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CREATION OF EPOXY COMPOSITES WITH ZEOLITE FOR THE MEDICAL IMPLANTS PRODUCTION

Kateryna Strukova
Dmitro Starokadomsky
National Center "Junior Academy of Sciences of Ukraine" under the auspices of UNESCO;

Kyiv, Ukraine

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Kateryna Strukova,
10th grade, Natural Science Lyceum #145 of the Pechersk district of Kyiv
Mentor: Dmitro Starokadomsky

Using Epoxy Resign in the Medical Implants Production

Abstract

The world's population is growing every year. The United Nations predicts that our global population will reach 9.7 billion people by 2050, with an average life expectancy of 77.1 years. In the United States, for example, life expectancy in 2020 was 77.3 years.

Growing urbanization and life expectancy, environmental degradation, and sedentary lifestyles that lead to joint damage and other serious health problems all require quality medical care for people. And quality medical care is impossible without new materials and the latest technology.

In this research, epoxy resin-based composites with a dispersed zeolite filler and with copper powder additive were synthesized and studied. It was considered whether these composites would be suitable for the imitation of cancellous bone tissue and the production of medical implants using 3D printing.

Experimental results show that zeolite is promising for strengthening the compressive strength, adhesion to steel, and microhardness of composites. It has been determined that the filling significantly increases abrasion resistance and chemical resistance in aggressive fluids.

Determination of strength and resistance was carried out according to the methods of the relevant standards (DSTU or ASTM).

Key words: epoxy composite, zeolite, copper powder, strength, resistance, adhesion.

Question

Is it possible to create a cheap 3D printing material for individual medical implants with the necessary physical, mechanical and chemical properties?

Variables

Independent Variable: time

Dependent Variables: viscosity, compressive strength F, abrasion resistance W, microhardness H, pull-off strength (adhesion) τ, swelling value Q

Table 1

Controlled variables

Experimental Group	**Controlled variables for all groups**
(H) unfilled epoxy polymer	Constant temperature 20 °C The same equipment, tools, and experimental conditions for physical-mechanical and chemical tests of different samples
(Z50%) epoxy polymer with zeolite filler	
(Z50%+Cu) epoxy polymer with zeolite and copper powder filler	

Hypothesis

The resin-based composite with a dispersed zeolite filler is suitable for simulating cancellous bone tissue and is cheap material to produce medical implants using 3D printing.

Background research

The world's population is growing every year. The United Nations predicts that our global population will reach 9.7 billion people by 2050, with an average life expectancy of 77.1 years. In the United States, for example, life expectancy in 2020 was 77.3 years. (The United Nations, 2021).

Growing urbanization and life expectancy, environmental degradation, and sedentary lifestyles that lead to joint damage and other serious health problems all require quality medical care for people. And quality medical care is impossible without new materials and the latest technology.

There is a general trend of increasing number of severe joint diseases and increasing number of patients requiring prosthetics in Ukraine and in the world. For example, in the United States, according to the 2021 annual report of The American Joint Replacement Registry (AJRR), the number of hip and knee joint replacements increased by 18.3% over the previous year (AJRR, 2021).

Therefore, research and work on the creation of cheap, biocompatible and wear-resistant endoprostheses is very relevant, because this problem can affect each of us.

Implant materials must meet several requirements: be non-toxic, durable and technological, and have physical properties close to natural tissues (Litvinenko, 2015). Given the need for structural integrity of such implants, the choice of materials for production is limited and includes metal, plastic and composites.

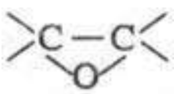
The development of 3D scanning and 3D printing technologies allows to create customized medical implants, so the materials that can be used on these devices are the most interesting to develop. Today, common materials for 3D printing are epoxy resin-based composites (Schwaar, 2021).

«Bone tissue is elastic, and implant's long-term operation depends on the physical and mechanical properties of the material from which it is made and the shape of its intraosseous part. Implants that are close to a cylinder in shape and have a porous surface better distribute the functional loads on the underlying bone tissues.» (Litvinenko, 2015, p. 8).

