. Silanization in the presence of tertiary amines may undergo a different reaction mechanism, and in spite of their high basicity, their effectiveness is low.

The near-infrared spectra of silica silanized with 3-methacryloxypropyltrimethoxysilane in cyclohexane with n-propylamine as a promoter, showed an absorption peak at 4630 cm\(^{-1}\), because of the C=C bond of the methacrylate groups present on the surface. This peak disappeared after the polymerization of silanized silica with methyl methacrylate, which means that few, if any, carbon-to-carbon double bonds
remained after cross-linking. It confirmed that silanized silica does co-polymerize with methyl methacrylate under slow-reaction conditions. However, it is not certain to what extent this copolymerization would take place using fast-curing conditions and with paste reactants of high viscosity [61].

Following the Chen’s study, I performed the IR spectra of silica modified with U-511, using different silanizing baths – with acetic acid (silanization 1 and 2), and diethylamine (3 and 3a) – Figure 38. The IR spectra analysis revealed no significant differences between the silica modified with different silanizing baths.

![Fig. 38 FTIR spectra of Aerosil 380 silica modified with different silanizing baths.](image)

However, it turned out that the modification of Aerosil 380 in the presence of diethylamine increases the abrasion resistance of the composites (Fig. 39). The excess of silane in silanization bath (3a, Composite 6) makes possible the introduction of larger amounts of filler to the matrix, but the wear volume significantly increases (by about 5 %) – Fig. 39. The abrasion kinetics of the Composite 6 is also the most similar to the commercial composite Enamel’s kinetics. It should be added here, that the choice of this commercial material as a reference sample was dictated by the presence of silica as a filler. Additionally, among all the commercial composites tested, Enamel is characterized by the most
homogeneous morphology. I expected that it would be the most similar morphologically to my own composites.

The tribological tests have shown that the Composites 4 and 5 are characterized by the lowest wear volume. These materials have similar characteristics of wear, in spite of the silanization of silica with two different silanes (Composite 4 – "vinyl" silane, and Composite 5 – "methacrylate" silane), and obtaining different contents of filler (respectively – 38 % and 53 % by weight).

One important detail should be pointed out here – in the presence of diethylamine and the appropriate amount of silane, I obtained the composites of relatively high resistance to abrasion (samples 3 and 4). The Composite 4, containing silica modified with vinyltrimethoxysilane (silanizing procedure 3b), exhibits low wear volume, despite the low filler content (38 wt. %). It was similar to the composite modified with the standard U-511 silane (composite 5). The influence of the presence of amine on the wear of composites is marked more strongly for vinyltrimethoxysilane than for silane U-511. Therefore, it could be said that the silica modification with vinyltrimethoxysilane (U-611) can be as effective as silanization with 3-methacryloxypropyltrimethoxysilane, if only we apply the appropriate silanizing bath, e.g. with the addition of amine.
Table 12 and Figure 39 indicate that there is no correlation between the hard phase content and the wear volume of dental composites, which only confirms the age-old rule of "quality over quantity". Therefore, the final mechanical properties of dental composites are connected not so much with the content of filler, but most of all – with the effectiveness of its modification (its quality), providing a strong filler-matrix interaction.

Nanohardness of the surface layer of the homemade composites achieves much lower values (about 100 MPa) than the commercial composites. At the same time, my samples seem to be more homogeneous – their nanohardness reaches similar values in the entire measuring range, with only slightly decreasing values when moving towards deeper parts of the material (Fig. 40). The commercial composites exhibit the gradient of hardness – the significant reduction of hardness with increasing nanoindentation depth.

![Fig. 40 Relationship between nanohardness and indentation depth of the composites studied.](image)

The results of nanoindentation measurements may point at a more homogeneous cross-linking of own composites. Perhaps, it is related to lower filler content, allowing the light beam to penetrate into deeper parts of the samples. The Composite 2 exhibits a different behavior, similar to the commercial composites. Its nanohardness is twofold higher than of the other own materials and strongly decreases with moving from the surface toward the interior part of the sample. The wear resistance of the composite 2 is the lowest.
Additionally, the sample broke during removal from the apparatus holder after second hour of tribological test, which indicates its poor mechanical resistance.

Sample 2 is characterized by the highest content of filler (68 wt. %). Hence, the hardness of its surface layer is increased. Additionally, such a high content of filler particles of nanometric size can be a barrier to the photons and hinder the deeper cross-linking. That would explain the increased fragility of the sample and the lower hardness of deeper parts of material.

The application of silanizing procedures, both 1 and 2 (and their "variations"), makes it difficult to obtain the samples of satisfactory mechanical properties. However, the acetone washing after drying of silica filler allows to remove most of the polysiloxanes and loosely adsorbed silane from the surface of Aerosil (silanizing procedure 1a). It makes possible to obtain a composite of high resistance to abrasion (composite 5). In light of my research, however, the use of small amounts of amines (instead of acetic acid) in silanizing baths seems to be more preferable.

10.2 Composites containing layered fillers

The satisfactory mechanical properties of different polymer composites containing fillers of layered structure (the montmorillonite-type fillers) led me to the question whether it is possible to use this kind of filler in the dimethacrylate-based dental composites.

The experiments were conducted on three types of aluminosilicates:

- Dellite® HPS (MMT Na+, unmodified)
- Nanomer® I.31PS (nanoclay modified with octadecylamine (15–35 wt.%) and 3-aminopropyltriethoxysilane (0.5-5 wt.%))
- Nanofil SE3010 (the basic surface treatment is a dimethyl-di(hydrogenated tallow)alkyl ammonium salt).

However, all attempts of introducing the layered filler into dimethacrylate resin have failed.

In the case of Dellite HPS (Composite 7), no binding of the filler with the resin matrix during grinding was observed. The problem is probably the hydrophilic nature of the montmorillonite surface and its incompatibility with the dimethacrylates. I attempted to silanize the filler, but it also did not bring the expected results. Although about 63 wt. % of Dellite HPS filler could be introduced to the resin matrix, the composite took a dark green
color (which made the cross-linking practically impossible). Additionally, the composite paste was incoherent and hardened after a month of seasoning in the syringe.

Other aluminosilicates behaved similarly. Organofilization did not significantly affect the possibility of their chemical binding with dimethacrylates. The content of Nanomer I.31PS in the resin matrix reached 60 % by weight (Composite 8), while the Nanofil SE3010 filled the matrix up to 80 wt. % (Composite 9). However, both compositions were incoherent and dark (brown-green) (Fig. 41). Their depth of curing was very small, and the samples were soft enough to scratch (Fig. 41a). Extrusion of the materials to the silicon mold after a month of seasoning in a syringe was problematic, and the preparation of the samples to the mechanical testing was not possible.

![Fig. 41](image)

**Fig. 41** The images of samples from stereoscopic optical microscope:

a) Composite 8, b) Composite 9.

At this moment, I think that any attempts to introduce such a large quantities of filler of such a high refraction coefficient to the dimethacrylate matrix, appear to be pointless.
10.3 Properties of composites containing other mineral fillers

Due to the fact that all attempts to introduce a non-modified fillers to the dimethacrylate matrix were unsuccessful, and that obtaining of desired morphology requires a combination of at least two fillers of different particle sizes, all the subsequent compositions were compounded using the microparticulate Arsil silica modified by 3-methacryloxypropyltrimethoxysilane and mineral additives (of nanometer-sized mainly) or nanosilica Aerosil 380 and micrometer-sized mineral filler (Tab. 13). Only the use of this combination of fillers made it possible to produce composites of satisfactory consistency. It turned out that the silanized silica may act as a factor ensuring the cohesion, even though the unmodified filler, theoretically completely incompatible with the resin matrix, is present.

Tab. 13 List of homemade composites containing silica and different mineral additives.

<table>
<thead>
<tr>
<th>No. of Composite</th>
<th>Type of silica</th>
<th>Type of additional filler</th>
<th>Total amount of filler [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Arsil</td>
<td>nano-zirconium dioxide</td>
<td>57,5</td>
</tr>
<tr>
<td>11</td>
<td>Arsil</td>
<td>wollastonite (VST 283-600.)</td>
<td>67,5</td>
</tr>
<tr>
<td>12</td>
<td>Arsil</td>
<td>aerogel</td>
<td>52,0</td>
</tr>
<tr>
<td>13</td>
<td>Aerosil</td>
<td>halloysite</td>
<td>60,5</td>
</tr>
<tr>
<td>14</td>
<td>Aerosil</td>
<td>expanded perlite</td>
<td>62,5</td>
</tr>
<tr>
<td>15</td>
<td>Arsil</td>
<td>Si-doped hydroxyapatite</td>
<td>59,5</td>
</tr>
</tbody>
</table>
Among all proposed compositions (Tab. 13), only the material containing halloysite did not exhibit the satisfactory optical properties. This mineral was chosen because of its interesting morphology. The results show that halloysite crystals exhibit euhedral lamellar, tubular or needle-like morphologies (Fig. 42a,b) and it could be an alternative to fibrous fillers. However, the brown color of the composite hindered its cross-linking, and the preparation of samples for further testing was unrealizable. Thus, the composite with halloysite behaved similarly to the samples containing other types of aluminosilicates.

