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Mechanical properties of composite material modified with amorphous calcium phosphate

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ABSTRACT

Purpose: The purpose of the study was to evaluate mechanical and physical properties of composite materials modified with amorphous calcium phosphate (ACP).

Design/methodology/approach: The study used two flowable composite materials: an experimental composite material based on dimetacrylic resin filled with colloidal silica (ECM) and commercially available composite material (SDR/Dentsply). Materials were modified with the addition of ACP as a powder. Three testing groups were created, depending on the amount of ACP – 0.12 g, 0.24 g and 0.36 g – added to 2 g of the basic composite. The composite without ACP was the control group. Diametral Tensile Strength (DTS) was evaluated using Zwick-Roell Z020. Vickers hardness test (HV1/10) was performed using the HV1/10 method in the ZHVμ (Zwick-Roell) hardness tester. The measurements of shrinkage stress that arose during polymerisation of the tested materials were conducted with the use of the FL200/Gunt circular polariscope.

Findings: In both composites modified with ACP the decrease of DTS was observed. ACP addition to experimental composite increased its hardness. Addition of 5.67 wt% of ACP to SDR resulted in significant decrease of its hardness. For both tested materials, the highest shrinkage stress was observed in composites modified with 5.67 wt% ACP addition. The lowest shrinkage stress was observed in ECM modified with 15.25 wt% ACP and SDR composite containing 10.72 wt% ACP.

Research limitations/implications: Additional investigations are needed to define the exact influence of addition ACP to composite materials on their mechanical and physiochemical properties.

Originality/value: In order to improve biological behaviour of composite materials it is possible to modify those materials with the addition of remineralising agents like ACP.

Keywords: Composites; Mechanical properties; Physical features of biomaterials and dental materials

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PROPERTIES

1. Introduction

Dental caries is probably one of the most common diseases. It is the result of a process, where the mineral elements of hard dental tissues are demineralized by organic acids produced by bacteria present in a biofilm adhering to the tooth surface [1]. When the calcium and phosphate are lost from the subsurface enamel, early caries lesion appears. At that stage, the caries lesion is reversible. The demineralizing process can be stopped via remineralization process, involving the diffusion of calcium and phosphate ions into the subsurface lesion to rebuild lost mineral structure [2]. Non-operative preventive treatment of early caries lesion and dental prophylaxis involve measures to reduce bacterial dental plaque and neutralize acidic substances in oral cavity by improving oral hygiene and stimulating the natural repairing process of remineralization. Remineralizing agents used in such treatment can have the form of remineralizing, ions-delivering dentifrices, chewing gums and mouthwashes. Another commonly used method of remineralization is systemic and/or topical fluoridation [3]. Incorporation of fluoride into tooth structure and creating fluoroapatite (FAP) decreases the solubility of tooth enamel and is a promising way to prevent caries [4]. Another way to initiate remineralization of dental tissues and inhibit mineral loss during the acid dissolution process is application of substances containing calcium and phosphate, such as amorphous calcium phosphate (ACP). The example of using this form of calcium phosphate in dental prophylaxis can be casein-phosphopeptide stabilized ACP (CPP-ACP) incorporated into sugar-free chewing gum or mouthrinses [5], CPP-ACP paste [6] or ACP-based polymeric composites [7]. Application of dental composites modified with ACP addition appears to be promising strategy to reduce occurance of secondary/recurrent caries, one of the most frequent cause of composite fillings replacement. However, a question arises, whether the addition of ACP would influence mechanical and physiochemical properties of such composite materials.

2. Materials and methods

2.1. Material and methods

The study used an experimental semi-flow composite material (ECM) based on dimetacrylic resin (BisGMA/TEGDMA 60/40 by weight) filled colloidal silica and commercial dental flow composite (SDR/Dentsply). Both materials were modified with the addition of ACP as a powder. Study groups were created depending on the weight of ACP – 0.12 g, 0.24 g and 0.36 g – added to 2 g of the basic composite. The control group was the composite without ACP (Table 1).

Table 1.
The proportion of ingredients (composite, ACP) in experimental groups (1, 2, 3, 0 - control group)

Group number	The amount of composite, g	The amount of ACP, g	The amount of ACP in the modified composite – wt %
0	2	-	-
1	2	0.12	5.67
2	2	0.24	10.72
3	2	3.36	15.25

Diametral Tensile Strength (DTS) and Vickers hardness test (HV1/10) were used to assess mechanical strength of materials. For the sake of the experiment, the composite material was applied into a silicone roller-shaped matrix (3x5 mm) in layering technique. Each layer was light-cured with Megalux Soft Start polymerizing lamp (Mega Physik Dental). Samples were stored in dry conditions, at room temperature, for 24 hours prior testing. DTS was performed using Zwick Roell Z020 device at crosshead speed of 2 mm/min. For each group 10 samples were tested. Maximum force [N], causing specimen fracture was recorded by the computer. DTS [MPa] values were calculated by the formula:

$$DTS = \frac{2F}{\pi dh}$$

where:
F – maximum force applied, N
d – diameter of the specimen, mm
h – height of the specimen, mm

The hardness was evaluated using the HV1/10 method in the Indentec ZHμ-S micro hardness tester (Zwick/Röell, Germany). The indenter was forced into tested specimens with the load of 1 kg for 10 seconds. From each group 3 samples were tested, hardness was measured fivefold.

