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Epoxy-Cement Compositions with effect of thermo-hardening at hard heat treatment for Applied Engineering & Technologies

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Abstract:

The composites "epoxy resin - microdispersed cement" were obtained and studied in a wide range of filling (5 - 65 wt%). It was shown that the filling significantly changes the appearance and viscosity (especially at 50-65 wt%), but has little effect on the curing kinetics of the composites. The obtained polymer composites are characterized by increased or acceptable physical, mechanical, and chemical-resistant properties. At the same time, the mechanical properties of the filled composites can be preserved or even enhanced after severe thermal heating (250-300 °C), which is not typical for unfilled polyepoxides (which degrades and weakens its properties at 250-300 °C). These properties open up new possibilities for using cheaper epoxy materials for work in extreme areas of service, industry, and technology.

Introduction

Cement is one of the oldest artificial inorganic construction binders. The history of the of cement began before our era. Its first recipes date back to the times of ancient civilizations of the Ancient Roman Empire, which used a relatively low-strength today, but then quite effective and durable "Roman cement" [1-2]. Technologies for its improvement were layered over the centuries, and by the 20th century they were formed into cement grades. In the post-war industrial period, the most popular cement was M300 (i.e. with a strength of 300 kgf/cm2), which quickly gave way to even more durable grades M400 and M500. The cement formula is complex and inconsistent. Common for cement is the content of CaO (up to 2\3 of the clinker mass), SiO_2 (20-25 wt%), Al_2O_3 (≈5%), Fe_2O_3 (≈3%). And also the need for a balance in the hardened cement of phases important for strength\resistance - alite, belite, etc. [1-4]. Epoxy compositions with cement became known, apparently, soon after the start of widespread production of industrial epoxy resins in the 50s (these compositions were used in secret industries). Regular scientific reports on cement-filled compositions are found in the scientific literature of the 70-80s. Now a number of informative works, articles and dissertations on this topic are known [5-16], including our previously published works [6-10]. But the question - what happens when cement "enters" the epoxy resin and polymer, remains an interesting little-covered segment of the science of plastics.

A purely practical question also remains open – this is: “how strong can be the influence of the structure of cement and its water-cured form (concrete) on the final properties of epoxy plastics”. As is known, the construction industry and private households have a constant reserve of illiquid cement residues, and the question often arises: will they have the same effect, for example, on the strength of a polymer-concrete self-leveling floor or compound? It can be assumed that the original cement will be prone to capturing moisture in the resin itself and the atmosphere, with the formation of some additional frameworks inside the polymerized composite. And vice versa, already hardened cement after crushing should be a crystallizing mass - although better structured, but also more inert in the resin. If the basic properties in both cases are approximately equal, this will have a serious practical outcome. For example, builders will be able to use crushed construction cement waste instead of fresh cement to create an epoxy compound or coating. Thus, this work comes out of practice, with several vectors of possible scientific and practical conclusions.

Our laboratory has almost 10-year experience in creating such materials, the properties of which we have published a series of works [6-10].

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2.1 Preparation of epoxy samples

Compositions «epoxy resin + M400 cement (10-66 wt%)» were studied Epoxy520 epoxy resin, M400 cement (TM Eurocement), and DETA hardener were used to make the samples. In 4 mixtures, the amount of cement is 10%, 25%, 50% and 65%. Then, relative to the epoxy resin, a hardener was added to the mixture in a ratio of 6 to 1. After making suitable mixtures of fillers and epoxy resin, they were sorted into different molds for further experiments.

Fig. 2.1. Compositions before adding the hardener and the workplace

2.2 Devices and methods

Compressive strength - were measured on cylinder samples with a diameter of 0.65 cm and a height of 1.1+-0.1 cm, on a LouisShopper press. Abrasion resistance - according to the mass of the abraded composite after 40 passes of 20 cm on P80 sandpaper. Abrasion resistance is calculated as an inverse characteristic, taking into account the relative density of the samples according to the formula $I = \rho/X\rho_o$ (ρ/ρ_o – the ratio of the density of the composite and H-polymer, X – the mass of the abraded composite, mg). Adhesion at separation (tear) was measured on steel cylinders with an area of 5 cm^2, on the UMM machine.

