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EVALUATION OF COMPOSITE EPOXY RESIN APPLICABILITY FOR CONCRETE COATINGS

The developed composite materials based on epoxy resins show high adhesion to concrete surfaces and good mechanical properties. Thermoplastic epoxy resins with various (380, 1830, 10 800) molecular weights and added polysulfide rubber can be used as coatings and glues. The epoxy composite with 10 800 molecular weight had better mechanical and adhesive properties than those of lower molecular weights. In this work the tensile strength, compressive strength, shear strength, tensile elongation and thermodynamic properties were studied. The materials for the compounds are called thermoplastics, which turn into a plastic state when heated and again solidify on cooling. Hot melt adhesives were first produced at the beginning of the 1950s and every year their production has increased. The new composite copolymer material, based on Bisphenol A, can be used as a thermoplastic composition for concretes, as well as a component or coating for various materials. Their use allows one to achieve high-speed mass production, where they significantly reduce the production time and labor intensity. In this article corrosion processes in concrete and reinforced concrete structures as well as their capability of preventing chemical degradation were examined. Composite materials based on epoxy resins have a great potential to solve this problem. Numerous materials have been developed and examined in the context of use for coatings in reinforced concrete structures. It should be noted that with protective coatings, the physical and mechanical strength of concrete structures increases to 50%, the chemical resistance is improved by several times, while water resistance is increased by 150%. This study also examined the technology for applying epoxy coatings on concrete and reinforced concrete surfaces. The study demonstrated that the coatings enhance the properties of reinforced concrete structures.

Keywords: coating, composite materials, epoxy resins

OCENA PRZYDATNOŚCI KOMPOZYTOWEJ ŻYWICY EPOKSYDOWEJ DO POWŁOK NA BETONIE

Nowoczesne materiały kompozytowe na bazie żywic epoksydowych to m.in. materiały wykazujące wysoką przyczepność do powierzchni betonowych i dobre właściwości mechaniczne. Poprzez modyfikację żywic epoksydowych o różnych masach cząsteczkowych (380, 1830, 10 800) za pomocą syntetycznego kauczuku polisiarczkowego otrzymano wzrost właściwości fizykochemicznych. Nowy kompozytowy materiał kopolimerowy na bazie bisfenolu A może być stosowany jako kompozycja do betonów, a także jako składnik lub powłoka do różnych materiałów. Dotychczasową stosowaną propozycją w przemyśle budowlanym jest zastosowanie farb nitro na bazie żywicy nitrocelulozowej oraz akrylowej o właściwościach hydrofobowych. Posiadają one jednak niskie właściwości adhezyjne podczas procesu eksploatacyjnego. Proponowanym w artykule rozwiązaniem tego problemu jest zastosowanie termoutwardzalnych i termoplastycznych żywic epoksydowych o optymalnych właściwościach mechanicznych, adhezji do podłoża oraz podwyższonej odporności chemicznej na działanie kwasów i zasad. Jak wskazują uzyskane wyniki badań, dzięki powłokom ochronnym wytrzymałość mechaniczna konstrukcji betonowych wzrasta o 50%, a odporność chemiczna w środowisku wodnym wzrasta o 150%. Jediną dostrzeganą przez autorów wadą tych materiałów jest aspekt ekonomiczny oraz brak jak dotąd standaryzacji technologii zastosowania żywic epoksydowych jako powłoki w budownictwie przemysłowym i cywilnym. Zagadnienie to, jak wskazuje analiza literaturowa, dotychczas nie zostało podjęte i stanowi innowacyjną propozycję autorów.

Słowa kluczowe: powłoki, materiały kompozytowe, żywice epoksydowe

INTRODUCTION

Analysis of the scientific literature shows that thermoplastic compounds have unique properties compared to other types of compounds [1-15]. They are characterized by an absence of organic solvents in their composition, ease of technology application, and are environmentally safe. Thermoplastic materials turn into the plastic state when heated and solidify after cooling [7].

Hot melt adhesives began to be produced in the 1950s, with the production level gradually increasing year by year. They can be used in high-speed mass production, significantly reducing production time and labour intensity. Polyamide, polyolefin and polyurethane are the most popular types of thermoplastic compounds available on the market. From this standpoint, epoxy resins

are innovative materials. This results from the fact [1] that thermoplastic epoxy resins have low mechanical properties. Some researchers [4] have proposed the use of epoxy composite material modified with polysulfide rubber.