Measurements of reduced stress value and analysis of stress around restorations were performed using photosensitive epoxy resin plates (Epidian 5/Organica),

4 mm thick with rounded-shaped perforations of 3 mm in diameter. The perforations were designed to simulate the dental cavities. The walls of the perforations were sandblasted using Al_2O_3 (50 μm), followed by application of the universal bonding system (Single Bond Universal/3M ESPE) and its polymerization according to manufacturer's instructions. Thereafter, the tested materials were applied into perforations in two layers and polymerized with Megalux Soft Start polymerizing lamp. For each group 3 samples were prepared. Measurements of shrinkage stresses during polymerization of tested material were performed after 24-hour storage in dry conditions at room temperature with the use of circular polariscope FL200/Gunt. Met-Ilo computer program was used to analyze the size and distribution of interference fringes in the plates around composite filling. Shrinkage stress of composite material was calculated based on the theory of elasticity formulas, using the Timoshenko equation [8]:

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

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

where:
σ_r, σ_θ - radial and circumferential stress
p_s – circumferential shrinkage stress
a – radius of perforation in the plate
b – radius of the greatest isochromatic fringe
r – radius measured between a and b

Sum and difference of main stresses for the filling and for surrounding dental tissues, respectively, are:

$$\sigma_r^w + \sigma_\theta^w = 2 \cdot p_s \tag{1.3}$$

$$\sigma^m{}_r - \sigma^m{}_\theta = 2 \cdot \frac{p_s \cdot a^2}{b^2 - a^2} \cdot \frac{b^2}{r^2} \tag{1.4}$$

Based on elastooptic measurements, the difference in main stresses was evaluated:

$$\sigma_1 - \sigma_2 = k_\delta \cdot m \tag{1.5}$$

where:
k_δ – elastooptic constant
m – amount of isochromatic fringes

It was assumed for the analyzed case that the difference between main stresses σ_1 - σ_2 equals the difference between radial and circumferential stresses σ_r - σ_θ so the shrinkage stresses at the filling – inner margin of perforation interface, for $r = a$, equals:

$$k_\delta \cdot m = 2 \cdot \frac{p_s \cdot b^2}{b^2 - a^2} \quad p_s = k_\delta \cdot m \cdot \frac{b^2 - a^2}{2 \cdot b^2} \tag{1.6}$$

2.2. Statistical analysis

Statistica 10.0 program (StatSoft Inc., 2011) was used for statistical analysis of obtained data. The following tests of significance were performed: Shapiro-Wilk test for normality, Levene's test for the homogeneity of variances, analysis of variance (ANOVA) without replication, and the Kruskal-Wallis equality-of-populations rank test. A level of $p < 0.05$ was considered statistically significant.

3. Results and discussion

3.1. Diametral tensile strength

DTS test results for experimental composite modified with ACP are presented in Table 2. There were no statistically significant differences in mean DTS values between control (0) and study (1-3) groups (F=1.03; p=0.3896).

Table 2.
Statistical analysis (ANOVA) of DTS [MPa] test results for experimental composite material (ECM) modified with ACP addition

Group	Mean value, MPa	SD	Confidence interval 95%Cl	F	p
0	26.41	5.09	22.77-30.05	1.03	0.3896
1	24.57	4.81	21.13-28.02		
2	23.20	4.97	19.65-26.75		
3	26.23	3.91	23.44-29.02		

DTS test results for SDR modified with ACP are presented in Table 3. Statistical analysis showed significant differences between tested groups (H=27.5; p=0.0000). The

highest mean values and median were in group 0 (control group) and the lowest in group 3 (15.25 wt% ACP). Group 1 and 2 presented similar values.

Table 3.
Statistical analysis (Kruskal-Wallis test) of DTS [MPa] test results for SDR composite modified with ACP (Me-median, LR-lowest result, HR-highest result)

Group	Me	LR	HR	H	P
0	43.8	37.03	51.26	27.5	0.0000
1	36.9	32.40	42.39		
2	37.5	33.14	38.15		
3	29.5	22.21	37.37		

3.2. Hardness

In research of ECM modified with ACP in group 0 (control group) mean HV1/10 values were significantly lower when compared to the study groups (1-3) (every p-value for pairs assumed inequality $p<0.0001$), (Table 4).

