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NEW EFFECTS OF THERMO-HARDENING AND THERMO-PLASTICIZATION AFTER HARD HEATING IN EPOXY-COMPOSITES WITH OPTIMAL MICRO-NANO-FILLERS

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Abstract

Based on a review of the literature (including the geography of specialized research centers), the prehistory and problems of the study of thermal effects in polyepoxides are shown. It is shown that the main research database is now concentrated in 50-60 research centers in India, China, Middle East, the ex-USSR and the EU countries.

The article summarizes the results of experiments on hardening a standard bisphenol epoxy-amine polymer. The existence of inorganic microfillers, which impart hardening properties to the epoxy, especially after destructive critical (250 - 300 °C) temperatures, is shown. These include inorganic binders (gypsum and cement), carbides and nitrides (SiC, TiN), metal microparticles (Fe). The ability of the epoxy polymers filled with them to harden or plasticize under the action of critical destructive temperatures, is proposed to be called "thermal hardening" and "thermal plasticization" of epoxy-composites. The work gives examples of these effects on specific compositions with 50 wt% fillers. The creation of these filled compositions makes it possible to expand the temperature range of the practical application of epoxy polymers - in areas with high requirements for the thermal stability of materials.

Keywords: Epoxypolymer, Strength at Compression, Abrasion, Modulus, Microhardness, Thermal Hardening, Thermal Plasticization, Micro-fillers.

Introduction

A. Epoxy-polymers-prehistory & modernity. Epoxy resin - is an epoxy-terminated oligomer typically cured with amines and anhydrides. Its invention in 1896 - 1906 by the Russian chemists Dianin and Prilezhaev [1] gave rise to the use of epoxy polymers. Of the dozens of types of such resins, the most widely used resin is called ED-20 in the USSR and then in the East Europe, and has different trademarks in the world (Epoxy520, DER33, Raseen, Eposir7120).

Popularity of epoxides is due to its ability to transform into a strong durable plastic in any (even poorly adapted - road, home, camping) conditions. Moreover, from the use of the most affordable fillers (sand, clay, stone chips, shavings, microspheres, grains etc.), it often only strengthens. Its distribution is restrained by the specificity of use (skills of mixing with a hardener are needed), the toxicity of hardeners (the liquid resin itself is also considered unhelpful), the need for complete drying and degreasing of the glued surfaces, and other inconvenient requirements.

B. Filled epoxy-composites. In the technology of polymers, it is possible to increase the physical and mechanical properties or durability of composites by simple filling. However, most often, the behavior of such filled composites copies the behavior of the initial polymer matrix, especially after severe heat treatment (destructive for this polymer matrix). Sometimes, we can reach new properties through an optimization of fillers.

Filling can produces effective thermo-durable epoxy composites (EC). Now a lot of eminent researchers in ≈50 researchers institutions are working at this field [1-51] (Table 1). A lot of him investigates thermo-mechanical properties of EC.

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Table 1: The Research Collectives with Regular or Creative Publications in Field of Thermo-Durability or Thermo-Mechanics of Epoxy Composites (EC), in 2017 – 2021 (selectively, estimated list)

