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Micro-nano-filled biocompatible polyepoxides for outclinical self-restoration of large dental carious and traumatic damages

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Annotation:
For the first time, a theoretical thesis for the need to introduce preventative and self-restorative methods in dentistry has been provided at the level of a popular scientific experimental publication, thanks to the use of compositions with nano-silica, nano-alumina and micro-sized mineral plant fillers. The thesis about possibilities of preventive and self-restorative methods in dentistry - has been experimentally prove on standard polyepoxy filled materials. The effect is achieved, thanks to the use of compositions with nano-silica and micro-sized biocompatible mineral fillers.
Our hypotheses were confirmed in the obtained results of observations in the well-being of volunteer patients by visual information (photo, x-ray image) of the treated groups of affected teeth.

The experimental part was based on the results of preclinical studies and was conducted on volunteers, with the involvement of consultants from dental clinics. All these assumptions and hypotheses were confirmed by the obtained results of observations of the patients' well-being and visual information (photos, X-rays) of the treated groups of affected teeth.

The physical, mechanical and resistance parameters of these epoxy compositions during curing in dry and wet (or underwater) conditions are indicated. Practical examples of fillings and restorations of real teeth are presented. It has been shown that the use of these compositions (subject to curing technology) provides highly effective dental fillings, with a minimal percentage of unsuccessful cases and the absence of post-effects. The results confirm the possibility of effective prevention and self-healing of dental systems through non-operative dental exposure of epoxy owerlays. The proposed method of using ordinary, commonly available epoxy resins allows us to open a new direction in dentistry - self-dental methods. This is very important for the majority of the world's population.

Key words: dental diseases, traditional dentistry, surface preparation problems, self-restoring prophylactic compositions, self-restoration possibilities, positive effects, highly filled epoxy composites, self-filling

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INTRODUCTION

The scenario of dental problems is familiar. A tooth starts to hurt (chip, fall out, become hypersensitive) just on the weekend or while traveling... The nearest time to treat it is in a week... A dentist you know is on vacation, for another three days, and a filling at a private dentist costs 1000 hryvnias. At the local clinic, the dentist refused to treat this "hopeless case" and wrote a referral for a surgeon to remove the tooth... Queues, uncertainty, money spent... These troubles, familiar from childhood, haunt most people throughout their lives, right into old age. Subsequently, you have to fork out for dentures, bridges, crowns... but these bring new problems – tooth loss, gum inflammation, a bad bite... Is it really necessary for it to always be like this, and will our teeth forever be a kind of fifth column, on which we must keep a constant guard of dentists and a separate wallet? Or try to ignore it and endure all the problems, cavities, gumboils and irritations of the teeth, right up to their loss?

Over the past half-century, medicine and preventive healthcare have made dramatic strides. While epidemics of cholera, diphtheria, malaria, and even typhoid and plague were considered normal in the 1930s and 1950s, we hardly even mention them now. Dentistry, however, has experienced a virtual renaissance, thanks to the advent of new polymeric materials. For example, polymer cements began to be widely introduced in the 1960s and 1970s, followed by photopolymers in the late 1980s. The quality of these materials continues to improve. However, typical medical inertia and, often, political processes have hindered progress in dentistry. Dentistry and dental diseases - their treatment methods and attitudes toward them are still stuck somewhere in the 1930s. Perhaps the drills are less painful and noisy, the chairs are more attractive, anesthesia is better, and fillings last 5-10 years instead of a year. But this isn't a breakthrough, merely an improvement on old, traditional methods. In particular, mass practical dentistry remains based on the methods of the 40s and 50s, according to which the treatment of caries remains a nerve-wracking, time-consuming and costly procedure – and often with lifelong side effects and complications.

Self-restoration of damaged dental areas today seems fantastic and even dangerous (due to sepsis, poisoning or inflammation).

