O R I G I N A L   A R T I C L E

Influence of water sorption on the shrinkage stresses of dental composites

Wpływ sorpcji wody na naprężenia skurczowe materiałów kompozytowych

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Abstract

Introduction. *The elimination or reduction of shrinkage stress generated during polymerisation is one of the major problems in the development of dental composites. Sorption of water by resin fillings in the moist environment of the oral cavity and in consequence its volume expansion should counteract the observed shrinkage contraction.* **Aim of the study.** *To evaluate the influence of water sorption in resin-based materials on polymerization shrinkage stress generated on the restoration-tooth interface.* **Material and methods.** *The shrinkage stress was measured immediately after curing. The samples stored in water were evaluated after 24 h for 7 days and then once a week up to 90 days. Photoelastic study was performed on photosensitive epoxy resin plates in Transmission Polariscope FL200. The study was based on the analysis of dimension and arrangement of fringes. Contraction stress was calculated on the basis of photoelastic theory. In order to measure the water sorption and its dynamics, the material samples were weighed on analytical scale in the above mentioned time intervals.* **Results.** *The tested materials during polymerization generated shrinkage stresses ranging*

Streszczenie

Wstęp. *Wyeliminowanie lub zmniejszenie skurczu objętościowego, który jest generowany podczas polimeryzacji jest jednym z ważniejszych problemów w rozwoju kompozytów dentystycznych. Sorpcja wody przez materiał kompozytowy w wilgotnym środowisku jamy ustnej i w konsekwencji zwiększenie objętości materiału powinno przeciwdziałać obserwowanemu skurczowi polimeryzacyjnemu.* **Cel pracy.** *Celem niniejszej pracy była ocena wpływu sorpcji wody w materiałach dentystycznych na naprężenia skurczowe generowane na granicy tkanek zęba i wypełniania.* **Materiały i metody.** *Naprężenia skurczowe mierzono bezpośrednio po sieciowaniu. Próbki przechowywane w wodzie oceniano po 24 h przez 7 dni, a następnie raz na tydzień przez 21 dni. Badania elastooptyczne przeprowadzono na płytach z optycznie czułej żywicy epoksydowej z użyciem polaryskopu kołowego FL200. Badanie oparto na analizie wymiarów i układu prążków. Naprężenia skurczowe obliczono na podstawie teorii elastooptycznej. W celu określenia sorpcji wody i jej dynamiki, próbki materiału były ważone na wadze analitycznej w wymienionych powyżej odstępach czasu.* **Wyniki.** *Badane materiały*

from 6 to 17 MPa. After conditioning in water, the decrease in shrinkage strain after 72 h was observed. The decrease in value stress in time depended on the type of material. **Conclusions.** *Polymerizing dental materials generated differentiated shrinkage stress that decreased in time due to water sorption. The dynamics of stress change is material dependent.*

podczas polymeryzacji generowały naprężenia skurczowe w zakresie od 6 do 17 MPa. Zaobserwowano spadek naprężeń po kondycjonowaniu w wodzie przez 72 godziny. Zmniejszenie wartości naprężeń w czasie zależy od rodzaju materiału. **Wnioski.** *Kompozytowe materiały stomatologiczne generują zróżnicowane naprężenia skurczowe, które pod wpływem sorpcji wody zmniejszają się w czasie. Dynamika zmian naprężeń jest zależna od materiału.*

Introduction

Curing processes of dental composites generate a shrinkage stress at the restoration-tooth interface (even 20 MPa, dependent on the material).[1] The consequences of the stress contraction reported in the literature are: deformed tooth structure or even cracks in healthy tooth structure and damage of the adhesive bond between restoration and dental tissue. Shrinkage stresses can also lead to marginal discoloration, post-operative sensitivity and secondary caries.[2-4] The elimination or reduction of shrinkage stress is one of the major problems in the development of dental composites. Despite the fact that restorative materials obtain dimensional stability by photopolymerization, they are not fully stable because of continuous interaction with the surrounding environment. The resin materials are constantly bathed in saliva, and therefore sorption and solubility constitute the principal interaction.[5,6] Sorption of water by resin fillings in the moist environment of the oral cavity and in consequence its volume expansion should counteract the observed shrinkage contraction.