Table 4.
Statistical analysis (ANOVA) of HV1/10 test results for experimental composite material (ECM) modified with ACP addition

Group	Mean	Standard deviation	F	P
0	17.2	2.6	54.3	0.0000
1	25.1	1.4		
2	23.3	1.5		
3	25.4	2.3		

Table 5.
Statistical analysis (Kruskal-Wallis test) of HV1/10 test results for SDR composite modified with ACP (Me-median, LR-lowest result, HR-highest result)

Group	Me	LR	HR	H	p
0	38	35	41	35.2	0.0000
1	35	29	39		
2	38	37	40		
3	40	36	47		

HV1/10 test results for SDR modified with ACP are presented in Table 5. The significantly lowest mean values of hardness were obtained in group 1 (G1 vs. G0: p=0.0023; G1 vs. G2: p=0.0025; G1 vs. G3: p=0.0000). The highest mean HV1/10 value was obtained in group 3.

3.3. Shrinkage stress

Elasto-optic studies results for ECM modified ACP are presented in Table 6. The highest shrinkage stress was observed in group 1, the lowest one in group 3. The stress values in group 0 (control group) and in group 2 were similar. The shrinkage stress values decreased with the increase of ACP concentration in ECM.

Table 6.
Mean values of stress generated by experimental composite material (ECM) modified with ACP

Group	Shrinkage stress p_s, MPa	Radial stress σ_r, MPa	Circumferential stress σ_θ, MPa	Difference in main stress $\sigma_r-\sigma_\theta$, MPa
0	3.4 ± 0.5	3.4 ± 0.5	-4.9 ± 0.4	8.3 ± 0.9
1	4.0 ± 2.0	4.0 ± 2.0	-5.4 ± 2.1	9.4 ± 4.1
2	3.5 ± 1.7	3.5 ± 1.7	-4.8 ± 1.9	8.3 ± 3.6
3	2.8 ± 1.7	2.8 ± 1.7	-4.0 ± 1.9	6.8 ±3.6

Elasto-optic studies results for SDR modified with ACP are presented in Table 7. Group 0 and group 1 generated the highest shrinkage stress (approximate values in both groups). The lowest mean value of stresses arising during polymerisation of composite was observed in group 2.

Table 7.
Mean values of stress generated by SDR composite modified with ACP

Group	Shrinkage stress p_s, MPa	Radial stress σ_r, MPa	Circumferential stress σ_θ, MPa	Difference in main stress $\sigma_r-\sigma_\theta$, MPa
0	1.8 ± 0.0	1.8 ± 0.0	-3.0 ± 0.0	4.8 ± 0.0
1	1.8 ± 0.0	1.8 ± 0.0	-3.0 ± 0.1	4.8 ± 0.0
2	0.5 ± 0.1	0.5 ± 0.1	-1.1 ± 0.1	1.6 ± 0.0
3	1.5 ± 0.1	1.5 ± 0.1	-2.8 ± 0.1	4.3 ±0.1

In general, when comparing both tested materials, the SDR composite generated the lower shrinkage stress values (0.5 - 1.8 MPa) than the experimental composite material (2.8 - 4.0 MPa).

3.4. Discussion

The use of light-cured composite materials is an integral part of restorative dentistry, bringing back the function and aesthetics of lost hard dental tissues. Good mechanical properties, appearance similar to natural dental tissues and remineralizing potential are the most desirable features of modern restorative materials. The development of bioactive polymeric composites is a promising way of improving their biological properties and widening indications for use. Research on mechanical characteristics and possible modifications is crucial for improving the quality of composite filling [9].

The color and shape stability, strength, hardness, polishability, scratch-resistance as well as withstanding the occlusal forces are important parts of restoration behavior [10-12]. Material hardness describes its ability to resist deformations caused by compressive force. One of the methods of testing surface hardness is Vickers hardness test (HV) [10]. Another important dental material feature is its resistance to tensile stress. Tensile force is one of the main components of forces generated in dental restoration during chewing process. Appropriate dental material's tensile strength is essential for restoration's clinical success. This parameter can be checked by diametral tensile strength test (DTS). Hardness testing, diametral tensile strength and wear resistance are common tests for dental composite [13-15]. It is reported that composite physical properties, like hardness, tensile strength and wear highly depend on type of resin, level of resin conversion, modulus of elasticity, water sorption, solubility in water, but most of all on the type and amount of filler.