Considering that epoxy fiberglass and epoxy carbon plastics have a cellular structure, thanks to which nerves, axons, and body cells can grow through their surface, I decided to use epoxy resin as the basis.

In (Shidlovsky, Bondar and Musienko, 2015) it was proposed to model the cancellous bone tissue, which connects the implant to the bone after regeneration, with a special composite material of epoxy resin with a polymeric porous filler. To evaluate the possibility of using as a cancellous bone tissue simulator, three different materials were chosen: cellular foam rubber soaked by liquid epoxy resin; cellular foam concrete; and a composite material made by mixing small spherical foam plastic grains with a diameter of 1-2 mm with epoxy resin.

Comparing the mechanical properties of cancellous bone tissue samples obtained directly from the proximal part of the femur and samples from the above composite materials based on epoxy resin in real experiments related to the evaluation of biomechanical characteristics of endoprostheses, a conclusion was made, that "the cancellous bone tissue can be replaced by a composite material of epoxy resin with the inclusion of small spherical foam plastic grains" (Shidlovsky et al., 2015, p. 136).

Epoxy resins are oligomers or monomers containing at least two glycidyl  or epoxy  groups in the molecule, which can turn into cross-linked, net-structured polymers under the action of hardeners (Knunyants, 2000, p. 712).

The biocompatibility of epoxy resins for the bone implants has been confirmed by studies and research of many scientists. Thus, in the article (Galatenko, Astapenko, Kulesh, Levenets, & Rozhnov, 2015) epoxydian oligomer ED-20 (MM 420: epoxy number 21.6, hydroxyl number 1.7) was used as a base. Within the framework of the research, the biocompatibility of epoxypolyurethane composites with poly-3-hydroxybutyrate was studied during their implantation in experimental animals. It was determined that «compositions based on ED-20 epoxy resin are biocompatible with tissues of experimental animals, do not cause acute and chronic inflammatory reactions, retain their structure during implantation» (Galatenko et al., 2015, p.109).

However, the composite material mentioned in the article (Shidlovsky et al., 2015) was designed for experiments outside the human body and foam plastic is not a biocompatible material.

Therefore, given the results of the above research, I was looking for an epoxy filler that would create a porous biocompatible material to simulate the cancellous bone tissue of a bone implant, was cheap, and had the necessary physical, mechanical, and chemical properties. I have hypothesized that zeolite could be a promising filler for epoxies in the medical implants production using 3D printing.

This group of minerals is widespread and more than 1000 large deposits are known in the world, including in Ukraine, the USA and Japan. « The zeolite structure is based on rings of tetrahedrons formed by SiO_4^{4-} , AlO_4^{5-} , large cavities between which are connected by tubules" (Biletsky, Omelchenko, and Gorvanko, 2016, p. 454). That is, zeolite has the necessary porous structure.

The general formula for zeolites is $M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$, where M is an alkali or alkaline earth metal, and n is its oxidation state. «Natural zeolite is available, cheap, heat- and acid-resistant.» (Knunyants, 2000, p. 675).

This group of minerals is used as adsorbents and as an additive in animal feed. Considering that some types of zeolites have already been used in medicine, namely in abdominal surgery (Bogomolov, Kulish, Minina and Bogomolova, 1998), this mineral can be considered biocompatible.

These characteristics make zeolites interesting objects for research and determination of their physical-mechanical and chemical properties as an epoxy filler.

Considering that the epoxy resin composition with zeolite may be too plastic, and considering that in medicine (dentistry), metals such as platinum, silver or copper are added to implant materials for hardness, I decided to consider copper powder as an additional filler for the epoxy composition. Since copper is the cheapest of these metals.

To create wear-resistant and strong endoprostheses, it is necessary to evaluate the physical-mechanical and chemical properties of the synthesized materials. This is done by testing under laboratory conditions and evaluating material samples for compressive strength (DSTU EN ISO 604:2019), abrasion resistance (GOST 20811-75), microhardness (DSTU ISO 6506-1:2007), resistance to swelling in liquids (ISO 62:2008). Considering that epoxy composite can be used also as a coating for metals implants, it is appropriate to study the bond strength of the epoxy composite with steel, that is, to evaluate samples of materials for pull-off strength (adhesion). (DSTU ISO 4624:2019).