Over rapid development of practical dentistry, strong stereotypes and instructions for the behavior of both patients and treating personnel have been formed \1A\. They provide for mandatory clinical care, ensuring sterility and inevitable surgical intervention. In recent decades, dental materials have been replenished with effective polymer systems - primarily polyacrylic \1-5\. Epoxy materials, however, were not included in the list of those approved for clinical use, due to the "bad image" of non-biocompatible materials.

Meanwhile, polyepoxides (with the correct filling and curing technique) prove to be a unique material for dental fillings and restorations—even without a dentist and outside of a clinical setting! It's important to know how and when the epoxy composition transforms into an effective "cold weld" for wet and mobile surfaces.

In Asian countries, such methods have long been used without any patents or scientific publications. For example, videos from European geobloggers periodically appear about methods of treating teeth with unknown quickly hardening compositions - right on the street (by street doctors) \6-11\. There are also reports of increased self-installation of dental fillings by international commercial residents (usually with materials based on polypropylene and acrylates).

Our laboratory has a good experience to optimization of self-dental polyepoxy composites \12-14\ and inorganic-herbal restorative powders \15-16\. This work combines previous experience with new results.

2. Research Methods

For mechanical studies, we used epoxy resin Epoxy520 (manufactured in the Czech Republic) or another analogue of the well-known brand ED20 (manufactured in Russia). The resin was cured with polyamine brand PEPA (manufactured in the Czech Republic).

For comparison, we used photopolymer acrylic dental materials of ether or urethane nature, based on oligocarbonate methacrylates or urea dimethacrylates (manufactured in the EU).

Bone material was taken by sawing cattle bones, dentin (enamel) was taken from extracted or fallen teeth of patients in dental clinics.

Mechanical tests were carried out using methods identical or close to ASTM or GOST standards.

Initial experiments on non-clinical (including self-testing) filling and bonding of chipped teeth - were conducted. An epoxy composition Epoxy520 resin + fresh PEPA hardener (5:1), filled with 65% of inorganic dispersions (gypsum, white or ordinary cement, micro-CaCO3, microquartz etc) or 3-5 wt% of nanodispersions (silica, alumina) - was used:. After adding the hardener, the composition was left for 3±0.5 hours to reach a semi-solid consistency with high tack. After this, the composition remained firmly bonded (within 1-2 minutes) to a wet tooth surface for 30±10 minutes. In all cases, priming of the tooth surface was not performed (since a priming composition of the same composition usually turned into a weakening layer). Tooth surface preparation was also simplified by a series of rinses, followed by wiping with a soft brush with nano-silica (or another drying agent) and applying a swab-napkin. The filling (or crown) was applied immediately after this drying, applying a certain amount of pressure and holding it in place for 1-2 minutes. The patient then adjusted the bite and shape of the filling or bonded portion of the tooth manually. Subsequently, for 3-7 hours (including overnight sleep), the surgical site was left undisturbed, only self-adjustments of the bite and shape were performed (including removal of any loose adhesive).

3. Research Results

3.1. Properties of polyepoxides. According mechanical and resistance properties (Table 1), epoxy polymers are quite suitable for materials used in dental technology. At the same time, they are softer than acrylic, metal and ceramic materials – due to which they do not lead to the gradual destruction of surrounding dental tissues.

Table 1. Comparison of the strength and durability of epoxy composites in their original form and after exposure to a warm aqueous environment. *-Estimated generalized data.

Epoxy polymer	in dry normal cond.	in H_2O
Compression, MPa	100 +-20	50+-10
Bending, MPa	10 +-2	6+-2
Adhesion to dentine, rel.un.	100%	80%
Adhesion to enamel, rel.un.	100%	35%
Microhardness, XF	80	40
Wear resistance, rel.un.	100%	50%
Water resist, (swelling), 30 ºC, % \ 3 monts	3%	10%
Bone\dentin		
Compression, MPa	20+-3	20+-3
Bending, MPa	15+-5	15+-5
Microhardness, XF	50	40
Wear resistance, rel.un.	80%	70%
Acrylates		
Compression, MPa	150+-20	-
Microhardness, XF	90	-
Wear resistance, rel.un.	100%	-

3.2. Results of practical in vivo restorations. The results of out- clinical experiental restorations “in vivo”, and on a poorly cleaned (without drilling of the dentin and enamel with a drill) surface can be considered important. The quality of the adhesive contact, the hardness and durability of the filling, as well as side effects - many consider insurmountable problems that require long-term study. Our experience has shown that with normal patient immunity,

such concerns can be neglected. Since their probability is comparable to complications after visiting quite respectable traditional dental offices.

