Effect of Rapid Polymerization on Water Sorption and Solubility of Bulk-fill Composites

Utjecaj brze polimerizacije na apsorpciju vode i topljivost bulk-fill kompozita

Abstract

Objectives: The aim of the study was to examine the impact of rapid high-intensity polymerization on water sorption and solubility of a new generation of bulk-fill composite materials. Materials and methods: Five materials were tested: a conventional composite Filtek Z250 (3M, St. Paul, USA) and four bulk-fill composites, Filtek One Bulk Fill (3M), Tetric PowerFill (Ivoclar Vivadent, Schaan, Liechtenstein), Tetric PowerFlow (Ivoclar Vivadent), SDR Plus (Dentsply, Konstanz, Germany). Composite specimens with a 9-mm diameter and a 2-mm height (n = 6) were polymerized with a high-intensity curing unit (Bluephase® PowerCure, Ivoclar Vivadent). The control group was polymerized for a total of 40 s on both sides (1193 mW/cm²) and 3 groups for 3 s on one side (3053 mW/cm²). Water sorption and solubility were measured by ISO 4049 method up to 30 days of immersion. The results were statistically analyzed using one-way ANOVA with Tukey post-hoc correction. Different polymerization protocols for the same material were compared by t-test (p < 0.05). Results: The 3s polymerization protocol increased the solubility of all materials. Filtek One Bulk Fill showed the highest water sorption and solubility values, and Tetric PowerFlow proved to be a stable material with low values of tested parameters. During immersion, a saturation of specimens was achieved in low-viscosity bulk-fill composites within two weeks, while in other materials it was not achieved within 30 days, or more, following the immersion. Conclusions: Rapid polymerization caused an increase in solubility, which could affect the biocompatibility of the investigated materials not intended for the 3s curing. SDR Plus and Filtek One Bulk Fill should not be polymerized with rapid high-intensity curing due to increased solubility that exceeds ISO 4049:2009 limits.

Introduction

To meet ever-increasing demands for a better management of restorations with conventional composites, it is essential for dentists to have simpler clinical procedures with reduced working time. For this purpose, bulk-fill composites have been introduced in the dental market as a new category of composite resins. Unlike a conventional composite, a bulk-fill composite allows for placement of a composite layer up to 4 to 5 mm thick in the cavity (1).

In addition to the placement of bulk-fill composites in thick layers, rapid polymerization with extremely high light intensity has recently been re-popularized to accelerate the clinical procedures of composite materials (2, 3). The concept of rapid polymerization is based on the principle of exposure reciprocity, which means the higher the light intensity, the less time is required for polymerization of the material, thereby reducing the curing unit exposure time (4).

Uvod

Da bi se zadovoljili sve veći zahtjevi za bolju izradu restauracija od konvencionalnih kompozita, stomatoložima su prijeko potrebni jednostavniji klinički postupci sa skraćenim vremenom rada. U tu svrhu na dentalnom su tržištu predstavljeni bulk-fill kompoziti kao nova kategorija smolastih kompozita. Za razliku od konvencionalnog kompozita, bulk-fill kompozit omogućuje postaviti u kavitet kompozit debljine od 4 do 5 mm (1).

Uz postavljanje bulk-fill kompozita u deblim slojevima, posljednjih se godina ponovno popularizira brza polymerizacija sjajem iznimno visokoga intenziteta radi ubrzanja kliničkoga rada s kompozitnim materijalima (2, 3). Koncept brze polymerizacije temelji se na načelu exposure reciprocity, odnosno što je veći intenzitet svjetlosti, to je manje vremena potrebno za polymerizaciju materijala i obratno, zato što uku-
and vice versa, because the total delivered energy required for a satisfactory polymerization remains the same (4). This concept of rapid polymerization dominated in the 1980s when plasma lamps gained their popularity. Plasma lamps could emit extremely high-intensity light, but only for a short period of up to 5 seconds (5). Higher light intensity means that more photons were emitted which could, in turn, simultaneously activate a higher amount of photoinitator molecules and ensure faster polymerization (6, 7). In the conventional composites, a myriad of initiation nuclei create a polymer network that rapidly reaches the gel point. At the post-gel stage, numerous monomers remain immobilized in the long-chain polymer network and the final polymerization of conventional composite remains significantly lower (8). The unpolymerized monomers with restricted mobility can form bonds within the same chain, so-called cyclization. Due to cyclization, the degree of conversion sometimes attains equally high values as with slower polymerization with lower radiation intensity. Still, the mechanical properties will be weaker and the polymerization stress higher (9). Because of this, many investigations have shown that the high-intensity polymerization concept is not sustainable for conventional composites (2, 3, 5, 8-10).

Recently, this concept has regained the interest of scientists due to the fundamental change in the chemical composition of the organic matrix of specific bulk-fill composites. The composite Tetric PowerFill (Ivoclav Vivadent, Schaan, Liechtenstein) is at the forefront. It has incorporated β-allyl sulfone reagent, allowing for addition-fragmentation chain transfer (AFCT) (2, 11). The aforementioned reagent allows for a step-growth polymerization process and a typical radical polymerization that forms a more homogeneous polymer network than the free radical reaction alone. After initiation and addition of the AFCT reagent, the AFCT reagent terminates the polymerization on one end of the polymer chain and simultaneously creates new sulphonyl radicals that further activate other monomers. The end result is a stable short kinetic chain network (2, 11). The fact that new initiation sites occur after the illumination has ended supports the rapid high-intensity curing. In that way, the material is customized to the concept of rapid polymerization.