Materials List

1. Low molecular weight Czech cold curing Epoxy520 (manufacturer SPOLCHEMIE).
2. Polyethylene polyamine (PEPA) (manufacturer SILKOR).
3. Zeolite, ECO Instinct 1-3 mm (manufacturer Ecoinstinct).
4. Copper powder PMC-1, <100 μm (manufacturer LLC «Grand Lada»).
5. Hydrogen peroxide "Medical"60% (LLC «INTER - SYNTEZ»).

6. Solvent "Acetone+" (manufacturer TM KHIMREZERV)
7. Solvent Ethylacetate (manufacturer TM KHIMREZERV)
8. Laboratory porcelain mortar and pestle.
9. Beakers and conical flasks.
10. Silicone test molds (cylinders (diameter 6.5 mm, height 11±1 mm); tablets (10x10x2±1 mm); plates (height 1.5±1 mm, width 10 mm, length 6 mm).
11. Steel tear-off plates, bonding area $3cm^2$.
12. Electronic scales, capacity 500g x 0.01g.
13. Tensile-testing machine DI-1.
14. Louis Schopper Press Testing Machine.
15. Portable micro-hardness tester PIM.

Experimental procedure

1. Synthesize three types of samples for the study: (H) unfilled epoxy polymer, (Z50%) epoxy polymer with zeolite, and (Z50%+Cu) epoxy polymer with zeolite and copper powder.
   - 1.1. Grind 250g of zeolite in a laboratory mortar to micro-sized particles and sieve it down to 100 μm.
   - 1.2. Harden 500g of epoxy resin «Epoxy520» by 100g of polyethylene polyamide in big beaker (manufacturer's recommended ratio of 5:1) at 20^0C and stir.
   - 1.3. Pour 250g of that liquid mixture into the first beaker and sign as sample (H).
   - 1.4. Pour 125g of that liquid mixture into the second beaker and sign as sample (Z50%).
   - 1.5. Pour 95g of that liquid mixture into the third beaker and sign as sample (Z50%+Cu).
   - 1.6. Add 125g of zeolite to the second beaker (ratio 1:1) to synthesize the sample (Z50%) and stir it until homogenized.
   - 1.7. Add 125g of zeolite and 30g of copper powder (ratio 38:50:12) to the third beaker to synthesize the sample (Z50%+Cu) and stir it until homogenized.
   - 1.8. Pour all type of samples into the silicone test molds (cylinders, tablets, plates) and sign.
   - 1.9. Lubricate and glue the steel tear-off plates with each of the three synthesized samples.
   - 1.10. Leave the samples in the molds and steel tear-off plates to harden for 3 days.
2. Analyze the physical, mechanical, and chemical properties of each of the three types of synthesized samples.
   - 2.1. Perform compressive strength tests.
     - 2.1.1. Take a cylindrical sample, compress it at a given constant rate of displacement of the active grip on a Louis Schopper Press Testing Machine to and measure the load P at complete destruction of the sample.
     - 2.1.2. Evaluate a destruction type.

2.1.3. Calculate the compressive strength F using the formula F = P\s, where P is the destructive load (kgf), s is the pressure area (cm^2).

2.1.4. Repeat step 2.1.1-2.1.3 four times for each sample type and write the results in the table.

2.1.5. Calculate the average value of F for each type of sample and write the results in the table.

2.2. Perform abrasion resistance tests.

2.2.1. Take a cylindrical sample and measure its mass in mg.

2.2.2. Make 40 runs at 10 cm on both sides with a cylindrical sample on the surface of the P60 emery cloth and measure the new mass in mg and the new height in mm for cylinder.

2.2.3. Calculate weight loss.

2.2.4. Calculate the abrasion resistance W using the formula $W=m_1/M$, where M is the weight loss, m_1 is the initial weight of the sample.

2.2.5. Repeat step 2.2.1-2.2.4 for each sample types and write the results in the table.

2.3. Perform microhardness tests.

2.3.1. Take the sample plate and press a 3 mm indentor into the plate surface to a depth of 10 μm and measure the resistance load using a portable micro-hardness tester PIM.

