STRENGTH AND CHEMICAL RESISTANCE OF COMPOSITES BASED ON EPOXY RESINS, FILLED WITH GYPSUM IN THE ORIGINAL AND WATER-HARDENED FORMS

This paper reports the results of studying epoxy compositions with gypsum taken in the form of dispersed powders in the original and water-hardened form. The exact pattern has been shown in the way the introduction of a gypsum additive in the amount of 50 % by weight affects the strength, chemical stability, and morphology of the composites.

Under conventional heat treatment (60–110 °C) of the hardened composites, the maximum stress at compression σ_m and the elasticity module at compression E_c, as well as wear resistance, decrease after the introduction of gypsums (of both types). At the same time, after a hard (destructive) heating at 250–260 °C, the elasticity module Ec of the hardened composites increases. The maximum stress at compression σ_m is also increased. The same applies to the wear resistance, which grows especially noticeably after 250 °C.

The micro-hardness after filling is prone to increase but the fragility of epoxy-gypsum composites does not make it possible to measure it when a punch (a steel hemisphere) penetrates it deeper than 20 µm. However, after the heat treatment at 250–260 °C, the unfilled polymer, on the contrary, is embrittled while the filled ones are plasticized, thus showing a high micro-hardness at significant (30–50 µm) immersion.

The composites with gypsum, in contrast to the unfilled ones, do not disintegrate in acetone and retain integrity at any aging duration (up to 75 days and beyond). In this case, the original gypsum produces a composite with less swelling in acetone than the hardened gypsum. Based on the data from atomic-strength microscopy (ASM) microscopy, the morphologies of the non-filled composite, the composites with the hardened gypsum and original gypsum are different. The original gypsum forms a composite with a more pronounced (possibly crystalline) filler structure; the morphology for the hardened composite reflects the distribution of inert particles; for the unfilled composite (H-composite), only pores are visible against the background of a relatively smooth relief

Keywords: epoxy composite, gypsum, micro-hardness, chemical resistance, thermal strengthening, strength, morphology, water hardening

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1. Introduction

G5 gypsum is a thin-ground white powder derived from the thermal treatment of gypsum raw materials – calcium sulfate dihydrate ($CaSO_4*2H_2O$) in various modifications [1]. In nature, it occurs in the form of rose-like druses, plates, and layers. It has limitations for hardness – it ranks second out of ten along the Mohs geopetrological scale (preceded by super soft talc and pyrophyllite). The gypsum is classified within a group of air-hardening binders (as opposed to cement binders that are hardened hydraulically) [1, 2].

As an inorganic binder, gypsum is capable of capturing impurity and atmospheric water, which may well contribute to its self-organization in the polymer matrix. This is quite possible in the case of the use of epoxy resin as such a matrix. It is known [3–6] that epoxy resin is not water-soluble, so water impurities have an undesirable effect in the process of polymerization, leading, in particular, to the clouding and

loss of mechanical properties of the polymer. The presence of gypsum-alabaster (binding such water) in resin can become an additional stimulant to enhance the epoxy polymer composite. In this case, of special interest is to elucidate how much the properties of the epoxy-composite with the original alabaster and the water-hardened gypsum stone on its basis (the same dispersion) would differ. Theoretically, the water-hardened gypsum micro filler should be more inert, and, therefore, a series of its indicators might prove different.

The relevance of our scientific area is defined in the context of the need for extensive scientific research. The results to be obtained could be useful for industrial, service, and construction practices as the technologies to form such formulations are currently mainly at the level of experimental application. Those large organizations that can afford specialized laboratories and appropriate research often do not report results for open access because of their commercial use.

2. Literature review and problem statement

The studies into gypsum rock are reported in works [1, 2]. It is shown that a particularly pure and well-crystallized form, also termed alabaster and selenite, refers to the sedimentary rocks of the Permian, Triassic, and Tertiary periods. Gypsum binders are the powders of semi-aquatic gypsum ($CaSO_4*0.5H_2O$), obtained by heat treatment, at 140 ± 40 °C, of the natural gypsum dihydrate ($CaSO_4*2H_2O$) or the technogenic or secondary wastes containing it. However, the issues related to the impact of impurities such as waste on the quality of the composite formulation remained unresolved. The reason for this may be the objective complexity of such research due to the large number of materials used.

