

Microfilled Epoxy-Composites, Capable of Thermo-Hardening and Thermo-Plasticization After Hard Heating (200-300 °C) - For “in-Field\Offroad” Use in Bio-, Agro-, Medservice

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ABSTRACT

The work is devoted to the study of a new type of composites for the manufacture of special details, parts, tools or adhesive repair in the field. We have developed epoxy compounds that preserve or increase strength and ductility after heating at 200-250oC. That let, if necessary, an effective thermo-disinfection of composite toolsproducts at elevated temperatures. It is believed that conventional epoxy resins are unable to retain their physical and mechanical properties after heating above 200°C. Their feature is in simplicity of making (ordinary filling with available\cheap microfillers) without special qualification of personnel and in any conditions (outside clinics, laboratories and service centers). In this work some of such compositions (with SiC, TiN, SiO₂-marshalite, cement) are considered. It offers to name such composites of “thermo-harden” or “thermo-plasticized”. Bioneutrality, durability and heat-resistance, at 200-300°C does him a good material for rapid repair and making of the special or failing instruments in the field, travelling, military and other difficult terms.

Introduction

Requirement in effective repair and 3D-copyright compositions for ambulances and research groups “in-field” is actual now. Even appearance of 3d-printers and single-use cheap instruments decides a problem only on the insignificant moving away from cities or service centers. In regions with the low level of hygiene, the deficit of instruments (special, new or quality) appears industry or populated constantly. And such regions even now is majority - and it is Sahara\Africa, Antarctic Continent or Siberia not only. Low-habitat and deprived many blessing of civilization even such regions as west of China, west of the USA, north-west of the USA and Canada, mountain districts of Asia and South America. Problems with the quality providing are present and in Europe and inhabited regions, in periods of geo-, techno-, military and social troubles. Epoxy resin is open 120 years ago by Russian chemists Dianine (his name in term “EpoxyDian resin”) and Prilezhaeff [1]. Until now, possibility

of epoxy resin as rapid repair-copying material still not used full. Her dignities also not always are estimated. We will lead a few from them:

- a) Widely accessible and used, is comparatively cheap (5-8 USD\kg).
- b) Does not depend in base properties from producer (USA, Russia, Czech Republic, SaudiArabia, Korea, China) nor from storage-time (at correct storage - 50 years and more).
- c) It is combined both with non-polar and by arctic liquids, and almost with all types of fillers.
- d) Is high interest both cleanly scientific and industrial research laboratories.
- e) Allows to get a construction (durable and proof) polymer without the special qualification and equipment.

f) Comparatively low-toxic (if not with hardener and solvents), and polymer is bio-compatible.

g) After harden have not a shrinkage, saving an initial volume (unlike acrilates, rubber and celluloid glues).

Lately service-domestic possibilities of epoxyresin are extended by commercial success of the high-filling "cold welding" (Blitz-Steel etc). But application of эпоксидных resins in biomedicine was limited to the traditional views on toxicity of her components (especially amine hardener). Opinions of biocompatibility of epoxy-polymers until now differentiate also, and often biomedicine prefer acrylic and thermoplastic polymers. Nevertheless last 5-10 the spectrum of the use of epoxides in biomedicine grew notably. In 2010-2019 were edited survey book that in leading scientific editions of the world - the authors of that dedicate to epoxides a head chapters and key places in text. We will give an examples. Iftekhar [2] in his book places a table (Table 12.1. Constituents of BiomedicalComposites), where epoxies occupy a first-ever column. In [3] can see a photo of prosthetic appliances from an epoxy-carbo-plastic (fig.12.6 etc). And such composites can successfully replace metals in External Prosthetics and Orthotics (p.12.8.3). BobbyMohammed&Samad dedicate a whole head 5 in her book [3] to the theme of "Epoxy composites in biomedical engineering". One of main theses here - "In the field of biomedical engineering, epoxy composites have been widely used to prepare components of devices for medical imaging, bone plate applications, as a novel material for dental applications, as scaffolds for tissue regeneration, and as implants for bridging large osteoperiosteal gaps". The theme of study of "cytotoxicity of such composite systems" is affected, from where a conclusion follows about biocompatibility of epoxy-polymers.

