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Water-Polymerisable Compositions "Epoxy Resin - Nanosilica – Mineral Fillers" for Out-Clinical Dental Prevention, and Self-Treatment of Carious and Traumatic Dental Damages

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ABSTRACT: In our new experimental works, the existence of highly filled epoxy-mineral compositions capable to polymerize in wet or water conditions. Their compositions consist of ordinary, cheap, commonly available components, and are filled with water-curing fillers (gypsum, cement). The technology of their curing provides for a combination of exposure and heating modes before application.

They water-cured epoxy-compositions can be use for fast dental filling and restoring damages of teeth, outside of clinical conditions. These hypotheses found confirmation in the obtained results of dental repair on volunteers. The tooth powders and epoxy-composites from cheap available components, for use by non-specialists in domestic and non-clinical conditions – were developed and proposed. These results will be very useful for people and communities who, for various reasons (wars, out-cities, voyages, poverty, workload), are left without access to quality dental services.

KEYWORDS: Epoxy, gypsum, cement, highly-filled composite, underwater curing, gluing, self-sealing, highly-resistant, dental.

1. INTRODUCTION

The main direction in modern dentistry should be the prevention of dental diseases, and their treatment with minimal surgical intervention. And the quality of these materials is constantly improving. However, practical dentistry remains conservative, based on improvement on traditional methods. Dentistry has experienced a rebirth - with emergence of new polymeric materials - polymer cements (1960−70's) and late – photopolymers (1980−90`s). Many other polymer matrices, (polyepoxides etc), were not considered then. Meanwhile, polyepoxides has unique restorative potential no only in engineering but medicine (prosthetics, gluing, etc.).

The Chuiko Institute of Surface Chemistry developed first in USSR/world acrylic photopolymer compositions for prosthetics and filling, [1−3]. We already have a positive experience in creating prophylactic powders for damaged teeth [4]. Now, work on the creation of epoxycomposites for dental-fillings represents a new special cycle, which has no analogues in the world dental science.

The review on this topic tells on the lack of the necessary publications. Today, in the available literature, there are lack of scientific sources on natural prophylactic formulations (homeopathic, self-crystallizing in the cavity, etc.). There are several reports of nanobiomaterials [10], prophylaxis with antibiotics [11] or artificial compounds for self-build-up of micro-damage to the enamel [9]. Most often, dentists and the dental scientists develops traditional methods. Which are really convenient - but not for all patients (especially the poor and remote from clinics), as well as for doctors and dental business. Even the terms "self-hardening", "self-healing", "prophylactic" - refer to dental filling and prosthetic masses [6-18] - but not preventive (preventing filling and prosthetics) or self-service systems.

Also, on the world market there are big number of toothpastes with enhanced protective and anti-carious activity. They are presented as "super-innovative" receptures from the world's leading institutions for enamel protection (in rare cases - restoration of damaged areas of the tooth [14]). Advertisements often contain phrases like “active calcium”, “liquid enamel”, “innovative glycerophosphate (amino-, gluconato-) calcium complex”, etc. [12-15].

However, a simple analysis of these pastes shows ordinary toothpastes compositions, only with an increased content of active components (hydroxyapatite, sodium monofluorophosphate, glycerophosphate and calcium gluconate). Like ordinary toothpastes, they (obviously - for custom attractiveness) contain components that are unnecessary and potentially harmful to the teeth - aroma, dyes, aspartame, surfactants and detergents. These commercial gels [9,12-15] do not contains natural ingredients (herbal powders, natural mineral micro-nano-particles) and nano-SiO_2 or nano-Al_2O_3.

Recent reviews in the scientific literature confirm the tendency to consolidate long-known trends in dental physical chemistry and practice (Vouvoudi [16], Raszewski [17], Gutiérrez [18]) .

The aim of the work was to find compositions for underwater application without using hard-to-find or expensive components. Therefore, ordinary conventional\cheap cold-hardening epoxy-dian resins (**Fig. 1**), were chosen as the polymer base for these compositions.

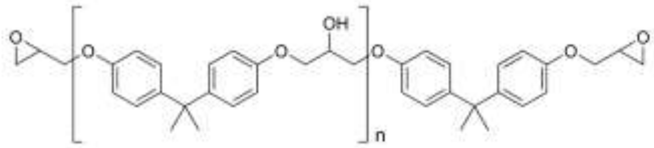

Fig.1. Epoxypolymer typical structure

2. METHODS

An ordinary epoxy composition Epoxy520 : PEPA in a ratio of 6:1 (Composition 1). It was filled (2/3 by weight of the polymer phase) with microdispersed powders of white-cement (Composiiton 2), greaze cement (3) and gypsum (4). The composition was applied by coating, adhesive or poured into molds under normal conditions. After special exposure and processing (the essence of the process is patent information), similar procedures with this composition were carried out under water. After 1-2 months of endurance, samples and coatings were pulled for testing. The hardening mass was held until it lost fluidity and was used as a coating or molding compound.