A series of promising gypsum epoxy polymers have been developed, described in several earlier published papers [3–6]. Thus, according to [3], the introduction of G-5 gypsum in the amount of 10–75 % by weight makes it possible to obtain composites with acceptable strength and durability; at the same time, certain characteristics considerably improve (adhesion to steel, resistance to organic solvents). Work [4] investigated the effect of gypsum at a practically convenient ratio of the filler to the epoxy composition of 1:1 (50 % by weight of gypsum): it is shown that the filler is able to increase the strength and elasticity of the composite, its resistance against aggressive environments. Paper [5] reports the results of the G-5 gypsum effect over a wide interval of concentrations, the analysis of destruction diagrams during compression tests, and microphotographs of composites. The authors explained possible changes in the nano-microstructure of composites after filling. The relevance of the reported study is the fact that exploring the influence of a gypsum state (original, semi-aquatic, and hardened dihydrate) on the structure makes it possible to effectively manage the physical and mechanical properties of polyepoxide.

Interest in the compositions of epoxy polymers with gypsum or cement is due, first of all, to its cheapness. However, the compositions also have the ability to self-crystallization with the binding of water, and it is both in the air and in the resin itself and the PEPA hardener. Since water is an agent that interferes with the polymerization of epoxides, its binding by the filler is a promising way to produce persistent composites.

This approach was implemented in the industry of bulk floors. There, as you know, the introduction of the epoxy component makes it possible to reduce the minimum allowable thickness of the coating by an order of magnitude – from 8–10 to 1 cm [1–5]. The introduction of a large amount of filler (up to 85 %) makes it possible to drastically reduce the ratio of linear expansion of the coating, bringing it closer to the corresponding indicator for the base made from an inorganic binder (gypsum, concrete, etc.) [8]. Therefore, when the temperature changes, there are almost no stresses in the area of contact with the base, which usually cause cracks and detachment of low-filled polymer coatings. All this suggests that it is appropriate to conduct a study on the effect of filler content on the durability and strength of the polymer composite.

It is known that polymer composites with gypsum (despite the wide scope of their domestic use) have not been studied in detail. Polyurethane is particularly important for research [7]. This work shows a marked difference between the properties of polyurethane with dihydrate and hemihydrate calcium sulfate. This is due to the fact that the hemihydrate calcium sulfate has the ability to hydrate and the water, in this case, hardens the prepolymer itself.

Many properties of the composites with non-hardened and hardened gypsums reported in the cited work (the equilibrium part of the elasticity module, the segment's molecular weight M_e, the cross-linking effective density) are not dependent on the type of gypsum taken. This follows from the fact that their curves on the corresponding diagrams are partially duplicated.

However, for example, the relaxation time of composites is very sensitive to the type of gypsum. The non-hardened (hemihydrate) gypsum yields an increase in the relaxation time before filling of 0.2 (20 % by volume); with further filling, it stops growing. The hardened (dihydrate) gypsum produces a monotonous and strong growth over the entire investigated range of fillings (up to 35 % by volume). Differences are also observed in the curves of the relaxing part of the composite modulus [7].

The authors explain the differences by the simultaneous formation of a "nanohybrid polyurethane mesh containing ... a filler capable of being structured by the redistribution of physical bonds in ... the matrix and the formation of an endless cluster of nanoscale gypsum particles" [7]. It should be taken into consideration that there would be no such cluster for the already hardened and formed gypsum, which predetermines differences in the properties of strength (in this work, it can be seen on the example of relaxation properties). It is stated in [7] that "such systems are characterized by the abnormally large relative elongation, elasticity module, maximum stress at compression σ_m, and the destruction work." At the same time, the inorganic filler in any structuring does not affect the molecular parameters of the polymer in the composite [7].

There are also a series of research papers [8, 9] on gypsum-based composites. In addition, we have already conducted and published several papers on gypsum-epoxy and epoxy-cement compositions.

The reinforcement of gypsum compositions is often carried out by the introduction of fibrous fillers [10] or polymeric additives such as PVA [11–13], latex [14, 15], plastic waste [16].

Thus, according to work [10], when gypsum is prepared, the composition is injected with waste from pulp and paper

production. Study [17] reports a 1.7-fold increase in compression strength after the introduction of 0.6 % of the SMF plasticizer into the gypsum.