2.3.2. Repeat step 2.3.1 for depths of 20 μm and 30 μm for same type sample of plate.

2.3.3. Repeat step 2.3.1-2.3.2 for each sample type and write the results in the table.

2.4. Perform a pull-off test for adhesion.

2.4.1. Take the glued steel tear-off plate and tear the sample on the tensile-testing machine DI-1, and measure the value of pull-off strength (adhesion) τ.

2.4.2. Repeat step 2.4.1 four times for each sample type and write the results in the table.

2.4.3. Calculate the average τ value and modified average value for each sample types and write the results in the table

2.5. Perform chemical resistance tests on the degree of swelling in aggressive fluids and water.

2.5.1. Weigh the sample tablets for the test and record the data.

2.5.2. Take the sample tablet and place it in glass beakers with a 1:1 acetone-ethyl acetate mixture, with a 60% hydrogen peroxide solution, and with water.

2.5.3. Repeat step 2.5.1 for each sample type.

2.5.4. Cover all flasks and leave the samples to swell at 20^0C temperature for 10-12 days.

2.5.5. Every 1 to 3 days, weigh the sample tablets by taking them out of the flasks and then putting them back in.

Data analysis and discussion

The concentration of 50 wt% zeolite was chosen in the second sample because it forms a viscous composition comfortable for work and allows mixing the components without precision scales. To increase the hardness in the third sample, a concentration of 50 wt% zeolite and 12 wt% copper powder was chosen. The synthesis of three types of samples H, Z50% and Z50%+Cu according to the scheme Fig.1 resulted in polymerized composites with and without zeolite. Fig.2. Description and labeling of experimental samples are presented in Table 2.

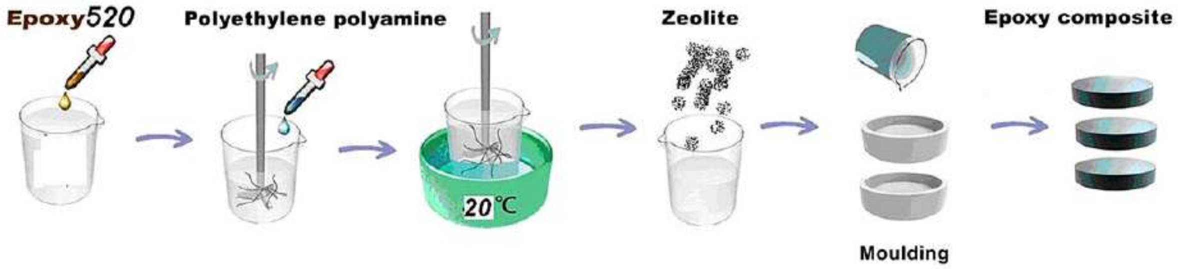
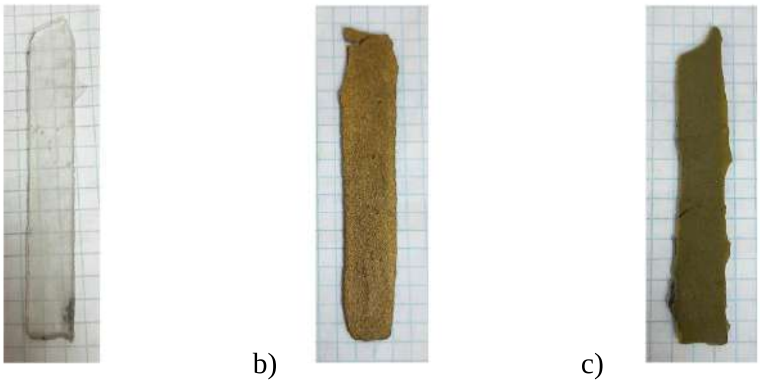


Fig. 1. Typical scheme of obtaining epoxyceolite composites



a) b) c)

Fig. 2. Plates appearance of samples: (a) H, (b) Z50% and (c) Z50%+Cu

Table 2

Samples' description and labeling

Sample	Description
H	Unfilled epoxy polymer
Z50%	Epoxy polymer with 50% zeolite
Z50%+Cu	Epoxy polymer with 50% zeolite and 12% copper powder

When testing the cylindrical specimens of Fig. 3 for compressive strength up to complete destruction, the destructive load P in kgf was measured for each sample.