Given that composite materials are used for direct composite restorations and constantly exposed to moist medium, it is essential to investigate the impact and consequences of water sorption on the properties of composite materials. Water causes hydrolysis of ester bonds in polymer networks in resin composites (12). In poorly polymerized resin composites, untreated monomers could leach out of the material facilitated by water ingress and pose threats to the biocompatibility of the material (5, 7, 13). In oral environment, the salivary esterase can even promote enzymatic monomer degradation (14, 15), possibly causing genotoxic, cytotoxic or allergic reactions to the oral mucosa (16-20). Besides, absorbed water can lead to hydrolytic degradation of resin matrix-filler bond and the silane-filler bond which can deteriorate mechanical properties (21). The amount of absorbed water and solubility of composite is conditioned by the type and amount of composite matrix, amount of filler, and degree

and with the total delivered energy required for a satisfactory polymerization remains the same (4). This concept of rapid polymerization dominated in the 1980s when plasma lamps gained their popularity. Plasma lamps could emit extremely high-intensity light, but only for a short period of up to 5 seconds (5). Higher light intensity means that more photons were emitted which could, in turn, simultaneously activate a higher amount of photoinitator molecules and ensure faster polymerization (6, 7). In the conventional composites, a myriad of initiation nuclei create a polymer network that rapidly reaches the gel point. At the post-gel stage, numerous monomers remain immobilized in the long-chain polymer network and the final polymerization of conventional composite remains significantly lower (8). The unpolymerized monomers with restricted mobility can form bonds within the same chain, so-called cyclization. Due to cyclization, the degree of conversion sometimes attains equally high values as with slower polymerization with lower radiation intensity. Still, the mechanical properties will be weaker and the polymerization stress higher (9). Because of this, many investigations have shown that the high-intensity polymerization concept is not sustainable for conventional composites (2, 3, 5, 8-10).

Recently, this concept has regained the interest of scientists due to the fundamental change in the chemical composition of the organic matrix of specific bulk-fill composites. The composite Tetric PowerFill (Ivoclav Vivadent, Schaan, Liechtenstein) is at the forefront. It has incorporated β-allyl sulfone reagent, allowing for addition-fragmentation chain transfer (AFCT) (2, 11). The aforementioned reagent allows for a step-growth polymerization process and a typical radical polymerization that forms a more homogeneous polymer network than the free radical reaction alone. After initiation and addition of the AFCT reagent, the AFCT reagent terminates the polymerization on one end of the polymer chain and simultaneously creates new sulphonyl radicals that further activate other monomers. The end result is a stable short kinetic chain network (2, 11). The fact that new initiation sites occur after the illumination has ended supports the rapid high-intensity curing. In that way, the material is customized to the concept of rapid polymerization.

Given that composite materials are used for direct composite restorations and constantly exposed to moist medium, it is essential to investigate the impact and consequences of water sorption on the properties of composite materials. Water causes hydrolysis of ester bonds in polymer networks in resin composites (12). In poorly polymerized resin composites, untreated monomers could leach out of the material facilitated by water ingress and pose threats to the biocompatibility of the material (5, 7, 13). In oral environment, the salivary esterase can even promote enzymatic monomer degradation (14, 15), possibly causing genotoxic, cytotoxic or allergic reactions to the oral mucosa (16-20). Besides, absorbed water can lead to hydrolytic degradation of resin matrix-filler bond and the silane-filler bond which can deteriorate mechanical properties (21). The amount of absorbed water and solubility of composite is conditioned by the type and amount of composite matrix, amount of filler, and degree
gree of conversion of monomer into the polymer (22, 23). Water sorption is a diffusion-controlled process mainly related to the organic part of the composite materials, and it is lower for the highly filled materials (24). Therefore, the water sorption characteristics of dental composite materials are vital for a better understanding and the appraisal of behavior of a material in human mouth.

Free volume theory and interaction theory are two theories used to explain water sorption. Free volume theory is explained by water sorption in free spaces of the polymer network. In contrast, interaction theory is defined by chemical bonds formed between water and the hydrophilic ionic groups of the polymer chain (25). Most of the restorative dental materials are sensitive to water sorption and solubility. Comparing water sorption with other restorative materials, composites exhibited the lowest amount of absorbed water (0.17%), followed by composites (1.1%) with the resin-modified glass-ionomer cements in the first place with the highest values (6%) (26).

Apart from Tetric PowerFill, the manufacturer also claims that Tetric PowerFlow (Ivoclar Vivadent) could be polymerized by rapid polymerization. Rapid polymerization was not successful in the past due to a decrease in the crosslinking density of the polymer network. So far, the influence of this type of polymerization on water sorption and solubility has not been investigated on contemporary composites, hence this study aimed to investigate the influence of rapid polymerization during 3 s with a high-intensity curing unit on water sorption and solubility of bulk-fill composites and to compare it with standard polymerization.

Material and methods

Material

Five materials were tested (Table 1): two high-viscosity bulk-fill materials: Tetric PowerFill and Filtek One Bulk Fill Restorative (3M, St. Paul, USA); and two low-viscosity bulk-fill materials: Tetric PowerFlow SDR Plus Bulk Fill Flowable, and one conventional composite: Filtek Z250 (3M).

Dimensions of composite specimens (n = 6) for water sorption and solubility were 9 mm in diameter and 2 mm in height. Polymerization was carried out using the fourth-generation light-emitting diode curing unit (Bluephase PowerCure, Ivoclar Vivadent) with one of two modes of polymerization (Figure 1): 1. during 3 seconds on one side with average values of radiant exitance 3053 (± 4.71) mW/cm² or 2. 20 seconds on both sides with average values of radiant exitance 1193 (± 4.71) mW/cm².

Light intensity was measured three times with a built-in radiometer of the curing unit (Bluephase PowerCure, Ivoclar Vivadent) before specimen production to calculate the average intensity value.

Water sorption and solubility

After polymerization and before placing specimens in a desiccator, the edges of specimens were gently ground on abrasive paper (Silicon carbide grinding paper, wet or dry, difuzijski je kontrolirani proces koji je vezan za organski dio kompozitnih materijala pa je obično smanjena kod materijala koji su više punjeni (24). Zato su karakteristike apsorpcije vode kompozitnih materijala od vitalnog značenja za bolje razumevanje i procjenu ponašanja materijala u ljudskim ustima.