Amorphous calcium phosphate (ACP) is the example of substance with desirable remineralising properties, that can be useful in preventive dentistry and that can be used as composite filler. Amorphous calcium orthophosphates (ACPs) belongs to biomedically relevant calcium orthophosphate salts [16]. ACPs can precipitate from aqueous solutions containing Ca^{2+} and PO_4^{3-} or made in different production ways. ACP is thermodynamically unstable compound and has tendency to transform spontaneously to crystalline calcium orthophosphates, mainly to calcium apatites. These effects are of a great biological relevance [16]. Having excellent biocompatibility and bioresorbability, ACP can be used in many biomedical applications like titanium implants coating, biocomposites and hybrid materials. It can also be used as anti-cariogenic and/or remineralizing agent in chewing gums, tooth mousses, bleaching gels, drinks or even in milk [15].

During the spontaneous precipitation, ACP forms large agglomerates [17]. Uneven distribution of highly agglomerated ACP particles in matrix is probably the cause of inadequate filler/resin interlocking and can impede material mechanical strength [18]. McCabe and Wessel studies [19] showed that material hardness grows with increasing amount of filler in composite materials. This phenomenon is more evident in materials with silanated filler than with unsilanated one. Present studies showed the increase of experimental composite hardness caused by addition of ACP as filler. But higher concentration of ACP did not cause hardness growth. When the commercial composite (SDR) was modified with ACP addition, in group with lowest amount of ACP (5.67 wt% ACP), the hardness was lower than in control group and the more ACP was added to the composite, the higher hardness was observed. Many authors describe attempts to improve ACP-modified material resistance by silanization of ACP with 3-aminopropyltrimethoxysilane (APTMS) or methacryloxypropyltrimethoxysilane (MPTMS) [3] or grinding [20]. Silanization of ACP allows chemical connection of ACP with organic matrix of composite, while grinding enhances ACP dispersion in polymeric matrix and prevents from forming big ACP agglomerations that destabilizes the structure of polymer chain [21].

The increase of the filler mass fraction determines the composite's mechanical properties, inter alia improves their hardness [22]. The study showed that experimental composite material modified with ACP addition (5.67 wt%, 10.72 wt%, 15.25 wt%) had significantly higher hardness in comparison to the control group (composite without ACP). But when ACP was added to the commercial composite (SDR) in group 1 (5.67 wt% ACP), the hardness was lower than in control group. Different basic filler included in these two materials and another type of organic matrix can be the cause of differences in material's hardness after modification with ACP.

Marovic et al. [23] observed in SEM images of the ACP-based composite that the cracks aroused during three-point bending test were mostly formed around large ACP agglomerates. This occurrence could be explained by the weak interaction of ACP with the resin. Park's et al. [24] study showed that DTS of the dry ACP composite (40 wt%), (21.8 MPa) was comparable with that of the hydroxyapatite (40 wt%), (22.8 MPa) and micro-sized

glass (50 wt%), (25.5 MPa) composites. The DTS results for ACP composite were also lower than that of the commercial visible light curable base/liner composite (36.2 MPa). In the present study, ACP addition to the SDR composite caused the decrease of DTS values (Table 5). ACP is an inorganic filler and does not combine chemically with organic matrix of composite and its addition can weaken the material strength.

Another essential phenomenon, which can have an influence on clinical performance of composite materials, is shrinkage stress during polymerization. Shrinkage stress is a consequence of multiple factors; inter alia the amount of material applied, the material formulation and dynamic development of elastic modulus during the polymerization [25]. Shrinkage stress can cause failure of the marginal integrity of a composite resin restoration resulting in recurrent caries, marginal staining, restoration displacement and post-operative sensitivity [25, 26]. Because of type, size, shape, volume fractions and distribution of filler particles affect the material properties [22], one of the ways of reducing the polymerization shrinkage is modification of filler technology. The following research showed that the addition of different volume of ACP as a filler to composite material can influence shrinkage stress during polymerization. There is little information in literature about shrinkage stress generated during polymerisation of ACP modified composites. In general, there was observed an inverse relationship: the increased inorganic filler content decreases shrinkage stress [27]. It is probably connected to the decrease of amount of organic resin, which is the main cause of shrinkage stress. In this research, the highest shrinkage stress in experimental composite was observed in group 1 (5.67 wt% ACP) and the lowest one in group 3 (15.25 wt% ACP). In case of SDR composite, the highest shrinkage stress was observed in control group, while the lowest shrinkage stress was observed in group 2 (10.72 wt% ACP). Domarecka el al. [28] proved that SDR, thanks to the modified matrix, generates the lowest shrinkage stress among other flowable composite materials with modified and conventional matrix.

4. Conclusions

1. ECM modified with 15.25 wt% ACP resulted in optimal mechanical properties: high DTS values, the highest hardness and the lowest shrinkage stress.
2. The higher ACP concentration in SDR composite, the lower DTS and shrinkage stress values were observed.
3. ACP-modified tested materials exhibited improved hardness in comparison control groups.

Additional information

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