Restoration of deep tooth lesions with epoxy can be classified into several categories. These are:

1) Installation of bridges and large tooth-like fillings in place of completely destroyed teeth, with roots remaining in the jaw and gum. The nerves in such teeth can be removed or are in a half-dead (or sensitive) state. In all these cases, pouring or pressing the tooth-replacing composition (without deep cleaning of the lesion) will close the affected area, while the outer side of the filling will take a perfect bite - under the influence of neighboring and opposite teeth. Such "mega-fillings", of course, have many risks for rapid loss - due to a very large area of adhesive contact with the contaminated surface. But our experience has shown that after loss, they only help to clean the affected surface - just like scotch tape or masking tape cleans chalk and dust from a painted wall. Subsequent similar installations increase the durability of the new filling, and now we know of cases where they stand well and work for 0.5-1 and even 1-2 years.

2) External filling-covering of damaged or fragmented surface. It often happens that part of the tooth or filling is damaged and gradually destroys. This is a very unpleasant situation, since it requires full-fledged surgical intervention in the established and years-old dental ecosystem. Often this intervention ends with the loss of both the filling and the tooth itself (or removal of its nerves), expensive and painful procedures for restoration. Therefore, patients with low-incomes or very-busy (actively working, family, remote from medical centers) often go the way of ignoring the problem, up to stopping chewing on the problematic side of the jaw. This can end in inflammation or preservation of destructive processes. We have also developed methods (described in [15-16]) for filling such problem areas with special plant-silicate dental powders. But the best solution to the problem would still be a quick sealing of the destructive fragment or area, at least with a temporary polymer composition. Self-sealing kits (and even installation of dentures) based on easily fusible polypropylene balls are now being actively sold. This is a new word in dental technology, but such seals do not provide strong adhesion (only mechanical).

In our case, epoxy restoration allows for ideal integration in terms of both mechanical and adhesive parameters. The epoxy composition hardens gradually, which allows it to self-spread and self-flow along the rust of the destroyed areas, and to harden slowly. Our first experiments show that with minimal care in installation (that is, with minimal requirements for drying the contact area and preparing the epoxy), such fillings will last quite a long time (2-6 months and sometimes up to 1-2 years) without destruction - and this is with an active chewing cycle.

Table 2. Statistics of restorations performed (on the teeth of three patients) of partially destroyed teeth.

Всего	Less 1 month	1-3 months	3-12 months	>1 year	Post-Inflammations
10	1	4	3	2	1

At the same time, epoxy overlays do not cause inflammation and sepsis, and due to their softness, they do not injure the soft tissues of the oral cavity.

It is also important that after the loss of such overlays, they are very easy to reinstall on your own, on the same day or in the near future. Reinstallation (unlike operations in a dental clinic) only cleans the contact area, improves the health and improves the conditions for subsequent overlays. At the same time, the bonds between the tooth and surrounding tissues (gums, adjacent teeth) that have been formed for years are not destroyed.

We think that epoxy gives such an effect due to its compatibility with amine, anhydride and other compounds - characteristic of putrefactive masses (which are carious masses). It can be considered that epoxy resin not only adheres well and flows with the surface of the damaged tooth, but also “eats” caries, partially converting it into a polymerization hardener (and partially incorporating it into the polymer network).