Dental composites are exposed to water and a variety of substances that contain acids, alcohols, salts, bases, etc. They may absorb these chemicals or release some components (unreacted monomers, erosion products) to the surrounding environment. These processes may have influence on the structure and function of the dental composition. These effects may include volumetric changes, plasticization or chemical changes such as hydrolysis and oxidation.[7,8] There are many factors which determine the influence of the surrounding environment on sorption and solubility of resin composites. These aspects need to be discussed individually.

Chemistry and structure of polymer matrix are the most important aspects determining sorption and solubility of dental composite. The most widely used dental resins are prepared from polymerization of monomers: bisphenol A glycol dimethacrylate (bis-GMA), urethane dimethacrylate (UDMA), triethylene glycol dimethacrylate (TEGDMA), bisphenol A ethoxylateddimethacrylate (bis-EMA). Their resultant polymer has heteroatom and hydrolytically receptive group. They are acknowledged as relatively hydrophilic. *Sideridou* and *Tserki*[9] show differences in absorption of water for polymer network composed of various monomers. They reported that the sorption of water takes place in the following order: TEGDMA>Bis-GMA>UDMA>Bis-EMA. The sorbed water disperses in polymer network using intermolecular spaces and porosity. Therefore, the density of polymer networks is another factor which influences the amount of uptaken water.[9] *Armira* et al.[10] have reported a correlation between solubility and concentration of cross-linking agents. The increasing amount of cross-links which do not contain hydrophilic ether linkages, reduce solubility of polymethacrylate polymer. Another aspect affecting the solvent's uptake and dissolution are fillers. They reduce the free volume in polymer matrices, decreasing sorption and solubility of dental material.[11,12] However, water can behave as an acid, and other substances of the surrounding environment may induce erosion of the ceramic filler. It has been demonstrated for a variety of glass-phased and all-crystallite ceramics that have been subjected to corrosion in aqueous environment.[13]

Bowen et al.[14] have shown that dental composite can be formulated to have hygroscopic expansion

sufficient to compensate for polymerization shrinkage. *Feilzer, De Gee* and *Davidson*[15] have reported that dental resin composed of bis-GMA/TEGMA and urethane dimethacrylate were fully relieved by sorption of water. In some cases, hygroscopic expansion caused the appearance of new "expansion stress". *Huang* et al.[16] have studied the effect of water sorption on the extent of marginal gap reduction in different types of dental materials. It has been shown that reduction of marginal gap resulting from water sorption is more extensive in resin-modified glass-ionomer cements, followed by compomers, whereas composites are relatively stable.[16] Although in the literature there are many publications about sorption characteristics of dental resin and its influence on properties of dental composite[8,9,17,18] what is still needed is analysis of the relationship between water sorption and the change of shrinkage stress generated during curing of dental materials.

Materials and Methods

In order to determine the sorption properties of selected composite materials, a study of the dental materials sorption was conducted. The composition of selected materials is presented in Table 1.

The samples were prepared using the silicone form (15 mm in diameter, 1 mm wide). The material was cured with LED light lamp (Mini L.E.D., Acteon) in nine partially overlapping zones (Fig. 1). Exposure time was consistent with the manufacturer's instructions. Direct contact of optical fiber with the sample surface was ensured. Five samples were prepared for each dental material and they were weighed (RADWAG AS 160/C/2) immediately after preparation and daily for 30 days. Based on these results, the absorbency of the material was calculated according to the formula:

$$A = \frac{m_i - m_0}{m_0} \cdot 100\%$$

where:
A – is the absorbency of water,
m_0 – is the mass of the sample in dry conditions,
m_i – is the mass of the sample after storage in water for a specified (i) period of time.