In our work [4] a possibilities of prosthetic works from cheap and accessible epoxycomposites are shown - that makes accessible prosthesis (at presence of specialists) for the wide layers of population in all regions. Very interesting and most modern is now a book of Grumezescu [5]. In that a few heads are devoted exactly to the epoxy-composites for biomedicine. Mainly the question is about stomatology and bone prosthetic appliances or implants (p.4.3.3 "epoxy composites...these materials play an important role in bone repair"). Authors of [5] cites many last works of colleagues : «An nanotubesECO was developed for application in prosthetic sockets in transfemoral amputees (Arun&Kanagaraj, 2016) [6]. ...Pineapple leaf fibers were loaded in different variations in thermoset Pester& E resin (Odusote&Oyewo,2016) etc. In [5-7] shows the frequent height of durability of epoxy (carbo-& glass-plastic) prosthetic appliances comparatively with titanic [5] Ch.5, p.5.2, page 149 are driven. According [10] prospect of their use in implantation yet wider, because of "The bone structure growth over the Epoxy/CarbonFiber Co was found to be pore bearing, implying a better degree of O₂ & nutrient accessibility compared to the titanium alloy - which lacked such features". [5], p.5.2 Artificial Implants & Bone Fixation Plates). The epoxy-systems can press even acrylic in stomatology (sphere where epoxides yet not so known). For

example inp.5.5 reported: «...glassfiber Epoxy Composites and found that a similar moduli ...would mean better distribution of ... stresses across the bonding interfaces of the Dentin/Dowel/Core system to the tooth with a potential to reinforce the weakened tooth in addition to reducing the probability of root fracture. Besides biomedicine, epoxyresin is very popular as in high-technology (engineering, aerospace, electronics) so in building-domestic spheres (polymer floors\tables, handmade, facade decor). Epoxyresin can be filled to practically all dispersions in order to her high adhesion to any surfaces (except fat and silicon). Already 30-40 syear such fillers come forward the hit of the following as silica [10] microspheres, carbon (CNT, Graphene [8]) , carbide [12-14], nitride [15,16], metals [9,17], cellulose, polymer dispersions (see online-accessible literature). Is many works, discusses seriously the results of filling by such "very innovative" fillers as rice and other husk, stones, coffee and cacao, vegetable and tissue fibres, and even "waste fillers". From the last works the article interesting for example Oladele et al. [11] about cow bone particulate reinforced epoxy composites for biomedical applications.

But epoxy resin (we do not talk about expensive and special resins) has traditional limitations characteristic for all polymers. So, accessible epoxy-composites save properties only to 180-200°C. Meantime, practically the important (for example at drying and treatment of food, medications, at термо-disinfection) is see an interval to 200-270 °C. Our collective presents the group of scientists from research centers in Ukraine - country where almost 85% of people are higher education. Since times of SovietUnion we have one of the best medical systems for a population, and innovative sector is highly developed in bio-, zoo-, agro-, medical sphere. Due to regular civil and military conflicts (2004-2006, 2014-2018), technical and social stresses (including nuclear accident in Chornobyl in 1986) - here is natural base for development of researches on composite prosthetics and implantation. Accordingly, in our practice there are queries on simple cheap technology to increase of working interval for epoxy compositions. Really, accessible fillers (and even wastes), fully can replace more expensive polymer in a composite, without worsening (or improving) of properties. However mostly behavior of filled composites copies initial polymer after hard (destroyed) heat treatment. This work shows an examples where the filling is capable of thermo-reinforcing a composite - in comparison with unfilled polymer and (sometimes) with a not-heated composite.