Fig. 2.2. Work near the tearing machine ID-1 (on the left), press machine L.Shopper Fig. 2.3. Working with PIM microhardness-tester and with Durometer (right).

Microhardness was measured by pressing the indenter into the composite materials in the shape of a flat hexagon with the help of the ASTM 2240 device. Swelling of samples of pyramids and cubes was classically determined by growth, calculated according to the formula $q = (m - m0)/m0$, wt.%, where m and m0 are the final and initial masses of the sample.

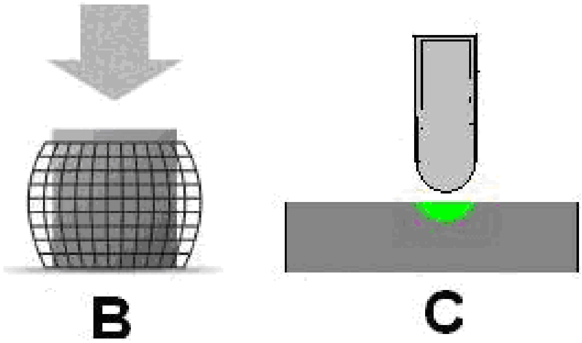

Fig. 2.4. Scheme of compression and microhardness tests.

3. Experimental Results

3.1. Visual info and microscopy.

The introduction of cement fillers into epoxy resin makes it possible to obtain dark sedimentation-resistant (that is, resistant to the settling of the filler) masses that are well-formed and harden in the usual mode (fig.1).

Fig.3.1. *Visual characteristics of compositions and composite cubes*

It is shown that as the composition increases, the viscosity increases, while maintaining the same ability to harden. Microscopy shows that morphologically (that is, at the level of microstructures), the compositions represent an aggregative mixture with its own filler structures (in particular, crystal-like formations) and rare air inclusions (Fig.2). According to SEM microscopy data, at the macro level, the epoxy-cement coating is a system similar to concrete, with areas (domains) separated by microcracks and single inclusions of various inhomogeneities. It can also be seen that cement is able to form agglomerates in the composition, clusters around air bubbles and certain structures similar to ordered (crystallized) structures.

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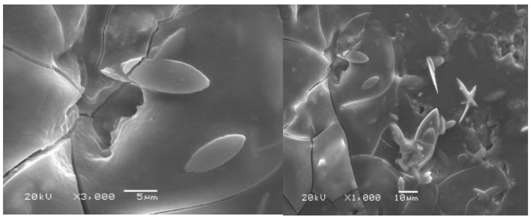

***Fig.3.2**. SEM-images of composite surface*

In all cases of filling, we see a noticeable (by 2-3 times), and sometimes a record (for 65% - by 5 times) increase in adhesion upon separation. There is also an increase in microhardness (both according to Shore and Brinell) and modulus of elasticity under compression (by 1.2-2 times).

3.2. Microhardness by different methods

It can be seen that the unheated samples are fragile, because it is not possible to push the sample through the hemisphere by more than 20-30 microns (tab. 2). The same - for the 10 wt% filled sample. For 25 wt%, there is no longer such fragility, and 50 and 65%-filled samples can be examined when immersed even up to 40 µm. After heating to 75 ^{o}C, unfilled and all samples become more plastic and withstand immersion up to 50 µm. A clear regularity can be seen - the growth of microhardness with increasing filling. At 50-65% by mass, we already have 20-30% growth, in particular. during deep dives

Table 1. Indicators of microhardness according to Brinell (H) at different depths of penetration into the hemispheres

	Deep of immersion, mcm				
Initial (at 25 ^{o}C) templates	10	20	30	40	50
0 (unfilled)	100	250	…		
10 мас%	200	250	…		
25 мас%	125	225	325	400	450
50мас%	-	-	-	-	-
65 мас%	250	350	450	…	
Soft-heated (at 75 ^{o}C) templates					
0 (ненаповнений)	100	200	300	400	500
10 мас%	100	200	300	400	-
25 мас%	150	250	350	450	-
50мас%	188	288	413	500	575
65 мас%	200	300	413	513	600

Table 2. Indicators of microhardness according to Brinell (H) at different depths of penetration into the 75^{o}C-treated templane hemispheres.