Fig. 3. Cylindrical samples for compressive strength tests

The compressive strength was calculated using the formula: F = P\s, where P is the destructive load (kgf), s is the pressure area (cm^2).

$s=2\pi(d/2)^2=2\pi(6,5/2)^2 \approx 33,2$ (mm^2)= 0,332 (cm^2), where d is the cylinder diameter 6.5 mm

The data obtained in Table 3 allows us to state that the addition of 50% zeolite to the epoxy polymer increases the compressive strength of the epoxy composite by 5.5%. And when copper powder is added to the composition, the compressive strength of the epoxy composite increases by 8.2%. Fillers also changes the character of destruction from plastic (the sample crumples like plasticine) to brittle (cracks along the lines).

Table 3

Measurement of compressive strength, assessment of the samples destruction character

Sample	**F_1, kgf**	**F_2, kgf**	**F_3, kgf**	**F_4, kgf**	**F average, kgf**	**Destruction character**
H	350	350	380	380	365	Plastic
Z50%	380	380	390	390	385	Brittle
Z50%+Cu	380	380	395	425	395	Brittle

The mechanical abrasion value of epoxy composites is an important parameter when selecting a material or coating, particularly for implants. So, when epoxy composites are used for joint prosthetics, the mutual friction of the surfaces can be significant, which can lead to the material destruction.

The weight loss M in milligrams has been determined for the sample as a result of abrasion of the cylinder surface against the surface of P60 emery cloth. The coating's abrasion resistance was calculated according to the formula $W=m_1/M$, $W=m_1/M$, where M is the weight loss, m_1 is the initial weight of the sample.

The results presented in Table 4 show that the addition of fillers leads to a marked increase in abrasion resistance.

Table 4

Resistance evaluation to mechanical abrasion

Sample	**Initial weight m_1, mg**	**Weight after abrasion m_2, mg**	**Weight loss M, mg**	**Abrasion resistance W**
H	37	28,5	8,5	4,35
Z50%	44	37	7	6,29
Z50%+Cu	55	48	7	7,86

According to the results of my experiment shown in Table 5, the addition of 50% zeolite increases the microhardness of the epoxy composite, while the addition of copper powder has no effect on microhardness.

Table 5

Surface microhardness measurement of epoxy composites

Sample	**Microhardness, H**		
	10 µm depth	**20 µm depth**	**30 µm depth**
H	100	300	450
Z50%	200	400	#
Z50%+Cu	200	400	#

Note. The # symbol indicates brittle cracking of the sample at the testing time

If epoxy composite is to be used as a coating for metal implants, it is appropriate to study the bond strength of epoxy composite coatings to steel. When testing samples of glued steel tear-off plates Fig. 4 for pull-off strength (adhesion), the value of adhesion strength Table 6 was measured.

Fig. 4. Glued steel tear-off plates for adhesive strength determination

The data of the measurements indicate that the adhesion to the steel at tearing off does not tend to strengthen in the second sample. This is evident from Table 6, the results of which are the most informative.

Table 6.

Load value when measuring adhesion to steel on pull-off

Sample	**F_1, kgf**	**F_2, kgf**	**F_3, kgf**	**F_4, kgf**	**F average, kgf**	**F modified average, kgf**
H	34	35	41	42	38	38
Z50%	22	30	38	51	35	40

Table 7 summarizes the research results for a visual comparison of the strength parameters of epoxy composites.

Table 7

Comparison of strength parameters in samples

Sample	**Compressive strength (avg/max), kgf**	**Abrasion resistance**	**Microhardness, H**	**Adhesion (avg/mod.avg), kgf**
H	365/380	4,35	100/300	38/38
Z50%	385/390	6,29	200/400	35/40
Z50%+Cu	395/425	7,86	200/400	-

According to my experiments on testing the samples-tablets of Fig. 5 for chemical resistance to aggressive hydrogen peroxide medium 60%, it can be stated that zeolite gives the composite more resistance to hydrogen peroxide, but the addition of copper powder to the composition somewhat weakens the positive effect of filling, bringing the swelling index to unfilled H (Table 8, Fig. 6).

