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Epoxy composites with 5 wt.% of nanodispersed magnetites and ferroxides. Strength, heat resistance, morphology.

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Abstract

The article summarizes a considerable amount of experimental material on the morphology and physico-mechanical properties of magnetically sensitive ferro-containing polypoxides. The purpose of the study was to determine what changes occur in the micro- and nanostructure of the polymer after filling, and how it affects the operationally important strength indices under different treatment conditions. Optical microscopy indicates the ability of magnets and ferroxides to form carcass-like structures that can enhance strength. AFM microscopy of the composites indicates a change in the surface morphology after filling and integration of structure heterogeneities. The data obtained indicate a negligible effect of 5 wt% -filling on compressive strength, both during the normal treatment of cured composites (50-60 ° C) and after exposure under aggressive conditions (250 ° C or soaking in water). Approximately such effect of these fillers is seen in the assessment of flexural strength. Therewith, the modulus of elasticity (both in compression and flexural) can be increased by 10-15% after filling. Therewith, the filling can significantly (2-2.5 times) increase the fire resistance of polyepoxide. These results open the way to technologies for creating magnetically sensitive polymer nanocomposites with susceptible strengths.

1. Introduction

Epoxy resins are used in almost all spheres of human activity, in the manufacture and repair of devices, as adhesives and compounds in construction, as osteoprostheses in medicine, hulls for yachts, aircraft and machines in the aerospace shipbuilding and engineering industries, in demand in the manufacture of toys (handmade) [1-4]. Therefore, on the basis of epoxy resin, new compositions are created that are resistant to various conditions of use and for solving various problems. In our work, the task was set to create a composite more resistant to aggressive environments and high loads, which included magnetite.

Mineral-filled epoxy composites is a popular area of research today [2-7]. Iron-containing epoxy composites have found application in industries requiring special adhesives and polymer composites - magnetically sensitive, heat-conducting, or similar in properties to iron and its alloys [8-13]. To a large extent, they are needed when repairing chips and equipment defects, when welding methods are expensive or unacceptable [2-4]. In particular, epoxy magnetite composites attract

ongoing scientific attention. Magnetite ($FeO \cdot Fe_2O_3$ or Fe_3O_4) is iron oxide, an ore mineral common in eastern Europe among other iron oxide minerals.

The authors of [10] placed CNT fibers with Fe_3O_4 (own synthesis) in an epoxy resin. Thus, they obtained magnetic and electrically conductive composites. The authors consider such composites necessary for the industry. At the same time, as a rule there is a decrease in strength and other properties, or inconsistency with their theoretically high ratings (see Introduction in [10]). They explain this by an imperfect distribution, poor interphase interactions and poor filler structuring.

In [12] magnetite powder with different weight percent (4, 8 and 12 wt%) was dispersed into epoxy resin (with ratio 2 : 1 epoxy and hardener) matrix mixture and poured into samples (22.86 width × 10.16 height ×2 thickness) mm. The 12 wt% composite had the highest value of real part of permittivity due to greater reflection coefficient and also highest dielectric loss factor. Each of the composite had very low magnetic loss mechanism and the value of μ_r was nearly unity. The σ of the composites increased with frequency where the 8 and 12 wt% contents showed highest value of conductivity. The particle size of nanomagnetites does not allow to introduce a lot of them into the epoxy resin, and already at 5-10 wt% the composition is significantly thickened. In this case, there are many structural changes that can significantly change the strength of the final cured product. It is known [3] that the epoxy resin is well combined with iron powders of micro- and nanoscale, and even capable of better curing in their presence.

When planning this work, it was decided to compare the properties of composites with several types of magnetites, as well as with yttrium ferrite and red iron-minium (α-Fe_2O_3). Their comparison can provide very complete and thereby valuable information about what to expect from the introduction of magnetites and ferroxides into epoxy resin (and this is often practiced on an industrial and repair-service scope). At the same time, the obtained data is logically correlated with visual information from various microscopy methods.