The topic of epoxy-gypsums is not so often addressed in the literature despite their widespread use in construction and repair. Of relevance today is work [18] that compares the resistance of finishing coatings based on conventional gypsum and (epoxy- or ester-) polymer-gypsums to fungus. The results show that polymer-gypsums are more resistant than the original gypsum, in particular, because of the greater resistance to the acids secreted by the fungus (micromycete).

However, the issue of the influence of gypsum forms (original, already hardened) remained insufficiently covered in the cited studies. The epoxy system, in contrast to polyurethane, is not hardened with water (which is rather considered an impurity that makes it difficult to polymerize). However, even here it is quite possible that a cluster forms from particles of the hardened gypsum (due to the impurities of water in the polymer). This means that it is logical to expect a difference in the properties of a polyepoxide with the non-hardened and hardened gypsum. Therefore, the verification of such a hypothesis (assumption) may make it possible to solve this issue.

3. The aim and objectives of the study

The aim of this study is to investigate the effect of the introduction of gypsum in epoxy resin depending on the type of gypsum (original hemihydrate, or hardened dihydrate). This would make it possible to obtain cheap composites for both large-tonnage and small production, as well as to determine the effect exerted on polyepoxides by the used gypsum of different quality (new, old, second-hand, construction waste, low-quality, etc.).

To accomplish the aim, the following tasks have been set:
– to determine the way the introduction of gypsum into epoxy resin alters the consistency of the composition and the morphology of composites;
– to determine the way the introduction of gypsum in the amount of 50 % by weight after a soft (55 °C) heat treatment of polymers affects the strength at compression, module, and wear resistance;
– to determine the way the introduction of gypsum in the amount of 50 % by weight after a hard heat treatment at 250 °C of polymers affects the strength at compression, module, and wear resistance;
– to determine the way the introduction of gypsum in the amount of 50 % by weight affects the resistance to acetone-containing solvents.

4. Materials and methods to study the effect of gypsum introduction in epoxy resin

In a simplified form, gypsum hardening can be divided into two stages [2]. These include:
1) dissolving in water and hydrating hemihydrate gypsum by the formation of the primary structure;
2) long-term consolidation of this structure due to the processes of its pre-crystallization.

Our samples were produced on the basis of the resin Epoxy-520 and the hardener PEPA (5:1). The hardening process was performed by mixing these components with gypsum of the same mass (50 % by weight), without vacuuming. The G-5 gypsum was used in its original and water-hardened and, then, dispersed form. The post-hardening of composite samples was carried out in 3 to 10 days after their polymerization, at 55–60 °C, over 6 hours (Fig. 1).
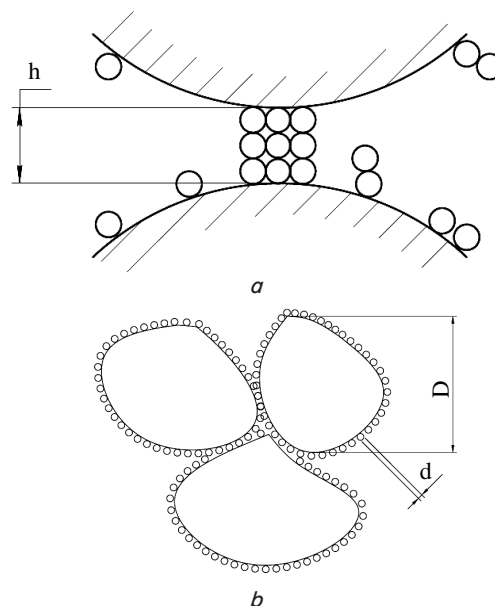

Fig. 1. Schematic cross-linking of the hardening structures of gypsum (large — primary, smaller — secondary):
a — the initial stage; *b* — the final stage [2]

Samples in the form of a cylinder with a diameter of 6.5 mm and a height of 10–12 mm, manufactured at 25 °C and thermally-treated, were tested for compression in line with GOST 4651-2014 (ISO 604:2002) at the "LouisShopper" press machine (Germany) at loading speed of 10 mm/min. Tests for adhesive detachment (GOST 32299-2013 (ISO 4624:2002) were performed on the cross-linked metallic "mushrooms" with a diameter of 2.2 cm with the examined binder, at the installation "UMM-10 Armavir". The force of detachment increased at an even speed of no more than 1 MPa/s. All rounding, including when averaging, is towards a higher value when the lowest 1–2 values are not taken into consideration. Tests for adhesive shift (GOST 14760-69) of the glued fiberglass plates with a gluing area of 3 cm^2 were carried out at the installation ZIP DI-1, the movement speed of the machine's clamp was 10 mm/min.