Fig. 5. Sample tablets for testing in in aggressive fluids

The degree of swelling is determined by the formula $Q=(m-m_0)/m_0$, where m and m_0 – weight of the reacted and initial sample, respectively.

Table 8

The degree of swelling of experimental samples in 60 % H_2O_2

Time, in days	Sample		
	H	Z50%	Z50%+Cu
0	0,0	0,0	0,0
0,04	1,5	1,7	3,5
1	2,0	2,3	4,7
2	3,5	1,7	4,1
3	4,5	2,9	3,5
5	4,5	2,9	3,5
12	5,1	4,0	4,7

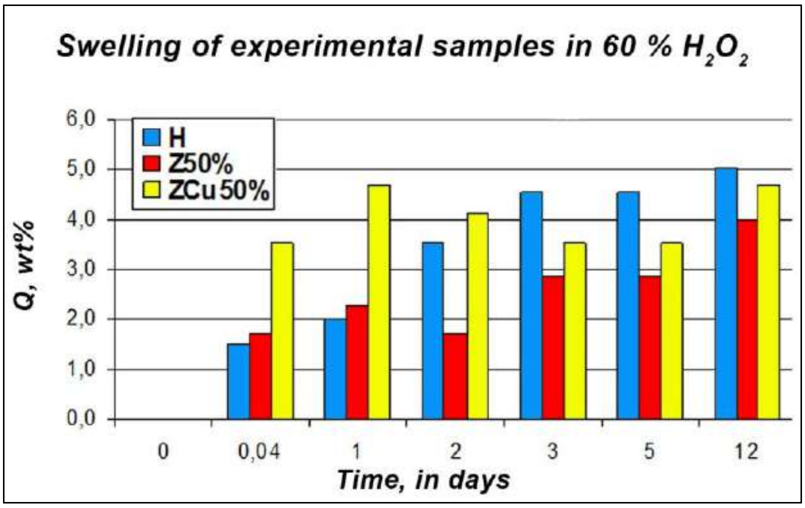


Fig. 6. Swelling histogram of experimental samples in 60 % H_2O_2

Among organic substances, acetone and acetone-based solvents are very aggressive. Unfilled epoxy polymer (especially freshly prepared) degrades in acetone solvents in a matter of days, sometimes even hours. At the same time, filling epoxies can significantly increase their resistance to these aggressive fluids. This can be seen from the results in Table 9 and Fig. 7.

The unfilled sample swells strongly during the first hours of exposure, and by the end of the 1st day of exposure it is completely destructive (crumbles in the solvent). After adding zeolite, the sample does not destruct, and swells much slower than the H sample. Adding copper powder enhances this effect.

Table 9

The degree of swelling of experimental samples in acetone - ethyl acetate mixture

Time, in days	**Sample**		
	H	**Z50%**	**Z50%+Cu**
0	0,0	0,0	0,0
0,03	6,7	2,2	1,1
0,05	7,9	3,1	0,5
0,08	12,1	2,6	1,6
1	destruction	12,7	9,3
2		17,5	12,0
4		17,9	15,3
5		18,8	15,3
8		20,1	18,6
12		21,4	18,6