![Fig. 42 SEM images (10000x): a) halloysite, b) Composite 13 containing halloysite, c) wollastonite.](image)

The analysis of the wear volume indicates that own materials do not differ significantly from commercial composites (Fig. 43). The graph illustrating the kinetics of wear includes (for comparison) the best, in terms of abrasion resistance, commercial material – Filtek Supreme.
Among the own composites studied, the highest wear resistance was exhibited by the samples 11 and 14, containing surface-modified wollastonite and expanded perlite, respectively. In the literature I could not find any mention regarding the possibility of using such fillers in dental composites. Especially wollastonite, which is a commonly and naturally occurring silicate, seems to deserve special attention, because of its interesting morphology (Fig. 42c) and the possibility of its silanization.

Nanohardness of the surface layer of own composites (Fig. 44) was measured according to the same procedure, which has been proposed for commercial samples. The cured composites were tested every time in seven places on the surface. The surface layer of material was penetrated with a Berkovich indenter with the loading/unloading rate of $dP/dt = 0.1$ mN/s up to the max. force of 5 mN.
The nanohardness is reversely proportional to the square of the indentation depth. The experimental data for dental composites are arranged in an exponential curve (Fig. 44), which can be described by the simplified equation (14):

$$H = \frac{1.95 \cdot 10^5}{h^2}$$

where: $H$ – nanohardness [MPa], $h$ – indentation depth [nm].

The Filtek Supreme composite posed the highest resistance to the Berkovich indenter. Its indentation depth varied from 450 to 650 nm, with the average nanohardness of about 650 MPa. The nanohardness of own composites was significantly lower than hardness of commercial samples, achieving the lowest value for the composite 12 (~ 85 MPa), and the highest in the case of composite 11 (approximately 465 MPa). It is probably connected with the summary content of filler – the highest for the composite 11 containing wollastonite, and the smallest for the aerogel-containing composite (sample 12). Generally, materials containing various fillers and with different filler contents should not be compared between themselves. Different chemical nature and varied surface areas suggested that searching for correlation between the content of the solid phase and the nanohardness is probably not the best solution.
Undoubtedly, supplementation of the research with model composites, differing only in the degree of filling, would be useful. However, such experiments have been conducted earlier and, as expected, they indicated that a higher filler content causes a higher microhardness of the composites [205].

In my opinion, dental composites are very inconvenient objects for any mechanical testing, because such a wide variety of fillers of different nature impede the formulation of general conclusions. It is quite obvious that the increase in silica content will increase the hardness of the material and the increase in filler particle size causes a similar effect [205]. The only questions are whether these findings can also be applied to other types of fillers, and whether it is possible to draw general conclusions about the effects of the inorganic phase (its amount and particle size) on the mechanical properties of hybrid dental materials, containing at least two kinds of filler of completely different nature.

During the preparation of own composites, I focused on obtaining the desired consistency, rather than on introducing a particular amount of filler(s) to the resin matrix. Moreover, in contact with dimethacrylate resin, the varied fillers behaved quite differently. It was therefore hard to predict the amount of unmodified filler which could be introduced to the resin matrix. However, I still made an attempt to compare the composites between themselves.
10.3.1 Morphology of the composites containing mineral fillers

The morphology of own composites (Composites 10–15) was imaged by the scanning electron microscope (Fig. 45). I was primarily interested in the dispersion and distribution of filler in resin matrix.
The analysis of the SEM images proves that the homogeneity of own composites is satisfactory. Dispersion of filler in the matrix is good – the unfilled areas are not observed.

Good distribution of fillers in the resin matrix indicates that process of preparation of own composites was carried out correctly, despite being made by hand, in a mortar, without any mechanical support. Satisfactory dispersion and distribution of the filler is probably the result of grinding of small portions of composite components. Filler was added gradually, in small quantities (approximately 0.2 g) and each time homogenized painstakingly for several minutes before adding the next portion.
The composites containing nano-zirconium dioxide (Fig. 45a), surface-modified aerogel (Fig. 45c) and Si-doped hydroxyapatite (Fig. 45f), are characterized by the morphology similar to commercial materials containing nanofillers [206]. The silanized silica appears in clusters, into which additional fillers incorporate themselves. Due to the similar chemical nature and spherical shape of particles, it is hard to assess how mineral fillers are distributed in the matrix resin.

The addition of irregularly shaped filler particles gives different images. Wollastonite, perlite and halloysite are characterized by relatively large, spindle-shaped particles, which are clearly visible on the SEM images. The size of particles of wollastonite (Fig. 45b) and perlite (Fig. 45e), ranges from a few to over a dozen microns and they are embedded between silanized silica agglomerates. Thus, the composites containing such fillers have a quite disordered structure, which is similar to the morphology of dental composites containing whiskers [64, 65]. If we assume that both wollastonite and perlite behave in a manner similar to the fibrous fillers, the morphology of materials 11 and 14 explains their increased resistance to wear (just as it has been observed for dental composites containing whiskers [65, 69]).
10.4 Positron Annihilation Lifetime Spectroscopy (PALS) of dental composites

Two commercially available resin composite formulations: Filtek Supreme and Gradia Direct, and two homemade composites (Composite 15 and 16) were the objects of examinations. The materials were selected for their significantly different morphologies and filler contents – Table 14.

The characteristic lifetimes $\tau_i$ are calculated as the mass centers of peaks, and the intensities $I_i$ as the related areas under the peaks. In the case of the dental composites studied, four peaks appeared in the obtained lifetime distributions. Discrete components of positron lifetime have been found. The first one, located close to $\tau_1 \approx 130$ ps, originates from the annihilation of para-Ps. The second one at $\tau_2 = 360–410$ ps, comes from the annihilation of free positrons. The third one, present at $\tau_3 = 890–1870$ ps, probably comes from the more densely packed regions of polymer in a composite. The fourth peak, at $\tau_4 = 2110–3370$ ps, corresponds to o-Ps annihilation in the main part of polymer matrix. The results of PALS analysis are given in Table 15.
Tab. 15 Parameters of PALS analysis for the dental composites studied.

<table>
<thead>
<tr>
<th>Kompozyt</th>
<th>( \tau_2 ) [ns]</th>
<th>( I_2 ) [%]</th>
<th>( \tau_3 ) [ns]</th>
<th>( I_3 ) [%]</th>
<th>( \tau_4 ) [ns]</th>
<th>( I_4 ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtek</td>
<td>0.410 ±0.003</td>
<td>60.0 ±0.9</td>
<td>1.303 ±0.016</td>
<td>16.0 ±0.9</td>
<td>2.534 ±0.071</td>
<td>11.7 ±0.7</td>
</tr>
<tr>
<td>Gradia</td>
<td>0.385 ±0.011</td>
<td>51.0 ±1.2</td>
<td>1.008 ±0.085</td>
<td>18.2 ±0.9</td>
<td>2.111 ±0.086</td>
<td>14.7 ±1.5</td>
</tr>
<tr>
<td>15</td>
<td>0.357 ±0.010</td>
<td>61.0 ±1.4</td>
<td>0.893 ±0.090</td>
<td>12.0 ±1.1</td>
<td>2.220 ±0.048</td>
<td>18.7 ±1.2</td>
</tr>
<tr>
<td>16</td>
<td>0.393 ±0.004</td>
<td>62.2 ±3.6</td>
<td>1.867 ±0.049</td>
<td>22.3 ±0.9</td>
<td>3.370 ±0.180</td>
<td>6.1 ±1.3</td>
</tr>
</tbody>
</table>

Based on the above analysis (Tab. 15) one can notice that Gradia Direct differs significantly from other composites in the value of \( I_2 \). The small deviation from the average value of \( \tau_2 \) for the composites studied is also observed for Composite 15. Lower value of the intensity of the second component reflects more difficult conditions for self annihilation of free positrons, and is likely to originate from some morphological constraints present in the highly filled composite. Contrary to other materials studied, Composite 15 represents a morphology which facilitates annihilation of free positrons, e.g. due to the decrease of micropore size present in the material.

However, the most important and fortunately the most distinct are the differences concerning \( \alpha \)-Ps annihilation, represented by the third and fourth component. The annihilation taking place in the filler-matrix interphase, being relatively similar between commercial composites, becomes completely different for the homemade materials. Composite 16 is characterized by much higher concentration of free volumes, additionally of bigger size in comparison not only to Composite 15, but to other materials studied as well. Similar tendency is followed by free volumes present in polymer matrix. This time however, Composite 16 revealed the lowest concentration of free volumes, but of the largest size. Composite 15 exhibited the highest concentration of free volumes in polymer matrix, of dimensions similar to the commercial composites.
The smallest value of $\tau_4$, together with higher value of $I_4$ obtained for Gradia Direct in comparison to Filtek Supreme, probably result from different polymer resins being applied as composite matrices. The UDMA molecule, which constitutes the matrix of Gradia Direct, is smaller and has a higher concentration of double bonds than Bis-GMA, the basic component of Filtek Supreme matrix [1]. Therefore the former resin exhibits the highest crosslink density and is able to form stronger networks. Some characterization, made for comparison between dimethacrylate resins is presented in Table 16 [20].