	0	10 %	25%	50%	65%
Microhardness by Shor, xF	*80*	*82*	*87*	*89*	*91*

3.3. Com pression strength

A high filling of 65 wt% deprives the composite of plasticity, turning it into an elastic-brittle state, as evidenced by a change in the type of compression diagrams (from two-stage to one-stage) and the modulus of elasticity. The introduction of cement gives an increase in resistance to abrasion and preserves the original index of compressive strength, and for 65% it greatly increases the compressive strength (from 700 to 900 kgf\cm^{2}, i.e. from 70 to 90 MPa). The reinforcing effect of cement (the stronger the higher the filling) on the stability of strength in the case of severe heating has been established. After 270 ^{o}C processing, the unfilled sample significantly reduces the strength index, while compositions with gypsum increase them. A particularly high index is given by the maximally filled composite (65%), when the compressive strength becomes 2-3 times higher (than for unfilled) and exceeds 100 MPa (1000 kgf/cm^{2}).

Table 3. Parameters of polymer composites.

	Compression strength M^{D} (кгс\см^{2}) & E* (rel.units)	
0	680^{880} & 1	440 & 1
10 wt%	680 ^{880} & 1	550 & 1,1*
25 wt%	700^{850} & 1,2	-
50 wt%	730^{800} & 1,7	800* & 1,8*
65 wt%	890 $^{=}$ & 2	1000 & 2,5

The plasticizing effect of cement for composites with hard heat treatment (270 ^{o}C) was noticed, which is indicated by the microhardness data. The work shows the high prospects of filling epoxies with water-hardening viscosities to strengthen and provide new properties. The revealed effects of thermosetting and thermoplasticization show that such filling gives epoxy previously uncharacteristic properties, which are very important in a number of important applied tasks for industry, repair, and creation of new materials.

3.4. Discussion

Thus, the introduction of cement provides the strength of polyepoxy with significant resistance to hard heat treatment, and this effect is greater the higher the degree of filling (tab.3). This can be considered an important result for the physical chemistry and materials science of composites. We can propose next scheme for effect of filling

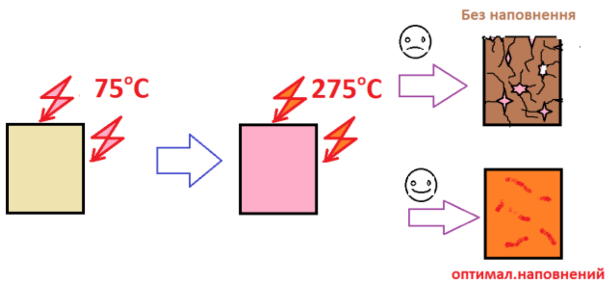

Fig.3.3. Shematic visualisation of possible thermo-hardening of composites.