Researchers (official @-mail)	Affiliation	Field
Starokadomsky D. [1,4-16], Gorelov B. [11], S. Shulga, N, Sigareva & M. Reshetnyk; km80@ukr.net	Chuiko Institute of Surface Chemistry & Natural Sci. History Museum, Nat. Academy of Sciences, Ukraine	Filled EC for repair & advanced devices
Danchenko Yu., M Kachomanova, Y Barabash [17-19] u_danchenko@ukr.net	Kharkov Nat. Univ. of Build & Architecture, Ukraine	acid-base interaction role in fire-resist. filled EC
A. Mostovoy, Yu. Kadykova & A. Yakovlev [22-23] Mostovoy 19@rambler.ru	Engels Institute of Technology, Yuri Gagarin State Technical Univ. of Saratov Russia	EC with chromites, graphites, polytitanates
A. Bekeshev, L. Tastanova & M. Akhmetova [22] lyazzatt@mail.ru	K. Zhubanov Aktobe Regional State University, Aktobe, Kazakhstan	Filled epoxy composites
T.A. Nizin, V.P. Selyaev, D.R. Lowland & A.Sulejmanov [24] Sulejmanov@kgasu.ru	Mordovsky University & Kazan State Archit.-Build. Univ. Russia	Climatic durability of epoxy polymers
E. Kupriyanova & V. Osipchik, T. Kravchenko, A. Pachina, T. Morozova [25]	Armokom-Center, Moscow & Mendeleev Russ. Chim. - Tech. Univ., Moscow Russia	Durability of Epoxy-binders
L.A. Gnibeda, V.M. Mikhalchuk; V.A. Krotova. [26]	Donetsk National University	thermoresist.EC-coatings with SiO_2 & TiO_2
Vovchenko, L., Lozitsky, O., Matzui, L., Oliynyk V.& Zagorodnii V [27]	Taras Shevchenko National University of Kyiv (Dep. Phys.& Dep. Radiophys.), Ukraine	EC with multiphase Fe, TiO_2, C - nano-fillers
Alexander J., Augustine B. & Paudel A. [28] vsjalexander@gmail.com	Sathyabama University, Jeppiaar India	Basalt/epoxy composites: hygrothermal effexts
M. Pawar, A. Patnaik & R. Nagar [29] patnaik.amar@gmail.com	Malaviya National Institute of Technology, Jaipur, India	Epoxy-granite composites: thermo-mech, properties
O. Daramola, O. Akintayo, J. Olajide, & E. Sadiku [30] oodaramola@futa.edu.ng; ojaythompsoms@yahoo.com	Dep. of Metallurgical and Mater. Engin., Federal Univ. of Techn., Akure, Nigeria & Inst. of Nano-Engin. Res; Tshwane Univ. of Technology, Pretoria	epoxy-silica & silicate clay composites
Y. Sun, L. Chen, J. Lin [31]	Key Lab. of Condition Monitor. & Control for Power Plant Equipment, North China Electric Power Univ.	Conductivity of epoxy composites
D. Shen, Z. Zhan, Z. Liu, J. Yu [32] zl_zhan@sohu.com	Kunming Univ. of Sci. and Techn., China & Ningbo Inst. of Materials Techn. and Engin., Chinese Academy of Sciences	EC filled with silicon carbide nanowires: thermo-conductivity
D. Matykiewicz [33]	Institute of Mat. Technology, Fac. of Mech. Engin., Poznan Univ. of Technology Poland	Fiber & powder EC: Thermomechanics
M. Amin, M. Ali & A. Khattak [33] abraiz.khattak@tdt.edu.vn	Ghulam Ishaq Khan Institute of Eng. Sci. & Techn., Topi, Pakistan; City Univ. of Sci. & Information Tech., Peshawar, Pakistan; Ton Duc Thang Univ., Ho Chi Minh City, Vietnam	epoxy/silica composites: thermal, and electrical characterization
G. Xue, B. Zhang, M. Sun, J. Li, L. Wang & C. Song [34]	College of Mat. Sci. & Chem. Engin., Harbin Enginю Univ.; Inst. of Petrochemistry; Inst. of	Epoxy/graphene-oxide adhesives: Thermal prop.