For compression tests (ISO 604:2002, GOST 4651-2014), cylindrical samples d=6.5 mm, h=12+-1 mm were taken, compressed on a press-machine LouisShopper until complete destruction. Based on the results of the tests, the strength was calculated: $f = P\backslash s$ (*P* is the load in kgf, ***s*** is the area equal to 0.332 cm^2) and the modulus E: $E=f\backslash e$ (*e* is the relative elongation).

Tests for adhesion (GOST 14760-69) with normal tearing were carried out on cylinders 5 cm^2 (**Fig. 2**).

Brinell microhardness (ISO 6506-1: 2005, GOST 9012-59) was measured as resistance load when a steel hemisphere (d=3 mm) was immersed in a sample-plate (b=1.5 mm) to 10-60 μm.

Abrasion was performed by passing composite cylinders (diameter 6.5 cm) on the emery P60 surface 40 times at a distance of 20 cm. Weight & matter loss (in mg & mm) was determined. Abrasion resistance was calculated as the inverse of the abrasion mass of the sample - by empirical (derived from experiments) formula W = 1 × (m / mH) / P = m / mH × P, where mH / m characterizes the increase in mass (density) of the sample after filling.

3. RESULTS AND DISCUSSION

3A. Experimental results. Physico-mechanics.

Under normal conditions, epoxy polymers are characterized by high strength and moduli in compression (about 100 MPa), bending, microhardness, resistance to abrasion and scratching.

According to experiments, exposure to water worsens all parameters for all studied compositions (**Tab.1**). The compressive strength is especially affected, for which a 2-3-fold drop is observed. Flexural strength, scratch resistance, abrasion resistance, and microhardness are also somewhat reduced.

Table 1. Parameters of composites with 66 wt % of filler obtained in water (and in air). *-estimated

	In water (*in normal conditions – in air at 20ºC*)			
	Compression, kgf on 0,33 cm^2	Microhardness, , X.F.	Wear, mg(mm) & wear-resistance	Adhesion, kgf
1. (unfilled)	100 (*330*)	65 (*70*)	11 (2) & 0.16	50 (*250*)
2. (wh.cem.)	150 (*350*)	72 *(77)*	10 (1,8) и 0,18	130 (*300*)
3. (cement)	160 (*370*)	73 *(80)*	10 (1,8) и 0,18	70 (*350*)
4. (gypsum)	120 (*350*)	70 (*75*)	8,5 (1,7) и 0,23	75 (*375*)

Qualitatively, the indicators of the obtained underwater coatings are clearly visible from **Table 2**. All of them give a shiny (in normal conditions) or matte (under water) coverage. Composites hardened “in normal conditions” have very good scratch resistance (up to 4 on the Mohs scale, i.e. almost at the level of glass). But when cured and exposed “under water”, scratch resistance is greatly weakened, and differences appear: Unfilled polymer - has poor resistance; the rest of the samples are acceptable or even good (**Table 2**). So, filling in all cases softens the decline in abrasion resistance when moving from normal conditions to underwater conditions.

Table 2. Some practical indicators of composites coatings or films

Underwater	**Wear,resistance**	**Scratch. resistance**	**Shape**
1. (unfilled)	Poor	Weak	Matte, solid
2. (wh.cem.)	Good	Good	Matte, solid
3. (Cement)	Good	Medium	Matte rough
4. (gypsum)	Good	Medium	Matte rough
Normal conditions	Wear,resistance	Scratch. resistance	Shape
1. (unfilled)	Good	Good	Matte-glossy
2. (wh.cem.)	Excellent	Excellent	Glossy
3. (Cement)	Excellent	Excellent	Glossy
4. (gypsum)	Good	Good	Matte-glossy

3B. Experimental results. Non-clinical “self-dental” applications.

The first experiments on non-clinical (including self-tested) filling and gluing of chipped teeth were carried out. Composition Epoxy520+ PEPA hardener (5:1) was filled with 65% of white-cement, and was kept for 3−4 h until a semi-solid consistency. After that, the composition was suitable for strong adhesion with a wet tooth surface. And the preparation procedure of tooth (or crown) surface is maximally simplified - it is limited to pre-rinsing and wiping with antiseptic. The filling applies with a pressure and holding for 1-2 minutes. After that, the patient personally self-corrected the bite and shape of the filled\glued part of the tooth. Subsequently, for 5-7 hours (for a night's sleep etc), the operation site remained at rest, with several self-corrections.