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Conclusions

1. The introduction of cement into epoxy-resin allows to obtain dark sedimentation-resistant (that is, resistant to the settling of the filler) masses that are well formed, hardened in the usual mode with unchanged kinetic of polymerisation.
2. Microscopy shows that morphologically (that is, at the level of microstructures), the compositions represent an aggregative mixture with its own filler structures (in particular, crystal-like formations) and rare inclusions of air. According to SEM microscopy data, at the macro level, the epoxy-cement coating is a system similar to concrete, with areas (domains) separated by microcracks and single inclusions of various inhomogeneities. It can also be seen that cement is able to form agglomerates in the composition, clusters around air bubbles, and certain structures similar to ordered (crystallized) structures. At a very high magnification (××3000-5000) it can be seen that there are cracks (just like in concrete) and formations of unknown nature similar to rhombuses\ellipses, bacteria, needles, and formations of other shapes (these may be crystalline formations of the cement itself in composites).
3. In all cases, there is a greater increase in tear adhesion (for 2-3 times). There is also an increase in microhardness (both according to Shore and according to Brinell) and elastic modulus during compression (by 1.2-2 times). A high surface content of 65 wt% reduces the composite's plasticity, transferring it to a spring-critic state, - which notes the change in the type of compression diagram (from double-stage to single-stage) and the elastic modulus. The introduction of cement increases the resistance to abrasion and preserves the output value of the compression value, and for 65% it increases the compression value (from 70 to 90 MPa).
4. The strengthening effect of cement (the stronger the higher the filling) on the stability of strength in the case of severe heating has been established. After **270** ^{o}C, the unfilled sample significantly reduces the strength index, while the compositions with gypsum **increase** them. A wery high index is given by the maximally filled composite (65%), when the compressive strength becomes 2-3 times higher (than for unfilled) and exceeds 100 MPa (1000 kgf/cm^2). The plasticizing effect of cement for composites with hard heat treatment (270 oC) was observed, which is indicated by the microhardness data.
5. The work shows a high perspective of filling epoxies with water-hardening viscosities to strengthen and provide new properties. The revealed effects of thermosetting and thermoplasticization show: such filling gives epoxy previously uncharacteristic properties, which are very important in a number of important applied tasks for industry, repair, and creation of new materials.

References

1. Starokadomsky D. On Strengthening of Epoxy-Composites by Filling with Microdispersions of SiC, TiN, and Cement // "Composite Materials Engineering Modeling and Technology" Editors: A.V.Vakhrushev, A.K.Haghi. – Apple Academic Press, NewYork, - Chapter 4. - 2019. - P. 49-60.
2. Starokadomsky D., Reshetnyk M. Study of restoration epoxy composites with initial and water-cured cement & gypsum fillers \\ Industrial laboratory Diagnostics of materials 87(8):34-41 - DOI: 10.26896/1028-6861-2021-87-8-34-41.
3. Starokadomsky D, Reshetnyk M. Microfilled Epoxy-composites, capable of thermo-hardening and thermo-plasticization after hard heating (200-300 ^{o}C) - for "in-field\offroad" use in bio-, agro-, medservice.// Biomedical J.of Scientific & Technical Research – 2019. - V.19, N 1 - P.14118-14123 - DOI: 10.26717/BJSTR.2019.19.003257
4. 1. Voronkov A.G., Yartsev V.P. **Epoxy polymer solutions for the repair and protection of building products and structures**. – Tambow. – Publishing house of Tambow State Tech. University, 2006. – p. 92.(in Russian).
5. Sia T., Mai Y., Cotterell B. **Strength and fracture properties of epoxy-cement composites** / *The Second Australian Conference on Engineering Materials, held at Sydney*, July 6-8, 1981. P. 512-529. https://trid.trb.org/view/1746523.
6. **Łukowski P.** Studies on the microstructure of Epoxy-Cement composites / Archives of Civil Engineering. 2016. V. LXII. iss.2. P.100-111. DOI: J0.1515/ace-2015-0068
7. **Czarnecki L., Łukowski P., Nejman R.** The statistical evaluation of epoxy concrete heterogeneity / Cement and Concrete Composites. 1996. Vol.18. P. 417-428.
8. **Ohama Y., Demura K., Endo T.** Properties of polymer-modified mortars using epoxy resin without hardener / in Polymer-Modified Hydraulic-Cement Mixtures. – Philadelphia. – Special Technical Publication ASTM-STP 1176, 1993. – P. 90-103.
9. **Mohammed A.A., Ali T.K.** Flexural Behavior of Composite Concrete–Epoxy–Reinforced Concrete Beams / Iranian J. Sci. Technol. Trans. Civil Eng.. 2020. Vol.44. P. 549–563. https://doi.org/10.1007/s40996-019-00255-1
10. **Bhutta M.A.R.** Effects of polymer-cement ratio and accelerated curing on flexural behavior of hardener-free epoxy-modified mortar panels / Mat Struct. 2010. Vol.43. P. 429-439. https://doi.org/10.1617/s11527-009-9578-8
11. **Jo Y., Do J.** Hardening Properties of Epoxy-Modified Cement Composites Without Hardener /