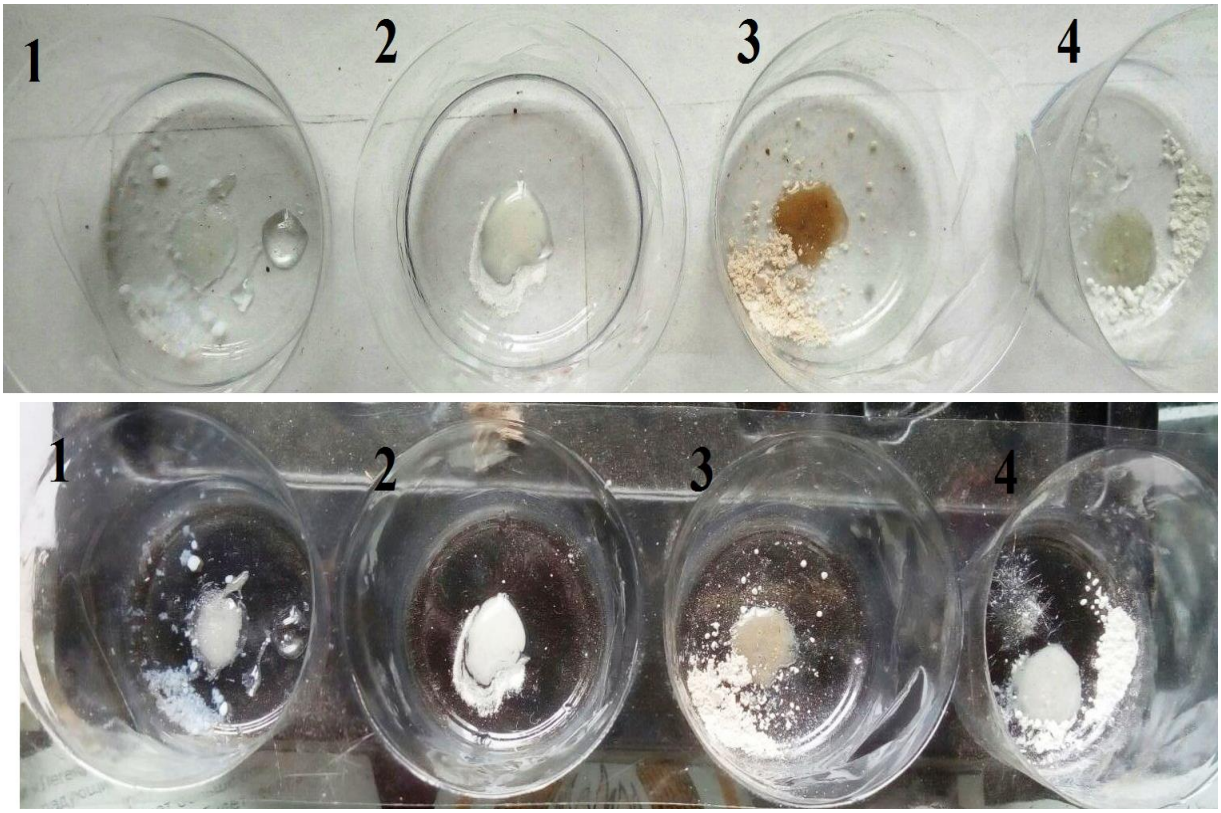


Fig.1. Type of epoxy composites available for dental restorations. Left-to right – compositions and their fillers: 1) Epoxy+SiO2 and Neat epoxy; 2) Epoxy + dentifrice or TiO_2 ; 3) Epoxy + Gypsum; 4) Epoxy + WhiteCement.

Can see (Fig.1) that self-restored compositions can compose from accessible and inexpensive materials. The colour of obtained composites can differ from transparent to gray and dark tones.

3) Deep cavities.

Теоретически это сложный случай, потому что глубокие полости (как считается) совмещаются с отравлением и постоянн усиливающейся деструкцией оставшегося зуба. This, of course, depends on the immune system, since one just needs not to overload the problem area (and it will self-preserve), while another will not be able to stop decay even with the best clinical care. But the general requirement of any organism (both weak and strong) to such a problem is to quickly close the cavity and provide peace to the immune system, correcting (or preserving) the situation.

