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THE EXPERIMENTAL RESEARCH ON ADHESION AND MASS LOSS FOR REINFORCING STEEL COVERED WITH POLYMERIC SULPHURIC COMPOSITES

This paper presents the results of the experimental research and analyses indicating the usefulness of polymer sulphur composites to the protection against corrosion of reinforcement. In paper presents materials also the domain of the personal investigations and the methodology are definite. After the analyze of the initial results the optimum compositions have been chosen to the experimental research. In paper the review of the literature have been done, among other things about select using polymer sulphur composites in buildings, about the methods of the surface protection against corrosion of reinforcement and about the methods of the evaluation of protection layer on these materials. The experimental programme comprised the adhesion of sulphur polymer composite layer to rebars under tension and bending, adjacent adhesion of sulphur polymer composite layer to reinforcing bars, adjacent adhesion of sulphur polymer composite to rebars in pushed-out test, adjacent adhesion of concrete to rebars coated with sulphur polymer composite, and mass loss of plain rebars in aqueous solutions of acids, hydroxides and salts and in water. In paper the usefulness of polymer sulphur composites to the surface protection against corrosion of the reinforcement have been evaluated.

Keywords: **adhesion, mass loss, polymer sulphur composites, surface protection against corrosion, reinforcement**

BADANIA EKSPERYMENTALNE PRZYCZEPNOŚCI I UBYTKU MASY PRĘTÓW ZBROJENIOWYCH POKRYTYCH POLIMEROWYM KOMPOZYTEM SIARKOWYM

Przedstawiono rezultaty badań eksperymentalnych i analiz wykazujących przydatność polimerowych kompozytów siarkowych do ochrony przed korozją stali zbrojeniowej. W artykule podano skład materiału, rezultaty badanych właściwości i metodykę przeprowadzonych badań. Wybrano do dalszych badań polimerowy kompozyt siarkowy, charakteryzujący się najkorzystniejszymi, spośród badanych, właściwościami. Dokonano przeglądu literaturowego, między innymi, w zakresie wybranych zastosowań polimerowych kompozytów siarkowych w budownictwie, metod i sposobów powierzchniowej ochrony przed korozją stali zbrojeniowej, a także metod i sposobów oceny szczelności warstw zabezpieczających ten materiał przed korozją. Przeprowadzono badania eksperymentalne dla wybranych polimerowych kompozytów siarkowych. Program badań eksperymentalnych obejmował zbadanie: przyczepności warstwy polimerowego kompozytu siarkowego do prętów zbrojeniowych rozciąganych i zginanych, przyczepności stycznej warstwy polimerowego kompozytu siarkowego do prętów zbrojeniowych, przyczepności stycznej polimerowego kompozytu siarkowego do prętów zbrojeniowych wypychanych z tego kompozytu, przyczepności stycznej betonu do prętów zbrojeniowych pokrytych warstwą polimerowego kompozytu siarkowego i ubytku masy prętów zbrojeniowych gładkich w roztworach wodnych kwasów, wodorotlenków i soli oraz w wodzie. Wykazano przydatność polimerowych kompozytów siarkowych do powierzchniowej ochrony przed korozją stali zbrojeniowej.

Słowa kluczowe: **przyczepność, ubytek masy, polimerowe kompozyty siarkowe, powierzchniowa ochrona przed korozją, stal zbrojeniowa**

INTRODUCTION

Some specific environments with varied corrosivity occur in agriculture and in food- and beverage-industries. Soil with varied composition, structure and corrosivity, fertilizers, organic environment of live-stock buildings, and the atmosphere of chemical industries manufacturing plant protectives and fertilizers are among the most significant [1-6].

As far as construction made of reinforced concrete is concerned the corrosivity of live-stock building environment is much higher than that typical for rural one and it may be compared to that of atmosphere of chemical industry. It depends on humidity and on concentration of compounds which make electrical conductivity of the condensate to increase and react chemically with after that they have dissolved in it [7].

There are several ways possible of protecting ferro-concrete constructions: pre-galvanizing steel, using alloy steel, cathodic protection, electrochemical extraction of chlorides, re-alkalizing carbonated concrete [1, 2, 6]. Protective coating, if needed, can be used to prevent corrosion of reinforcing steel, e.g. when concrete envelope may not to be tight, too thin or none, on connecting parts of precast concrete units. Sulfuric polymeric coating may be an example [2-5].

Surface protection of the reinforcing steel, in the form of a hermetic protective coating, considerably reduces or prevents the access of the surrounding gas or water environment to the reinforcing steel [1, 7, 8]. Various materials, e.g. polymer epoxy resins [7, 8], inhibiting agents (inhibitors) [6, 9], noble metal admixtures [1, 6], or cathodic protection [1, 6, 9] are used for this purpose. It seems that such protection can be provided by coating rebars with a polymer sulphur composite composed of a sulphuric binder, fillers and proper additives. Even though sulphur binders show: resistance to many aggressive water solutions, low absorbability, surface hydrophobicity and quite high (tangent and normal) adhesion to the surface of many materials (including metallic surfaces), they have not been used for this purpose before [2, 4].