For bend tests (GOST 56810-2015), plates measuring 6×1×0.2 cm were fabricated. Their bending fracture was tested at the bending testing machine DI-1. Based on the test results, we calculated the strength *i*. Where $i=3PL\backslash 2h^2b$, *P* is the obtained 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, 2 mm, *b* is the width of the sample equal to 10 mm. The module of elasticity at bending *I* ($I=PL^3\backslash 4bh^3W$, where *W* is the displacement on a scale of 1 cm=20 μm).

The wear of composites was measured according to a change in the mass of the sample after the sample was rubbed with the sandpaper P180, by a 100-fold scraping at a scraping path diameter of 5 cm.

The wear resistance *T* was calculated from the proposed empirical formula

$$T = \frac{\rho}{X \cdot \rho_0}, \qquad (1)$$

where $\frac{\rho}{\rho_0}$ is the ratio of the density of filled to unfilled polymers; X is the wear magnitude.

In fluid resistance tests, lens-shaped tablets were placed in the mixture of acetone:ethyl acetate, or 20 % nitric acid. A change in the mass was registered gravimetrically as a percentage of weight gain. In this case, the time before the transition to a foamed state (in nitric acid) was taken as a "lifetime" of the sample.

The study adopted the following designations: H-composite is a pure epoxy mixture, without filler; the filled composite is subdivided into G_h – an epoxy mixture with a filler in the form of non-hardened gypsum, G_o – an epoxy mixture with a filler in the form of hardened gypsum. Samples $H1$ and $H2$ refer to the category of samples consisting of a pure epoxy mixture, differing in weight and size.

5. Results of studying the effect of gypsum filling with composites in various states

5. 1. The composites' mechanical parameters

Despite the different effects of gypsums of different brands, including an increase in strength [3], in this case, one can see a clear weakening of the maximum stress at compression σ_m after filling. Under a soft heat treatment (50–60 °C), the introduction of both types of gypsum (hemihydrate G_h and dihydrate G_o) yields almost the same reduction of load C by about a third (Table 1).

Table 1

The load and module when the composites' cylinders are compressed (diameter, 6.5 mm; height, 11±1 mm). The index shows the limit of total destruction (if registered)

Sample	Averaged destruction load C in kgf (% to the C of non-filled)	Module E*10³, MPa	Wear, mg\wear resistance, mg⁻¹
Non-filled (H)	350 (100 %)	1.35 (100 %)	8\0.125
With non-hardened gypsum (G_h)	220 (63 %)	0.85 (63 %)	12\0.124
With hardened gypsum (G_o)	220 (63 %)	0.9 (67 %)	11.5\0.13
Additional treatment 100+10 °C, 1 hour			
Non-filled (H)	350 (100 %)	1.35 (100 %)	8\0.125
With non-hardened gypsum (G_h	240 (69 %)	1.0 (74 %)	10\0.15
With hardened gypsum (G_o)	210 (60 %)	0.96 (71 %)	11\ 0.136
Additional treatment 250 °C, 1 hour			
Non-filled (H)	245 (100 %)	1.0 (100 %)	8.5\0.118
With non-hardened gypsum (G_h)	280 (114 %)	1.2 (120 %)	8\0.188
With hardened gypsum (G_o)	215 (87 %)	1.2 (120 %)	8\0.188

A significant characteristic indicating the strengthening of these compositions by thermal heating is the micro-hardness of the material. Table 2 shows that the H-composite has high plasticity (a punch penetrates without cracking at 50–60 μm) and acceptable micro-hardness (M). The introduction of gypsum makes it possible to increase the micro-hardness (a G_h sample filled with non-hardened gypsum has the highest indicator) but noticeably embrittles the composite.

Table 2

The micro-hardness load when the indenter penetrates for 10–60 μm. * denotes cases where destruction is observed in half of the similar series of samples taken for measurement

Sample	Micro-hardness (MPa) at different penetration, μm					
Thermal treatment 55 °C	10	20	30	40	50	60
$H1$	509.6	242.0	318.5	382.2	509.6	573.2
$H2$	509.6	229.3	293.0	382.2	Cracked	–
G_h	764.3	267.5	Cracked	–	–	–
G_o	611.5	254.8	Cracked	–	–	–
Thermal treatment 250 °C	10	20	30	40	50	60
$H1$	509.6	254.8	382.2	Cracked	–	–
$H2$	509.6	242.0	293.0	Cracked	–	–
G_h	509.6	191.1	293.0 (T*)	Cracked	–	–
G_o	509.6	254.8	356.7	394.9	407.6 (T*)	Cracked

Table 3 shows that the introduction of gypsum contributes to the strengthening of adhesion to steel when detached.