Pracrtically. we can close a narrow deep hole with anything - even chewing gum or cement mass. The only question is - how long will it stay there and what will be under it. Ведь в процессе жевания, контакт с зубом сразу нарушается и пломба сразу выпадает. Контакт вообще может не образоваться – из-за слоя гнтлостных и мокрыъ масс на поверхности зубной ткани.

It is generally accepted that without thorough cleaning of such a cavity, closing it will lead to the same suppuration as closing a festering wound with tape (or a non-breathing plaster).

Epoxy compositions make it easy and long-lasting to close such cavities. But in this case, deep carious processes may not be affected by contact with epoxy and are left to themselves. In this case, the process is transferred to the immune system, and the carious cavity (in most normal cases) will be preserved or absorbed (Fig. ...). In other cases, the epoxy composition can flow to the site of deep caries and come into contact with it, absorbing part of the carious masses. The porosity of epoxy composites provides another useful effect - the filling "breathes", does not block gas exchange and can even act as a capillary drainage system (for removing liquid waste) from the carious cavity.

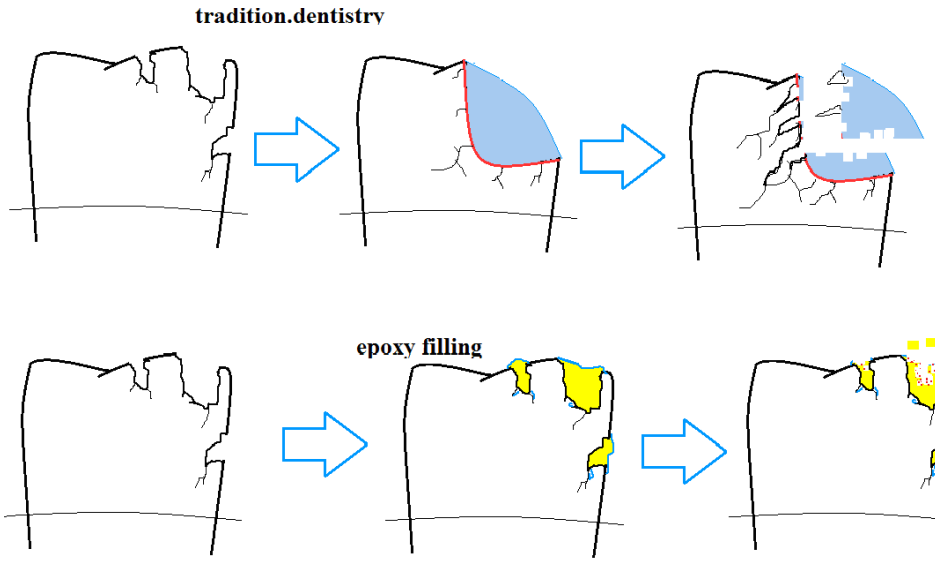


Fig. 2. Restoration and its subsequent aging/destruction with traditional and epoxy execution.