2. Material and Methods

For testing, a resin EPOSiR-7120 (Italian prod.) was used, which is characterized by frost resistance (does not freeze at 0-10 °C) and heat resistance of the polymer. The reason for this heat resistance is evident in the characteristics of the resin modifiers. The manufacturer claims the presence of a certain «epoxyalkyl diluent», which gave it such properties. The same chemical modification obviously led to a decrease in compressive strength by almost a factor of 2 - in our case, from 400 + -50 kgf (for standard tfademarks Epoxy520, Czech and ED-20, Soviet/Russian) to 270 + -20 kgf. And this same additive interferes with determining the adhesion for EPOSiR to steel, since it does not allow the surfaces to be glued (possibly due to the release of alkyl on the interphase surface). As can be seen from Table 1, after 250 °C the properties of the polymer from EPOSiR do not changes; even the plasticity of the material is not violated (as can be seen from the diagrams). The following fillers were used for the study:

1 (M) Magnetite M - nanoscale, with an average size of primary particles 30 nm
2 (A) Magnetite A - nanoscale, with an average size of primary particles 50 nm
3 (T) Magnetic toner for HewlettPackard printers.
4 (Y) Nano-microdispersed Yttrium Ferrite of the general formula $Y_4Fe_5O_{12}$.
5 (C) Ferroxide micron-sized industrial “Meerkat red pigment” (production of Ukraine)

Strength tests were carried out in accordance with or taking into account standard methods (ISO, GOST or ASTM).

Compression tests (ISO 604: 2002) were subjected to cylinder-shaped samples with a diameter of 6.5 mm and a height of 10-12 mm (using a LouisShopper press machine) manufactured at 25 ° C and heat-treated. The adhesive peel tests (GOST 14760-69) were subjected to gluing of metal cylinders with a diameter of 2.2 cm on a test binder, on a UMM-10 Armavir installation. All rounding, including averaging, is done towards a larger value, and the smallest 1-2 values are not taken into account.

Bending strength – (**ISO** 178:2019, GOST 56810-2015, ASTM D790). For bending tests, plates 6 × 1 × 0.2 cm in size were made. Their bending during bending was carried out on the basis of L = 3 cm of the test bending machine DI-1. According to the test results, the strength i was calculated (i = 3PL \ 2h2b, P is the received load in kgf on a scale of 1 cm = 1 mm, L is the length of the fracture base equal to 30 mm, h is the thickness of 2 mm, b is the width of the sample is 10 mm) and the module bending elasticity I ($I=PL^3\backslash 4bh^3W$, where W is the displacement on a scale of 1cm = 20 microns).

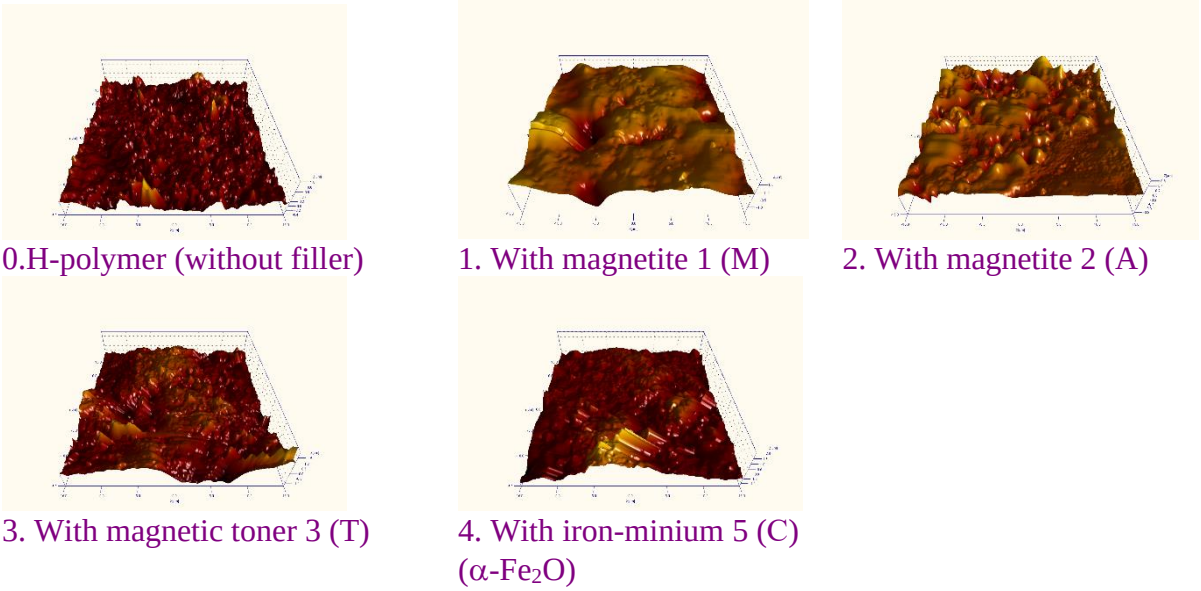
Optical microscopy was performed on a DRESSER microscope. SEM-microscopy was performed on electron microanalysator JEOL. AFM-microscopy was performed on Scanning microscope NanoScope.