Table 3

Adhesion to steel (breaking stress at detachment, MPa) when testing cross-linking by composites containing original non-hardened (G_h) and hardened (G_o) gypsum

Normal detachment	Non-filled	G_h	G_o
Averaged load, kgf	125	280	120
Load, MPa	2.5	5.6	2.0
Shear	Non-filled	G_h	G_o
Load, MPa	11	11	11

Table 4 shows that the strength at bending is not so sensitive to the type of filler.

Table 4

The maximum stress at bending σ_m and the elasticity module at bending the plates of composites with original non-hardened (G_h) and hardened (G_o) gypsum

Test type	Non-filled	G_h	G_o
Maximum stress at compression σ_m, MPa	32	41	40*
E, ×10³, MPa	1.7	3.4	3.4

Table 5 demonstrates that the unfilled polymer is naturally unstable in the mixture of acetone-containing solvents – it noticeably swells already in the first hours, and then disintegrates.

Table 5

Data on the stability and swelling of samples in the mixture acetone:ethyl acetate. H — non-filled, G_h — filled with non-hardened gypsum, G_o — filled with hardened gypsum

Day	Weight gain percentage, %		
	H	G_h	G_o
0.02	3.7	0.0	1.0
1	6.5	0.5	1.0
9	9.3	2.3	4.1
14	12.0	1.4	2.6
75	35.2 disintegrated	7.5 whole	11.9 whole

5. 2. The composites' stability in aggressive environments

When aging in a highly acidic environment (20 % nitric acid), as we can see from Table 6, the unfilled polymer is capable of a noticeable monotonous swelling.

Table 6

The swelling of samples without (H) filling, with 50 % by weight of original gypsum (G_h) and chalk (M) in 20 % nitric acid

Day	Weight gain percentage, %	
	H	G_h
0	0.0	0.00
0.083	0.0	−0.48
1	2.2	4.83
9	6.0	24.64
14	7.6	28.50
22	8.7	26.09
37	11.4	22.71
84	20.7	17.87

Table 6 shows that the filling drastically changes the ratio of the polymer composite to nitric acid with a relatively high concentration (that is, to a highly acidic and oxidizing environment). The non-filled polymer is comparatively stable in it. Almost a week later, the destructive effect of HNO_3 has to be taken into consideration because a 6-% swelling (Table 6, in 9 days) is unacceptable in many technological cycles. Then the swelling process only increases; after 3 months, it exceeds 20 %, and proceeds further to complete destruction.

The composite with gypsum demonstrates in the first stages a multiple (about 3–4 times) increase in the intensity of swelling, that is, much worse stability. Further swelling slows down, due to the activation of the process of washing out dissolved products. It should be noted that the sample did not look destroyed.

Based on our results (Table 7), one can see that gypsum filling drastically improves the resistance of polyepoxide to such an aggressive oxidizer as highly concentrated H_2O_2. The non-filled polyepoxide has much less resistance, and, within a few weeks, it "swells" and disintegrates. At the same time, samples from the gypsum-filled composite show similar swelling dynamics; and the original non-hardened gypsum (G_h) in the composite exerts a stronger stabilizing effect than the hardened gypsum (G_h). This confirms the assumption about the activity of the original gypsum in the composition both in the process of kneading and hardening

(as opposed to the inert hardened gypsum). The duration of aging has little effect on the stability of the filled samples; after more than 3 months, they do not disintegrate and even reduce their degree of swelling (Table 7). The resulting patterns make it possible to use such formulations for the manufacture of oxidizer-resistant composites and adhesives. One should note that the special properties of gypsum-epoxides have allowed them to be applied where the use of conventional epoxy and acrylic glues is ineffective. Specifically, we carried out a set of works to repair key parts of large printing equipment (Fig. 2). The problem with such equipment was the relatively rapid failure of expensive "heads" of the printer-plotter – devices for spraying ink from the printer on a sheet of paper. As the aggressive and environmentally harmful solvents in the course of operation corrode the glued body of these units, the solvent and dyes dissolved in it start seeping through. Without repairs, such parts should be replaced, which, given their high cost (on the order of a thousand dollars) and the need to import them, is extremely unprofitable.