Teorija slobodnoga volumena i teorija interakcije dvije su teorije kojima se objašnjava apsorpcija vode. Teorija slobodnog volumena objašnjava se apsorpcijom vode u slobodne prostore polimerne mreže, a teorija interakcije stvaranjem kemijske veze između vode i hidrofilnih ionskih skupina polimernoga lanca (25). Većina restaurativnih dentalnih materijala podložna je apsorpciji vode i topljivosti. Uspoređujući apsorpciju vode kompozita s ostalim restaurativnim materijalima, kompoziti su pokazali najmanju količinu apsorbirane vode (0,17 %), slijeđe kompomeri (1,1 %), pa smolom modifičirani staklenoionomerni cementi koji su pokazali najviše rezultate (6 %) (26).

Osim Tetric Power Filla, proizvođač također tvrdi da se Tetric Power Flow (Ivoclar Vivadent) može polimerizirati brzoj polymzracijom. Brza polimerizacija u prošlosti nije bila uspešna zbog smanjenja gustoće umrežavanja polimerne mreže. Utjecaj vrste polimerizacije na apsorpciju vode i topljivost dosad nije istražen na suvremenim kompozitima, sto ga je cilj ovoga istraživanja bio ispitati utjecaj brze polimerizacije tijekom 3 sekunde s polimerizacijskom svjetiljkom visokoga intenziteta na apsorpciju vode i topljivost bulk-fill kompozita i usporediti ih sa standardnom polimerizacijom.

Materijal i postupci

Materijali

Ispitalo se pet kompozitnih materijala (tablica 1.), od toga dva visokoviskozna bulk-fill materijala – Tetric Powerfill i Filtek One Bulk Fill Restorative (3M, St. Paul, SAD), dva niskoviskozna bulk-fill materijala – Tetric PowerFlow i SDR Plus Bulk Fill Flowable (Dentsply, Konstanz, Germany) te jedan konvencionalni kompozit – Filtek Z250 (3M).

Kompozitni uzorci za apsorpciju vode i topljivost (n = 6) bili su sljedećih dimenzija: promjer 9 mm i visina 2 mm. Polimerizacija je obavljena svjetiljkom s diodama četvrtog generacije (Bluephase Power Cure, Ivoclar Vivadent) s jednim od dvaju načina polimerizacije (slika 1.): 1. tijekom 3 sekunde s jedne strane s vrijednostima prosječnoga emitiranoga zračenja od 3053 (± 4.71) mW/cm² ili 2. 20 sekunda obostrano s vrijednostima prosječnoga emitiranoga zračenja od 1193 (± 4.71) mW/cm². Mjerenje intenziteta svjetlosti provedeno je tri puta radiometrom ugrađenim u postolje svjetiljke (Bluephase Power Cure, Ivoclar Vivadent) prije izrade uzoraka da bi se izračunala srednja vrijednost intenziteta.

Apsorpcija vode i topljivost

Poslije polimerizacije i prije postavljanja uzoraka u ekiskator, njihovi su rubovi nježno ispolirani na abrazivnom papiru (Silicon carbide grinding paper, wet or dry, Grit500/
Table 1 The composition of the materials used in the research according to the manufacturer’s instructions and the recommended layer thickness.

| Material • Materijal | Manufacturer • Naziv proizvođača [Ec rep]; [Lot (i) exp] | Organic matrix • Organska matrica | Inorganic filler • Anorgansko punilo | Filler particle size • Veličina čestica punila | Weight / volume content of fillers • Maseni / volumni udio punila (%) | Recommended layer thickness • Preporučena debljina sloja |
|----------------------|------------------------------------------------------------|-----------------------------------|-------------------------------------|---------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| 3M™ Filtek™ Z250 Universal Restorative | 3M ESPE Dental Products; St. Paul, MN, SAD [NC4979 27.7.2023.] | UDMA, Bis-GMA, Bis-EMA, TEGDMA | zirconia/silica | 0.01-3.5 μm | -60 | from 2 to 2.5 mm • od 2 do 2.5 mm |
| Tetric® PowerFill IVA | Ivoclar Vivadent AG; Schaan, Lichtenstein [X56571 14.9.2022.] | monomer matrix - dimethacrilates (w = 20 - 21 %) | barium glass, ytterbium trifluoride and copolymers (w = 79 - 80 %) | 40 nm – 3 μm | 76 - 77 / 53 - 54 | up to 4 mm • do 4 mm |
| 3M™ Filtek™ One Bulk Fill Restorative A2 | 3M ESPE Dental Products; St. Paul, MN, SAD [NA61219 28.5.2022.] | AUDMA, UDMA, 1,12-dodecanediole-DMA | non-aggl./non-aggr. silica f. | 20 nm | -76.5 / -58.5 | up to 5 mm • do 5 mm |
| SDR® Plus Bulk Fill Flowable U | Dentsply Caulk; Milford, DE, SAD [Dentsply DeTrey GmbH; Konstanz, Njemačka] [00028647 12.8.2022.] | resin matrix – modified UDMA, TEGDMA, dimethacrylate resin and trimethacrylate resin | silanated barium-alumino-fluoro-borosilicate glass, silanated strontium alumino-fluoro-silicate glass, surface treated fume silicas, ytterbium fluoride, synthetic inorganic iron oxide pigments and titanium dioxide | - | 70.5 / 47.4 | up to 4mm • do 4mm |
| Tetric® PowerFlow IVA | Ivoclar Vivadent AG; Schaan, Lichtenstein [Y15023 09.4.2021./E00V4H 20.7.2022.] | monomer matrix - dimethacrilates (w = 28 %) | barium glass, ytterbium trifluoride and copolymers (w = 71 %) | 0.1 μm – 30 μm | 68.2 / 46.4 | up to 4 mm • do 4 mm |

non-aggl.: non-agglomerated, non-aggr.: non-aggregated, aggr.: aggregated, aggl.: agglomerated, f.: filler, DMA: dimethacrylate, UDMA: urethane-dimethacrylate • neagl. – neaglomerirano, neagr. – neagregirano, agr. – agregirano, aggl. – aglomerirano, p. – punilo, DMA – dimetakrilat, UDMA – uretan-dimetakrilat, TEGDMA – trietilenglikol-dimetakrilat

Figure 1 Comparison of 3s polymerization (left) and control groups of specimens (right)

Slika 1. Usposrebila trosekundne polimerizacije (lijevo) i kontrolne skupine uzoraka (desno)
Apsorpcija vode pri trosekundnoj polimerizaciji

Klarić i sur.