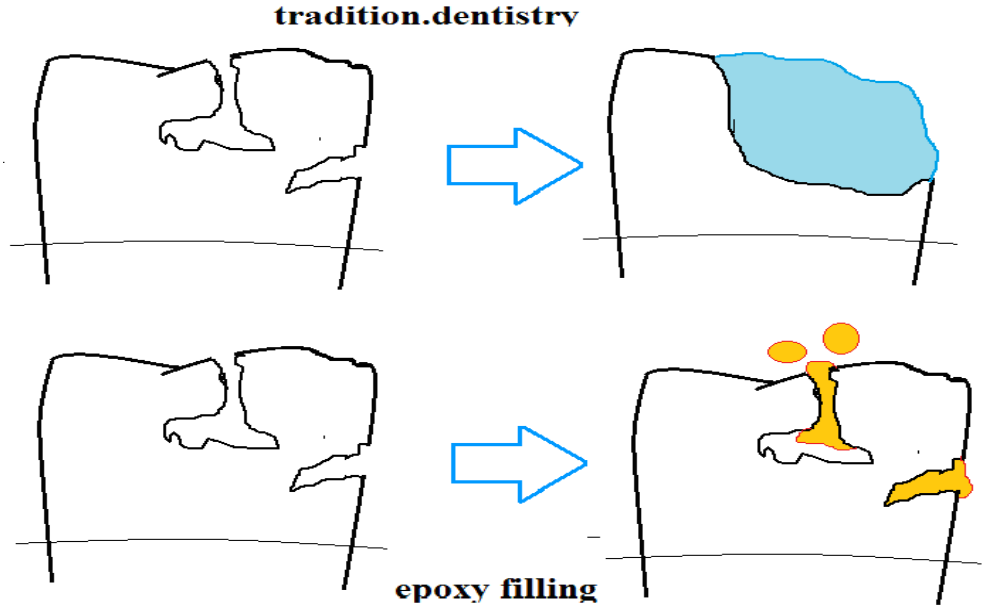


Fig. 3. Comparison of traditional and epoxy fillings

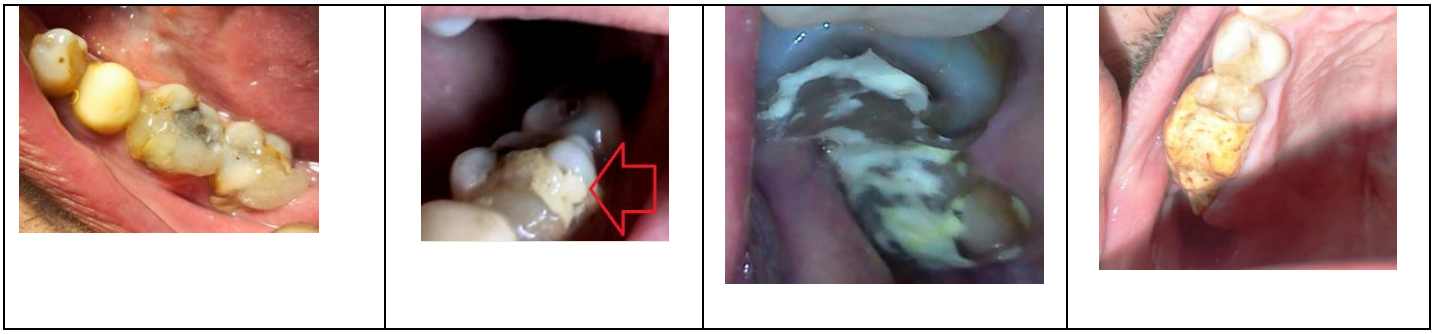
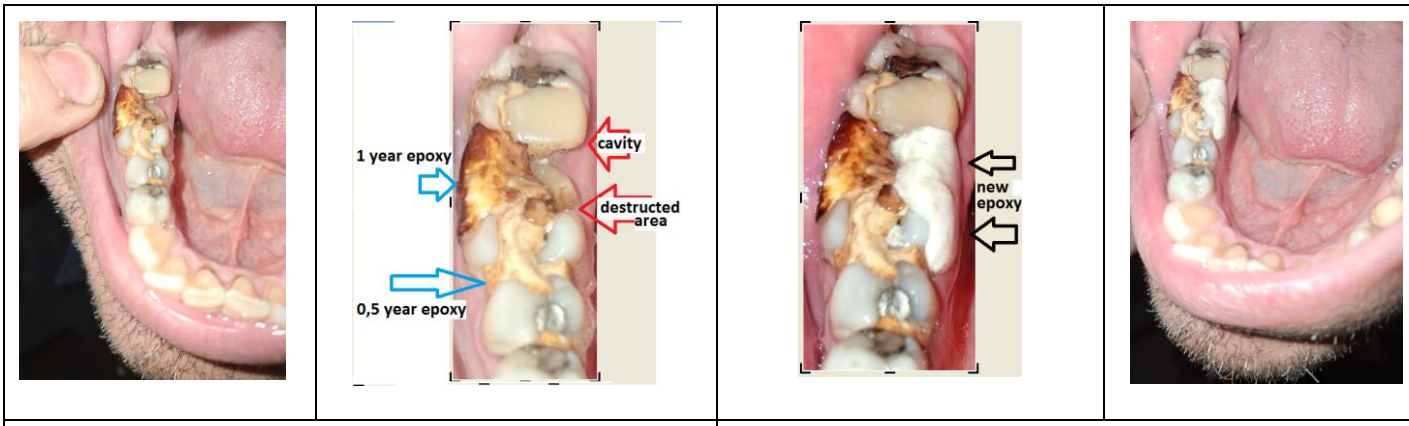