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>$M_w$</th>
<th>Concentration of double bonds [mol/kg]</th>
<th>Limiting degree of conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis-EMA</td>
<td>540</td>
<td>3.70</td>
<td>52.2</td>
</tr>
<tr>
<td>Bis-GMA</td>
<td>512</td>
<td>3.90</td>
<td>39.0</td>
</tr>
<tr>
<td>UDMA</td>
<td>470</td>
<td>4.25</td>
<td>69.6</td>
</tr>
<tr>
<td>TEGDMA</td>
<td>286</td>
<td>6.99</td>
<td>75.7</td>
</tr>
</tbody>
</table>

The matrix in Composite 15 and 16 is the same – the mixture of Bis-GMA and TEGDMA resins. However, higher value of $\tau_4$ for Composite 14 means probably that the polymer network in this sample has lower crosslink density. Because of the same kind of polymer matrix and the same time of light curing, the difference most likely be explained by the addition of silver nanoparticles to Composite 16. They worsened the conditions of polymerization by changing the color and transparency of material, making the polymer matrix less dense.

Reasons for the differences in $\tau_3$ between the composites studied are related not only to filler loading, but also depend on morphology of the materials and interphase interactions. SEM morphology of the composites was analyzed in order to correlate the images with values of the third and the fourth component of positron annihilation (o-Ps annihilation) for the materials (Fig. 46).
II. EXPERIMENTAL PART

B. HOMEMADE COMPOSITES

\[
\begin{align*}
\tau_3 &= 1.30 \text{ ns}, \quad I_3 = 16 \%, \\
\tau_4 &= 2.53 \text{ ns}, \quad I_4 = 11.7 \%
\end{align*}
\]

\[
\begin{align*}
\tau_3 &= 1.01 \text{ ns}, \quad I_3 = 18.2 \%, \\
\tau_4 &= 2.11 \text{ ns}, \quad I_4 = 14.7 \%
\end{align*}
\]

\[
\begin{align*}
\tau_3 &= 0.89 \text{ ns}, \quad I_3 = 12 \%, \\
\tau_4 &= 2.22 \text{ ns}, \quad I_4 = 18.7 \%
\end{align*}
\]

\[
\begin{align*}
\tau_3 &= 1.87 \text{ ns}, \quad I_3 = 22.3 \%, \\
\tau_4 &= 3.37 \text{ ns}, \quad I_4 = 6.1 \%
\end{align*}
\]

Rys. 46. SEM cross-section morphology of the composites studied: a) Filtek, b) Gradia, c) 15, d) 16 in comparison with 3	extsuperscript{rd} and 4	extsuperscript{th} components of positron lifetime.

Although the filler loading of Composite 16 is only 54 wt. %, the material exhibits the highest \(\tau_3\) and \(I_3\) values. The analysis of SEM images (Fig. 46d) does not give any simple explanation. Probably all solid phase particles in this composite form big, loose agglomerates, infiltrated and separated by tiny layers of polymer. It explains the lowest values of \(I_4\) in this case. Free volumes seldom appear in the polymer matrix, but if they are there, their dimensions are large (the highest value of \(\tau_4\)).

Images of commercial composites exhibit a significantly different morphology from the homemade ones. The former show bimodal size distribution of filler particles (for Gradia Direct particles additionally vary in shape), whereas the latter present solid phase particles organized in loosely packed big agglomerates. SEM analysis confirms that the degree of particle packing for Composite 15 is significantly higher in comparison to Composite 16 (Fig. 46 c,d). Also the separation layers between agglomerates are bigger for the latter. This is reflected by the parameters of PALS analysis. Probably the morphology of homemade composites in reality looks like it is presented schematically in Figure 47.
PALS provides information on size and concentration of free volumes in polymer matrix and in polymer-filler interphase. Based on the analysis it is possible to estimate crosslink density or compare the quality of polymer-filler interactions.

PALS together with the SEM analysis proved to be useful experimental techniques for determination of dental composites morphology. Based on the analysis of time and intensity of o-Ps annihilation it was possible to differentiate composites, previously selected due to their different mechanical and tribological properties. In my opinion, only the application of both these techniques allows for the precise characterization of morphology of dental materials with such a high filler content.

11. Attempts of production of antibacterial dental composites

Dental composites based on dimethacrylate resins are characterized by the smallest resistance to bacteria action. It is incomparably worse than the resistance of amalgams, or glass ionomers and results in the formation of secondary caries around composite fillings.

In the light of the literature review, the issue of development of dental composites for permanent fillings, which could have the bactericidal properties, appears to be an important task, though still little explored. Although attempts have been made of incorporation into the resin matrix of fluorine compounds, or antibiotics that could be released from fillings and act as biocides, to this moment no antibacterial composite has been elaborated yet. In this line, I have made attempts to develop such a composite material.

11.1 Preparation of composites containing antibacterial additives

Arsil silica (Z.Ch. Rudniki, Poland) modified with U-511 (Unisil, Poland) was the basic filler. Besides Arsil, different potentially antibacterial additives have been applied:

- SiO$_2$ with nanosilver (SiO$_2$+nAg), 32000 ppm (synthesized in the IChP, Warsaw, Poland).
- dibutyrlychitin (DBC) – synthesized by IMPiB, Torun, Poland;
- nano-titanium dioxide (nTiO$_2$) (Aldrich)
- nanosilver on titanium dioxide (TiO$_2$+nAg), 1000 ppm Ag (Amepon, Poland)
- nanosilver on nanotitanium dioxide (nTiO$_2$+nAg), 1000 ppm Ag (Amepon, Poland)
- nanosilver on silica Arsil (AR+nAg), 1000 ppm (Amepon, Poland)
- nanosilver on silica Aerosil 380 (AE+nAg), 1000 ppm Ag (Amepon, Poland)

The list of composites containing antibacterial additives, including the volume of individual components, is presented in Table 17. In order to compare the materials, this time I decided to introduce similar amounts of antibacterial additive (10–15 wt. %).
II. EXPERIMENTAL PART

B. HOMEMADE COMPOSITES

Tab. 17 Homemade composites containing antibacterial additives.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Type of antibacterial additive</th>
<th>Amount of additive [wt. %]</th>
<th>Amount of Arsil [wt. %]</th>
<th>Mass of matrix [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>SiO$_2$ + nAg</td>
<td>2,2</td>
<td>54,0</td>
<td>43,8</td>
</tr>
<tr>
<td>19</td>
<td>SiO$_2$ + nAg</td>
<td>0,4</td>
<td>56,5</td>
<td>43,1</td>
</tr>
<tr>
<td>20</td>
<td>DBC</td>
<td>11,7</td>
<td>41,4</td>
<td>46,9</td>
</tr>
<tr>
<td>21</td>
<td>nTiO$_2$</td>
<td>12,2</td>
<td>43,6</td>
<td>44,2</td>
</tr>
<tr>
<td>22</td>
<td>TiO$_2$ + nAg</td>
<td>11,7</td>
<td>41,4</td>
<td>46,9</td>
</tr>
<tr>
<td>23</td>
<td>nTiO$_2$ + nAg</td>
<td>11,7</td>
<td>41,4</td>
<td>46,9</td>
</tr>
<tr>
<td>24</td>
<td>nTiO$_2$ + nAg</td>
<td>1,1</td>
<td>53</td>
<td>45,9</td>
</tr>
<tr>
<td>25</td>
<td>AR + nAg</td>
<td>14,1</td>
<td>36,0</td>
<td>49,9</td>
</tr>
<tr>
<td>26</td>
<td>AE + nAg</td>
<td>14,6</td>
<td>26,8</td>
<td>58,6</td>
</tr>
<tr>
<td>&quot;0&quot;</td>
<td></td>
<td>–</td>
<td>–</td>
<td>50,1</td>
</tr>
</tbody>
</table>

For samples 18 and 19 the reduced amount of bactericidal additive was applied, because the concentration of nanosilver on the filler surface was very high (32000 ppm). Unfortunately, this filler had such an intensive dark color, that even the reduction of SiO$_2$+nAg amount to about 0.4 wt %., changed the color of the composite paste to dark gray, which persisted after the curing (Fig. 48b).

![Fig. 48 Images of samples from stereoscopic optical microscope: a) Composite 18, b) Composite 19.](image-url)
11.2 Disc diffusion tests of homemade composites.

Selected cured composites in form of flat discs with a diameter of 8 mm were subjected to the diffusion test. In this method, after incubation of selected strains of bacteria on Petri dishes containing the samples deposited on a growth medium, the size of the zone of bacterial growth inhibition around the materials is estimated. If the sample exhibits a bactericidal action, we observe a "brightening" (an inhibition zone) around the sample (as in Fig. 49), indicating no bacterial growth. The larger the zone of inhibition, the higher is the bactericidal potential of material.

![Fig. 49](image)

**Fig. 49** An example of a sample exhibiting bactericidal properties (here: vulcanizate of natural rubber).

Unfortunately, none of the homemade composites showed antibacterial action. The disc diffusion experiments showed no presence of inhibition zones of bacterial growth around the own dental composites tested (Fig. 50).