These effects have not been covered in the literature. May be that this effect was first described in 2017 by Starokadomsky [17] - on epoxy composites with micronano-iron particles. He suggest to call them "thermo-strengthening" and "thermo-plasticization" (when warming up improves flexibility/plasticity). The difference from the well-known thermally-reinforcing effects of polymers is discussed temperature. So, it is well-known that polyepoxides are strengthened by heating at 50-120°C. But they can work no higher than 150-200°C (when the final destruction begins). In our case, after such a "deadly" warming up for polyepoxides as 240-270°C, these composites only improve the physical properties, or reduce

them insignificantly - by 5-15% (but not in 1.5-2 times as for unfilled epoxy-polymer). For the biomedical use this is important by possibility of disinfection at warranty-effective temperatures (150-250°C), that it easily to get 'in-field' from accessible electric devices or from above an open fire. Unlike widespread now thermoplastic composites (PP, PE, PET) epoxy wares will not be melted at this heating. Thus, they can be easily done "in place" and to replace more expensive or scarce wares (spatulas, capacities, details) from a PTFE, nickel and titan [2-7,16].

Methods and Reagents

Samples were prepared on the basis of classic dianepoxy resin (Epoxy520, Czech product.(2015), Eurounion) and PEPA (Czech prod.) hardener (5:1). Compositions were filled by 50 wt% of SiC or TiN (Donetsk reagents plant(1987), USSR), SiO2 marshalite (Ukraine prod. (2015)) or cement M400 (Eurocement prod. (2018), Ukraina) and gypsum "Alabaster G-5" (Gypsovyk prod. (2018), Ukraina). After 7-10 days composites were treated at 55 oC during 5 hours (or 55 oC 5 hours after that 250 oC 1 hour). Compression tests were subjected to cylindric samples (diameter 6.5 mm, height 10-12 mm) on a "LouisShopper" press machine [17]. Microhardness tests were subjected on a Rockvell testing portative machine (immersion of steel sphere into template plate on 10-60 mcm). SEM-images were scanned on JEOL GSM microscope.

Experimental Results

Compression tests. The first example of hardening and plasticization after destructive heating. Filling only in some cases (for SiC) allows to increase the compressive strength F (Figures 1 & 2). But the unfilled polymer after heating significantly (25%) loses its strength. And, all the microfilled composites taken after 250°C gave a higher than H-polymer index. All of them practically retain his strength indicator after a hard heat treatment - unlike unfilled. Two of them (with cement and gypsum) increase their strength after hard heating. Note - that the studied nano-fillers and a number of micro-fillers (basalt fiber, etc.) do not give such effects, losing strength as shown in the example of epoxide with 0.01 wt% graphene oxide (sample GrOx, Figure 1). The same picture was observed when such an epoxy resin was filled with a micro-iron in the work of Starokadomsky [9]. There, unfilled also have a maximal strength, but significantly reduced it after 250°C. On the contrary, the iron-filled samples were strengthened (sometimes by 40–45%, Figure 2) precisely after a hard heating. Microhardness. A twist example of hardening and plasticization after destructive heating. The reduction of shrinkage (Table 1) can be considered a practically important consequence of filling. This suggests the effect of filling on microhardness.