Photoelastic analysis allows for quantitative measurement and visualization of stress concentration that develop during

Table 1. Composition of materials used in the original study

| Material	Manufacturer	Composition			
		resin matrix	filler	filler loading [%] by weight	type
SDR	Dentsply	Patented urethane dimethacrylate resin, dimethacrylate resin and difunctional diluents	Barium and strontium-alumino-fluoro-silicate glasses	68	Resin – modified-flowablecomposite
DyractFlow	Dentsply	Ammonium salt of PENTA (dipentaery-thritolpenta acrylate monophosphate), N,N-dimethyl aminoethyl methacrylate, Carboxylic acid modified methacrylate macromonomers, Diethylene glycol dimethacrylate (DGDMA)	Strontium-alumino-fluoro-silicate glass, Highly dispersed silicon dioxide	65	Compomer Polyacid-modifiedresin-composite
Filtek Ultimate Flow	3M ESPE	BisGMA, TEGDMA and Procrylat resins	Silane treated zirconia/silica, ytterbium trifluoride	65	low-viscosity flowable nanocomposite
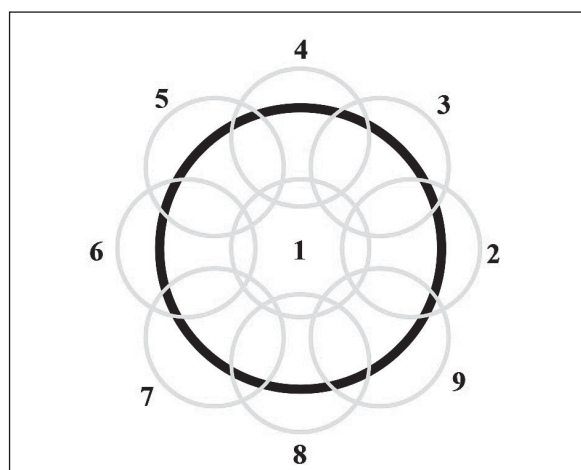
Fig. 1. *A diagram of partially overlapping zones of curing samples.*

photopolymerization of resin composites. Photoelastically sensitive plates of epoxy resin (Epidian 53, Organika-Sarzyna SA, Poland) which becomes optically double-refractive under stress was used in this study. Calibrated orifices of 3 mm in diameter and thickness of 4 mm were prepared in resin plates. The diameter of the orifices (3 mm) has been selected to mimic a tooth cavity and clinical conditions of average size. The plate was stored in distilled water for a period of three months before photoelastic examinations. In order to ensure bonding of the resin composite to the plates, the inner surfaces of resin plates were sandblasted with a 50-μm grain corundum Cobra (Renfert, Germany) and a dedicated bonding system was applied and cured with Elipar S10 lamp. The orifices were filled with selected material in one layer and cured according to the manufacturer's instructions. The polymerization was carried out on both sides of the plate to ensure a satisfactory degree of conversion in the whole volume of material. Three samples were prepared for each dental material and stored in distilled water at room temperature. After selected period of time (24-504 h) the generated strains in the plates were visualized in circular transmission polariscope FL200 (Gunt, Germany). Photoelastic images were recorded by digital camera (Canon EOS 5D Mark II/Canon Inc., Japan) both in parallel and perpendicular orientation of filter

polarization planes. Next, Met-Ilo computer program was applied to analyze arrangement and dimension of interference fringes. Stress intensity around composite filling was determined on the relevant equations. The analysis of stress and strain was carried out in a two-dimensional state of the stresses and three-dimensional state of deformations. Additionally, the calculation was conducted following this assumption: the relative change in volume of the composite material causes its extension and extension of the base material which is "tooth model" (epoxy resin plate). Therefore, photoelastic strain calculations were based on the Timoshenko's equation[19]:

$$\sigma_r = \frac{a^2 \cdot p_s}{b^2 - a^2} \cdot \left(\frac{b^2}{r^2} - 1 \right) (1.1)$$

$$\sigma_\theta = \frac{a^2 \cdot p_s}{b^2 - a^2} \cdot \left(\frac{b^2}{r^2} + 1 \right) (1.2)$$

where:
σ_r – is radial stress,
σ_θ – is circumferential stress,
p_s – is the shrinkage stress around composite filling,
a – is the radius of the internal orifices in the plate,
b – is the radius of the largest of isochromatic fringes,
r – is the radius contained in the region from a to b.