Fig. 4. Examples of successful restoration of destroyed areas



before | after

Fig. 5. An example of successful restoration of destroyed areas of the lateral teeth of a 50-year-old patient.

A | B | C

Fig.6. Fully destroyed teeths (6 and 7) before (A) and after self-restauration, and sample of used dental epoxy prosthesis after 1 month of in-vivo working.

Fig.7. Example of mobile dental workstation (A) and samples of epoxy-filling in molar (B), fallen epoxy-filling for molar (C) and epoxy-filling for permanent adult tooth (C).

Conclusions

1. On the basis of well-known analogies with the phenomena of **self-rehabilitation** in wildlife and in industrial and construction industries, the **first foundations** for the theory of self-healing of the human dentition have been created, with the implementation of a number of hygiene rules, and the regular use of optimal plant-mineral mixtures (powders). On the example of experimental work, the **possibility** of the existence of highly filled epoxy-mineral compositions capable of filling and restoring lesions and mechanical damage to teeth, independently and outside of clinical conditions, **is shown**.

1. A simplified method of non-clinical self-restoration of dental damages of any complexity (carious, traumatic,crack etc) is proposed. It involves the use of epoxy compositions, including those filled with waterproof micro-nano-

dispersed powders. The self-restoration technique eliminates a number of traditional painful stages that are inconvenient for the patient (cleaning dentin/enamel with a dental machine, removing nerves, etching the drilled surface, etc.), does not require money or time, eliminates the patient's total dependence on the dentist and clinics. It also encourages responsibility for the condition of one's own teeth, develops the ability to independently observe and recognize their behavior, and enhance self-prevention of dental diseases.

2. It has been experimentally shown that polyepoxy-filled composites (including those cured in water and wet conditions) have high mechanical and resistance properties, quite comparable with traditional dental materials. The comparative slowness of their curing (2-3 hours before dental installation and 1-2 hours after) contributes to the thorough self-formation of the current (compatible with the characteristics of adjacent teeth and soft tissues) bite of the new dental filling. This eliminates inconvenient procedures of clinical grinding and reinstallation of poorly installed dental fillings and dramatically reduces the risk of inflammation due to errors in installation.

3. It has been experimentally shown that polyepoxides have higher (or comparable\) microhardness than bone tissue, but lower than dental polyacrylates. This allows you to easily replace an outdated or fallen out epoxy filling with a new one, without destroying the living tissues of the tooth (which occurs when traditional acrylic and cement fillings fall out or become loose).

4. Examples of successful self-restorations are shown. As examples, successfully working epoxy inserts (including dentures and bridgesy h, dsdddsddd ds) in children, adults and pensioners are given. A number of self-restorations have been successfully carried out on teeth that do not respond to traditional clinical treatment (sent for extraction or pinning).

5. Thus, we can talk about the discovery of a new highly demanded direction in medical materials science and dental technology - self-sealing. This will be very useful both in cases of difficult access to quality treatment, and for the treatment of low-income human groups. The proposed materials and methods allow you to create an alternative methodology for independently restoring dental damage (including deep and extensive carious \ traumatic cases).

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