![Rys. 50](image)

**Rys. 50** Action of homemade composites against different bacteria (no inhibition zones).

However, it seems that this method does not allow a full evaluation of antibacterial properties of dental composites. Disc diffusion tests give some results only if materials contain a biocidal substance which is released to the environment. It is more likely that in the case of own samples such a process does not occur, because the antibacterial agents are immobilized in the bulk of the material or on its surface.
These studies do not provide full knowledge of the bactericidal properties of dental materials also due to the type of bacteria used. The most common strains of Gram- (E. coli) and Gram+ (B. subtilis, S. aureus) bacteria were applied, but none of them is a standard inhabitant of the oral cavity. Therefore, the test of bactericidal properties had to be supplemented with the fluorescence analysis, which allows to quantify the viability of bacteria in direct contact with the samples tested.

11.3 Viability of *S. mutans* bacteria on the surface of samples.

*Streptococcus mutans* is widely recognized as the main etiological agent of dental caries [145]. It is obvious, therefore, why the usage of this strain in studies of bactericidal properties of dental composites is the most reasonable.

The same set of samples was tested as previously, only Composite 18 of small cure depth was replaced by Composite 10 which contains an addition of nanozirconia. I was interested in whether other nanoparticles, such as nano-ZrO$_2$, may exhibit bactericidal properties.

In addition, the Aerosil 380 modified with the dispersion of nanosilver in vinyltrimethoxysilane (1000 ppm, Amebox) was introduced to the resin matrix. The final content of nanoAg in the Composite 16 was approximately 100 ppm. The suspension of nanosilver in the TEGDMA (1000 ppm, Amebox) was used to prepare the matrix with a concentration of 100 ppm of nanosilver (according to the procedure described in Section 1.2.2.2), which then was filled with silanized Arsil – Composite 17. The broad spectrum of samples containing nanosilver introduced to the composition in different ways, and other additives "suspected" of antibacterial properties, was subjected to fluorescence tests.

The results of viability of bacteria on the surface of the samples studied are presented in Table 18.
Tab. 18 Viability of bacteria on the surface of homemade composites.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Type of antibacterial additive</th>
<th>Amount of additive [wt.%]</th>
<th>AVERAGE VIABILITY [%]</th>
<th>stand. deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>nZrO₂</td>
<td>4,4</td>
<td>87,30</td>
<td>2,53</td>
</tr>
<tr>
<td>16</td>
<td>AE+nAg* (*own modification)</td>
<td>13,5</td>
<td>97,38</td>
<td>0,81</td>
</tr>
<tr>
<td>17</td>
<td>matrix with nAg</td>
<td>4,8</td>
<td>91,51</td>
<td>1,56</td>
</tr>
<tr>
<td>19</td>
<td>SiO₂+nAg</td>
<td>0,4</td>
<td>82,77</td>
<td>2,85</td>
</tr>
<tr>
<td>20</td>
<td>DBC</td>
<td>11,7</td>
<td>89,28</td>
<td>2,32</td>
</tr>
<tr>
<td>21</td>
<td>nTiO₂</td>
<td>12,2</td>
<td>76,60</td>
<td>3,15</td>
</tr>
<tr>
<td>22</td>
<td>TiO₂+nAg</td>
<td>11,7</td>
<td>47,82</td>
<td>11,64</td>
</tr>
<tr>
<td>23</td>
<td>nTiO₂+nAg</td>
<td>11,7</td>
<td>74,74</td>
<td>2,87</td>
</tr>
<tr>
<td>24</td>
<td>nTiO₂+nAg</td>
<td>1,1</td>
<td>77,13</td>
<td>5,40</td>
</tr>
<tr>
<td>25</td>
<td>Ar+nAg</td>
<td>14,1</td>
<td>86,57</td>
<td>4,75</td>
</tr>
<tr>
<td>26</td>
<td>AE+nAg</td>
<td>14,6</td>
<td>67,40</td>
<td>3,95</td>
</tr>
<tr>
<td>“0”</td>
<td></td>
<td>–</td>
<td>98,30</td>
<td>1,15</td>
</tr>
<tr>
<td>CONTROL</td>
<td>(incubation on a coverglass)</td>
<td></td>
<td>98,92</td>
<td>0,17</td>
</tr>
<tr>
<td>NEGATIVE CONTROL</td>
<td>(incubation on a coverglass with 95% ethanol)</td>
<td></td>
<td>0,14</td>
<td>0,1</td>
</tr>
</tbody>
</table>

In all cases, the decline in populations of S. mutans in contact with the surface of samples tested was observed. Definitely the worst effect was observed for Composite 16 and 17, where I introduced nanosilver from solutions myself. Already at the stage of sample preparation I had doubts whether such a "homemade" modification would be effective. The nature of the silanization process excludes in principle the possibility of chemical binding of nanosilver to the surface of silica. It is probable that washing the filler with acetone after silanization removed a part of adsorbed nanosilver. On the other hand, in the case of Composite 17, after a month seasoning of matrix in a glass bottle, probably the sedimentation of nanoparticles took place and at the bottom of the bottle I observed a black precipitate. It is well known that making a lasting and stable dispersion of nanoparticles in a solvent is a crucial and the most difficult issue in the preparation of nanosilver solutions. The suspension of nanoAg in TEGDMA (Amepox) was stable,
but at the stage of matrix preparation at elevated temperature, it was likely to lose its stability. In this case, despite thorough mixing of the matrix just prior to grinding the composite paste, probably a lower amount of nanosilver was introduced to the composite, and consequently its effectiveness against the *S. mutans* was lower.

The viability of bacteria on the surface of reference sample "0" was similar to the CONTROL. It confirmed that microparticulate silica did not act as an antibacterial agent.

The composites containing additives which individually show no antibacterial activity, exhibited the smallest bactericidal action (Fig. 51). It should be added, that the presence of dibutyrylchitin in this set of samples is no coincidence. DBC is known for its high biocompatibility and ability to support regeneration of damaged tissue, so it is a bioactive factor [207]. In this context, the concept of introducing dibutyrylchitin to the dimethacrylate resin (or using it as a “primer”) seemed interesting and reasonable, nevertheless DBC-contain composite exhibited a poor antibacterial activity.

![Fig. 51 Viability of *S. mutans* in contact with composites: "0", 17, 20, 10.](image)

Comparing the addition of silica fillers containing nanosilver (Fig. 52 – blue bars), it is noticeable that the combination of two types of nanoparticles: silicon dioxide and silver,
acts the most effectively. The synergistic action of these two components certainly occurs. The preliminary studies indicated that viability of bacteria in contact with the material containing only 53% by weight of silanized Aerosil (AE, Composite 3) was 82% (Fig. 52 – the first bar). Perhaps the addition of pure Aerosil 380 nanosilica works antibacterially to some extent, but its high content in Composite 3 indicates that it is less efficient than nanozirconia.

Composite 22, containing nanoparticles of silver deposited on the surface of titania, exhibited the strongest bactericidal activity. In this case, over 50% did not survive the contact with the surface of the cured composite (Fig. 52). More interestingly, the addition of nanosilver on nano-titanium dioxide (Composite 23 and 24) resulted in only a slight improvement in bactericidal activity, and the observed effect was not specifically dependent on the amount of the additive. Despite the tenfold reduction of nTiO₂+nAg in the Composite 24 (relative to 23), only a slight increase in average viability of bacteria was observed. What is more, I suspect that in the case of nanosilver deposited on nano-titanium dioxide, it is rather the carrier itself that exhibits antibacterial properties.
The addition of pure nTiO₂ (Composite 21) caused a similar effect as the introduction of a similar amount of nTiO₂, but with nanosilver (Composite 23).

Absence of the composite with pure microparticulate TiO₂ in this set of samples follows from the fact that it is widely used as a pigment in dental composites, and generally does not exhibit antibacterial properties. Moreover, the bactericidal effect (even if it occurs) will be unnoticeable because really small quantities of TiO₂ are applied.

Nevertheless, I have noticed the best bactericidal effect against *S. mutans* for the sample containing nanosilver deposited on microparticulate titanium dioxide (Composite 22). Such a combination of fillers works much more efficiently than nanosilver deposited on nano-sized titanium oxide (Composite 23). Geometric considerations may correspond to such differences. It seems that microTiO₂ rather serves a carrier function (just as in the case of catalysts), on which the nanosilver particles are deposited, and it is a more effective system than deposition of nanosilver on nanoTiO₂. In the latter case, probably both kinds of nano-sized particles "compete" with each other, leading to a situation where one deactivates the other. It would explain why we do not observe a synergistic effect in this case.

### 11.4 Surface free energy of dental composites

Although the analysis of the viability of bacteria on the surface of samples gives clear numerical values, the reason for antibacterial action (or inaction) of the examined composites is not obvious. It is well known that the adhesion of a biofilm to the tooth surface is the key factor responsible for the formation of dental caries. The first stage of the biofilm formation is the overlap between the acquired pellicle and the tooth surface [147, 148]. I decided to check whether the viability of bacteria may, in any way, be correlated with the values of surface free energy of composites. I made the assumption that the more hydrophilic is the surface of composite, the more favorable should be the formation of bacterial biofilms. In the literature I have not found such a juxtaposition of experimental data. In the context of adhesion of bacteria to the surfaces or dental fillings, it is rather roughness which is considered as a determinant of the rate of material surface colonization by bacteria. This study
did not include a measurement of roughness. I looked for a correlation between the size of the polar component of the surface free energy and the activity of composites against *S. mutans*.