After calculating the shrinkage stress on the circumference of the orifices, the radial and circumferential stresses were determined on the basis of formulas (1.1) and (1.2).

Results and discussion

All of the resin matrix dental materials shrank during the hardening process and contraction stress was observed. During immersion in water all samples increased in weight. Due to hygroscopic expansion of composites contraction stress was reduced significantly. Water sorption and contraction stress mean values are presented in Fig. 2-7. On the basis of our measurements it has been found that Dyrect Flow composite is characterized
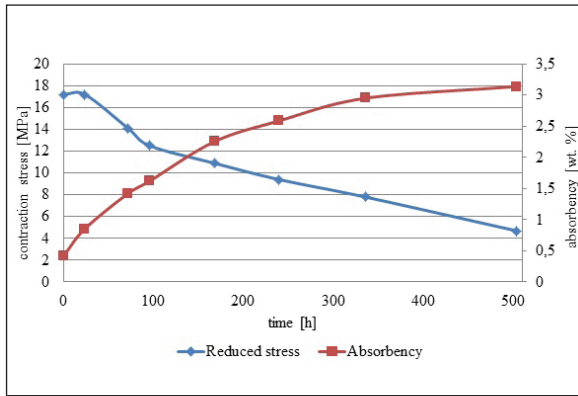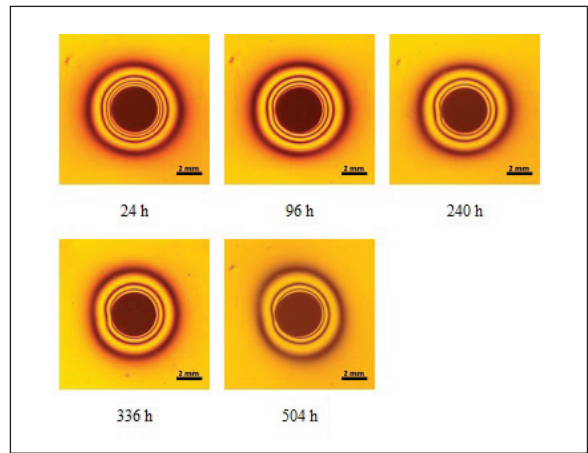
Fig. 2. *The influence of water sorption on absorbency and contraction stress generated during curing of Dyract Flow.*
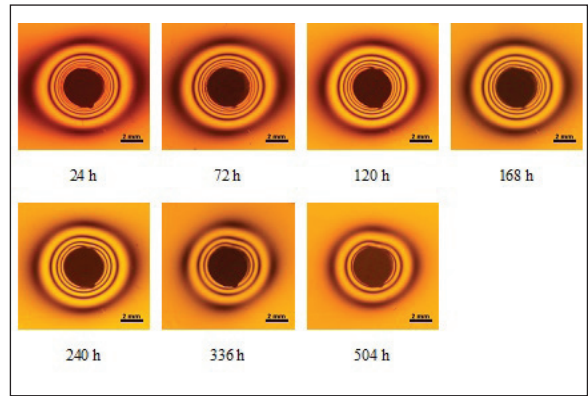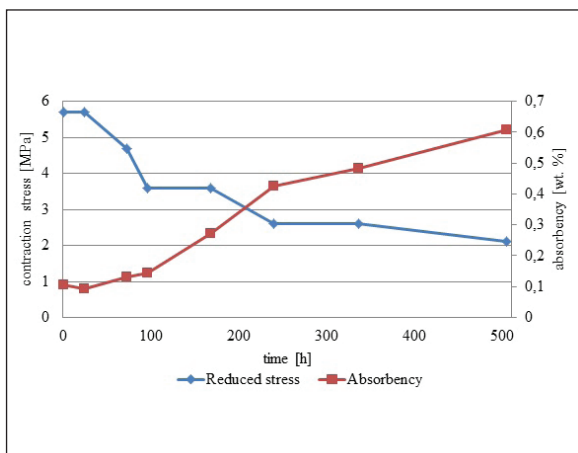