Reinforced concrete structures are a component of almost every building. Most often, these structures have contact with the environment - atmospheric humidity, precipitation, and aqueous media. Concrete is capable of absorbing water and wetting. Over time, in constant contact with moisture, corrosion develops in the concrete, which leads to chemical destruction of the material. This study examined the LC 40/44 concrete used in bridge structures and components used in supporting structures that are in contact with water. Deterioration of the physical and mechanical characteristics caused by different fluids during 45 days is shown in Figure 1. An alternative method to protect concrete from corrosion is to apply polymer reinforcements. The use of polymer reinforcement has not been researched to date to allow practical application in skyscrapers and various types of concrete in order to improve their functional properties. Another proposition is to use coatings on the concrete. Polyacrylic coatings, nitro paints and coatings with a water repellent are most frequently used in practice [5].

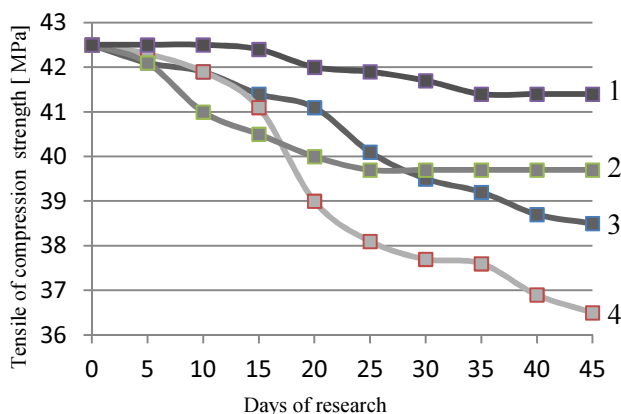


Fig. 1. Compressive strength (MPa) of concrete in: 1 - water, 2 - NaCl (20%), 3 - KOH (20%), 4 - HCl (20%)

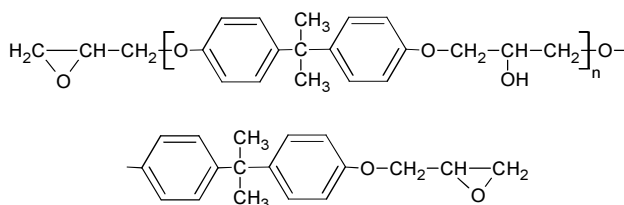
Rys. 1. Wytrzymałość na ściskanie (MPa) betonu w: 1 - wodzie, 2 - NaCl (20%), 3 - KOH (20%), 4 - HCl (20%)

However, protective coatings generate substantial costs. Furthermore, these substances can be destroyed even at low stress values. An excellent solution to this problem is offered by thermosetting and thermoplastic polymer epoxy resins. They are characterized by high mechanical properties, improved adhesion to concrete and improved chemical resistance to acids and alkalis. This makes them promising for use in industry. One drawback of these materials is that they are expensive and no standardized application technology has been developed for epoxy resins as coatings in industrial and civil construction. This paper presents investigations of different epoxy resins as chemical and water-resistant coatings for protecting reinforced concrete structures.

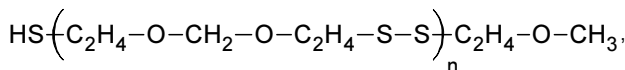
Various kinds of epoxy resins (thermoplastic and thermosetting) of different molecular weight were used for comparison. Study [3] presented a polysulfide rubber formula to enhance stabilization of the physico-mechanical properties of the epoxy resins.

MATERIALS AND METHODS

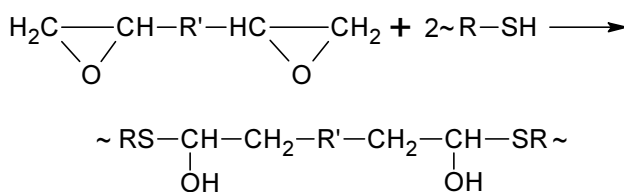
Most imported liquid epoxy resin has a molecular weight of 350÷450. Furthermore, most thermoplastic epoxy resins of a molecular weight < 10000 crack at room temperature due to the large internal stress between the molecules in the material [2]. Epoxy resin with 10 800 molecular weight has distinctive properties due to its longer linear structure. The adhesive characteristics of thermoplastic polymer with regards to metal surfaces can be improved by modification, stabilization and flexibilisation. The structure of epoxy resin (DGEBA/propanol) is:



The structure of liquid polysulfide rubber ($n = 6-10$), viscosity = 28 Pa*sec, HS- = 3.1% is:



The reaction of epoxy resin (DGEBA/propanol) with liquid polysulfide rubber is:



The optimal epoxy resins and their tensile strength characteristics are shown in Table 1.