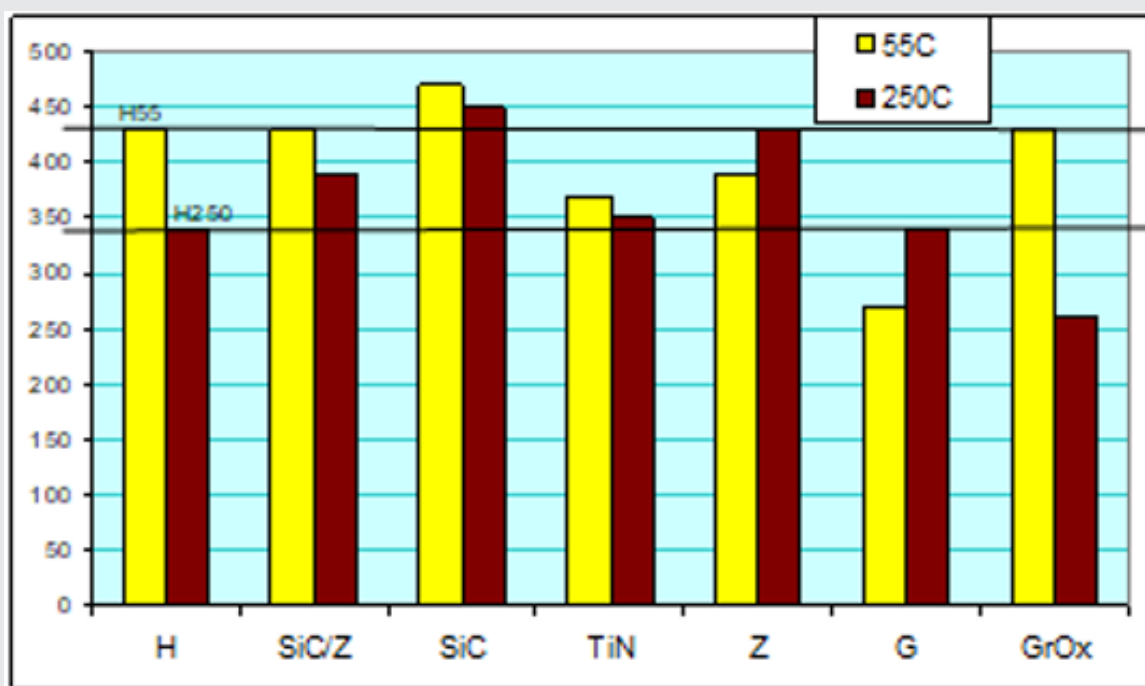


Figure 1: Compression load (kgf) for composites without filling (H) and with 50 wt% SiC and cement (1: 1, SiC \ Z), SiC, TiN, cement M400 (Z), gypsum G5 (G) and from 0.01 wt% graphene oxide (GrOx). Line H55 shows the level for H after 55 °C, H250 - after 250°C (1 hour).

Table 1: Shrinkage (mm) of cylindrical specimens with a height of 12 mm.

Unfilled	SiC	Sic/Zement	TiN
1,5	0.8	1	1

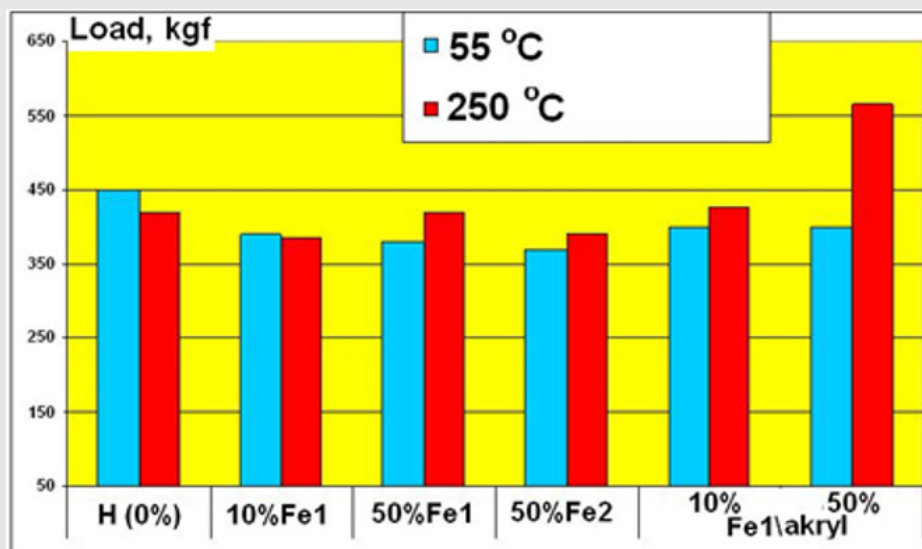


Figure 2: [17] Compression load (kgf) for composites (treated at 55 oC and 55; 250 oC) without filling (H) and with 10-50 wt% of micro-iron neat and surface-modified by acrylate (Fe1\akryl).