3. Results and discussion

Microscopic morphology

AFM microscopy of the surface of composites

The AFM does not always provide complete information about the structure, but is very useful for assessing surface changes — roughnesses, pores, smooth zones. It can be seen from them (Figure 1) that composites with magnetite tend to enlarge and group «micro-islands» of the surface, to form zones of a smooth surface - up to their dominance (Figure 1-2).



0.H-polymer (without filler) 1. With magnetite 1 (M) 2. With magnetite 2 (A)

3. With magnetic toner 3 (T) 4. With iron-minium 5 (C) (α-Fe_2O)

Figure 1: AFM images of the surface of composites

The initial unfilled composite is characterized by a fairly uniform distribution of pores and irregularities. That generally corresponds to modern ideas about the fibrillar-pack structure of three-dimensional thermosetting plastics. The AFM clearly shows the difference in the structures of epoxy magnetites from the epoxy-suric composite - which does not change the polymer structure so much (Figure 3). Possible reasons for this we do not undertake to explain.

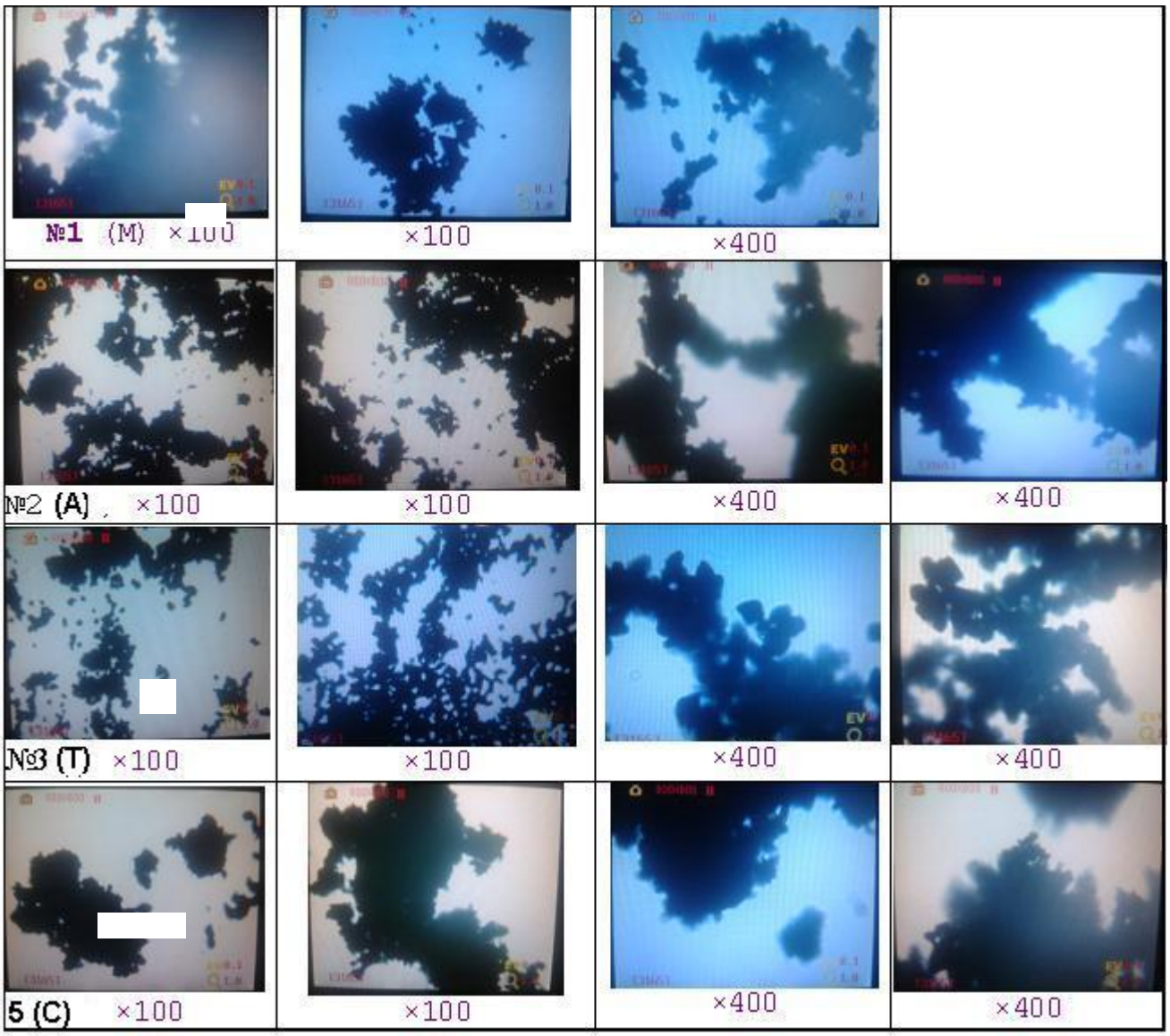