TABLE 1. Mechanical properties of epoxy compositions
TABELA 1. Właściwości mechaniczne kompozytu epoksydowego

No	Molecular weight	Weight of epoxy groups [%]	Crystallization temperature [°C]	Tensile strength (ISO 6922) [MPa]		
				Titanium «Grade 1»	Aluminium A356.0 A13560	Steel C30
1	390**	22.8	-40÷(-30)	10.3*	23.8*	46.2*
2	1830	4.7	120÷125	0.6	0.9	0.6
3	10800	0.1	210÷220	12.1	14.9	20.1

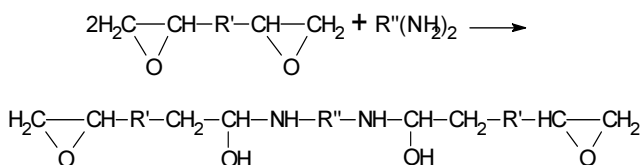
* - hardener: polyethylene polyamine 100:5

** - liquid epoxy resin

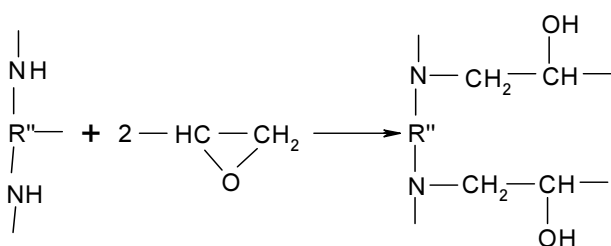
The structure of polyethylene polyamine ($n \geq 4$) is:



When polyethylene polyamines (primary or secondary amines) are added to reactive epoxy resin, the following reaction occurs:



Furthermore, secondary amine or adduct activators interact with the epoxy resin groups, which leads to the formation of cross-linked polymers:



To study the chemical resistance a 20% aqueous solution (sodium hydroxide, potassium hydroxide and hydrogen chloride) was used.

The tensile strength was determined by the ISO 527-2 procedure «Plastics-Determination of tensile properties» and the ISO 6922 procedure «Adhesives-Determination of tensile strength of butt joints». Chemical resistance (W) tests were carried out according to the formula:

$$W(t) = \frac{m(t) - m_0}{m_0} \cdot 100\% \quad (1)$$

where: m_0 - the initial mass of the sample; $m(t)$ - the mass after exposure to an aggressive environment for time (t). The microstructure was examined using the microscope KEYENCE VHX-5000.

RESULTS AND DISCUSSION

The structures of the epoxy resin and epoxy composite are shown in Figures 2 and 3. These Figures show the stabilization effect of polysulfide on the epoxy resin, which mainly leads to amine hardening of the structure and reduction of internal stress. A large amount of polysulfide leads to isolation of the polymer chain. Numerous cracks in the structure were revealed.

The optimal modification of the epoxy resin is presented in Table 2. These are composites that were used as coatings on concrete.

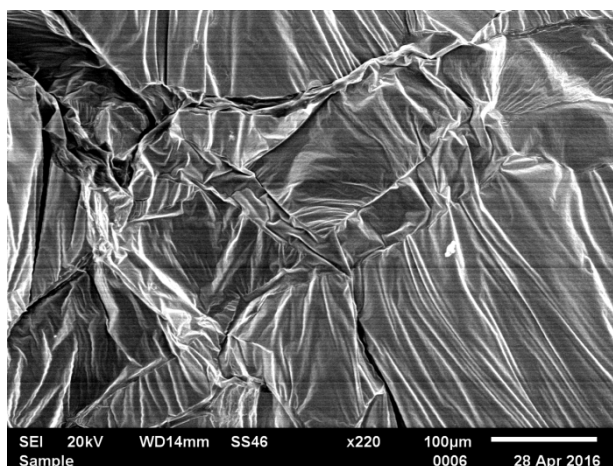


Fig. 2. Structure of epoxy resin (molecular weight: 1830)

Rys. 2. Mikrostruktura żywicy epoksydowej (masa cząsteczkowa: 1830)

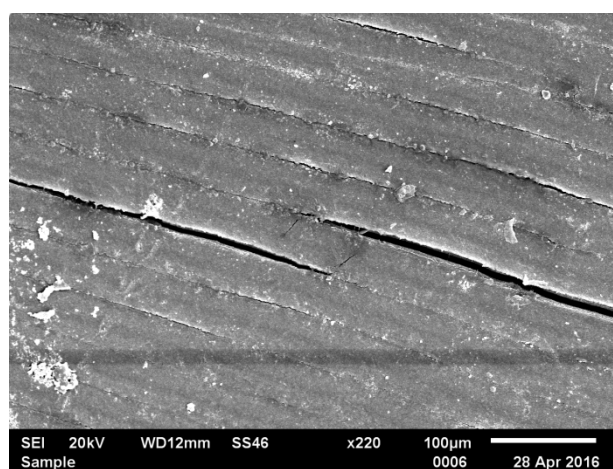


Fig. 3. Structure of epoxy resin (molecular weight: 1830) with polysulfide rubber. 100:60