The total surface free energy ($L$) and its components: dispersive ($L_d$) and non-dispersive ($L_p$), were measured according to the procedure proposed by Owens and Wendt [198]. To obtain a complete set of data, surface energy measurements of the homemade samples were supplemented by two commercial composites: Gradia Direct (GR) and Filtek Supreme (FS) – Table 19.

| Composite | $L$ [mJ/m$^2$] | $L_d$ [mJ/m$^2$] | $L_p$ [mJ/m$^2$] | % $L_d$ | % $L_p$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;0&quot;</td>
<td>57,22</td>
<td>34,46</td>
<td>22,76</td>
<td>60,2</td>
<td>39,8</td>
</tr>
<tr>
<td>20</td>
<td>52,60</td>
<td>35,96</td>
<td>16,64</td>
<td>68,4</td>
<td>31,6</td>
</tr>
<tr>
<td>21</td>
<td>49,47</td>
<td>42,41</td>
<td>7,06</td>
<td>85,7</td>
<td>14,3</td>
</tr>
<tr>
<td>22</td>
<td>54,88</td>
<td>36,41</td>
<td>18,47</td>
<td>66,3</td>
<td>33,7</td>
</tr>
<tr>
<td>23</td>
<td>50,43</td>
<td>38,54</td>
<td>11,89</td>
<td>76,4</td>
<td>23,6</td>
</tr>
<tr>
<td>24</td>
<td>55,63</td>
<td>33,90</td>
<td>21,73</td>
<td>60,9</td>
<td>39,1</td>
</tr>
<tr>
<td>25</td>
<td>52,79</td>
<td>40,59</td>
<td>12,20</td>
<td>76,9</td>
<td>23,1</td>
</tr>
<tr>
<td>26</td>
<td>51,18</td>
<td>40,10</td>
<td>11,08</td>
<td>78,3</td>
<td>21,7</td>
</tr>
<tr>
<td>GR</td>
<td>45,72</td>
<td>34,42</td>
<td>11,30</td>
<td>75,3</td>
<td>24,7</td>
</tr>
<tr>
<td>FS</td>
<td>47,10</td>
<td>33,55</td>
<td>13,55</td>
<td>71,2</td>
<td>28,8</td>
</tr>
</tbody>
</table>

Generally, the surface energy of polymers ranges between 20–60 mJ/m$^2$. The values obtained for the dental composites are very high. They reach the upper limit, which suggest good adhesive properties [208]. Total surface energy of the commercial composites is slightly lower than of the homemade ones. Perhaps it is connected with higher filler content in the former samples (in both cases it is about 78 % by weight).

The highest surface free energy is exhibited by the reference sample "0", containing silanized silica Arsil only. The addition of other fillers causes a slight decrease in the total surface free energy. However, the total surface energy is not as important as the values of its
components. They determine the energetic character of the surface of dental composites and indicate on possible behavior of composite fillings in contact with the moist oral environment.

The percentage shares were calculated of the dispersive and polar component in the total surface free energy of the examined composites (Fig. 53).

![Graph showing the percentage shares of polar and dispersive component in total surface energy of composites studied.](image)

**Fig. 53** Shares [%] of polar and dispersive component in total surface energy of composites studied.

The comparison between sample "0" and Composite 23 and 24 makes it possible to determine the effect of addition of nanosilver deposited on nanoTiO$_2$ on the surface hydrophilicity of composites. It turns out that its small amount – about 0.04 g (1 wt. %) – Composite 24, does not cause visible changes in the surface energy. However, if we introduce a tenfold higher amount of nanoTiO$_2$+nAg (Composite 23, 11 wt. %), the share of dispersive component increases, decreasing the hydrophilicity of the material. It is also clear that nanoTiO$_2$ (Composite 21) causes a greater increase in the value of $L_d$ than titanium dioxide with nanosilver (samples 22–24). Probably titania is therefore an active hydrophobizing agent.

The influence of particle size of titanium dioxide, which is the carrier of nanosilver, on the values of dispersive and polar component, is also visible. In the case of microparticulate TiO$_2$ (Composite 22) the surface energy does not change as significantly as
in the case of nanoparticulate titanium dioxide (Composite 23). Perhaps a different character of nanosilver-dioxide interactions plays a role, or the process of cross-linking proceeds in a different way, depending on the size of the carrier.

A similar effect could not be observed in the case of silica fillers. Samples containing silica (including commercial GR and FS) are generally slightly more hydrophobic than the others. However, both for microparticulate (Composite 25) and nanoparticulate silica (Composite 26), similar values of the dispersion component are observed, only slightly higher for nanosilver on Aerosil.

The results of surface free energy measurements do not correlate with the values of the average viability of bacteria on the composite materials. It seems to confirm the supposition that not only physical and chemical properties of dental composites determine the viability of bacteria in contact with the material. The optimal hydrophilicity seems to be not as important as the effectiveness of bactericidal activity of the additive. From a theoretical point of view, an antibacterial agent works, when bacteria are in direct contact with them, so the hydrophilic nature of the sample surface would be desirable. On the other hand, too low hydrophobicity may cause too strong adhesion of bacteria to the surface of the filling, rendering the antibacterial agent ineffective.
11.5 Mechanical properties of composites containing antibacterial additives

11.5.1 Measurements of curing depth

Satisfactory results of bactericidal properties of homemade dental composites provoked the necessity of checking their mechanical properties. I wanted to verify whether the samples containing bactericidal additives could be applied in clinical practice.

Especially the composites containing titanium oxides aroused some doubts. Specific optical properties of TiO$_2$, which is capable of absorbing light, caused the problems with cross-linking of composites. The curing depth of Composites 21–23 after 60-second exposure was too small (especially Composite 22 – Tab. 20), to apply these restoratives in dental practice.

<table>
<thead>
<tr>
<th>Composite</th>
<th>&quot;0&quot;</th>
<th>20</th>
<th>21</th>
<th>22</th>
<th>23</th>
<th>24</th>
<th>25</th>
<th>26</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curing depth [mm]</td>
<td>4.7</td>
<td>4.0</td>
<td>0.8</td>
<td>0.4</td>
<td>0.8</td>
<td>1.8</td>
<td>2.0</td>
<td>1.6</td>
</tr>
</tbody>
</table>

10-fold reduction of the nanosilver content on nano-titanium dioxide (Composite 24) increased the depth of cure from 0.8 mm to the acceptable value of 1.8 mm. Probably the reduction of the amount of titania with nanosilver in Composite 22 will allow to achieve a similar result, without losing the very good bactericidal properties.
11.5.2 Nanoindentation

Mechanical properties of the surface layer of dental composites were determined with a NanoTest instrument (Tab. 21). Composite 22 is not present in this set of samples due to the small depth of curing.

<table>
<thead>
<tr>
<th>Composite</th>
<th>average indentation depth [nm]</th>
<th>average hardness, H [Mpa]</th>
<th>Reduced modulus, $E^*$ [MPa]</th>
<th>$H/E^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;0&quot;</td>
<td>1160</td>
<td>211</td>
<td>4005</td>
<td>0,0527</td>
</tr>
<tr>
<td>20</td>
<td>1265</td>
<td>185</td>
<td>3170</td>
<td>0,0583</td>
</tr>
<tr>
<td>21</td>
<td>1245</td>
<td>227</td>
<td>2480</td>
<td>0,0915</td>
</tr>
<tr>
<td>23</td>
<td>1275</td>
<td>171</td>
<td>3545</td>
<td>0,0482</td>
</tr>
<tr>
<td>24</td>
<td>1375</td>
<td>154</td>
<td>2745</td>
<td>0,0561</td>
</tr>
<tr>
<td>25</td>
<td>1190</td>
<td>198</td>
<td>3990</td>
<td>0,0496</td>
</tr>
<tr>
<td>26</td>
<td>1205</td>
<td>202</td>
<td>3555</td>
<td>0,0568</td>
</tr>
</tbody>
</table>

The top layer of the Composite 21 containing nanoTiO$_2$ is the hardest one (~230 MPa) and significantly differs from the others in terms of $H/E^*$ ratio – its value is almost twice higher than for other materials. This phenomenon partially depends on the presence of nanoparticles of titanium dioxide strongly absorbing light radiation. In effect, the effective cross-linking of the surface layer of Composite 21 occurs, affecting the increased surface hardness of the material (and the surface only). Shallow depth of cure obtained in this case indicates that after cross-linking of surface layer the penetration of radiation quanta in the deeper parts of the material may be blocked by nanoTiO$_2$ particles. Similar effect is also observed for samples 23 and 24. In these cases, the tenfold reduction in amount of nanotitanium dioxide in the Composite 24 results in lowering the hardness of the surface layer by about 10%.

The addition of nanosilver changed the color of samples from cream to brown. The higher the amount of nanosilver in a material, the darker was the color and the curing process was more difficult. Thus, the reduction in cross-linking density and curing depth have
been observed, which was also reflected in a lower, compared to the reference material "0", the hardness of the surface layer of composite 23–26 (Tab. 21).