	Advanced Techn. Heilongjiang Academy of Sciences, China	
J. Prabhudass & K. Palanikumar [35] prabhu.mech@sairamit.edu.in	Sathyabama University & Sri Sai Ram Institute of Technology, Tamilnadu, India	Coir-kenaf reinforced EC: Thermal prop.
H. Sepetcioglu, A. Gunoz, M. Kara. [36]	Selçuk University, Konya; Mersin University, Turkey	Graphene/basalt EC: ageing & mechanics
J. Wang, P Ren, F Ren, G Zhu, A Sun, C You [37]	School of Materials Science and Engineering, Xi'an University of Technology, China	highly thermally conductive EC
W. Guo, X. Wang, J. Huang, W. Cai, L. Song, Y. Hu. [38]	State Key Laboratory of Fire Science, University of Science and Technology of China	anti-flammable and self-toughened phosphorylated EC
B. Earp, J. Hubbard, A. Tracy, D. Sakoda, C. Luhrs [39]	Naval Postgraduate School, Monterey; United States Naval Academy, Annapolis; USA	Electrical prop. of CNT EC for space
A. Pai, R. Shetty, N. Gagan, N. Padmaraj, N.C. Kini [40]	Manipal inst. of Techn.; Manipal Acad. of high Education, India	Thermo-mech. of coconut endocarp ash reinforced EC
R.T. Selvan, P.V. Raja, P. Mangal, N. Mohan, S. Bhowmik [41] b_shantanu@cb.amrita.edu	Department of Aerospace Engineering, Amrita School of Engineering, India	Recycling of epoxy glass & carbon fiber composites
C. Bogiatzidis, L. Zoumpoulakis [42] k_bogiatzidis@hotmail.com	National Technical University of Athens. Greece	EC with Constr. Wastes : Thermal analysis
Zhou T., Wang X., Liu X. & Xiong D. ztltianle999@hotmail.com	Nanjing University of Science and Technology, China	Thermal conductivity of carbon nanotube/micro-SiC/ EC
M. Li, C. Tang, L. Zhang, S. Qi [43]	Key Lab. of Polymer Sci, School of Sci., Northwestern Polytech. Univ., Xi'an, China	conductive EC with nanowires & graphene oxide
Z. Oguz, A. Erklig, Ö. Bozkurt [44] oguzeynal02@hotmail.com	Muhendislik Faculty, Gaziantep University, Ganziantep, Turkey	Aging on Mech. Properties & Water Absorption of Glass/Aramid EC
Zhou T., Wang X., Liu X. & Xiong D. [45]		Thermal conductivity of EC + carbon NT/microSiC
EP Ayswarya, AB Nair, ET Thachil [46] ethachil@cusat.ac.in	Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, 682 022 Kerala, India	Rice-husk-ash & SiO2 - filled EC^ thermal prop.
S Kumar, A Saha [47]	Indian Institute of Technology Guwahati, Guwahati, Assam, India	Graphene/wood dust composites: physical, and thermal characterization
T. Gao, F. Wang, Y. Xu, C. Wei, S. Zhu, W. Yang luhdo@hfuu.edu.cn [48]	School of Energy, Materials and Chemical Engineering, Hefei University, 99 Jinxiu Avenue, Hefei, Anhui 230601, PR China	Luteolin-based epoxy resin with heat resistance, mechanical and flame retardant properties
Mousavi-Bafrouyi S., Eslami-Farsani R. & Geranmayeh A. [49]	Department of Mechanical Engineering, South Tehran Branch, Islamic Azad University, Tehran, 15847-43311, Iran	Thermo effects in Carbon-basalt Fibers/Epoxy Hybrid Composites
E. Saidane, D. Scida, R. Ayad	Université de Haute Alsace, Laboratoire de Physique et Mécanique Textiles EA 4365, 68093, Mulhouse, France el-hadi.saidane@uha.fr	Thermo-mechanical behaviour of flax/green EC
Y. Baghdadi, J. Sinno, K. Bouhadir, M. Harb, S. Mustapha (sm154@aub.edu.lb), D. Patra, A. Tehrani-Bag.	American University of Beirut, Liban & School of Chemical Engineering, Alto University, Espoo, Finland	Thermal properties of graphitic carbon nitride (g-C3N4)-based EC

Theory of the physical chemistry of filled thermo-reactive polymers is well interpreted by the well-known generalizing theory of Soviet chemist Lipatov [2], which has not lost its significance now. As you know, modern concepts of the structure of filled polymers provide for the existence of compacted boundary layers at the surface of the filler particles, plus a loosened (weakening) layer tens of microns thick [2, 2A]. The ability of the filler to reinforce is also associated with the formation of chains, frameworks, aggregates, and other own filler structures. In works of Starokadomsky, this model were expanded in polyepoxides [14] and polyacrylates [15]. The experimental hypotheses for reinforcing and thermo-reinforcing of epoxy-composites by filling were proposed in different works [1-44].

The working temperature range of pure and filled epoxy-polymer is limited by 200-250 °C. This is due to relaxation and destruction processes at these temperatures. Their study in recent years has allowed Gorshunov and Sichkar [3] to classify them into 5 types.