Figure 2: Optical microphoto of magnetite powders, with an increase of 100 or 400 times (with a screen length of 7 cm).

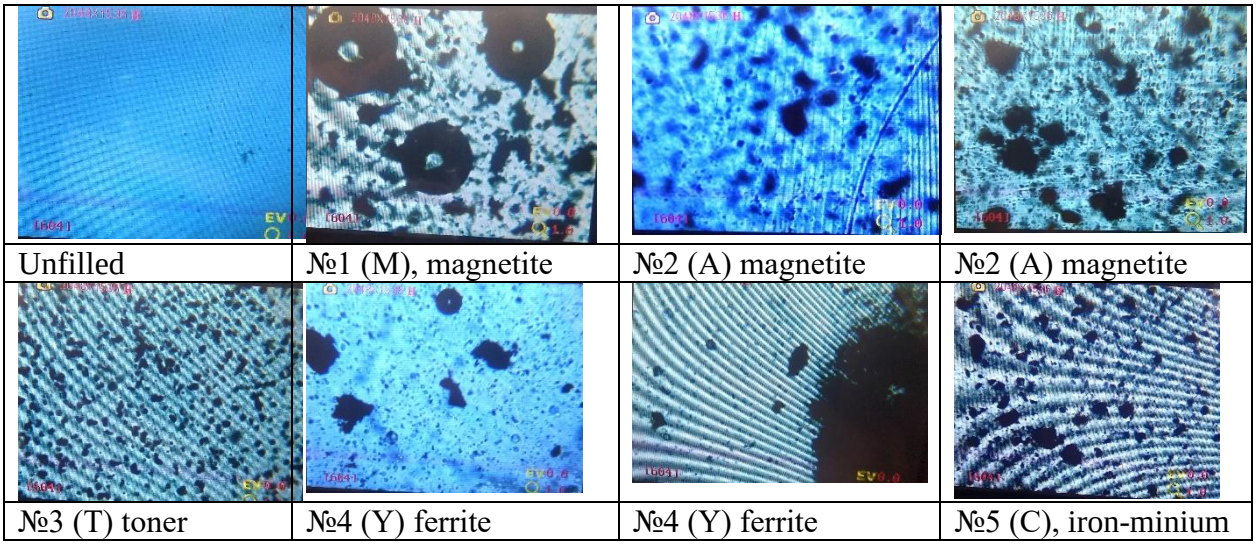


Figure 3: Optical microphotographs of epoxy compositions with magnetites, with an increase of 100 times (with a screen base length of 7 cm).

Optical microscopy.

It can be seen from Figure 2 that magnetite powders have a granular aggregate structure. Sometimes dendritic structures are manifested in magnetite agglomerates, which are even more common in α-Fe_2O_3 (meerkatat). This makes it possible to predict a very good compatibility and distribution of these powders in the epoxide. From the optical photos (Figure 4) of epoxy compositions, a fairly uniform distribution of almost all magnetites (except for coarsely dispersed No. 4) and meerkat is noticeable. And sometimes magnetite can «tighten « in the system and stabilize very large air bubbles by the surface layer of nanoparticles (sm.№1 and №4). As we see, the unfilled composite has practically no serious defects (bubbles, inhomogeneities). The uniform distribution of magnetite can be useful for enhancing hardened composites in a number of ways.

