The aim of the study was to evaluate the influence of different fillers on the chosen functional properties of experimental composites based on typical polymeric matrix, in order to understand the effect of different fillers on their properties and to develop a simple base composite for further investigations with experimental fillers, e.g. with antimicrobial properties. Previous experiments have been usually based on commercially available composites of unknown composition or compilation of monomers, without reinforcing fillers. Scanning electron microscopy was used to investigate the quality of fillers’ dispersion, which was satisfying. Results showed significant differences between materials’ diametral tensile strength ($p = 0.0019$), compressive strength ($p < 0.0001$), Vickers micro-hardness ($p < 0.0001$), flexural modules ($p = 0.0018$), and the degree of conversion ($p < 0.0001$), but flexural strength was not significantly different ($p = 0.0583$). Investigations indicated that no filler type had an especially positive impact on the mechanical properties, but reinforcement effect was achieved by proper compilation of silica nanofiller and variable glass fillers. Nanofiller decreased the degree of conversion.

Keywords: resin composites, dental materials, filler, mechanical properties, degree of conversion

1. Introduction

Despite the continuous progress in dental material science, there has been no reconstructive material that could ideally repair hard dental tissues [1]. Nowadays, the most popular direct restorative materials are photopolymerizable resin-based composites. They were introduced to replace amalgams in the restorative treatment [2]. These materials, in comparison to others, are characterized by very good esthetics and show a quite durable bonding with dentin or enamel, proper biocompatibility as well as satisfying physical and mechanical properties. Additionally, dental composites are reasonably easy to use, which is an additional advantage from a clinical point of view. However, the durability of the direct restorative material is limited and often worse in comparison to amalgams [3-5]. The most common reason for filling replacement after a few years is secondary caries and fractures [6]. Secondary caries is related with microleakage, which leads to the presence of bacteria, liquid, and chemical substances between restorations and teeth [7,8]. Insufficient adaptation between the material and the tooth as well as volume change in the dental composite due to shrinkage are major factors determining the formation of microleakage [8]. Additionally, thermal stresses created by intra-oral temperature changes may be the cause of problems in composite-tooth interface due to the differences in thermal contraction/expansion coefficient between composites/adhesives and tooth tissues [9,10]. Occlusal forces during mastication and parafunctional activities like bruxism have a deleterious impact on the marginal adaptation of restorative composites [11]. The problem of microleakage has not been resolved yet, so secondary caries is still a limitation related with the use of dental filling materials.

Dental composites consist of three essential components: a highly cross-linked polymeric matrix, reinforcing fillers and silane coupling agents [14]. Those materials additionally contain activator-initiator systems, pigments, ultraviolet absorbers to improve color stability, and polymerization as well as inhibitors to prolong storage life or provide suitable working time for chemically activated materials [15]. The matrix in most dental restorative composites contains a blend of dimethacrylate monomers such as 2,2-bis-[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane, known as Bis-GMA resin, and 1,6-bis-(methacryloxy-2-ethoxycarbonylaminoo)-2,4,4-trimethylhexane, called the urethane-dimethacrylate monomer (UDMA) [15-17]. Those monomers create highly cross-linked, durable polymer structures, and are responsible for the mechanical properties of the polymer composite matrix. Because of their high viscosity (especially Bis-GMA, 800 Pa·s), those monomers are difficult to blend or manipulate, so they are often used in...
combination with the so-called diluting monomers, which give the composition a consistency suitable for application and allow for the introduction of large amounts of inorganic fillers [15]. Oligoethylene glycol dimethacrylates are added for this purpose, in the amount from 20 to 50 wt%, of which triethylene glycol dimethacrylate (TEGDMA), characterized by dynamic viscosity of 0.005-0.03 Pa·s, is the most popular [15,16]. Unfortunately, the application of diluent monomers leads to greater polymerization shrinkage, which partially compensates the benefit of using “large” monomers, such as bis-GMA. However, copolymerization of these basic monomers with TEGDMA is very advantageous and causes an increase in the degree of conversion of the polymer network. Hardness, modulus and impact strength of poly(di(meth)acrylate)s depend on the degree of conversion of the resin more than mechanical strength. To achieve higher values the latter property requires the presence of aromatic rings (Bis-GMA) and groups in the structure, willing to form strong hydrogen bonds, such as the hydroxyl group (Bis-GMA) or the urethane group (UDMA) [15]. In the current study we have used a typical mixture of Bis-GMA, UDMA and TEGDMA monomers, however other monomers are also frequently used in modern dental restorative materials. Fillers are used to increase strength, stiffness, and wear resistance, but they also reduce polymerization shrinkage and decrease thermal expansion. A typical dental composite is reinforced by fillers varying in terms of chemical composition, size and shape, which significantly affects its mechanical properties [12,13]. Nowadays, numerous fillers are used, such as glass particles, silica particles, metal oxide particles, resin-reinforcing filler particles, sometimes short fibers [15,18].