11.5.3 Tribological experiments

Samples containing antibacterial additives have also been tested on tribometer to determine the friction characteristics and abrasive wear. Unfortunately, in the case of composites containing titanium oxides, the depth of cure was too small to prepare the samples. Although I tried to apply the technique of layered curing (irradiation of thin layer, covering it with another layer of material and re-irradiation), but this treatment did not bring the expected results either. The samples were too brittle and it was impossible to mount them in the apparatus and apply the load.

On the other hand, in the case of Composite 26, containing nanofillers (Aerosil 380 with nanosilver), only one-hour measurement was performed, as after that time the sample broke.

For samples "0", 20, 25, the stabilization of friction force was observed after about 20 minutes (Fig. 54). Their tribological characteristics were similar to the commercial Filtek Z250 (see Chapter 8.1, Fig. 22). However, the average value of the friction force of samples "0" and 20 in the first hour of tribological measurements was higher than in the following hours, and reached the value ~ 80 N (in the first hour), and ~ 60 N (in the last hour). Tribological characteristics of Composite 25 were the most similar to the commercial material Filtek Z250, except that the friction force finally reached the value of about 20 N less.
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Fig. 54 Changes to the median of friction force in time for dental composites:

a) Composite "0", b) Composite 20, c) Composite 25, d) Composite 26 (during the 1\textsuperscript{st}, 3\textsuperscript{rd} and 6\textsuperscript{th} hour of experiment).
The friction coefficients ($\mu$) for each hour of tribological experiment were calculated based on the analysis of median of friction force (Tab. 22).

**Tab. 22 Coefficients of friction and relative wear of samples.**

<table>
<thead>
<tr>
<th>Composite</th>
<th>&quot;0&quot;</th>
<th>20</th>
<th>25</th>
<th>26</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time [h]</td>
<td>$\mu$</td>
<td>relative mass loss [%]</td>
<td>$\mu$</td>
<td>relative mass loss [%]</td>
</tr>
<tr>
<td>1</td>
<td>0.52</td>
<td>0.33</td>
<td>0.73</td>
<td>0.71</td>
</tr>
<tr>
<td>2</td>
<td>0.54</td>
<td>0.20</td>
<td>0.58</td>
<td>1.45</td>
</tr>
<tr>
<td>3</td>
<td>0.41</td>
<td>0.31</td>
<td>0.58</td>
<td>1.79</td>
</tr>
<tr>
<td>4</td>
<td>0.54</td>
<td>0.16</td>
<td>0.59</td>
<td>1.60</td>
</tr>
<tr>
<td>5</td>
<td>0.54</td>
<td>0.06</td>
<td>0.46</td>
<td>0.98</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>0.23</td>
<td>0.52</td>
<td>0.86</td>
</tr>
<tr>
<td>median of $\mu$ /or $\Sigma$ wear</td>
<td>0.52</td>
<td>$\Sigma 1.29 %$</td>
<td>0.58</td>
<td>$\Sigma 7.39 %$</td>
</tr>
</tbody>
</table>

Despite the introduction of similar amounts of bactericidal additives to the resin matrix, the wear volumes of the composites studied were different. It indicates that it is not the quantity but rather quality of antibacterial additive (their physical and chemical nature, and compatibility with the resin matrix) is the most important factor. This phenomenon is clearly visible in the case of the composite containing dibutyrylchitin (Composite 20), which has no affinity to the dimethacrylate resins. It was already conspicuous at the stage of the grinding of composite paste. Dibutyrylchitin does not bind with the matrix as well as the other additives, although, after the addition of surface-modified silica Arsil, I managed to obtain a homogeneous composite paste. However, the final abrasive properties of the DBC-containing composite were not good. Composite 20 wore off several times more than the other composites, what would confirm the complete incompatibility of DBC with resin matrix, resulting in weakening of the internal structure of material.

The tribological measurements indicate that there is no direct correlation between the average values of friction coefficients and wear rate of samples studied. The coefficient of friction of reference material (Composite "0") is the lowest (0.52), and abrasive wear after 6 hours of friction equals 1.3 wt.%. Higher coefficients of friction of Composites 20 and 26 translate to their higher wear rate (up 7.4 wt. % for Composite 20, with DBC). However, Composite 25 containing a small addition of nanosilver, despite the highest average coefficient of friction (0.63) shows the lowest wear (0.6 wt. %) – more than twofold smaller...
than the reference sample. In fact, however, the question is whether the addition of nanosilver may affect the abrasive wear directly, or it is rather a factor which influences the wear in an indirect way – by affecting the cross-linking process, and thus the changes of mechanical properties of the surface layer of material. Composite 25 shows a lower hardness than the reference sample, which probably translates into a lower wear.

In fact, it has to be considered what parameters should characterize the surface of composite filling to make it beneficial for dental applications. Certainly, materials use for the reconstruction of occlusal surfaces of teeth should be durable and resistant to abrasion. It concerns mainly the molar teeth, where the loads are larger and friction forces are higher.
12. Cost estimation of manufacturing a single dental composite filling

Light-cured dental composite filling costs about 80 PLN (18.5 €), in most dental offices in Poland. I decided to check how strongly this price is dependent on the cost of reagents. In my calculations I deliberately took into account the gross prices, although it is known that rather the wholesale orders are used in the mass production. Therefore, the calculated price will be slightly higher than actual, however, I was more interested in the order of magnitude than the exact price of the syringe of composite.

The list of reagents required to produce a dental composites does not include all possible substances – I focused only on the most commonly used materials (Tab. 23).

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Manufacturer</th>
<th>Size of the smallest (most expensive!) packaging</th>
<th>Net price of packaging [PLN]</th>
<th>Brutto price [PLN]</th>
<th>Brutto price of 1g [PLN/€]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis-GMA</td>
<td>Aldrich</td>
<td>100</td>
<td>116.1</td>
<td>151.7</td>
<td>185.07</td>
</tr>
<tr>
<td>TEGDMA</td>
<td>Fluka</td>
<td>250</td>
<td>273</td>
<td>213.6</td>
<td>260.59</td>
</tr>
<tr>
<td>CQ</td>
<td>Aldrich</td>
<td>-</td>
<td>5</td>
<td>262.0</td>
<td>319.64</td>
</tr>
<tr>
<td>BHT</td>
<td>Aldrich</td>
<td>-</td>
<td>100</td>
<td>77.1</td>
<td>94.06</td>
</tr>
<tr>
<td>DMAEMA</td>
<td>Aldrich</td>
<td>100</td>
<td>93.3</td>
<td>81.6</td>
<td>99.55</td>
</tr>
<tr>
<td>Silan A-174</td>
<td>Aldrich</td>
<td>100</td>
<td>104.5</td>
<td>363.3</td>
<td>443.22</td>
</tr>
<tr>
<td>Aerosil 380</td>
<td>Degussa</td>
<td>-</td>
<td>10000</td>
<td>500</td>
<td>610.00</td>
</tr>
<tr>
<td>Arsil</td>
<td>Rudniki</td>
<td>-</td>
<td>25000</td>
<td>200</td>
<td>246.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Aldrich</td>
<td>-</td>
<td>100</td>
<td>184.1</td>
<td>224.60</td>
</tr>
<tr>
<td>nanoZrO₂</td>
<td>Aldrich</td>
<td>-</td>
<td>25</td>
<td>382.1</td>
<td>466.16</td>
</tr>
</tbody>
</table>

**Tab.23** List of reagents for matrix preparation and their prices.
The following amounts of reagents are needed to produce 50 g of resin matrix (Tab. 24):

Tab. 24 Reagents necessary to prepare 50 g of matrix.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Brutto price/ 1g [PLN]</th>
<th>Necessary amount [g]</th>
<th>Total price [PLN]</th>
<th>Total price [€]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis-GMA</td>
<td>1.59</td>
<td>30</td>
<td>47.70</td>
<td>11.10</td>
</tr>
<tr>
<td>TEGDMA</td>
<td>0.95</td>
<td>20</td>
<td>19.00</td>
<td>4.40</td>
</tr>
<tr>
<td>CQ</td>
<td>63.93</td>
<td>0.2</td>
<td>12.79</td>
<td>2.99</td>
</tr>
<tr>
<td>BHT</td>
<td>0.94</td>
<td>0.05</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>DMAEMA</td>
<td>1.07</td>
<td>0.5</td>
<td>0.54</td>
<td>0.12</td>
</tr>
<tr>
<td>TOTAL</td>
<td>50.75</td>
<td></td>
<td>80.07</td>
<td>18.62</td>
</tr>
</tbody>
</table>

Dental composites are filled to 85 % by weight (max.), so about 284 g of filler will be needed per 50 g of the matrix. I assume that Aerosil 380 and Arsil are used half and half (Tab. 25).

Tab. 25 Reagents necessary to fill 50 g of matrix.