Fig. 1−4 shows examples of restorations implemented in 2020-2021 by our epoxy-composites. As a result of the tests, it was found that these compositions can effectively glue the fallen fragments of dental crowns, artificial jaws or teeth (**Fig. 1**). They hold well in this position and withstand all loads. They are no less effective when gluing fallen fragments of living teeth - for example, broken or broken ones (**Fig. 2**). These restorations may require repeating the gluing procedure (under errors or non-optimal post-curing process), after which the composite is firmly embedded and well withstands dental loads for many years (**Fig. 2**).

a *b* *c* *d*

Fig. 1. The drop-down “crown” of a old patient, in the states: *a* - initial, *b* -prepared, *c* - smeared with the composition, *d* - inserted back.

A B C D

Fig. 2. Damaged (A) by a marginal chip of enamel (B) and rejected for further treatment of the 7th tooth of a man; filling composition (C); restored tooth one month after the chip was glued back (D)

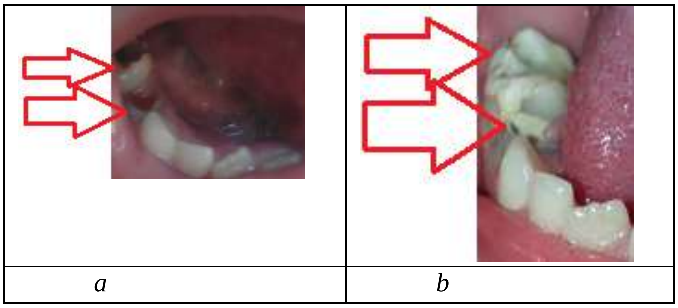

Fig. 3. Extreme milk teeth (molars) of a schoolgirl: *a* - in a completely degraded condition, *b* - their appearance after a month of self-filling (B)

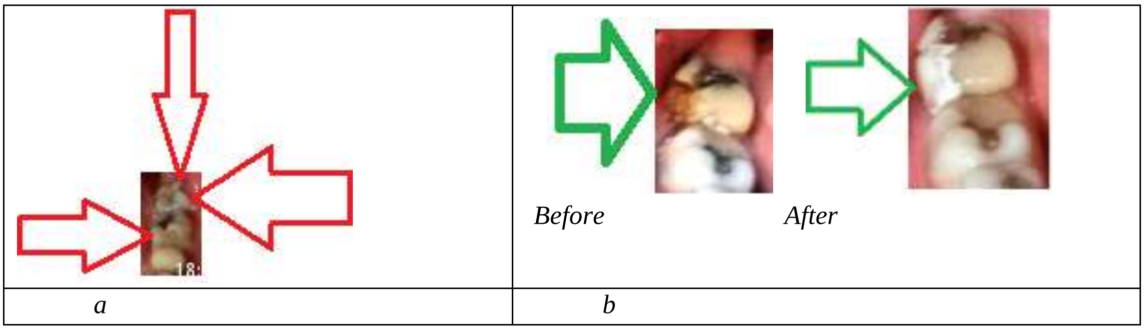

Fig. 4. Examples of other effective dental restaurations by epoxy-composite: a – at everyday home conditions and in offroad / field conditions (without fixtures and lighting, by touch).

It is effective to use these compositions in home and family conditions for the restoration of damaged children's teeth (**Fig. 3**). At the same time, an important problem is solved - the fear (or even panic) of the child in the doctor's office. Figure 3 shows an example of a completely destroyed tooth 4 and a severely affected molar 5. They were not accepted for treatment by any doctor and were sent for urgent removal (because they were periodically sick). But after restoration at home (by our parents during our observation), the polyepoxy mass stood firmly on the affected surface. At the same time, the ideal bite-compatibility with the upper teeth was restored, respectively, the problem of chewing was solved. Such an operation (**Fig. 3**) has been successfully performed on the teeth of several patients.

The effectiveness of these composites is seen from **Tab.3**.

Table 3. The recorded effects according to the results of the first out-of-clinical restorations with epoxy composites.

	Positive	Negative
Filling of dental holes / caverns	6	0
Chip restoration	4	1
Crown restoration	2	0

4. CONCLUSIONS

The highly filled water-cured epoxy-mineral compositions capable of filling and restoring dental lesions and mechanical damages, outside of clinical conditions, are obtained. The resulting composites are cheap, available and harden in the conditions of the dental cavity into biocompatible polymer fillings of high strength and resistance. This allows them to serve for a long time. These results will be very useful for people who, for various reasons (remoteness from cities, voyages, poverty, workload, war), are left without access to dental services.

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