Grit500/P1000, Buehler, Lake Bluff, Illinois, SAD) to remove overhangs and ensure that the same volumes and surfaces of all the specimens were maintained. Their mass was daily measured using an analytical balance (MS NewClassic, Mettler Toledo AG, Switzerland) until the daily difference in weight dropped below 0.1 mg, meaning that the equilibrium of the specimen mass had been established. The measured value indicated the initial mass of the specimen (m₁). Subsequently, each specimen was immersed in a conical bottom plastic container filled with 4mL of distilled water and stored in the dark in an incubator at 37 ± 1°C. Specimens were weighed after 1, 2, 3, 7, 14, 21, 28 and 30 days of immersion (m₂(t), where t stood for the interval from the beginning of immersion). During the immersion measurements, specimens were taken out from the water. According to the instructions of ISO standard 4049, each specimen was blotted with cellulose pads on both sides until it was free from visible moisture and waved in the air for 15 seconds. After immersion, specimens were again stored in a desiccator and weighed until they established a mass equilibrium (mass difference between the two subsequent measurements was below 0.1 mg) that denoted final mass (m₃). The total time of desorption was 48 days. Water sorption and solubility were calculated by the following formulas and presented in abso-
lute values in grams:

\[
\text{water sorption} = \frac{(m_2(\text{eq}) - m_3)}{V} \text{ (µg/mm}^3\text{)}
\]

\[
\text{solubility} = \frac{(m_1 - m_3)}{V} \text{ (µg/mm}^3\text{)}
\]

where \(m_2(\text{eq})\) represents mass equilibrium.

Statistical analysis

Water sorption and solubility values were compared using a mixed-model ANOVA that included two between-subject factors ("material type" and "polymerization protocol"), as well as one within-subject factor ("time point") that represented repeated observations. As statistically significant interactions of all three factors were identified, instead of interpreting the main effects overall, separate analyses were performed for each factor separately, at fixed levels of the remaining two factors (27,28). This led to using one-way ANOVA with Tukey’s correction for the comparison among materials, t-test for independent observation for the comparison between two curing protocols, and repeated-measurements ANOVA with Bonferroni’s corrections for the comparison among time points. Using the results of statistical comparisons among different time points obtained by repeated-measurements ANOVA with Bonferroni correction, the “plateau” of stable values was defined as the absence of statistically significant differences between at least two successive time points (29,30). For each test, p-values below 0.05 were considered statistically significant. The statistical analysis was performed using SPSS (version 25, IBM, Armonk, NY, USA).

Results

Filtek One Bulk Fill exhibited the highest water sorption in both groups of specimens, while Tetric PowerFlow exhibited the lowest water sorption in both groups compared to other materials. The polymerization method affected the water P1000, Buehler, Lake Bluff, Illinois, SAD) to be used for this purpose. The values of water sorption and solubility for the different materials are presented in Table 1. The statistical analysis revealed significant differences in water sorption and solubility between the two groups of specimens, with Tetric PowerFlow showing the highest values for both endpoints. Further analysis using post-hoc tests identified the specific groups that differed statistically from each other.

Rezultati

Filtek One Bulk Fill pokazao je najveću apsorpciju vode u obje skupine uzoraka, a Tetric Power Flow pokazao je najma-
niju apsorpciju u obje skupine u odnosu prema ostalim mate-
rijalima. Način polimerizacije utjecao je na apsorpciju vode.
sorption of all materials except Tetric PowerFlow and SDR Plus. For Filtek One Bulk Fill, Filtek Z250 and Tetric PowerFill, water sorption was higher in the control group of specimens when they were polymerized in the standard manner (Figure 2).

The solubility was higher for all specimens polymerized with the 3s protocol. SDR Plus specimens polymerized by standard protocol exhibited the highest solubility for this group of specimens, while Filtek One Bulk Fill and SDR Plus exhibited the highest solubility for the 3s group. Negative solubility values were established by the conventional control material Filtek Z250 for both polymerization groups and Tetric PowerFill for the control group of specimens polymerized by the standard protocol (Figure 3).

Figure 4 shows that specimens of Tetric PowerFlow and SDR Plus materials reached the plateau of mass change during immersion of all materials, except Tetric PowerFlow and SDR Plus. For Filtek One Bulk Fill, Filtek Z250 and Tetric PowerFill, water sorption was higher in the control group of specimens when they were polymerized in the standard manner (Figure 2).

The solubility was higher for all specimens polymerized with the 3s protocol. SDR Plus specimens polymerized by standard protocol exhibited the highest solubility for this group of specimens, while Filtek One Bulk Fill and SDR Plus exhibited the highest solubility for the 3s group. Negative solubility values were established by the conventional control material Filtek Z250 for both polymerization groups and Tetric PowerFill for the control group of specimens polymerized by the standard protocol (Figure 3).

Figure 4 shows that specimens of Tetric PowerFlow and SDR Plus materials reached the plateau of mass change during immersion of all materials, except Tetric PowerFlow and SDR Plus. For Filtek One Bulk Fill, Filtek Z250 and Tetric PowerFill, water sorption was higher in the control group of specimens when they were polymerized in the standard manner (Figure 2).

The solubility was higher for all specimens polymerized with the 3s protocol. SDR Plus specimens polymerized by standard protocol exhibited the highest solubility for this group of specimens, while Filtek One Bulk Fill and SDR Plus exhibited the highest solubility for the 3s group. Negative solubility values were established by the conventional control material Filtek Z250 for both polymerization groups and Tetric PowerFill for the control group of specimens polymerized by the standard protocol (Figure 3).

Figure 4 shows that specimens of Tetric PowerFlow and SDR Plus materials reached the plateau of mass change during immersion of all materials, except Tetric PowerFlow and SDR Plus. For Filtek One Bulk Fill, Filtek Z250 and Tetric PowerFill, water sorption was higher in the control group of specimens when they were polymerized in the standard manner (Figure 2).