Fig. 3. *Isochromes in epoxy plate around restoration made from Dyract flow, acquired in polarized light with parallel polarization facets, before and after water storage 24-540 h.*
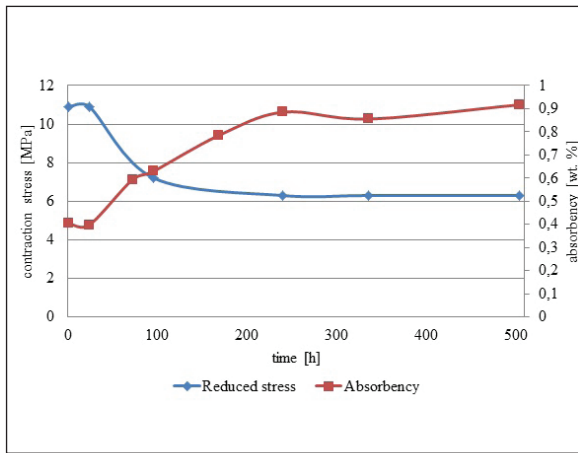

Fig. 4. *The influence of water sorption on absorbency and contraction stress generated during curing of Filtek Ultimate.*

Fig. 5. *Isochromes in epoxy plate around restoration made from Filtek Ultimate, acquired in polarized light with parallel polarization facets, before and after water storage 24-540 h.*

Fig. 6. *The influence of water sorption on absorbency and contraction stress generated during curing of SDR.*
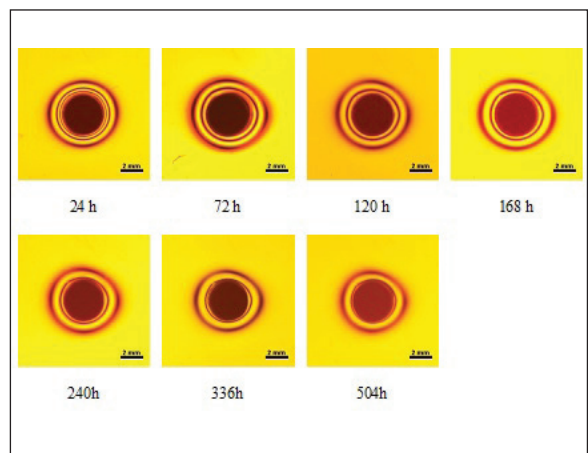
Fig. 7. *Isochromes in epoxy plate around restoration made from SDR, acquired in polarized light with parallel polarization facets, before and after water storage 24-540 h.*

by the highest contraction stress ~17 MPa, Filtek Ultimate Flow ~12 and SDR has contraction stress on 5.7 MPa level. After 21 days (504 hours) of Dyrect Flow water storage its contraction stress has been reduced to 4.7 MPa (Fig. 2 and 3). The water sorption means in weight% increased up to 3.1. The contraction stress of Filtek Ultimate Flow during 21 days in water decreased from ~11 to 6.3 MPa (Fig. 4 and 5). SDR composite during its water conditioning minimalized from 5.7 to 2.1 MPa (Fig. 6 and 7).