In the presented study we have used two different-size barium borosilicate glass fillers (mean particles size up to 2 μm), and nanosilica filler (mean particles size up to 20 nm). The borosilicate glass is a typical “hard” filler, and it shows a negative coefficient of thermal expansion, good refractive index, and additionally, due to the presence of heavy metal atoms, it imparts radiopacity. Silica nanofiller also plays a role in composite reinforcing, and additionally provides improved functional properties like polishability important for esthetics and smoothness to the tongue. Due to the used fillers composition, investigated materials are expected to present properties similar to materials recommended for moderate-stress areas, and according to the Anusavice [15] should be classified as hybrid (also called minifilled) when only glass fillers were used or nanohybrid, when silica nanoparticles were additionally compounded. Presented work is focused on investigating the effect of those fillers on the properties of composites. Therefore, the aim of the study was to evaluate the influence of different types of fillers on the chosen functional properties of experimental composites based on typical polymeric matrix, and to develop an experimental base composite for further investigations, with new specific fillers. This seems to be especially important if we consider that available studies were usually concentrated on commercially available materials, where compilations of fillers were, in fact, unknown. This causes difficulties in choosing a starting compilation of fillers for obtaining experimental composites with fillers characterized by special (e.g. antimicrobial) properties to limit the risk of secondary caries [19]. Currently, these works often use materials existing on the market [20,21], which restricts achievements due to the high initial viscosity of composition, and risk of large aggregation of filler. Optionally, they are focused on the modifications of matrix without reinforcing fillers, what provides low mechanical properties [22], and different characteristics in comparison to available restorative materials.

2. Materials and methods

2.1. Materials preparation

The base monomer mixture consisted of bisphenol A glycicydyl methacrylate (BisGMA), urethane-dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA) (all Sigma-Aldrich, Germany) at a weight ratio of 42:38:20. The monomers were mixed with: 0.4 wt% of camphorquinone (CQ, Sigma-Aldrich) as the photosensitizer and 1 wt% of N,N-dimethylaminoethyl methacrylate (DMAEMA, Sigma-Aldrich) as the reducing agent. The prepared matrix was loaded with 65 wt% of fillers. Two silanized barium borosilicate glass fillers with mean particle size 2 μm (FA) or 0.7 μm (FB) declared by the manufacturer (Esscherm, The Great Britain) and one silanized silica nanofiller Aerosil R7200 (NF) (Evonic, Germany) were used. Six composites with different weight ratios of fillers were obtained (Table 1). All materials were polymerized with a DY400-4 LED lamp (Denjay Dental, China); power 5W, intensity 1400-2000 mW/cm², optical wave length 450-470 nm.

<table>
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<tr>
<th>Composite symbol</th>
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2.2. Methods

Samples for the scanning electron microscopy (SEM) were polymerized in silicone mold and included. Investigations were carried out on the specimens after standard wet-grinding and polishing using diamond pastes and etching with orthophosphoric acid. The obtained sections were sputtered with gold and finally observed using a Zeiss SUPRA 35 scanning electron microscope at accelerating voltages from 1 to 5 kV.
Three-point bending test were prepared in accordance with the ISO 4049 standard [23] with minor adjustments regarding samples preparation. Specimens measuring $25 \times 2 \times 2 \text{ mm}$ were fabricated using silicone (Zetalabor Platinum 85Touch, Zhrmack, Italy) molds placed in a stainless steel frame. The composites were packed into the mold, covered with polyester foil at the top and pressed with microscope slide glass. Glass was taken from the top and material was polymerized with the use of four overlapping irradiations. After polymerization samples were carefully taken out of the mold and wet-ground with P800 and P1200-grit abrasive paper to remove excess material. The distance between the supports was 20 mm, and test was performed at a cross-head speed of 0.75 mm/min [23] using a universal testing machine (Zwick Z020 GmbH & Com, Germany). Flexural strength and flexural modulus were calculated according to the following equations:

$$\sigma_f = \frac{3PL}{2bh^2} \quad (1)$$

$$E = \frac{PL^2}{4bh^3\delta} \quad (2)$$

where: $\sigma_f$ is flexural strength, MPa; $E$ is flexural modulus, GPa; $L$ is distance between the supports, mm; $b$ is specimen width, mm; $h$ is specimen height, mm; $P$ is maximal force, N; $P_1$ is the load at a selected point at the elastic region of the stress-strain plot, kN; $\delta$ is deflection of the specimen at $P_1$, mm.

Diametral tensile strength (DTS) tests were prepared with the method presented by Penn et al. [24], with necessary specifications regarding samples preparation. The samples were prepared in a teflon mold 3 mm in thickness and 6 mm in diameter. The mold was placed at a microscope slide glass covered with 50 µm thick polyester foil, composite material was packed into the mold, covered with polyester foil at the top and pressed with microscope slide glass. Top glass was taken away and material was polymerized. After removing the polyester foil, samples in the mold were wet-ground sequentially with P800, P1200, and finally P2400-grit abrasive paper. The samples were polymerized in a teflon mold and wet-ground sequentially with P800, P1200 and finally P2400-grit abrasive paper. The samples were stored in distilled water at 37°C for 24 h. Compressive strength test was performed at a cross-head speed of 0.5 mm/min using a universal testing machine (Zwick Z020 GmbH & Com, Germany). Compressive strength was calculated according to the following equation:

$$\sigma_c = \frac{F}{A} \quad (4)$$

where: $\sigma_c$ is compressive strength, MPa; $F$ is force at rupture, N; $A$ is the initial cross-sectional area of specimen, mm$^2$.

Vickers hardness was investigated on specimens measuring 10 mm in diameter and 2.5 mm in thickness. They were polymerized in a teflon mold and wet-ground sequentially with P800, P1200 and finally P2400-grit abrasive paper. The samples were stored in distilled water at 37°C for 24 h. Hardness was measured using the Future-Tech FM-700 (Future-Tech Corp, Tokyo, Japan) microhardness tester with a 100 g load and loading time 15 s [27]. Measurements were made 30 times at randomly chosen locations on 3 specimens for each material (10 measurements for a specimen). Vickers hardness was calculated by the formula:

$$HV = \frac{1,8544F}{d^2} \quad (5)$$

where $F$ is the applied load, kgf; $d$ is the average length of the diagonal left by the indenter, mm.

The degree of conversion (DC) was determined using a FTIR spectrophotometer (Perkin Elmer Spectrum Two (Perkin Elmer, USA), and the method presented by Barszczewska-Rybarek [16]. The spectra of the monomers and polymers were recorded with 128 scans at a resolution of 1 cm$^{-1}$. The absorption intensity of selected peaks was measured in the 1800-1500 cm$^{-1}$ region as a baseline. The monomer samples were tested as thin films on KBr pellets. The cured samples were pulverized into powder of a particle diameter less than 24 µm, and it was analyzed as pellets with KBr. The DC was calculated from the decrease of absorption band at 1637 cm$^{-1}$ (referring to the C = C stretching vibration, $A_{(C-C)}$), in relation to the peak at 1718 cm$^{-1}$ (assigned to the C = O to aromatic stretching vibrations, $A_{(C=O)}$):

$$DC(\%) = 1 - \frac{(A_{(C=C)} / A_{(C=O)})_{\text{polymer}}}{(A_{(C=C)} / A_{(C=O)})_{\text{monomer}}} \times 100 \quad (6)$$

The results were subjected to statistical analysis with Statistica 12.5 software. The distributions of the residuals were tested with Shapiro-Wilk test and the equality of variances was tested with Levene test ($\alpha = 0.05$). When the distribution of the residuals was normal and the variances were equal, the one-way ANOVA with Tukey HSD post-hoc tests were used ($\alpha = 0.05$).
3. Results and discussion

In Fig. 1 the morphologies of used fillers were presented. However, for FA and FB a large number of particles were characterized by a much smaller size, and some were a few-times larger than the mean particle size declared by the manufacturer (2 μm and 0.7 μm respectively). So in fact, FB should be specified as submicrofiller and FA as microfiller, because using mean particle sizes to describe the applied glass fillers can be confusing. Observations clearly showed irregular shapes of FA and FB fillers which is typical after the milling process. Representative SEM images illustrating the morphology of composites were presented in Fig. 2 and Fig. 3. Composites reinforced with FA and FB showed morphology without aggregation. Glass particles, measuring from approximately 50 nm to a few micrometers, were densely distributed in matrix (Fig. 2). For materials with NF, FA and FB, called nanohybrid composites [28], very good distribution of nanoparticles between submicroparticles and microparticles was observed (Fig. 3). Large aggregations of NF were not detected which is preferred because of the unfavorable influence of aggregation on the mechanical properties of composites [29,30].