<table>
<thead>
<tr>
<th>REAGENT</th>
<th>Brutto price/ 1g [PLN]</th>
<th>Necessary amount [g]</th>
<th>Total price [PLN]</th>
<th>Total price [€]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosil 380</td>
<td>0.06</td>
<td>142</td>
<td>8.52</td>
<td>1.98</td>
</tr>
<tr>
<td>Arsil</td>
<td>0.01</td>
<td>142</td>
<td>1.42</td>
<td>0.33</td>
</tr>
<tr>
<td>Silane A-174 for Aerosil modification</td>
<td>4.24</td>
<td>170.4</td>
<td>722.50</td>
<td>167.63</td>
</tr>
<tr>
<td>Silane A-174 for Arsil modification</td>
<td>85.2</td>
<td>361.20</td>
<td>83.81</td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>539.6</td>
<td>1093.64</td>
<td>253.75</td>
<td></td>
</tr>
</tbody>
</table>

In this way we obtain 334 g of the composite (summarizing the weight of fillers and matrix only). In fact, this weight will be slightly higher because of the presence of silane, chemically bonded to the surface of silicas. So, in general, we produced approximately 400 g of the composite for about 1200 PLN (275 €). One syringe typically contains 4 g of the composite. The raw materials for its production cost about 12 PLN (2.75 €) (other costs such as energy, water, or salaries are not included). One syringe of composite paste is sufficient for approximately 10–20 patients. Without energy, electricity and labour, the price of one dental filling is about 1 PLN (0.25 €).
13. Conclusions

COMMERCIAL COMPOSITES

1. Studies have shown large differences between samples of commercial dental composites, even from one batch, which can indicate the problems in obtaining uniform dispersion of filler in commercial materials. Commercial dental composites are characterized by very diverse morphology, which implies differences in mechanical properties.

2. Some of composites (Filtek Supreme, Valux Plus) show increased resistance to abrasion during the first hour of tribological measurements, which proves the existence of the so-called "skin surface" of a different nature and different mechanical properties than the bulk of materials. The gradient of mechanical properties moving from the surface into the deeper parts of material has been observed (in the literature, there is no information about this phenomenon in relation to dental composites).

3. There is a certain correlation between the nanohardness of the surface layer of commercial composites, determined with using the nanoindentation technique, and the abrasive wear during the first hour of tribological experiments – the higher the nanohardness, the higher the wear rate.

4. There is a correlation between the value of H/E*, and the abrasive wear of the surface layer – the higher the H/E * ratio, the larger the wear volume.

5. The highest wear resistance is exhibited by materials with the highest diversity of shapes and sizes of filler particles. The "bimodal" morphology favors the best packing of filler particles in the resin matrix.

6. The increasing of filler content and its high heterogeneity (the presence of filler particles of different shapes and sizes) increases the energy absorbed by the material, while the time needed to reach the maximum force is shorter – the material exhibits a higher fracture toughness.
7. The analysis of the properties of surface layer (not reflected in the literature) should be an important aspect of dental composite research. In the light of my studies, the top layer often exhibits quite different nature and mechanical characteristics than the bulk of material, probably due to the usage of photopolymerization technique to cure dental fillings, which results in a gradient of cross-linking.

HOMEMADE COMPOSITES

8. The type and amount of silane used for modification of the filler and the composition of the silanizing bath, significantly affect the interaction between inorganic phase and the resin matrix. Modification of Aerosil 380 silica with a bath containing diethylamine improves the abrasion resistance of the composites.

9. Application of excess silane allows the introduction of more filler to the matrix, however, it increases its susceptibility to abrasion (by about 5 vol. %). It may be caused by the formation of thick polysiloxane multilayer structure on the silica surface, acting as a plasticizer of the polymer matrix.

10. Aluminosilicates (even after organofilization) are not compatible with the dimethacrylate resins. The high refractive index of MMT results in worsening the conditions of photo-curing.

11. Silanized silica can act as a factor ensuring the cohesion of composite paste, even in the presence of additional filler which is not surface-modified and theoretically completely incompatible with dimethacrylate resins.

12. Wollastonite provides high mechanical resistance and, due to the interesting morphology and possibility of modification with silanes, is an interesting alternative for whiskers.

13. PALS together with the SEM analysis proved to be useful experimental techniques for determination of dental composites morphology. Based on the analysis of time and intensity of o-Ps annihilation it is possible to differentiate composites in terms of their internal structure.
14. The addition of nanosilver deposited on silica or titania to dental composites effectively adds bactericidal activity against *S. mutans*, however, mechanical characteristics of the composites require fine-tuning.

15. The approximate cost of manufacturing of dental composite is about 10–12 PLN (2.30–2.80 €) per syringe (4 g). In fact, its market price reaches about 100–150 PLN (23–35 €). The question is, therefore, what is the reason of such a high difference? Perhaps, at least from an economic point of view, the production of dental composites in Poland would be beneficial.
14. Summary

Over the past years, dimethacrylate-based dental composites for the reconstruction of occlusal surfaces of teeth, evolved into a truly satisfactory form. For aesthetic reasons, they leave far behind other types of fillings, like amalgams, but their relatively low mechanical strength, shrinkage during polymerization and the tendency to accumulate dental plaque, resulting in the formation of secondary caries around fillings, still represent a significant problem.

Analysis of the subject literature leads to a series of alarming conclusions. Above all, the lack of cooperation between dentistry and materials engineering is visible. Availability of a number of different materials on the dental market, which vary in the quality and content of the inorganic phase, translates into significant differences in their internal structure. Different morphology, in turn, results in different behavior of composites in the oral cavity. The knowledge about the real impact of the size, shape and quantity of filler particles on the mechanical properties of composites is not systematized. What is more, each batch of a commercial composite is significantly different from another, which makes difficult the formulation of clear conclusions regarding its mechanical properties.

The aim of my study was an attempt to clarify, how the morphology of dimethacrylate-based dental composite affects the properties of dental fillings. I examined the possibility of producing dental composites, which – retrofitted with bactericidal properties – reduce the tendency to dental plaque accumulation within the light-cured fillings.

I also undertook to prove the thesis that the surface layer has the greatest impact on the durability of composites and, for that reason, the current methodology of research of dental composites, taking into account only bulk properties, requires some modifications.

The experiments were carried out bidirectionally:

1). The analysis of commercial samples – focused on searching for correlations between morphology and mechanical properties of cured composites, especially their surface layer properties;

2). I prepared own composites with fillers not currently used: aerogel, wollastonite, expanded perlite and halloysite, including also the ones with antibacterial additives, such as nanosilver deposited on silica or titanium dioxide and dibutyrylchitin. Next, these composites were characterized.
in terms of morphology, tribological behavior, mechanical properties of surface layer (determined by nanoindentation) and bactericidal action.

I proposed a set of tests on samples sized similarly to the dimensions of dental fillings, which seems to be more appropriate than measurements performed according to the ISO 4049 standard: "Dentistry. Polymer-based filling, restorative and luting materials". Positron Annihilation Lifetime Spectroscopy (PALS) supplemented by the SEM analysis, proved to be a useful experimental technique for the determination of dental composite morphology. Based on the analysis of time and intensity of o-Ps annihilation it is possible to differentiate composites in terms of their internal structure.

It turned out that some commercial composites exhibit an increased resistance to abrasion during the first hour of tribological measurements. It proves the existence of the so-called "surface layer" of a different nature and mechanical properties than the bulk of material. It is probably a consequence of the use of photo-polymerization technique for curing of dental fillings and may result in a gradient of mechanical properties moving from the surface to deeper parts of filling. Therefore, the analysis of the top layer (practically absent in the subject literature), should be an important aspect of research of dental materials.

An important parameter for evaluation of abrasion resistance of materials (e.g. thin coatings) is the H/E* ratio, which may constitute a measure of wear. And indeed, in the case of commercial dental composites some correlation is observed – the higher the H/E* ratio, the larger the wear rate of the samples. The literature suggests rather the occurrence of inversely proportional relationship, but in the case of commercial dental composites, the points on chart are arranged in a manner indicating a directly proportional relationship. It indicates probably a much higher significance of hardness in the estimation of mechanical resistance of the composites (brittle by nature), than of the Young's modulus.

The composites containing mineral fillers with the highest diversity of shapes and sizes of particles exhibit the highest wear resistance. The "bimodal" morphology favors the best packing of filler particles in the resin matrix. The increase of filler content and its high heterogeneity (the presence of filler particles of different shapes and sizes) increases the energy absorbed by the dental composite, while the time needed to reach the maximum force is shorter – the material exhibits the higher fracture toughness.

In the case of homemade composites I have observed that the type and amount of silane used for modification of the filler and the composition of the silanizing bath, significantly affects the interaction between the inorganic phase and the resin matrix, which translates into functional properties of the composites. Modification of Aerosil 380
silica with a bath containing diethylamine improves the abrasion resistance of the composites. The application of excess silane allows the introduction of more filler to the matrix, however, it increases its susceptibility to abrasion (by about 5 vol. %). It might be caused by the formation of thick multilayer structure of polysiloxanes on the silica surface, which acts as a plasticizer of the resin matrix. It also appeared that silanized silica can act as a factor ensuring the cohesion of composite paste, even in the presence of an additional filler, which is not surface-modified and theoretically completely incompatible with dimethacrylate resins. However, aluminosilicates (even after organofilization) are not compatible with dimethacrylate resins, as their high refractive index worsens the conditions of photo-curing.

Wollastonite is an interesting alternative to the commonly used fillers. It is characterized by a lower refractive index, exhibits an interesting morphology (similar to whiskers), and its modification with silanes is possible. Moreover, the introduction of wollastonite into resin matrix provides a high mechanical resistance of composite.