The solubility was higher for all specimens polymerized with the 3s protocol. SDR Plus specimens polymerized by standard protocol exhibited the highest solubility for this group of specimens, while Filtek One Bulk Fill and SDR Plus exhibited the highest solubility for the 3s group. Negative solubility values were established by the conventional control material Filtek Z250 for both polymerization groups and Tetric PowerFill for the control group of specimens polymerized by the standard protocol (Figure 3).

Figure 4 shows that specimens of Tetric PowerFlow and SDR Plus materials reached the plateau of mass change during immersion of all materials, except Tetric PowerFlow and SDR Plus. For Filtek One Bulk Fill, Filtek Z250 and Tetric PowerFill, water sorption was higher in the control group of specimens when they were polymerized in the standard manner (Figure 2).

The solubility was higher for all specimens polymerized with the 3s protocol. SDR Plus specimens polymerized by standard protocol exhibited the highest solubility for this group of specimens, while Filtek One Bulk Fill and SDR Plus exhibited the highest solubility for the 3s group. Negative solubility values were established by the conventional control material Filtek Z250 for both polymerization groups and Tetric PowerFill for the control group of specimens polymerized by the standard protocol (Figure 3).
ing their immersion after only two weeks, whereas other materials did not reach it within 30 days. The exception is Tetric PowerFill polymerized with 3s protocol after 28 days.

Discussion

This research examined the effect of 3s light polymerization with an intensity of approximately 3000 mW/cm² on water sorption and solubility of contemporary bulk-fill composite materials. The results showed an increased solubility for all materials polymerized with the 3s protocol. In contrast, standard polymerization of 20 s with a moderate light intensity of 1200 mW/cm² affected an increased water sorption in three of the five tested materials. The exceptions were low-viscosity materials with equal sorption values regardless of the polymerization protocol.

The amount of solubility of each composite material is determined by the amount of unreacted monomer, polymerization promoters, oligomers, filler particles, and products of degradation processes in the composite material (24, 31, 32). In this study, the rapid polymerization protocol markedly increased the solubility. The very high light intensity of 3053 mW/cm² emitted in the 3s program of the Bluephase Power-Cure used in this study released two and a half times more energy per second than the standard protocol with 1193 mW/cm². Such polymerization is much faster with the 3s program than with the standard program because a large number of free radicals that trigger a radical polymerization reaction are generated at the same time. In Tetric PowerFill, the AFCT reagent will condition the formation of short-chain polymers without much cross-linking, resulting in a more complete and more homogeneous polymer network. Therefore, its solubility values are one of the lowest in this study. For other materials, due to the increased rigidity of the polymer network, a large amount of unpolymerized monomers will remain, which dissolve and leach out of the specimen surface during prolonged exposure to water, causing increased solubility. Some studies have reported that the size of the unreacted monomer plays a role in the amount of solubility, e.g., triethylene glycol dimethacrylate (TEGDMA) is reported to have a higher and faster tendency to release from the material due to lower molecular weight (13,33). The solubility values for 3s polymerization of SDR Plus and Filtek One Bulk Fill were the highest, exceeding 7.5 µg/mm³, which is not within the recommended values by ISO 4049:2009. The high solubility values for Filtek One Bulk Fill in 3s polymerization can be explained by its reduced degree of polymerization, which was determined in a previous study by Marović et al. (2). Apart from unpolymerized monomers, it is possible that filler nanoparticles were also eluted from the surface of Filtek One Bulk Fill, thus contributing to its solubility.

Water sorption and dissolution of their individual components occur simultaneously during exposure of composite specimens to water. It is usually difficult to distinguish the effect of solubility while the specimens are still in the aqueous medium because water sorption is dominant, leading to an overall increase in mass. The exact extent of solubility could be determined only after the second drying of the ISO 4049:2009 standard after 30 days. It is usually difficult to distinguish the effect of solubility while the specimens are still in the aqueous medium because water sorption is dominant, leading to an overall increase in mass. The exact extent of solubility could be determined only after the second drying of the ISO 4049:2009 standard after 30 days. It is usually difficult to distinguish the effect of solubility while the specimens are still in the aqueous medium because water sorption is dominant, leading to an overall increase in mass. The exact extent of solubility could be determined only after the second drying of the ISO 4049:2009 standard after 30 days.

Rasprava

Ovo istraživanje proučavalo je utjecaj trosekundne polimerizacije svjetlom intenziteta oko 3000 mW/cm² na apsorpciju vode i topljivost suvremenih bulk-fill kompozitnih materijala. Rezultati su pokazali da je topljivost bila povišena za sve materijale polimerizirane trosekundnim protokolom. Su- protono tomu, standardna polimerizacija od 20 sekunda svjetlom umijerenog intenziteta od 1200 mW/cm² utjecala je na povisenu apsorpciju vode kod triju od pet ispitanih mate- rijala. Iznimke su bili niskoviskozni materijali koji su ima- li jednake vrijednosti apsorpcije bez obzira na polimerizacijski protokol.