Rys. 3. Mikrostruktura żywicy epoksydowej (masa cząsteczkowa: 1830) z kauczukiem polisiarczkowym. 100:60

TABLE 2. Optimal modification of epoxy composite material with polysulfide rubber

TABELA 2. Optymalna modyfikacja kompozytu epoksydowego z kauczukiem polisiarczkowym

No	Molecular weight of epoxy resin	Concentration of polysulfide rubber per 100 molecular weight of resin	Tensile strength [MPa]	Shear strength [MPa]	Compression strength [MPa]	Operating temperature range [°C]
1	390**	20	45.7*	12.1*	114*	-30 ... +150
2	1830	60	21	2.5	34	-30 ... +120
3	10800	10	27	5	62	-40 ... +210

* - hardener: polyethylene polyamine 100:5

** - liquid epoxy resin

Investigation of the chemical stability in acid and alkali solutions shows that the modified resin has very good resistance to acid, which is $< 0.7\%$ (Table 3). Chemical resistance tests in an aqueous solution of KOH composite of epoxy resin with polysulfide rubber indicate that the composites have a weight loss less than

2% in the case of composites with a ratio of 100:60. At high concentrations it is up to < 4.2% (Fig. 4).

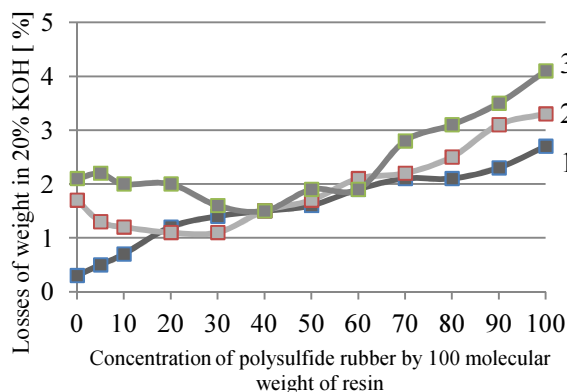


Fig. 4. Dependence of weight loss on concentration of polysulfide rubber (30 days). Molecular weight of epoxy polymers: 1 - 390; 2 - 1830; 3 - 10 800

Rys. 4. Zależność ubytku masy od dodatku kauczuku polisulfidowego. Masa molekularna polimeru: 1 - 390; 2 - 1830; 3 - 10 800

TABLE 3. Resistance of epoxy resin composition with rubber to NaCl and HCl water solutions (30 days)

TABELA 3. Odporność kompozytu żywica epoksydowa z kauczukiem polisulfidowym w roztworze NaCl i HCl (30 dni)

No	Molecular weight of epoxy resin based	Loss in weight [%]	
		HCl 20%	NaCl 20%
1	390*	< 0.4	< 0.3
2	1830	< 0.7	< 0.7
3	10800	< 0.2	< 0.1

* - hardener: polyethylene polyamine 100:5

In the next step, the strength properties of the concrete with and without the composite coating were determined. It should be noted that the strength properties of concrete immersed in a solution of water, salt and acid are less than 1% (0.4 MPa). The graph of the compressive strength of the concrete samples with a composite coating immersed in a solution of KOH is presented in Figure 5.

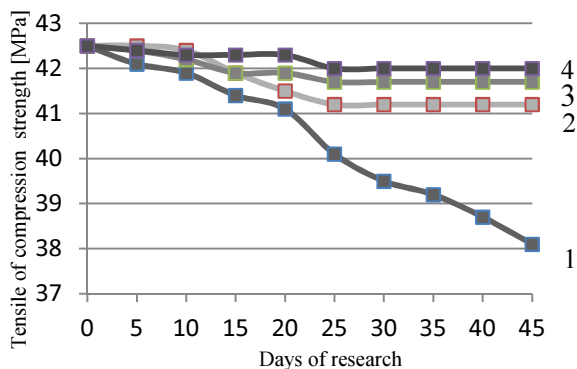


Fig. 5. Dependence of compression strength [MPa] on day of study. Molecular weight of epoxy polymers: 1 - 1240; 2 - 1830; 3 - 640; 4 - 10 800

Rys. 5. Wytrzymałość na ściskanie w funkcji czasu badania. Masa cząsteczkowa żywicy epoksydowej: 1 - 1240; 2 - 1830; 3 - 640; 4 - 10 800

The main results are listed in Table 4. In addition, the test results in Table 4 show that concrete with composite coatings exhibits higher compressive strength after 45 days in alkali, salt and acid. From the research results it can be concluded that modified epoxy resin can be used as protective coatings for concrete.