And really, fom Table 2 it is clear, that discussed composites can be essential plasticized after 250°C. This is indicated by the possibility of deeper penetration of steel sphere - up to 60 microns or more (instead of 30-40 microns without 250°C) - unlike the H-polymer, which naturally loses plasticity after 250°C. Indeed, during mild heat treatment, the filled compositions have, as a rule, 30-50% higher microhardness than the Unfilled polymer. But unlike the unfilled polymer, they do not differ in plasticity, and are fragile when a punch is dipped over 20-30 microns (Table 2). The reinforcing and plasticizing effect of the fillers is noticeable after destructive heat-treatment (250°C), when the unfilled samples retains its microhardness Table 3, but loses its plasticity, significantly destructuring. And really, the maximum immersion

without cracking for Unfilled in this case is no 50-70 microns, and only 30-40 microns. On the contrary, a composite with SiC after 250°C acquires significant plasticity, while maintaining (and even increasing) the microhardness (Table 2). The same, although to a lesser extent, can be said of the SiC/Zement mixture Figure 3. The composite with TiN was initially (after 55 °C) harder than the H-polymer (Table 2), but it is much more fragile. After 250°C, its plasticity increases markedly,- which, however, is accompanied by a drop in microhardness (but it remains higher than for the Unfilled polymer). That is, with any heat treatment, the composite with TiN gives a higher microhardness than the Unfilled polymer, moreover, after 250°C, it acquires plasticity.

Table 2: Microhardness of the filled composites, at different thermal modes. Italic indicates the measurement at which or to which the sample was destructed. Designations for the destruction of samples: T - cracked, (T) - most samples in this series of tests were cracked.

Soft = 55 °C 5 hours	20	30	40	50	60 mcm
Unfilled	150	230	310	380	450 (T)
SiC	210	300 (T)	420(T)	550(T)	T
SiC/Zement (1:1)	200	250	300(T)	T	
TiN	270	350	440 (T)	550(T)	T
SiO ₂ (marshalite)	400	500	550 (T)	T	-
<i>Hard = 250°C 1 hour</i>					
Unfilled	170	250	330(T)	T	-
SiC	210	330	430	530	570 (T)
SiC/Zement (1:1)	100	200	290	390	450(T)
TiN	180	300	370	460	500 (T)
SiO ₂ (marshalite)	370	450	550	600	700 (T)

Table 3: Fire resistance of composites at the time of ignition from an open fire (in brackets - the type of ignition).

Unfilled	SiC	Sic/Zement	TiN
1,3 (active self-inflames)	2 (inflames)	3 (weakly inflames)	2 (inflames)

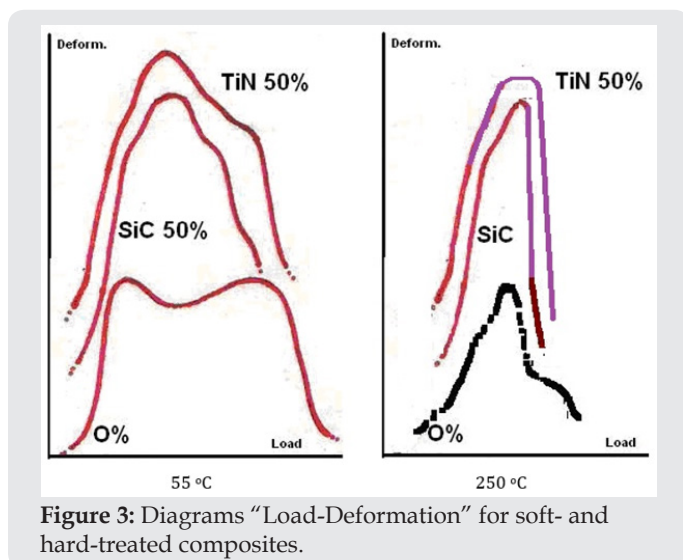


Figure 3: Diagrams “Load-Deformation” for soft- and hard-treated composites.