Količina topljivosti pojedinog kompozitnog materijala uvjetovana je količinom nereagiranog monomera, promo- torima polimerizacije, oligomerima, česticama punila te pro- duktima degradacijskih procesa u kompozitnom materijalu (24, 31, 32). Rezultati topljivosti u ovome istraživanju pokaza- li su iznimno povećanu topljivost brzim polimerizacijskim protokolom. Emitiranjem svjetlosti vrlo visokoga intenziteta od 3053 mW/cm², poput trosekundnoga programa Bluepha- se Power Cure svjetljike rabiljene u ovom istraživanju, oslobodi se nešto više od dva i pol puta energije u sekundi u uspo- redbi sa standardnim protokolom od 1193 mW/cm². Takva polimerizacija mnogo je brža u trosekundnome programu nego u standardnome zato što se istodobno stvara velika koli- čina slobodnih radikala koja pokreću radikalnu reakciju poli- merizacije. U slučaju Tetric Powerfill, AFCT reagens uvje- tovati će stvaranje više kratkolančanih polimera bez velikoga ukrštenog polimeriziranja te potpuno izomologiju poli- mernu mrežu. Zbog toga su njegove vrijednosti topljivosti jedne od najnižih u ovom istraživanju. Kod ostalih materij- a, zbog povećane rigidnosti mreže, zaostat će veća količina nepolimeriziranih monomera koji se pri dugotrajnom izlag- nju vodi otapaju i izlaze s površine uzorka uzrokujući poveća- nu topljivost. Autori određenih istraživanja navode da veliči- na nereagiranog monomera igra ulogu u količini topljivosti, npr., za trietilenglikol-dimetakrilat (TEGDMA) navode se da ima veću i bržu tendenciju otpuštanja iz materijala zbog manje molekularne mase (13,33). Vrijednosti topljivosti za trosekundnu polimerizaciju materijala SDR Plus i Filtek One Bulk Fill bile su najviše – više od 7,5 µg/mm³ što nije unutar preporučenih vrijednosti prema standardu ISO 4049:2009. Visoke vrijednosti topljivosti za Filtek One Bulk Fill pri trosekundnoj polimerizaciji možemo razjasniti i njegovim sma- njenim stupnjem polimerizacije koji su utvrdili Marović i su- radnici (2). Osim nepolimeriziranih monomera, moguće je da su nanočestice punila također bile eleuirane s površine Fil- tek One Bulk Fill pridonoseći tako njegovoj topljivosti.

Apsorpcija vode i otapanje pojedinih komponenta doga- đaju se istodobno tijekom izlaganja kompozitnih uzoraka vo- di. Obično je teško razaznati utjecaj topljivosti dok su uzorci u vodenome mediju zato što je apsorpcija vode dominantna, dovodeći do ukupnoga povećanja mase. Točan stupanj toplji-
4049 testing protocol. Our research unquestionably showed increased solubility after 3s polymerization for all materials, hence it is reasonable to suspect that this is the reason for the seemingly reduced water sorption in the 3s group. This led to the increased water sorption in the control group of specimens in high-viscosity materials in the statistical analysis. According to accepted theories of water diffusivity in composite materials (24), the amount of water sorption is inversely proportional to the degree of conversion because greater binding of monomers to polymer reduces the free space for water diffusion between polymer networks (31). In addition to the maximum achievable degree of conversion of individual material, it is important to study the post-cure polymerization kinetics after light illumination. Par et al. demonstrated that the long-term post-cure polymerization of the SDR continues up to 7 days, which leaves a more extended period for the release of unreacted compounds and thus higher solubility values (34). This could explain the higher solubility values of its successor SDR Plus than those of other materials tested in this study.

Filttek One Bulk Fill and Fitek Z250, as two of the most filled materials in our research, exhibited the highest water sorption for both polymerization methods. Although the high content of fillers slows down the diffusion of water, the type of fillers and the percentage of their silanization affect the final water sorption values, which have been considered in previous studies (35, 36). Nano-fillers that tend to agglomerate and silane on their large surface easily hydrolyze when exposed to water. This creates free spaces that facilitate the diffusion of water in such a polymerized composite. Our previous long-term study of water sorption of specimens polymerized by standard protocol over 90 days confirms the current results because the same sorption patterns were observed for Filttek One Bulk Fill (37, 38). In addition, Filttek One Bulk Fill also contains a long chain aromatic urethane dimethacrylate (AUDMA) with a small number of reactive groups added to reduce polymerization shrinkage. However, their polymerization leads to a lower degree of cross-linking of the polymer network. The lower density of the polymer opens up free spaces within the network, thus leaving room for water sorption according to free volume theory (14). Filttek Z250 does not contain nano-fillers, but includes a hydrophilic bisphenol A-glycidyl methacrylate (Bis-GMA) resin which, by interaction of its numerous hydroxyl groups with water, forms hydrogen bonds and enhances water sorption (35). Another reason for the increased sorption of Filttek Z250 could be TEGDMA resin residues. Although the manufacturer has replaced most of the hydrophilic resin TEGDMA with more hydrophobic resins (Table 1), its traces could still contribute to increased sorption, which was also observed in the study of Baor et al. (39).

The lowest solubility was demonstrated by Filttek Z250 and Tetric PowerFill (40). Filttek Z250 has negative solubility values, which can be explained by strong and numerous hydrogen bonds within Bis-GMA molecules, which is why water cannot be completely removed during desorption. However, the low solubility values of Tetric PowerFill compared to other bulk-fill composites in 3s polymerization can also vosti mogao se odrediti tek nakon drugog sušenja protokola ispitivanja ISO 4049. Naše istraživanje neupitno je pokazalo pojačanu topljivost pri trosekundnoj polimerizaciji i to za sve materijale, pa je opravdano posumnjati da je to razlog za izgled sniženu apsorpciju vode u trosekundnoj skupini. To je u statističkoj analizi rezultiralo povišenom apsorpcijom vode u kontrolnoj skupini uzoraka kod visokoviskoznih materijala. Prema dosad prihvaćenim teorijama difuzivnosti vode kod kompozitnih materijala (24), količina apsorbirane vode oznacuje se kao proporcionalna stupnju konverzije jer se većim povezivanjem monomerova u polimera smanjuje slobodni prostor za difuziju vode između polimerne mreže (31). Dodatno maksimalno ostvarivom stupnju konverzije pojedinog materijala bitno je pružiti i kinetiku polimerizaciji koja se dugoročno naknadno događa nakon svjetlosne polimerizacije materijala. Par i suradnici učili su dugoročno naknadnu polimerizaciju SDR materijala koja maksimalni stupanj konverzije postigne do 7 dana, što ostavlja veće razdoblje za otuđivanje nereagiranih reaktivnih spojeva kompozitnoga materijala te time veće vrijednosti topljivosti (34). To bi moglo biti objašnjenje za veće vrijednosti topljivosti njegova nasljednika – SDR Plusa od drugih ispitanih materijala u ovom istraživanju.