Mechanical–contraction stress in resin restorations is one of the main reasons for failures of the tooth-filling bond. Contraction stress is the consequence of polymerization shrinkage.[20] The restoration is exposed to the oral fluids and for that reason some part of this contraction stress relief may arise from water swelling. The water that diffuses into the material causes a gradual expansion up to a certain value.[15] Uptake of water into a polymer matrix is controlled by the Fickian (type I) diffusion process.[21] The patterns of diffusion are governed by the "free volume theory", in which water passes through nanopores without any chemical reaction with polymer chains, or by the "interaction theory" in which water diffuses through the material binding successively to the hydrophilic groups.[22] Therefore, absorbed water exists in two distinct forms: "unbounded" that occupied free volume between the polymer chains and the nanopores created during polymerization[23] and "bound water" that is attached to polymer chains via hydrogen bonding.[24] The highest value of water absorbency by weight% is observed for Dyract flow material. This is the consequence of composition of that compomer, low stability and high hydrophilic character of carboxylic acid modified methacrylate monomers and diluent ingredient such as diethylene glycol dimethacrylate. A distinctive feature of compomers is that following the initial polymerization reaction, they take up small amounts of moisture in situ, and this triggers an acid–base reaction between the reactive glass filler and the acid groups of the functional monomer. Among other features, this process causes fluoride to be released from the glass filler to the matrix and the most important fact is that the sorption of water plays a significant role

in reducing these stresses *in vivo*.[25] Compomers are designed to absorb water,[26,27] and are able to up of the order of 2–3.5% by mass of water on soaking. This water uptake has been shown to be accompanied by neutralization of the carboxylic acid groups.[26] Dyract flow has very high value of contraction stress (~17 MPa) generated during photopolymerization associated with volumetric shrinkage. From our measurements it transpires that observed contraction stress can be significantly relieved or converted into an "expansion stress" by hydroscopic expansion. The reduction of contraction stress about 77% after 21 days of water storage was observed. The hydroscopic relaxation proceeds slowly in comparison to rapid polymerization contraction stress development. The rate of water sorption is dependent on speed of diffusion process connected with the type of resin, polymer network, type and amount of filler and filler-matrix adhesion.[15,28] The rate of contraction stress decreasing in Dyract Flow is in direct proportion to the time the samples were immersed in water

Filtek Ultimate Flow is dental composite characterized by conventional composition of polymer matrix containing bis-GMA and TEGDMA as diluent. The stress relaxation means 42% after 21 days of water storage was observed. The kinetics of contraction stress relaxation is different in comparison with Dyrect flow and SDR. After 10 days of water immersion and absorption about 1 wt.% of water samples reached certain equilibrium solubility. Due to SDR water storage 63% reduction of contraction stress value was noted, accompanied by water absorbency on 0.6 wt.% level. Taking into account the influence of chemical and physical structure on polymer network on the moisture sorption, it seems that the higher absorbency of Filtek Ultimate Flow in comparison with SDR is most probably due to the stronger hydrophilic character of its monomer units. Hydroxyl groups from bis-GMA form stronger hydrogen bonds with water molecules than urethanes groups. This is the result of the value of cohesive energy density of –OH groups equal to 2980 J/cm^3, and of urethane groups 1425 J/cm^3.[29]

It is worth stressing that stronger relief effect is observed for SDR than Filtek Ultimate Flow. It could be explained by the character of the network in polymer matrix of dental composites. Bis-GMA/TEGDMA matrix in Filtek Ultimate Flow absorbs more water than SDR but plasticizing effect of water sorption is not strong enough to reduce interchain interactions, such as entaglements and secondary bonding connected with contraction stress. SDR polymer matrix formulation is based on a new dimethacrylate-urethane monomer with high molecular weight of 845 g/mol. Therefore, it can be expected that the SDR curing process, as compared to those containing traditional polymer matrix only (bis-GMA – 513 g/mol), will create a smaller number of bonds, which will reduce its polymerization shrinkage. For this reason after water immersion of SDR samples contraction stress is also reduced.

Conclusions

Resin dental materials during photopolymerization generate differentiated shrinkage stress that decreases in time due to water sorption. The value of water absorbency, magnitude of reduction and dynamics of stress change is material dependent.

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