Addition of bactericidal agents to the dimethacrylate matrix (e.g. nanosilver deposited on a silica or titania) is effective against S. mutans, however, mechanical characteristics of the composites containing antibacterial additives require fine-tuning before introduction to the dental market.

The approximate cost of manufacturing of one syringe (4 g) of dental composite is about tenfold lower than its market price. Therefore, the question is, what is the reason of such a huge difference? If it mainly comes from the fact that dental composites are imported, maybe we should regret that we do not produce them in Poland.
Streszczenie

Na przestrzeni kilkudzięściu ostatnich lat, kompozyty dentystyczne żywic dimetakrylanowych, służące do odbudowy powierzchni zwarców zębów, ewoluowały do naprawdę zadowalającej postaci. Ze względów estetycznych, pozostawiają one daleko w tyle inne rodzaje wypełnień, jak chociażby amalgamaty, jednak ich relatywnie niska wytrzymałość mechaniczna, skurcz oraz tendencja do akumulacji płytki nazębnej, skutkująca powstawaniem próchnicy wtórnej w obrębie wypełnień, ciągle stanowią znacznny problem.

Analiza literatury dotyczącej kompozytów na bazie żywic dimetakrylanowych prowadzi do szeregu niepokojących wniosków. Widać przede wszystkim brak współpracy między stomatologią a inżynierią materiałową. Na rynku dostępny jest szereg różnorodnych materiałów, różniących się jakością i zawartością fazy stałej, co przekłada się na znaczne różnice w ich budowie wewnętrznej. Zróżnicowana morfologia skutkuje z kolei odmiennym „zachowaniem się” kompozytów w czasie eksploatacji. Brak jest usystematyzowanej wiedzy, co do rzeczywistego wpływu rozmiaru, kształtu i ilości cząstek fazy stałej, na właściwości mechaniczne kompozytów. Co więcej, każda szarża danego kompozytu komercyjnego potrafi w sposób znaczący różnić się od kolejnej, co znacznie utrudnia formułowanie jednoznacznych wniosków odnośnie jego właściwości mechanicznych.

Celem mojej pracy była próba wyjaśnienia, jaki wpływ ma morfologia dentystycznych materiałów kompozytowych na bazie żywic dimetakrylanowych, na właściwości użytkowe wykonanych z nich wypełnień. Sprawdziłam również możliwość wytworzenia kompozytów dentystycznych, które – doposażone we właściwości bakteriobójcze, ograniczają tendencję do akumulowania się płytki nazębnej w obrębie światłoutwardzalnych wypełnień. Podjęłam się także próby udowodnienia tezy, iż największy wpływ na trwałość kompozytów ma warstwa wierzchnia i chociażby z tego właśnie względu, modyfikacji wymagałoby stosowana dotychczas, w odniesieniu do kompozytów dentystycznych, metodyka badań, uwzględniająca jedynie pomiary właściwości objętościowych.

Badania prowadzone były dwukierunkowo:

1. Analizie poddalam próbki komercyjne, skupiając się na poszukiwaniu korelacji pomiędzy morfologią a właściwościami mechanicznymi usieciowanych kompozytów, przede wszystkim – ich warstwy wierzchniej;
2. W oparciu o nie stosowane dotychczas napełniacze: aerożel, wollastonit, perlitr ekspandowany i haloizyt, w tym również – zawierające dodatki
o charakterze bakteriobójczym, takie jak: nanosrebro osadzone na ditlenku krzemu lub tytanu i dibutyrylochitynę, opracowałam własne materiały kompozytowe, które scharakteryzowałam pod względem morfologii, poddałam testom tribologicznym, oznaczeniom metodą nanoindentacji i badaniom bakteriobójczości.

Zaproponowany przeze mnie zestaw badań, z wykorzystaniem próbek zbliżonych rozmiaarami do wymiarów wypełnień stomatologicznych, wydaje się być bardziej adekwatny, niż standardowe pomiary prowadzone według normy PN-EN ISO 4049: „Stomatologia. Polimerowe materiały do wypełnień, odbudowy i cementowania”. Technika PALS, uzupełniona o analizę SEM, umożliwiła dokonanie kompleksowej oceny morfologii kompozytów polimerowych. Okazało się, że na podstawie długości czasu życia oraz intensywności anihilacji o-Ps możliwe jest różnicowanie kompozytów pod względem ich budowy wewnętrznej.

Okazało się, że niektóre kompozyty komercyjne wykazują podwyższoną odporność na ścieranie w czasie pierwszej godziny pomiaru tribologicznego, co dowodzi istnienia tzw. „wierzchniej warstwy”, o odmiennym charakterze i parametrach mechanicznych, niż wnętrz materiału. Jest to najprawdopodobniej następstwem wykorzystywania techniki fotopolimeryzacji do utwardzania wypełnień i może skutkować gradientem właściwości mechanicznych w miarę przesuwania się od powierzchni w głąb wypełnienia. Ważnym aspektem badań kompozytów dentystycznych powinna być więc analiza ich warstwy wierzchniej, właściwie nie uwzględniana w literaturze przedmiotu.

Jak wynika z przeglądu literatury, ważnym parametrem przy ocenie odporności na ścieranie materiałów (np. cienkich powłok), jest wartość stosunku H/E*, mogąca stanowić miarę zużycia. I rzeczywiście, w przypadku komercyjnych kompozytów dentystycznych, zaobserwowana była pewna korelacja – wraz ze wzrostem wartości H/E* rośnie zużycie ścierne próbek. Analiza literatury dowodzi raczej występowania zależności odwrotnie proporcjonalnej, niemniej jednak w przypadku komercyjnych kompozytów dentystycznych, punkty układają się w sposób wskazujący na zależność wprost proporcjonalną. Świadczyłoby to o dużo większym udziale twardości w szczawaniu odporności mechanicznej kompozytów (z natury kruchych), niż samego modułu sprężystości.

Największą odpornością na zużycie ścierne odznaczają się materiały napelnione mineralną fazą stałą o największym zróżnicowaniu kształtów i rozmiarów cząstek. Najlepszemu upakowaniu cząstek napelniaca w matrycy sprzyja morfologia „bimodalna”. Wraz ze wzrostem zawartości fazy stałej w kompozytach oraz przy jej dużej niejednorodności
STRESZCZENIE

Ocena efektywności stosowania nanosrebra osadzonego na ditlenku krzemu lub tytanu w kompozytach dimetakrylanowych wykazały, że zastosowanie w kompozytach z nanosrebrem osadzonym na dimetakrylanie lub tytanu, działa efektywnie względem S. mutans, jednak żeby materiały te zyskały znaczenie praktyczne, dopracowania wymagałyby ich charakterystyki wytrzymałościowej.

W przypadku kąpielisilanizującej stosowanej do modyfikacji napełniacza, w znaczący sposób wpływają na oddziaływania krzemionki z żywiczną matrycą, co przekłada się na właściwości użytkowe kompozytów. Modyfikacja z wykorzystaniem dietyloaminy, wpływa na wzrost odporności próbek na ścieranie. Zastosowanie nadmiaru silanu, umożliwiające wprowadzenie do matrycy większych ilości napełniacza, skutkuje z kolei znacznym wzrostem (o ok. 5 % obj.) zużycia ściernego kompozytu, co może być spowodowane tworzeniem się wielowarstwowej struktury polisiloansowej na powierzchni krzemionki, działającej jak plastyfikator w odniesieniu do matrycy. Okazało się również, że silanizowana krzemionka może spełniać rolę czynnika zapewniającego układowi spoistość, nawet mimo obecności dodatkowego napełniacza, nie zmodyfikowanego powierzchniowo i teoretycznie zupełnie niekompatybilnego z matrycą żywiczną. Niemniej jednak, glinokrzemiany, nawet po organofilizacji, nie sprawdzają się jako napełniacz żywic dimetakrylanowych. Wysoki współczynnik refrakcji MMT znacznie pogarsza warunki sieciowania kompozytów.

Interesującą alternatywą dla stosowanych dotychczas napełniaczy, stanowi wollastonit. Oznacza się on niższym współczynnikiem refrakcji, posiada interesującą morfologię (zbliżoną do whiskerów), a dodatkowo – można modyfikować go silanami. Wprowadzony do matrycy dimetakrylanowej, zapewnia kompozytowi wysoką odporność mechaniczną.

Próby przeprowadzone z wykorzystaniem dodatków o charakterze bakteriobójczym wykazały, że zastosowanie w kompozytach nanosrebra osadzonego na ditlenku krzemu lub tytanu, działa efektywnie względem S. mutans, jednak żeby materiały te zyskały znaczenie praktyczne, dopracowania wymagałyby ich charakterystyki wytrzymałościowej.

Przybliżony koszt wytworzenia jednego opakowania kompozytu na bazie żywic dimetakrylanowych jest ponad 10-krotnie niższy od ceny materiałów oferowanych na rynku. Pytanie zatem, skąd bierze się ta różnica? Jeśli wynika ona głównie z tego, że kompozyty takie importujemy, pozostaje chyba żałować, że nie produkujemy ich w kraju.
15. Bibliography


16. List of publications