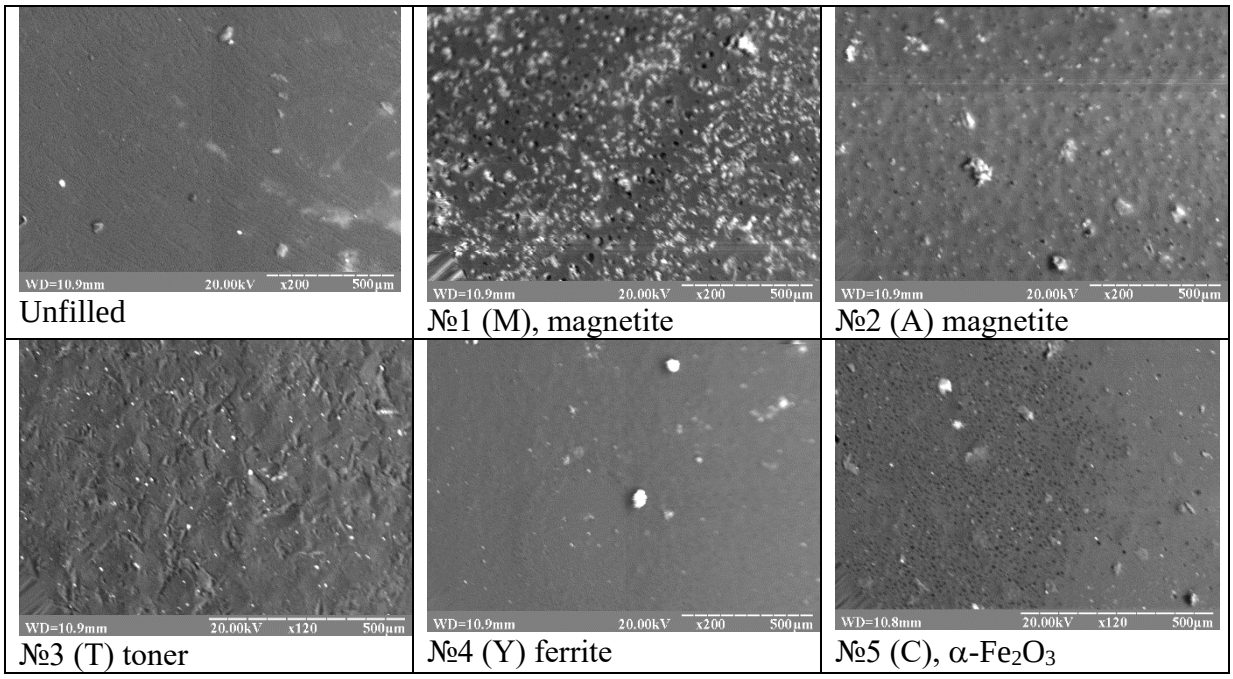


Figure 4: SEM photo of composites (× 200).

SEM microscopy.

Although the initial resin does not contain obvious inhomogeneities in the photo of non-hardened compositions, in the hardened epoxy polymer they are still visible as separate shapeless inclusions up to 50 microns (Figure 4).

Strength

It can be seen from the experiments that, according to the compressive strength, the unfilled polymer based on EPOSiR-7120 resin (heat-resistant) is insensitive to either hard heating or 7-day exposure in water (7 days). The strength practically does not change (by 2-3% - see Table 1, samples «H»), and if the module E decreases slightly then by 2-3% (to 10.8 instead of 11.1. Table 1 see samples «H»). This is uncharacteristic for standard epoxides, since from our recent work (on resin ED20 and Epoxy520 [1-4]), it is clear that heat treatment and holding in water led to a noticeable drop in the indicators of unfilled epoxy polymers. Recall that an ordinary resin like ED20 after such heating loses strength by a third or more (see our early works [1-4].

Table 1: Strength parameters of samples of composites with 5 wt.% Filler. Designations of the samples correspond to the numbering of magnetite in the section «Methods and reagents». Resin - EPOSIR-7120 (Italy).