Filttek One Bulk Fill i Filttek Z250, kao dva najviši punje- na materijala u našem istraživanju, pokazala su najveće apsorpciju vode tijekom oba načina polimerizacije. Iako visok udio punila usporava difuziju vode, vrsta punila i postotak njihove silanizacije utječe na konačne vrijednosti apsorpcije vode, što je rezultat proizvodno i prijašnjim istraživanjima (35, 36). Nanopulkna imaju tendenciju prema aglomeraciji i silan na njihovoj velikoj površini lako hidrolizira pri izlaganju vodi. To stvara slobodne prostore pa je olakšana difuzija vode u tako polimeriziranom kompozitu. Naše prethodno dugoročno istraživanje apsorpcije vode uzoraka polimeriziranih standardnim protokolom tijekom 90 dana potvrđuje sadašnje rezultate jer su uočeni isti oblici apsorpcije na Filttek One Bulk Fillu (37, 38). Uz to, Filttek One Bulk Fill također sadržava dugoglasanđeni aromatični uretan-dimetakrilat (AUDMA) s malim brojem reaktivnih skupina koji je dodan radi smanjenja polimerizacijskog skupljanja. No njihova polimerizacija potiče manje ukrčeno povezivanje polimerne mreže. Manja gustoća polimera otvara slobodne prostore unutar mreže i ostavlja prostor za apsorpciju vode prema teoriji slobodnoga volumena (14). Filttek Z250 ne sadržava nanopunila, ali sadržava hidrofilni bifensol A-glicidil metakrilat (Bis-GMA) smolu koja interakcijom svojih mnogobrojnih hidroksilskih skupina s vodom stvara vodotuve veze i pojačava apsorpciju vode (35). Drugi razlog za povećanu apsorpciju Filtkeka Z250 mogli bi biti ostaci smole TEGDMA. Iako je proizvođač većinu hidrofilne smole TEGDMA zamijenio hidrofobnijim smolama (tablica 1.), ipak bi u nekim ostacima mogli pridonijeti povećanoj apsorpciji, što se razmatralo i u istraživanju Baora i su- radnika (39).

Najmanju topljivost pokazali su Filttek Z250 i Tetric PowerFill (40). Filttek Z250 ima neugodne vrijednosti topljivosti, što se može objasniti čvrstom vodikovim vezama s Bis-GMA-om, zbog čega se voda ne može potpuno ukloniti pri desorpciji. No niške vrijednosti topljivosti Tetric Power Filla u usporedbi s ostalim bulk-fill kompozitima pri trosekundnoj
be explained by step-growth polymerization using β-allyl sulfone, the so-called AFCT, which leads to more stable polymerization in which there are no remaining unreacted monomers (2,11).

The observed water sorption curves (Figure 4) are increased at the beginning of the immersion, after which the highest level of absorbed water is reached, i.e., the highest measured mass followed by the plateau. Both low-viscosity materials in this study achieved water saturation after 7 and 14 days for both polymerization methods, while SDR Plus showed a slight decrease, which means that the process of releasing soluble components began to prevail (41, 29). Different proportions of inorganic and organic parts between high-viscosity and low-viscosity composites could play an important role in the obtained results. A higher proportion of the organic matrix creates a higher diffusion gradient of water to the specimen center, leading to faster water saturation of the material, especially if that organic matrix contains a hydrophilic resin such as TEGDMA found in SDR Plus.

The step-growth polymerization of Tetric PowerFill could explain the mass change curves during immersion (Figure 4). It is observed that Tetric PowerFill polymerized with 3s program reached a plateau after 28 days, while other tested high-viscosity materials did not achieve the plateau even after 30 days. Although Tetric PowerFill does not have a higher proportion of organic matrix than low-viscosity materials, it does have AFCT polymerization. Therefore, cross-linking of the polymer network plays a more important role in water sorption kinetics than in the final values, i.e. water sorption by volume (42).

This study was based on ISO 4049:2009 standard, hence 2 mm thick specimens were used, which enabled us to compare our results to the recommended values. For the extension of this study it would be interesting to evaluate properties of bulk-fill composite materials on 4 mm specimens, which would be more similar to clinical conditions. However, owing to this experimental design, we were able to determine that all materials in both polymerization protocols had less than 40 µg/mm³ water sorption and satisfied the ISO recommendation. On the other hand, rapid curing of SDR Plus and Filtek One Bulk Fill exceeded the maximum acceptable value for solubility (7.5 µg/mm³).

**Conclusions**

The solubility of all of the test samples significantly increased during rapid polymerization with very high light intensity, which could be associated with the elusion of unreacted monomers and possible adverse reactions of gingival and mucosal cells. The solubility values of SDR Plus and Filtek One Bulk Fill exceeded the recommended values by ISO 4049:2009 standard, hence rapid polymerization is not recommended for those materials. The effect of rapid polymerization on water sorption was material-dependent, with the low-viscosity bulk-fill materials being insensitive to the polymerization protocol.

Polimerizacija, mogu se objasniti i skokovitom polymerizacijom s pomoću β-ail sulfona, tzv. AFCT-a čime se postiže stabilnija polymerizacija u kojoj nema ostatnih nereagiranih monomera (2, 11).

Promatrane krivulje apsorpcije vode (slika 4.) sadržavaju povećanje na početku imerzije nakon kojega se postiže najviša razina apsorbirane vode, odnosno najviša izmjerena masa te nakon toga „plato“. Oba niskoviskozna materijala u ovom istraživanju postigli su zasićenje vodom već nakon 7 dana, odnosno 14 dana za oba načina polymerizacije, a kod SDR Plusa uočen je i blagi pad, što znači da je počeo prevladavati proces otpuštanja topljivih komponenti (41, 29). Različit udio anorganskoga i organskoga dijela između visokoviskoznih i niskoviskoznih kompozita mogao bi biti važan u dobitnim rezultatima. Veći udio organske matrice stvara veći difuzijski gradijent vodi u unutrašnjost uzorka, što rezultira bržim zasićenjem materijala vodom, pogotovo ako ta organska matrica sadržava hidroofilnu smolu poput TEGDMA-e koja se nalazi u SDR Plusu.