Studies generally associate mechanical properties with filler percentage in volume. In this work the filler percentage content in weight was used. This remains in accordance with Rodrigues et al. [31] who found that it is justified especially if we take into account different density of fillers and variation of the fillers’ morphology. In the presented work we used only one mass concentration of all fillers limited to 65% and those three fillers were characterized by a much diversified density before compounding (silica filler – approx. 0.23 g/mL and glass fillers approx. – 3 g/mL) and different morphology (Fig. 1). Additionally, we did not study the influence of total concentration of fillers on the properties of composites, as it is usually practiced for commercially available materials, but the effect of weight ratio of different fillers.

For the analyzed composites statistically significant differences in flexural strength were not registered (Fig. 4a), but the highest value of 99.8 MPa was obtained for the 50FA35FB15NF composite. These results were similar to numerous commercially available materials characterized by comparable organic matrix compositions or/and filler contents, but simultaneously lower than the most modern materials characterized by higher filler concentrations and/or new types of matrices [32-37]. Additionally, they were similar or even better than numerous experimental composite materials [38]. Simultaneously, the ISO 4049 standard requires lower minimal flexural strength values of 80 MPa for occlusal tooth surface restoration and 50 MPa for others [23]. The registered mean flexural modulus values were from 5.1 to 6.1 GPa. Some statistical differences were noted (Fig. 4b), but in fact all materials were similar and typical for dental composites [31,39]. This can suggest that flexural strength and modulus were associated with matrix composition and filler loading [31] rather than with filler type. Anyway, limitations of the presented study should be taken into account, because only a few types of fillers were studied. The pre-polymerized particles, clusters, spherical microparticles, alumina and zirconia particles, other types of glasses and unsilanized glasses were not analyzed.

The diametral tensile strength test is widely accepted to evaluate tensile strength of composites due to their brittle behavior. This method is acceptable if minimal or no plastic deformations occur, deformations are still small, and the area of contact is near to theoretical [24]. The results of DTS investigations were shown in Fig. 5. The mean values were from 35.7 to 40.1 MPa and the highest value was registered for the 50FA35FB15NF composite. Powers et al. [14] state that average DTS values for
composite materials should exceed 30 MPa so all investigated materials meet this guideline. Our results were also comparable with the ones obtained for commercially available materials by Della Bona et al. [32] and Łukomska-Szymańska et al. [1,19], and better than for similar experimental materials [1,38].

Most of the masticatory forces are qualified into the category of compressive forces, so the assessment of compressive strength is of great importance [26,25]. If we take into account that values of compressive strength with plastic limit of enamel and dentin are diversified in numerous works [15,40], and these results may create a standard to select the strength of composites.
[26,25], we can conclude, that 230 MPa should be considered as a secure value. The results of compressive strength measurements were presented in Fig. 6. The obtained mean values were from 225 to 277 MPa. Statistical analysis showed, that the lowest compressive strength was registered for the materials where there was the majority of FA filler (100FA and 65FA35FB). Composites with a greater concentration of smaller size fillers, and materials with three different fillers showed much better properties, and those were comparable with results reported for commercially available materials [26,41].

Vickers microhardness test is a commonly accepted method to evaluate and compare composite resins which may suggest their preselection [42,43]. Direct restorative materials for dentistry should demonstrate Vickers microhardness at a level of 40-50 or higher [1,44]. The results obtained for investigated materials were presented in Fig. 7 and HV0.1 was from 38.3 to 50.1, so three out of six composites meet the cited assumption and show properties similar to materials used in dentistry [27,36]. Nevertheless, these values were rather at the lower limit, because numerous most modern composites show microhardness at a level of 80-100 [25,27,36]. This can be associated with
relatively low filler levels. Generally, increased filler content, which may be over 80 wt.%, resulted in higher microhardness [30,27,45]. However, it should be noted that in the presented work fillers' mass concentration was limited to 65% due to the planned purpose of the material. The highest microhardness was obtained for 50FA35FB15NF. This result, together with the previously described, remains in accordance with Tornavoi et al. [46] who suggested that smaller-sized particles may be more promising in terms of mechanical properties, because the distance between particles becomes reduced.