50-60 °C	**Compression C, load on a column with a diameter of 7.5 and a height of 12 + - 1 mm (all received values). In an index - loading of total destruction**	**C_{aver}**	**Module E × 10^3 Kgf / cm^2 (all values) and average Ea**
H (Unfilled)	250^{340} - 280 - 280^{450} - 290^{460} Brittle-plastic failure	275	10,7 - 11,1 – 11,1- 11,5 Ea= **11,1**
№1 (M)	260^{290}– 270^{330}– 280^{330} Fragile-plastic fracture, with longitudinal. Cracks	270	12.1 –12.1 - 13.5 Ea= **12.8**
№2 (A)	270^{350} - 270^{450} – 280^{410} – 290 Plastic fracture, with longitudinal cracks	275	9.8 – 9.8 – 9.9- 10.1 Ea = ***9.9*** *(estimated data)*
№3 (T)	280 – 280^{370} - 300^{440} Fragile-plastic fracture, with longitudinal cracks	290	10.5 – 11.2 - 11.9 Ea= 11.2
№4 (Y)	290^{410} – 300^{410} - 300^{430} – 310^{340} Fragile-plastic fracture, with longitudinal. Cracks	300	10.7 – 11.5 –12 - 12.3 – 12.8 Eaver = **12**
№5 (C)	270^{490} - 280^{480} - 290^{400}	280	11.2 -12 – 12.7 Eaver= **12**
250-270 °C (after 50-60 °C)			
H(Unfilled)	250^{440} – 290^{390} - 310^{450} Plastic fracture (barreling)	285	9.9 – 10.3 – 11.8 Eaver = **10.8**
№1 (M)	250 – 270^{430} - 280^{360}	270	10.5 – 10.7, Eaver=10.6
№2 (A)	260 – 275 - 290 Plastic fracture (barreling)	275	11.9 – 12.8 , Eaver= 12.4
№3 (T)	*160* – 160 Very fragile destruction.	160	10.1 – 10.5, Eaver= 10.3
№4 (Y)	150 – 160 - 170 Very fragile destruction.	160	12.8
№5 (C)	240^{290} - 310^{360}	275	11.5 - 11.9, Eaver= 11.7
7 days in H_2O (after 50-60 °C, *estimated data***)**			
H (Unfilled)	270^{300} – 270 Brittle-plastic failure	270	10.4 – 11.1, Eaver = **10.8**
№1 (M)	270^{430} Plastic fracture (barreling)	270	11.2
№2 (A)	260^{360} Plastic fracture (barreling)	260	10.6
№3 (T)	270^{390} Plastic fracture (barreling)	270	10.1
№4 (Y)	250^{420} Plastic fracture (barreling)	250	12.2
№5 (C)	290^{430} Plastic fracture (barreling)	290	11.0

It can be seen that the presence of magnetite particles (as well as iron oxide) is not very significant on the compressive strength (see Tab. 1, samples 1 (M) and 2 (A). True, for a mixture of magnetite with a thermoplastic (toner 3 (T), Tab. 1), the load of yield stress C increases by 5-6% (for compression tests this also matters), and for ferrite 4 (Y) it grows even by almost 10% (Tab. 1). It does not change, only in some cases changing by 5-10% (Tab. 1). On the contrary, the modulus of compression elasticity can noticeably change. So, it grows by 5-8% for ferrite 4 (Y) and ferroxide pigment 5(C), and for magnetite 2 (M) - even by 15%. That is, iron oxides, even at 5 wt%, can give the polymer much higher elasticity, and this, by the way, can also be seen from the diagrams (Figure 2 - 4). This is also true for samples aged in water. That can be considered a very acceptable result for the tasks of creating magnetic, or iron-containing epoxides. After harsh heat treatment, the compressive strength of the filled polymers drops, sometimes substantially, Tab. 1. The elastic modulus E, on the contrary, can noticeably increase with filling (Figure 4). For several templates (N 2(A) and 4(Y)) E increases after hard heat-treatment (Tab.1). Thus, for epoxy-ferroxides we can observe the effects of "thermo-hardening of composites", which we described earlier for filled epoxides after destructive heating 250-300 ºC [1,3,4].

Type diagrams «load – deformation» for composites shows a certain increase in elasticity after filling. Indeed, an unfilled polymer after a load of the plastic limit (letter P in Figure 5) already weakly resists further loading (Figure 6). This can be seen by the small angle of the slope before the final destruction (letter D in Figure 6). But almost all filled composites have a steeper slope angles before D.