Table 7

Data on the stability and swelling of samples in a 60-% H_2O_2 concentrate. H — non-filled, G_h — filled with non-hardened gypsum, G_o — filled with non-hardened gypsum

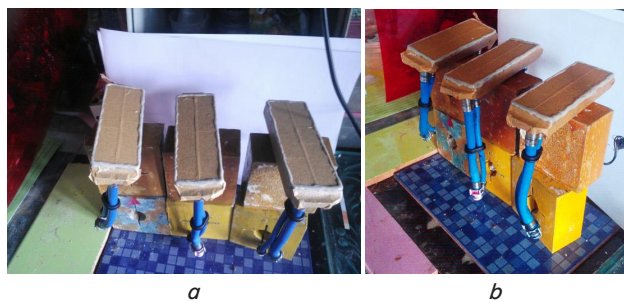| Day of aging	Weight gain (% by weight)		
	H	G_h	G_o
0	0.0	0.0	0.0
0.08	7.9	3.1	6.1
0.21	14.4	4.4	9.4
1	37.2	7.5	17.3
2	55.8	10.3	22.7
3	69.8	10.8	26.1
6	88.4	9.3	22.7
8	110.2	13.9	26.7
9	115.8	14.4	27.3
10	115.8	11.1	22.7
13	144.2	12.6	26.4
15	166.0	13.1	22.1
62		10.6	8.2

Fig. 2. The components of plotters glued (grey adhesive seam along the edges) by gypsum-epoxide (in this work, designated "G_h"): a — a side view; b — top view

The glue-based repair involving gypsum-epoxides (at low cost, due to the small volumes required for gluing a composite), which showed very high resistance to acetone and solvents, became an acceptable technique for a series of commercially available printer models. After repair, the glued

parts (Fig. 2) demonstrate high durability and reliability equal to the lifespan of a new part.

A second notable way of using gypsum-epoxides is the industry of bulk floors, including the private sector. The high resistance to atmospheric moisture, sun, and alkaline makes it possible to use these composites as the cheaper (compared with pure polyepoxides, polyesters, acrylates, and well-known putties), eco-friendly, and reliable filling compounds.

6. Discussion of results of studying the effect of epoxy resin filling on its properties

It can be considered that under such conditions the filling only disarranges the polymer system. After warming up at 100–110 °C (the most recommended thermal mode for post-hardening and stress removal [12]), the gypsum also weakens the maximum stresses at compression σ_m, although not so noticeable (by a quarter).

The situation changes if the composites are warmed up at 250 °C (Table 1). One can see that the non-filled epoxy polymer loses maximum stresses at compression σ_m by a third (from 350 to 245 kgf). The module is also similarly reduced, as well as wear resistance. This is natural because, at these temperatures, the epoxy polymers of cold harden-ing are considered to be completely inoperable: for example, at 200–250 °C, it is recommended to warm the products they glued together to clean them from an epoxy glue [12]. However, the gypsum-filled composites, after warming up at 250 °C, do not lose but increase the maximum stresses at compression σ_m and the module at compression (Table 1). Compared to the warmed H-composite, the gypsum-epox-ides demonstrate the higher indicators C (for the original gypsum), E, and T. In the case of the composite G_o (with pre-hardened gypsum), warming does not give a gain in C, but there is almost no weakening (as for the H-compo-site) as well.

These phenomena, the strengthening or maintaining strength after the limit for polyepoxide warming, are termed by us the thermal strengthening of epoxy composites. This effect was first observed and reported in [5].

The practical prospects for employing thermal strength-ening are very broad. Polyepoxides are still limited to the working interval of up to 150–200 °C, although the industry requires plastics resistant to temperatures of 200–300 °C.

A different pattern is observed in the study of samples warmed up to 250 °C. The H-composite retains micro-hard-ness but is embrittled and cracked already when punches penetrate for 40 μm (Table 2). On the contrary, the heated gypsum-epoxides become more plastic than the non-heated ones – especially G_o (with pre-hardened gypsum). It is possi-ble to measure their micro-hardness at a deeper penetration, up to 50 μm. We suggest designating this effect the thermal plasticization of epoxy-polymers at extreme (destructive, harsh, etc.) temperatures.