Table 2: (from [3]). Characteristics of Relaxation Processes (γ..δ) in An Epoxy Polymer

T, °C (at ν=1 Hz)	$E_{activation}$, kJ/mol	Kinetic Unit
Minus 165 +-15	10 … 20	Side groups -CH_2, -OH, etc.
Minus 90 +-40	30…120	Fragments of basic chain
105 +-30	70…140	Linear segment or pulsed Stitched micro-volume
250 +-100	80…100	Decay of physical nodes (clusters, etc.)
390 +-40	144… 175	disintegration of chemical bonds C-C, C-O, etc.

Table 2 shows that there are low-temperature transitions (which we will not touch upon) and high-temperature ones. There are no transitions in the range of practically applicable temperatures of 0 - 65 °C. The first of the high-temperature relaxation transitions is observed during soft heating of epoxy-polymer (EP), which is widely used to complete post-processes and impart final properties to EP. These transitions have a relatively noticeable activation energy, and are responsible for the optimization of the structure at the supramolecular level. The optimizing and enhancing effect of these transitions is well known in the practice of using EP, which is why mild heat treatment has become a component of most technologies for producing cold curing epoxy materials [3].

Up to 150 ° C, the temperature has little effect on the EP-relaxation (although visually the materials turn yellow), and then the first signs of decomposition appear. Responsibility for them, in particular, is borne by λ-relaxation - or the decay of physical units. In epoxides, such are clusters, domains, spherulites, and a number of other pseudo crystalline formations. Resistance to these processes can already be considered an important property of an epoxy composite. However, with an increase in temperature, all epoxy composites undergo λ-relaxation, and in parallel, already from 250 °C, signs of chemical destruction are clearly visible.

Table 1 indicates that it starts only from 350 °C, but in fact, the disintegration of chemical bonds becomes clearly visible already 100 °C earlier. Depending on the type of EP, in the range of 300-350 °C, carbonization of a part of the polymer occurs, i.e. complete disintegration of chemical bonds with "tarring" (koxation according Mostovoy [17-19]) of the composite. The fillers, however, can greatly inhibit the degradation process. Not the least role in this is obviously played by the heat capacity of the filler, the compaction of the polymer at its surface, and, in general, a decrease in the percentage of the burned-out polymer phase with its replacement with a non-combustible one.

Note that Gorshunov [3] made one of the best literary reviews of this topic. He admitted that the literature on thermal relaxation of polyepoxides, especially those filled with their composites, has not been identified or even absent. That is, 10 years ago the issue was not worked out at all - and there is too little evidence that the situation has changed dramatically. Since then, we have not found information about any epoxy composites that harden after exposure to destructive temperatures of 200-300 ° C.

Of the thermal effects on the hardening of epoxy composites, only thermal relaxation methods of soft treatment at 50-120 ° C have been well studied and are widely used (which we will also touch upon in this work for comparison) [3-44]. However, thermosetting plastics are valuable because (unlike thermoplastics such as PE and PP) they do not melt/soften at 120-150 °C, and can partially replace stone and metal products.

Formulation of the Problem

Is it possible, by simple filling with affordable and cheap binders, to change the epoxy resin - to the level of a thermo-fire-resistant composite? A number of our [4-16] and other works [18, 29, 31,

34, 43, 44, 37] confirm this. But as regards the possibility of maintaining high (or simply sufficient) strength and durability after hard heating, there is much less work [4, 5, 12]. This is especially true for the basic indicators of strength (in compression, bending, abrasion, impact, etc.) and resistance (to oxidants, organosilvents, acids).

Note that this effect was first discovered in 2017 on epoxy composites with micronuclear iron [5]. In 2017, Starokadomsky first published a work with a cursory description of a new interesting effect - hardening of an epoxy composite with micro-iron [5] after destructive heating of the composite. This effect looked strange and even artifact, but later it was observed on epoxy composites with silicates [4], gypsum [8, 10] and carbide [12, 16] fillers. Thus, we are talking about a phenomenon that allows the creation on the basis of conventional (non-heat-resistant) polymer components of epoxy composites with high durability (and even hardening & strengthening) of their characteristics in the "hot" range of 250 – 350 °C, which is uncharacteristic for plastics (even standard epoxy plastic).

Examples of the effects of thermo-hardening and thermo-plasticization.