*Corresponding Author: D. Starokadomsky

Polymers & Polymer Composites; Shropshire. 2016. Vol.24. Is.3. P. 195-204.
12. **Łukowski P., Adamczewski G.** Self-repairing of polymer-cement concrete / Bulletin of the Polish Academy of Sciences – Technical Sciences. 2013. V.61. P. 195-200.

1. Введення цементних в епоксидну смолу дозволяє отримувати темні седиментаційно-стійкі (тобто стійки до осідання наповнювача) маси, що добре формуються, отверждаемые в звичайному режимі.
2. Мікроскопія показує що морфологічно (тобто на рівні мікроструктур), композиції представляють агрегативну суміш із власними структурами наповнювача (зокрема кристалоподібними утвореннями) та рідкісними включеннями повітря. Згідно з даними СЕМ-мікроскопії, на макрорівні епокси-цементне покриття являє собою систему подібну до бетону, з областями (доменами) розділеними мікротріщинами та поодинокими включеннями різних неоднорідностей. Також видно що цемент здатний формувати в композиції агломерати, скупчення навколо бульбашок повітря та певні структури, схожі на упорядковані (кристалізовані) структури. При дуже великому збільшенні (у 3-5 тис.раз) видно що трапляються тріщини (так само як у бетоні) та невідомої природи утворення схожі на ромби\еліпси, бактерії, голки та утворення інших форм (це можуть бути кристалічні утворення самого цементу у композиті).
3. У всіх випадках наповнення ми бачимо помітне (у 2-3 рази), а іноді рекордне (для 65% - у 5 разів) зростання адгезії при відриві. Також має місце зростання мікротвердості (як по Шору так і по Брінеллю) та модуля пружності при стисканні (в 1.2-2 рази). Високе наповнення 65 мас% позбавляє композит пластичності, переводячи в пружно-крихкий стан, про що свідчить зміна виду діаграм стиснення (з двоступінчастого на одноступінчастий) та модулі пружності. Введення цементу дає підвищення стійкості до стирання і зберігає вихідний показник міцності стиснення, а для 65% сильно збільшує міцність стиснення (з 700 до 900 кгс см2, тобто з 70 до 90 МПа).
4. Встановлено посилюючий вплив цементу (тим сильніший ніж вище наповнення) на стійкість міцності у разі жорсткого прогріву. Після 270 оС обробки, ненаповнений зразок суттєво знижує показник міцності, тоді як склади з гіпсом збільшують їх. Особливо високий показник дає максимально наповнений композит (65%), коли міцність на стискання стає вищою в 2-3 рази (ніж для ненаповненого) і перевищує 100 МПа (1000 кгс\см2). Помічено пластифікуючий вплив цементу для композитів із твердою термообробкою (270 оС), про що говорять дані по мікротвердості
5. Введення даних наповнювачів дозволяє суттєво підвищити стійкість композиту до агресивного розчинника. Так, у суміші ацетон-етилацетат 10, 25, 50 і особливо 65%- наповнені композити не деструктують так як ненаповнений полімер (який розпадається в перший день витримки). Зразки з 25- 65 мас.% цементу дають композити більш стійкі до набухання у концентрованому H2O2. Однак стійкість у кислому водному середовищі (35%-й азотній кислоті) знижується (перевірити!).
6. Робота показує високу перспективність наповнення епоксидів водотвердіючими в'язкими, для посилення та надання нових властивостей. Виявлені ефекти термозміцнення і термопластифікації показують: подібне наповнення надає епоксиду нехарактерні раніше властивості, дуже важливі в ряді відповідальних прикладних завдань для індустрії, ремонту та створення нових матеріалів.
7. The introduction of cement filler allows you to significantly increase the resistance of the composite to an aggressive solvent. Thus, in a mixture of acetone-ethyl acetate 10, 25, 50, and especially 65%, the filled composites do not destroy like the unfilled polymer (which disintegrates on the first day of exposure). Samples with 25-65 wt.% of cement give composites more resistant to swelling in concentrated H2O2. However, stability in an acidic aqueous environment (35% nitric acid) decreases (check!).