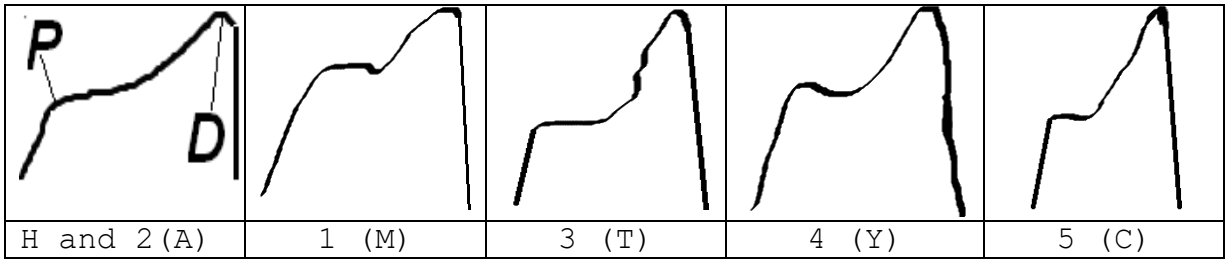


Figure 5: The type of compression diagram «load-deformation « for different composites, after conventional heat treatment (50-60 °C).

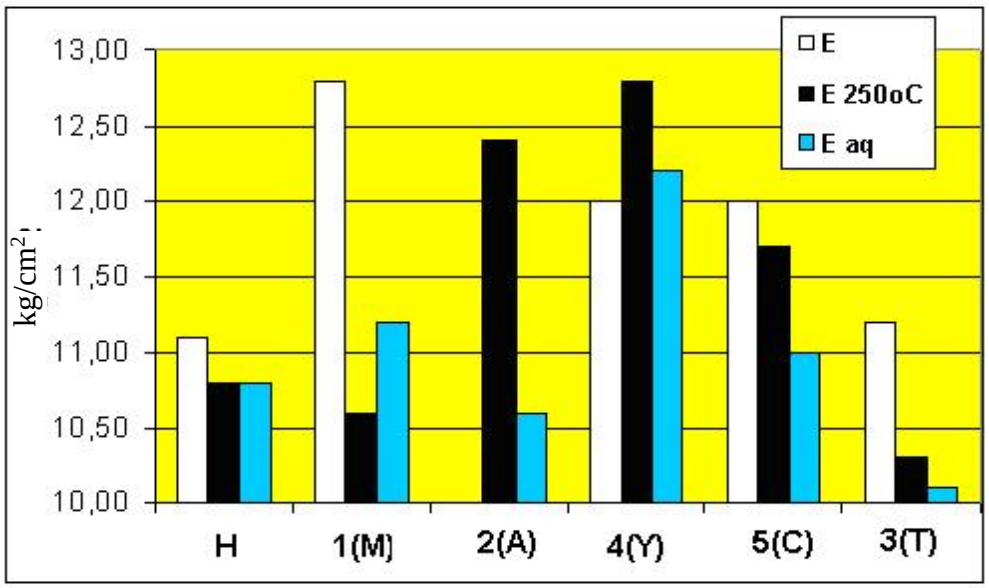


Figure 6: A comparative histogram of the values of the modulus of elasticity of compression of the samples at different exposure modes - the usual 60 °C; hard 250 °C and exposure in water for 7 days (Eaq).

From Table 2 it is seen that the tensile-strength deteriorates after filling (which is typical after filling of polyepoxides). At the same time, the elastic modulus can appreciably increase in good agreement with literature [8,15-18].

Table 2: Strength and modulus of elasticity in bending plates (1.5 mm thick, 1 cm wide).

	H	**1 (M)**	**3 (T)**
Bending Strength, kgf/mm^2	3,8	3,1	2,8
Bending modulus, 1000 kgf/cm^2	19	16	23

Conclusions

1. Epoxy composites with a 5% content of iron oxide nanodispersed fillers are characterized by a high modulus of elasticity and acceptable (100-115% compared to unfilled polymer) compressive strength. Bending strength is reduced, while the modulus of elasticity in bending can increase markedly.
2. After heat treatment, the compressive strength of filled composites decreases, while the elastic modulus can increase significantly.
3. Microscopy shows significant morphological changes after filling. A larger number of pores and large agglomerates, as well as air bubbles stabilized by nanoparticles, appear in the structure of composites.

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