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, and I suggest to call them “thermo-strengthening” and “thermo-plasticization” (when warming up improves flexibility / plasticity). The difference from the well-known effects of polymers thermally reinforcing 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 very insignificantly (by 5 - 15%, but not in 1.5 - 2 times as it happens with unfilled epoxy-polymer).

Figure 1 shows examples of thermal strengthening for a number of composite systems. All the microfilled composites taken after 250 °C gave a higher than H-polymer index, while without such heating only a composite with SiC was such. Note - that the studied by us other nano-fillers and a number of micro-fillers (basalt fiber [6], magnetite [7], cellulose [9] etc.) do not give such effects, losing strength as shown in the example of polyepoxide with 0.01 wt% graphene oxide (sample GrOx, Fig.1).

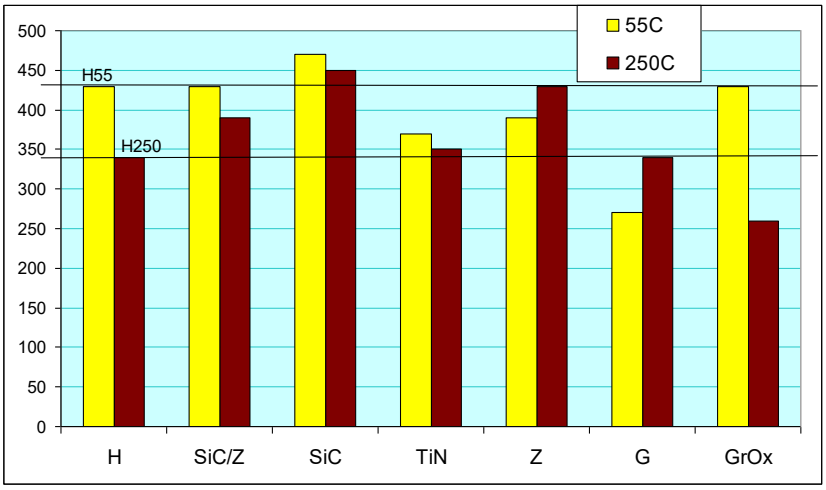


Figure 1: Compression Load (kgf) for Composites without Filling (H) and with 50 wt% SiC and Cement 1:1 (SiCZ), SiC, TiN, Cement M400 (Z), Gypsum G5 (G) and from 0.01 wt% Graphene Oxide (GrOx). Line H55 shows the Level for H after 55 °C, H250 - After 250°C (1 hour).

From tab.3 it is clear, that discussed composites can be also plasticized after 250 °C. This is indicated by the possibility of deeper penetration of Rockewll-s SteelSphere - up to 60 microns or more (instead of 30-50 microns without 250 °C) - unlike the H-polymer, which naturally loses plasticity after 250 °C. At the same time, fillers were found, the microhardness of which is almost insensitive to heating (see tab.1) or even grows after it (for marshalite).

Table 3: 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.

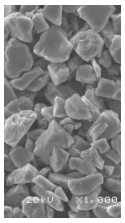
Soft = 55 ºC 5 h	20 mcm	30	40	50	60
Unfilled (H)	150	230	310	380	450 (T)
SiC	210	300 (T)	420 (T)	550 (T)	T
TiN	270	350	440 (T)	550(T)	T
SiO2 (marshalite)	400	500	550 (T)	T	-
Hard = 250 ºC 1 h					
Unfilled (H)	170	250	330(T)	T	-
SiC	210	330	430	530	570 (T)
TiN	180	300	370	460	500 (T)
SiO2 (marshalite)	370	450	550	600(T)	700 (T)

Another example of thermal hardening and thermal plasticization (elimination of unwanted brittleness) is observed for compositions of epoxy with water-binders - gypsum G5 and cements M400-M500 (table 4). These effects were recorded and published by us in works [4, 8, 10, 12, 16]. After 250 ° C, the compressive strength of composites with the neat (non-hydrated) cement almost does not change, and with pre-cured it increases, while the unfilled polymer noticeably (by one third) loses its strength. The neat (non-hydrated) gypsum gives approximately the same reinforcing effect in the composite heated at 250 °C. In all cases, after 250 °C, the abrasion resistance increases noticeably (the weight of the abraded mass decreases), while for the unfilled one, the resistance decreases (tab.4).