On the example of 50 wt% marshalite, the effects of thermo-plasticization and thermo-hardening (after 50 μm immersions, Table 2 are even more noticeable. Thus, is possible find a fillers that make the microhardness insensitive to heating or even grows after it. The increase in heat resistance after filling is also manifested in a noticeable increase in fire resistance - in 1.5-2 times (from 1.3 to 2 or 3 seconds, Table 3. This is due to the appearance of a large amount of non-combustible filler in the composite. Microscopy: something happens to the size and distribution of particles A SEM-microscopy shows morphology of composite. Main is an interesting fact of change (making small and enlargements) of size of microparticless of filler. It must give influence on durability of compo. Maybe, the described effects of “thermo-hardening” and “thermo- plasticization” are related also to increasind of conversion-degree and heat-resistance of compacted by filler layers of polymer Figure 4. The theory of this question yet coming to study.

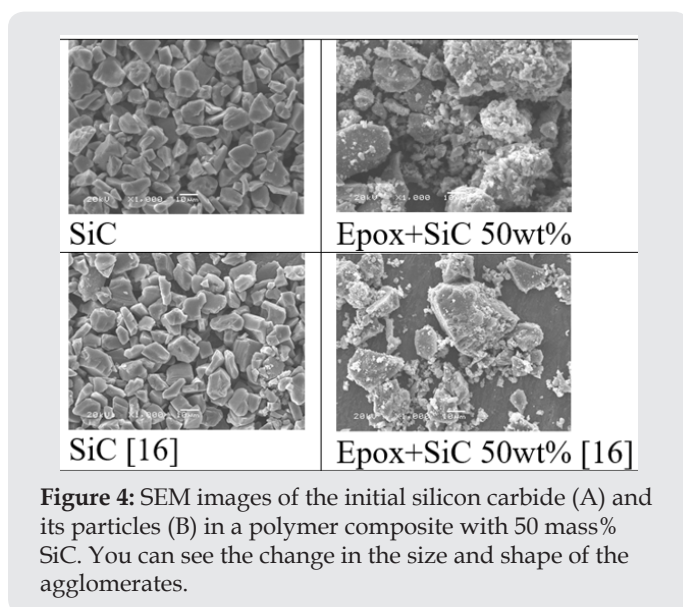


Figure 4: SEM images of the initial silicon carbide (A) and its particles (B) in a polymer composite with 50 mass% SiC. You can see the change in the size and shape of the agglomerates.

Conclusion

- The review of last literature, from that high perspective of the use of epoxy-composites ensues in biomedical direction, is presented. Thus, there is possibility of creation work-hardened and cheap composites by the simple filling within any terms accessible powders.
- Fillers and compositions that strengthen or retain after hard heat-treatments (that is impossible or difficult for standard unfilled polyepoxides) are found. The examples of them are shown (50 wt% of SiC, TiN, cement, gypsum, marshalite).
- The effect of preserving or enhancing strength (compressive strength, microhardness, resistance to abrasion etc) after 250+-20°C of warm-up is proposed to be called “thermo-hardening.” The effect of increasing plasticity after 250+-20°C of warm-up has been proposed to be called “thermo-plasticization”. These effects (according to our search) are not yet described in the scientific literature; therefore, they may have been identified for the first time.
- The exposure of such epoxy-composites takes off traditional limitations (150-200°C) from ordinary polyepoxides. It opens very wide possibilities of the use of him in the field terms - especially for biomedical or research necessities (considering disinfection procedures at guaranteed temperatures).

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