Skokovita polymerizacija Tetric Power Filla mogla bi objasniti krivulje promjena mase tijekom imerzije (slika 4.). Uočava se da je Tetric Power Fill polymeriziran trosekundnim programom postigao „plato“ nakon 28 dana, a drugi ispitani visokoviskozni materijali to nisu postigli ni nakon 30 dana. Iako Tetric Power Fill nema veći udio organske matrice poput niskoviskoznih materijala, ipak ima AFCT polymerizaciju. Zato bi umreženje polimernih mreža bilo važnije za kinetiku apsorpcije vode, nego za konačne vrijednosti apsorpcije vode, odnosno apsorpciju vode po volumenu (42).

Ovo istraživanje temeljilo se na standardu ISO 4049:2009, pa su korišteni uzorci debljine 2 mm kako bismo mogli usporediti naše rezultate s preporučenim vrijednostima. Za proširenje ovog istraživanja bilo bi zanimljivo ispitati navedena svojstva bulk-fill kompozitnih materijala na uzorcima deblije 4 mm koji bi bili sličniji kliničkim uvjetima. No zahvaljujući ovom eksperimentalnom dizajnu uspjeli smo utvrditi da svi materijali u oba polymerizacijska protokola imaju apsorpciju vode manju od 40 µg/mm³ i zadovoljavaju preporuke ISO-a. S druge strane, brza polymerizacija SDR Plusa i Filtek One Bulk Filla premašuje maksimalno dopuštena vrijednosti topljivost od 7,5 µg/mm³.

**Zaključci**

Topljivost svih ispitanih materijala značajno se povećala tijekom brze polymerizacije s vrlo visokim intenzitetom svjetlosti, što bi moglo biti povezano s eluzijom nereagiranih monomera i mogućim štetnim reakcijama stanica gingive i služnice. Vrijednosti topljivosti SDR Plusa i Filtek One Bulk Filla premašile su preporučene vrijednosti prema standardu ISO 4049:2009 i zato se za te materijale ne preporučuje brza polymerizacija. Učinak brze polymerizacije na apsorpciju vode ovisio je o materijalu, pri čemu su niskoviskozni bulk-fill materiali bili neosjetljivi na protokol polymerizacije.
Sukob interesa

Autori nisu bili u sukobu interesusa.

Conflict of interest

None declared

Author’s contribution: D.M., M.P. and Z.T – conceived the study and were in charge of overall direction and planning; N.K. and M.M. – performed the experiment and analyzed the data; D.M., Z.T. and M.P. – supervised the work; N.K., D.M. – wrote the manuscript and constructive feedback and editing from M.P. and Z.T. All authors discussed, reviewed, and approved the contents within the manuscript.
22. Braden M, Clarke RL. Water absorption characteristics of dental microfine composite filling materials. I. Proprietary materials. Biomaterials. 1984 Nov;5(6):369-72.

23. Braden M, Causton EE, Clarke RL. Diffusion of water in composite filling materials. J Dent Res. 1976 Sep-Oct;55(5):730-2.

24. Sideridou I, Tserki V, Papanastasiou G. Study of water sorption, solubility and modulus of elasticity of light-cured dimethacrylate-based dental resins. Biomaterials. 2003;24(4):655–65.

25. Yu CK, King NM, Pashley DH, Suh BI, Carvalho RM, Carrilho MR, et al. Effect of resin hydrophilicity and water storage on resin strength. Biomaterials. 2003 Feb;24(4):655–65.

26. Musanje L, Shu M, Darvell BW. Water sorption and mechanical behavior of cosmetic direct restorative materials in artificial saliva. Dent Mater 2001; 17(5):394–401.

27. Par M, Sspanovic N, Mohn D, Attin T, Tauböck TT, Tarle Z. Curing potential of experimental resin composites filled with bioactive glass: A comparison between Bis-EMA and UDMA based resin system. Dent Mater. 2001 Sep;17(5):394-401.

28. Par M, Sspanovic N, Bjelovucic R, Marovic D, Schmalz G, Gamulin O, Tarle Z. Long term water sorption and solubility of experimental bioactive composites based on amorphous calcium phosphate and bioactive glass. Dent Mater J. 2019 Jul 31;38(4):555-564.

29. Par M, Hubler A, Attin T, Tarle Z, Tauböck TT. Anti-demineralizing protective effects on enamel identified in experimental and commercial restorative materials with functional fillers. Sci Rep. 2021 Jun 3;11(1):11806.

30. Ferracane JL. Hygroscopic and hydrolytic effects in dental polymer networks. Dent Mater. 2006 Mar;22(3):211-22.

31. Ferracane JL. Hygroscopic and hydrolytic effects in dental polymer networks. Dent Mater. 2006 Mar;22(3):211-22.

32. da Silva EM, Gonçalves L, Guimarães JG, Poskus LT, Fellows CE. The diffusion kinetics of a nanofilled and a midfilled resin composite immersed in distilled water, artificial saliva, and lactic acid. Clin Oral Investig. 2011;15(3):393–401.

33. Putzeys E, Nys S De, Cokic SM, Duca RC, Vanoirbeek J, Godderis L, et al. Long-term elution of monomers from resin-based dental composites. Dent Mater. 2019 Mar;35(3):477-485.

34. Marovic D, Par M, Macan M, Klaric N, Klarić M, Plazonić I, Tarle Z. Aging-Dependent Changes in Mechanical Properties of the New Generation of Bulk-Fill Composites. Materials (Basel). 2022 Jan 15;15(3):902.

35. Boaro LC, Gonçalves F, Guimarães TC, Ferracane JL, Pfeifer CS, Braga RR. Sorption, solubility, shrinkage and mechanical properties of “low-shrinkage” commercial resin composites. Dent Mater. 2013 Apr;29(4):394-404.

36. Pongprueksa P, De Munck J, Duca RC, Poels K, Covaci A, Hoot P, et al. Monomer elution in relation to degree of conversion for different types of composite. J Dent. 2015 Dec;43(12):1448-55.

37. Asaoka K, Hirano S. Diffusion coefficient of water through dental composite resin. Biomaterials. 2003 Mar;24(6):975-9.

38. Peutzfeldt A. Resin composites in dentistry: The monomer systems. Eur J Oral Sci. 1997 Apr;105(2):97-116.