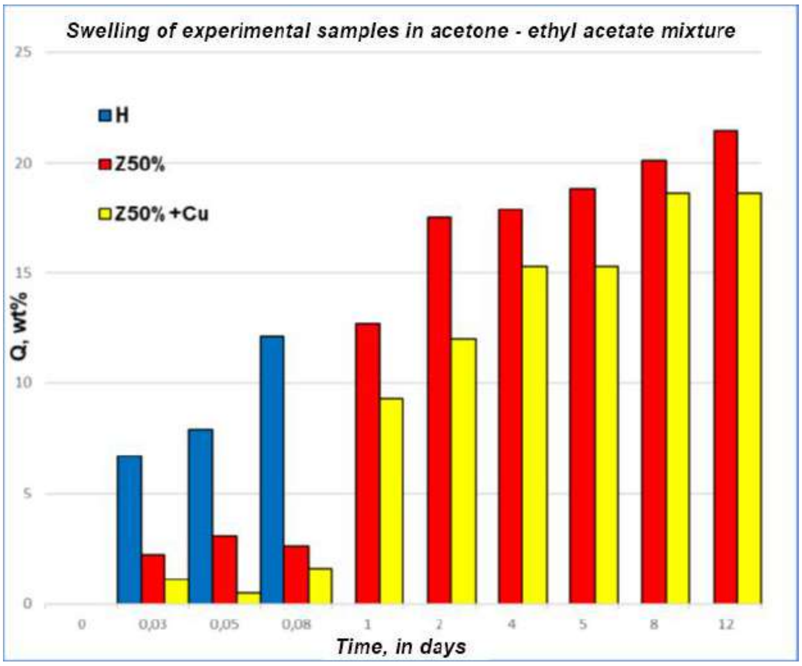


Fig. 7. Swelling histogram of experimental samples in acetone - ethyl acetate mixture

Epoxy composites are generally quite stable in water. Normal is considered a water absorption rate of 1-2% in a month of ageing. Often, however, even this rate needs to be improved. In addition, medical implants have to be in water for many years and high waterproofness is essential.

From my study we can conclude that the addition of zeolite makes the epoxy composite more resistant to the action of water (Table 10, Fig. 8) in the first half month of exposure. Filling even gives the effect of a slight weight loss, which may be caused by the phenomena of substances washout from the zeolite filler structure.

Table 10

The degree of swelling of experimental samples in H_2O

Time, in days	**Sample**	
	H	**Z50%**
0	0,0	0,0
0,04	1,7	1,1
1	1,3	-2,3
2	1,7	-1,5
4	1,7	-1,1
5	0,4	-1,1
12	2,6	-1,1
15	2,8	-1,1

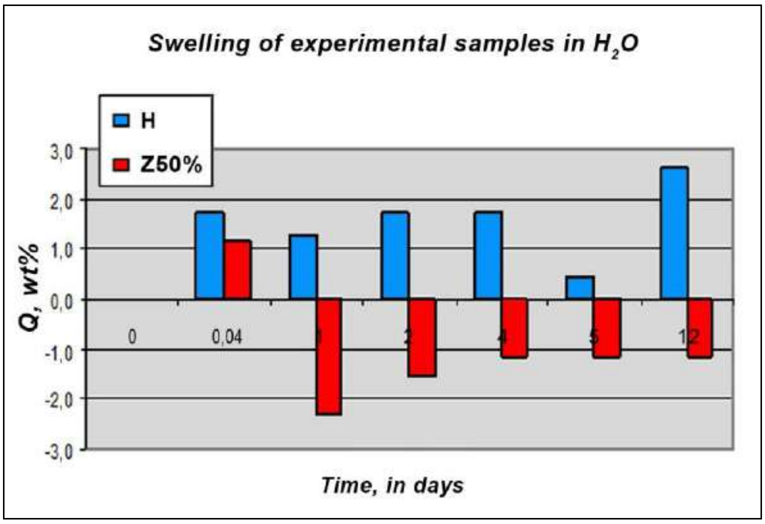


Fig. 8. Swelling histogram of experimental samples in H_2O

Thus, according to my experiments, the synthesized samples with the addition of 50% zeolite to the epoxy composition increased the strength (up to 6%), and with the addition of 12% copper powder to the composition the effect is increased to 8% respectively. It was also found that zeolite significantly increases the resistance of the composite to abrasion and chemical resistance to aggressive fluids and water. The addition of copper microparticles to epoxyceolite compositions allows to vary some properties in several cases. For example, to increase the quality and strengthening effect of composites.

All this has great importance and improves the material properties for medical implants.

Conclusions

My hypothesis that a composite material based on epoxy resin with a dispersed zeolite filler is suitable for imitation of cancellous bone tissue was confirmed. The results indicate that zeolite is promising for bio- and eco-compatible composites.

Ideas for future research

An interesting future experience could be the study of epoxyceolite composites with copper or silver powder to create electro- and thermally conductive materials for medical purposes (prosthetics).

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