TABLE 4. Chemical resistance of composites based on epoxy resin after 45 days of study

TABELA 4. Odporność chemiczna kompozytu na bazie żywicy epoksydowej po 45 dniach badania

	Compression strength [MPa]							
	Water		Salt (20% in water)		Alkali (20% in water)		Acid (20% in water)	
	Index	Difference [%]	Index	Difference [%]	Index	Difference [%]	Index	Difference [%]
Concrete (42.5 MPa)	41.4	3.1	39.7	6.6	38.5	9.5	36.5	14.5
Concrete \Epoxy 390	42.3	0.5	> 42.1	0.9	41.3	3.1	> 42.1	0.9
Concrete \Epoxy 1830	42.0	1.2			41.7	2.9		
Concrete \Epoxy 10800	42.1	1.1			42	2.5		

CONCLUSIONS

The results of this work show that modifying epoxy with polysulfide rubber leads to an increase in the mechanical properties of the composite materials. These composites can be used as protective and waterproof coatings in concrete. Therefore, the solution presented in the study offers an alternative method for protecting concrete and reinforced concrete structures that are used in contact with water and aggressive environments.

REFERENCES

- [1] Bezgin V.S., Adhesive properties of compositions based on solid epoxy resins, Ukrainian Conference of Macromolecular Compounds, Kiev. Coll. rep. 2013, 11-15.
- [2] Kochergin Y.S., Bezgin V.S., Structural hot melt adhesives with improved consumer properties, Vestnik DonNABA 2013, Makeevka, 2013, 133-138.
- [3] Bezgin V.S., Hot melt adhesives based on polyhydroxy. Conf. Recent advances in the field of adhesives and sealants, Materials. Raw. Tehnoogii, Dzerzhinsk, Nizhegor. region 2013, 121-124.
- [4] Pushkareva K.K., Bezgin V.S., New kinds of epoxy composites in building, The X International Scientific Conference for students and young scholars «Science and education - 2015», Astana 2015, 2015, 6366-6371.
- [5] Jonesa A.R., Watkinse C.A., Whited S.R., Sottosc N.R., Self-healing thermoplastic-toughened epoxy, Polymer 2015, 74, 15 September 254-261.

- [6] Yongtao Yao, Jingjie Wang, Haibao Lu, Ben Xu, Yongqing Fu, Yanju Liu, Jinsong Leng, Thermosetting epoxy resin/thermoplastic system with combined shape memory and self-healing properties, *Smart Materials and Structures* 2016, 1.
- [7] Functional polymer blends: synthesis, properties and performances, ed. V. Mittal, Taylor and Francis Group, New York 2012.
- [8] Rui Liu, Jinyan Wang, Jinlong Li, Xigao Jian, An investigation of epoxy/thermoplastic blends based on addition of a novel copoly(aryl ether nitrile) containing phthalazinone and biphenyl moieties, *Polymer International* 2015, 64, 12, 1786-1793, December.
- [9] Yingfeng Yu, Gebin Shen, Zhuoyu Liu, Morphology of Epoxy/Thermoplastic Blends, *Handbook of Epoxy Blends*. 1-34. Date: 09 January 2016.
- [10] Williams J.G., Fracture mechanic copolymers, *Polymer Eng. Sci.* 1977, 17, 144-149.
- [11] d'Hooge E.L., Edwards C.M., *Advanced Materials* 2000, 12, 23, Dec. 1.
- [12] Van Rijswijk K., Bersee H., Reactive processing of textile fiber-reinforced thermoplastic composites, An overview, *Composites Part A: Applied Science and Manufacturing* 2007, 38, 666-681.
- [13] Martone A., Formicola C., Giordano M., Zarrelli M., Reinforcement efficiency of multi-walled carbon nanotube/epoxy nano composites, *Composites Science and Technology* 2010, 70, 1154-1160.
- [14] Allaoui A., How carbon nanotubes affect the cure kinetics and glass transition temperature of their epoxy composites? - A review, *EXPRESS Polymer Letters* 2009, 3, 588-594.
- [15] Deng S., Djukic L., Paton R., Ye L., Thermoplastic - epoxy interactions and their potential applications in joining composite structures - A review, *Composites Part A: Applied Science and Manufacturing* 2015, 68, January, 121-132.