Given the importance of strength tests, a composite can-not be considered durable if it disintegrates or weakens its properties after being aged in a series of widely used liquids. It is convenient to use a widely used acetone-ethyl acetate mixture as a model environment. It is known that polyepox-ides made from resins of the type ED-20 are very unstable either in acetone or in its mixture with ethyl acetate. This,

in particular, underlies a method for cleaning products from unnecessary epoxy stitching or coatings. And it also se-verely limits the use of epoxy products without additional modification in the home and industry. However, we have proven that the addition of gypsum (as well as cement) produces a drastic improvement in resistance in acetone solutions (Table 5).

The decay time in this case (over 14 days) is longer than usual (1–2 days), as the composites were not freshly pre-pared. Accordingly, the internal stresses and post-effects in them were not so influential. At the same time, composites with gypsum are much more resistant to an acetone solu-tion; they are many times less active in swelling and retain integrity at any duration of aging. It should be noted that there is a marked difference in the swelling degree between the original non-hardened and the hardened gypsum. The non-hardened original gypsum (G_h) does not swell on day 1 while the level of swelling remains quite low even on days 9–14 (Table 5). After 2.5 months of aging, the swelling rate is quite small (7–8 %) – 5 times lower than that for an unfilled polymer. The hardened gypsum at all stages shows approximately twice the degree of swelling (it can be assumed that it is about half as stable) but it is also much more resistant to swelling than the non-filled gypsum. It should be noted that both gypsum-filled com-posites do not even disintegrate at small swelling, even after 2–3 months or longer aging in acetone. The resulting patterns can be used in solving the industrial-practical task to strengthen the resistance of polyepoxide to aggressive organic solvents (primarily, acetone).

The samples with gypsum show a weight loss in the first hours of the experiment. Further, the weight loss is re-placed with an active swelling for 2 weeks, after which the swelling is blocked by a competing process of washing out (as the degree of swelling decreases). The process of wash-ing out under the influence of acid is quite expected for a composite with chalk (given for comparison in Table 6). The resistance of polyepoxide to nitric acid decreases after gypsum filling.

The appearance and morphology of the composites, ac-cording to ASM and optical microscopy, allow us to note some differences between G_o and G_h (Fig. 3).

Fig. 3. The appearance of composites with the hardened (G_o) and original (G_h) gypsums