СПИСОК ЛІТЕРАТУРИ

1. Д.Л.Старокадомский, М.Н.Решетник. Исследование реставрационных эпокси-композитов с исходными и водоотверждёнными гипсовыми и цементным наполнителями.\\ **Заводская лаборатория. Диагностика материалов**, 2021, Т.87, №8, с.34-41 - DOI: https://doi.org/10.26896/1028-6861-2021-87-8-34-41
2. Химическая Энциклопедия. – Москва, БРЭ, 1992, Т.4.
3. H.Taheri, , N.Heidari, A.Perrot, G.Siqueira, G.Nyström, S.Kawashima. **Selection of suitable cellulose nanofibers derived from eco-friendly sources for the production of lightweight cementitious composites with tuned rheological, mechanical, and microstructure properties**.\\ *Cement and Concrete Composites*. V.151, August 2024, 105586 https://doi.org/10.1016/j.cemconcomp.2024.105586
4. https://www.sciencedirect.com/science/article/abs/pii/S0958946524001586
5. Starokadomsky D.. **On Strengthening of Epoxy-Composites by Filling with Microdispersions of**

*Corresponding Author: D. Starokadomsky

SiC, TiN, and Cement // *"Composite Materials Engineering Modeling and Technology"* Editors: A.V.Vakhrushev, A.K.Haghi. – Apple Academic Press, NewYork, - Chapter 4. - 2019. - P. 49-60.
6. Starokadomsky D, Reshetnyk M. Microfilled Epoxy-composites, capable of thermo-hardening and thermo-plasticization after hard heating (200-300 ^oC) - for "in-field\offroad" use in bio-, agro-, medservice.// Biomedical J.of Scientific & Technical Research – 2019. - V.19, N 1 - P.14118-14123 - DOI: 10.26717/BJSTR.2019.19.003257
7. Старокадомский Д.Л. Возможности создания огнехимстойких, термоупрочняемых и термопластифицируемых при 250°C эпокси-композитных пластмасс с микродисперсиями SiC, TiN и цемента. // Пластические Массы. – 2019. - №5-6. – с.40-43. - DOI : 10.35164/0554-2901-2019-5-6-40-43
8. Старокадомский Д., Решетник М., Матвеева Л.. Структура и физ.-мех. характеристики эпоксидных композитов с микродисперсным цементом. // Пластические Массы. - 2020. - №11-12. - С.43-49.
9. Starokadomsky D., Reshetnyk M., Rassokhin D.. Epoxy composites with 5 wt.% of nanodispersed magnetites and ferroxides. Strength, heat resistance, morphology. // J. Material & Environmental Sciences.- 2020. - N.11(8). - P. 1241-1249 - https://www.jmaterenvironsci.com/Document/vol11/vol11_N8/JMES-2020-11109-Staromsky.pdf11. 12.. Vol.25, Is.2. P. 411-423. https://doi.org/10.1016/j.conbuildmat.2010.02.035.
10. Старокадомский Д.(2018) **Длинный век эпоксидки**. *Наука и жизнь*. 2018, с.66-71.21.
11. Л.Охрименко. **Термохимстойкие полимеры**. Конспект лекций. – Ленинград, 1976, 30 стр
12. К.-У.Бюллер. **Тепло- и термостойкие полимеры**. – М., Химия, 1984, 1056 с.
13. Dr.K.Buhler. **Spezialplaste**. - Berlin, Deu.Demokr.Resp, Akademie-Verlag, 1978.

*Corresponding Author: D. Starokadomsky