Table 4 :The Strength Parameters of The Cylinders (diameter = 6.5 mm; height 11 + -1 mm) of Composites

Sample (50 wt% of filler)	Load P (kgf)	Modulus, $\times 10^3$, kgf/cm^2	Abrasion Resistance
Unfilled polyepoxide	350 (100%)	13,5 (100%)	0.12
Gypsum neat	220 (63%)	8,5 (63%)	0.12
Gypsum hydrated (hardened)	220 (63%)	9 (67%)	0.13
Cement neat	345 (99%)	14 (104%)	0.18
Cement hydrated (hardened)	320 (91%)	14,6 (108%)	0.23
0.01wt% graphene oxide	350 (100%)	16,5 (122%)	0.10
Unfilled polyepoxide	350 (100%)	13,5 (100%)	0.12
Gypsum neat	240 (69%)	10,0 (74%)	0.18
Gypsum hydrated (hardened)	210 (60%)	9,6 (71%)	0.15
Cement neat	335 (96%)	13,0 (96%)	0.15
Cement hydrated (hardened)	300 (86%)	12 (89%)	0.12
0.01wt% graphene oxide	320 (91%)	14 (104%)	0.11
Unfilled polyepoxide	245 (100%)	10 (100%)	0.12
Gypsum neat	280 (114%)	12 (120%)	0.19
Gypsum hydrated (hardened)	215 (87%)	12 (120%)	0.19
Cement neat	300 (123%)	12,4 (124%)	0.21
Cement hydrated (hardened)	350 (143%)	12,2 (122%)	0.21
0.01wt% graphene oxide	215 (87%)	-	-

It is still difficult to explain the nature of this effect. It is probably related to the nature of the distribution and self-organization of some fillers in the polymer. Thus, SEM-Microscopy exhibits the morphology of a polymer composite with SiC (fig.2). Here, an interesting fact is visualized of a change (crushing and coarsening) of the size of filler microparticles (SiC), their transformation into a reinforcing, bonded system (fig. 2). This should have a positive effect on the strength of the composite in the initial and strongly heated state. The same effect should be given by the frameworks of the structures of the cement in the epoxy (seen in Figure 3D). Changes in the size and shape of agglomerates are visible.


A

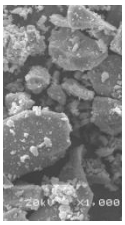
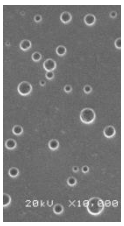

B

Figure 2: SEM Images of Initial Silicon Carbide (A) and Its Particles (B) in a Polymer Composite with 50 wt% SiC.


C

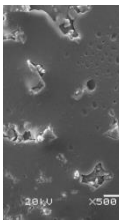

D

Figure 3: SEM Images of The Initial Unfilled Polymer (C) and Its Composite with 50 wt% Cement.

My working with many other fillers (graphite, graphenes, sands, nanosilica, cellulose, alumina) did not yet give us information about new heat-strengthened epoxy systems. Thus, now can talk about the property of silicate, carbide and some other (metallic - micro-iron [5]) fillers as optimal for the manifestation of declared effects in polyepoxides.

Conclusion

1. There are fillers capable of imparting the ability to harden (or plasticize) polyepoxide after heating at extreme (critical) temperatures. 250-300 °C, degrading pure polyepoxide or usually fillerd epoxy-composites. These effects are called "thermo-hardening" and "thermo-plasticization" of epoxy composites, and the corresponding fillers are called thermo-hardening (thermoplasticizing).

2. The reinforcing effect of fillers after heating at extreme temperatures is clearly visible on the example of compressive strength, micro-hardness, and abrasion wear resistance. These fillers include M500-cement, G5-gypsum, Fe-microparticles and SiC-carbide, and to some characteristics (microhardness) - TiN-itride and SiO2-marshalite.

3. The work shows a high perspective of filling of epoxides - for strengthening and imparting a new properties. The discovered effects of thermal-hardening and thermal-plasticization show that such filling gives the epoxy composite previously uncharacteristic properties - that are very important in a number of critical applications for industry, repair and creation of new materials. They show good reserves for strengthening the thermal-strength of epoxies through simple filling by available fillers.

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