Visually, the composites are little different; both are gray-green (G_o is slightly lighter); before the hardening, they have a viscous consistency; the time of hardening is comparable (Fig. 3). ASM images show that the original gypsum forms a composite (G_h) with a more pronounced filler structure – ASM (Fig. 4, a) demonstrates the relief areas with a clearly crystalline nature. The composite with the hardened gypsum (G_o, Fig. 4, c) does not have such pronounced structures, its morphology reflects the distri-bution of inert (albeit very evenly distributed in the ep-oxide) particles. Both ASM images noticeably distinguish the composites from the image for the H-polymer, where only pores are visible against the background of a relatively smooth relief (Fig. 4, c).
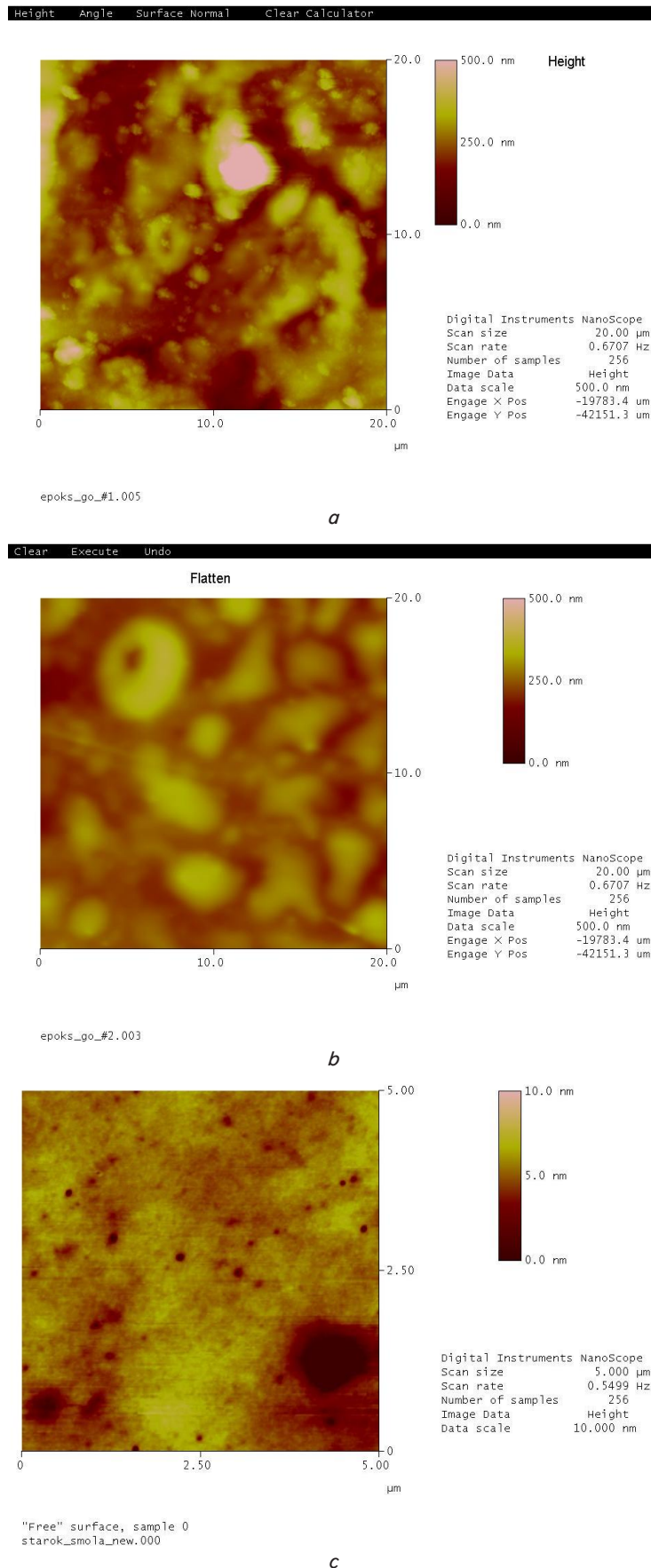
Fig. 4. ASM images of the following compositions: $a - G_h$ (50 % of the original gypsum); $b - G_o$ (50 % of the hardened gypsum); c — non-filled

Optical microscopy shows a completely different morphology for the composites with non-hardened and hardened gypsum.

Thus, the hardened gypsum is inert and does not form any noticeable structures in the composite. The non-hardened gypsum is structurally active. The ASM images make it possible to distinguish the orderly formations of the crystal-like type, which can be figuratively termed "wool-like". Air bubbles are also visible in the structure of both types.

Further research should be aimed at studying similar compositions at different concentrations, as well as with impurities of nano-additives (silica, alumina, nanotubes) and binders (cement, clay). Also, worth further consideration is the effect exerted by the ability of water-hardening (crystallization) of gypsum on the polymerization of epoxides. The "thermal strengthening effect", which could open up opportunities for the use of epoxides in the traditional niches of relatively heat-resistant polymers (which are now difficult to access or expensive), has not been fully studied. The current work can serve as a starting point for such research, which is in demand in practical materials science and the physical chemistry of composites.

8. Conclusions

1. The introduction of gypsum to the epoxy resin alters the consistency of the composition and the morphology of the composites, which also depends on the type of gypsum (the original hemihydrate or hardened dihydrate).

2. The introduction of 50 % by weight of gypsum after a soft (55 °C) heat treatment of polymers leads to a drop in the strength at compression, the module, and wear resistance. After treating at 100 °C, the strength of the gypsum-filled increases slightly but remains significantly lower than that for the non-filled (retaining the same indicators as at 55 °C).

3. After hard heat treatment at 250 °C, the maximum stress at compression σ_m and the module of the non-filled sample are reduced by about a third while the wear resistance decreases by 5–6 %. In contrast, a composite filled with hardened gypsum shows a slight increase in strength and a very noticeable growth of the module and wear resistance. A composite with non-hardened gypsum demonstrates the growth of strength (exceeding the strength of the non-filled analog) and a noticeable increase in the module and durability. We suggest that these effects should be termed the thermal strengthening of epoxy composites.

4. The filling renders composites a particularly high resistance to acetone-containing solvents, which neither the non-filled nor many filled exopolymers possess.

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