Presented investigations didn’t show particularly beneficial effects of one type of filler on all mechanical properties. It should be noted that all used fillers were after salinization. This process is usually conducted with organosilanes, as such as γ-methacryloxypropyltrimethoxysilane, and leads to attachment of silanes to the surface of silica and glass fillers [15]. Organosilane methacrylate groups have polymerizable carbon-carbon double bonds which react with the methacrylate groups of the resin matrix, when composite is polymerized [47]. It is essential for good mechanical properties of dental composites. Investigations show the best mechanical properties for the composite with tree different fillers (50FA35FB15NF) and generally good properties for composites with NF. This may be linked with the differentiation of particle sizes. If particles are uniform, large spaces will exist between them, but when smaller particles are introduced among the larger, the spaces will be reduced, so the contact area increases which is favorable for mechanical properties [46]. Additionally, in the same mass or/and volume of nanofiller a much greater number of particles are present than in microfiller. This situation may have effect on the crosslinking process, because a low distance between a very large amount of silanized nanoparticles with methacrylate groups on the surface may react with groups from matrix, and enhance properties, like hardness [48]. Significantly enhanced number of groups with carbon-carbon double bonds in composites resulting from NF introduction may also lead to a decreased degree of conversion, because total number of reacted double bond form fillers and matrix may be higher, but the percentage of reacted bonds may be lower due to their very high initial number. Although this supposition requires further confirmation, it may explain increased hardness values for composites with NF, when DC is decreased, what was registered by Fugolin et al. [49], and in our study. The degrees of conversion values for investigated composites were shown in Fig. 8. The mean values were from 55.7 to 61.1 %. These values were similar to the ones registered for modern composite materials with methacrylate-based resin matrix, which ranged from 45 to 68 [50,51]. Composites with NF show a significantly lower DC than 100FA and 50FA50FB. Additionally, the 50FA35FB15NF shows a significantly lower DC in comparison to all materials without NF. This stays in accordance with studies, where the presence of nanoparticles was associated with a lower degree of conversion [49,52-54]. Another reason of DC reduction may be that the particles can affect scattering of the light by particles. As light moves through a material with increasing density, its intensity is reduced. Silva, et al. [54] reported that non-agglomerated silica nanoparticles in nanofilled composites may scatter the light, reduce the power density inside the sample and finally decrease the DC. On the other hand, some reports showed larger scattering of the light, when the particle size is circa one half [55] or close to that [52] of the curing light wavelength, but NF or their aggregations in our study had a few times smaller dimensions, so they shouldn’t have a strong negative effect on DC from this point of view. Additionally, refractive index may also have an influence on DC. The used NF has an index of 1.46 and indexes of the resin matrix and glass filler are initially higher. De Oliveira [52] reported that during curing the refractive index of the matrix becomes even more different than that of the nanofillers, what can be the reason for the increase in light scattering within the composite and the decrease of DC. The presented considerations indicate that the reasons for lowering the DC of composites with NF probably complex. Investigations in that direction should be conducted in future, because DC is considered to be an important property of dental composites due to the risk of biological responses, because unsuitable conversion can increase the potential for monomer release and affect pulp tissues [56].

Fig. 8. Degree of conversion values (mean and standard deviation), the results marked with different lowercase letters are significantly different at the $p<0.05$ level

4. Conclusions

The typical matrix consisting of monomers used in dental materials was successfully modified with three different fillers, and the obtained composites showed satisfying properties. Within the limits of this study, the most advantageous compilation of properties was achieved by the material where a micrometric-size glass filler was used simultaneously with a submicron and nanometric filler. However, the results showed, that there was no filler, which had an especially positive impact on the mechanical properties, but the reinforcement effect was achieved by proper compilation of fillers of different sizes. Additionally, the results showed that the use of nanofillers can decrease the
degree of conversion, albeit in an acceptable range. The properties of dental composites result from a complex combination of compositional and microstructural factors that should not be considered in isolation, as is often done.

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