In order to demonstrate the suitability of sulphur polymer composites for the surface protection of concrete steel experimental research was carried out in the Institute of Building Engineering at Wrocław University of Technology. The research included: the experimental determination of sulphur polymer composite composition and manufacturing conditions, tests of the composite's selected physical, chemical and mechanical properties, tests of its tangent and normal adhesion to plain and ribbed reinforcing bars and to standard cement mortar and concrete, the determination of the mass decrement resulting from storage in aqueous solutions of acids, hydroxides and salts and in water and the polarization investigation of rebars subjected to tension in a solution modelling the pore liquid in carbonated concrete contaminated with chlorine ions [4].

DESCRIPTION OF INVESTIGATIONS

Sulphur polymer composites were investigated in two stages. In the first stage, compositions were fixed and thirty test sulphur polymer composites were prepared and pretested. When fixing the compositions, the binder (S_8) content was changed in a range of 55÷65%. Mineral powder, silica dust from a drying plant, high-silica sand and plain sand and cement were used as the filler. Carbon black and anthracene oil were used as the additive. The pretesting included preparing composites and determining their basic physical and mechanical properties, such as: bulk density, absorbability by wt., bending strength and splitting tensile strength. The experimental results are reported in detail in [4].

The results of the preliminary tests were analyzed and the sulphur polymer composite having the best properties among the tested composites was selected for further studies. The composition of the composite is given in table 1 and its experimentally determined properties are shown in Table 2 [4].

TABLE 1. **Composition of selected sulphur polymer composite [4]**
TABELA 1. **Skład polimerowego kompozytu siarkowego [4]**

Content in [%] of total composite mass		
Binder	Filler	Additive
Sulphur S_8 %	Mineral quartz dust %	Carbon black %
63	33	4

The adhesion of a 0.2÷4.0 mm thick sulphur polymer composite layer to plain St3S reinforcing steel samples and ribbed 34GS steel samples, 10 mm in diameter and 160 mm long, was tested. The adjacent adhesion of a 1.5 mm thick sulphur polymer composite layer to rebars under tension and bending and to rebars being pushed out of this composite was tested on plain steel St3S samples and ribbed steel 34GS samples, 10 and 20 mm in diameter and 160 mm long. Also the adjacent adhesion of concrete to reinforcing bars coated with a 1.5 mm thick layer of the sulphur polymer composite was tested on plain reinforcing steel St3S and ribbed steel 34GS samples, 10 mm and 20 mm in diameter and 160 mm long.

TABLE 2. **Experimentally determined properties of sulphur polymer composites [4]**
TABELA 2. **Rezultaty badanych właściwości polimerowego kompozytu siarkowego [4]**

Average bulk density ρ_{pm} g/cm^3	Average absorbability by wt. n_{wm} %	Average bending strength f_{dm} MPa	Average splitting tensile strength $f_{ct,sp}$ MPa	Average compressive strength f_{cmc} MPa	Coefficient of fragility k -	Coefficient of direct elasticity E_{dm} under bending MPa	Coefficient of direct elasticity E_{cm} under compression MPa
2.10	0.05	<u>11.9</u> 4.9%	<u>3.4</u> 6.1%	<u>51.2</u> 6.2%	0.93	64840	66969

Note: the percentages under the line are coefficients of variation

The decrement in the mass of rebars coated with the composite and stored in aqueous solutions of acids and salts and in water for 1 year was determined using plain St3S steel samples, 10 mm and 20 mm in diameter and 160 mm long.

TEST RESULTS AND THEIR ANALYSIS

Adhesion of sulphur polymer composite layer to rebars under tension and bending

Figure 1 shows at what average values of stress σ_{pm} tensioning plain and ribbed rebars 10 mm in diameter a 0.2÷4.0 mm thick layer of the tested sulphur polymer composite gets unstuck from the surface of the rebars. According to this Figure, regardless of the polymer layer thickness, this stress is higher for the ribbed reinforcing bars. In this case, the maximum stress σ_{pm} (amounting to 560 MPa) occurs when the thickness of the polymer layer is in a range of 1.3÷1.6 mm. Whereas in the case of the plain rebars stress $\sigma_{pm}$is less dependent on the polymer composite layer, although at a thickness of 0.5÷0.6 mm this stress is higher, amounting to 320 MPa.

Figure 2 shows at what average bending stress σ_{dm} in plain and ribbed rebars 10 mm in diameter a 0.2÷÷3.0 mm thick layer of the tested sulphur polymer composite separates from the surface of the rebars. Also here this stress is higher in the ribbed rebars. According to Figure 2, stress σ_{dm} is the highest when the polymer composite layer is 0.2 mm thick. Also as the thickness of the layer increases, the bending moment at which the layer gets unstuck generally decreases. But at the layer thickness of about 1.4÷1.6 mm the downward trend of stress σ_{dm} clearly slows down, reaching a distinct local minimum. For example, in the ribbed rebars coated with the composite this stress amounts to 48.4 MPa. The tests have shown that the separation of a 0.2÷4.0 mm thick layer of the sulphur polymer composite from the surface of tensioned and bent ribbed rebars always occurs at higher values of stress than in the case of plain rebars of the same diameters. The optimum thickness of the layer for ribbed reinforcing bars is 1.5 mm. In the case of bent plane and ribbed reinforcing bars, the optimum thickness of the layer is 0.2 mm, though it seems that it can be as well 1.5 mm.

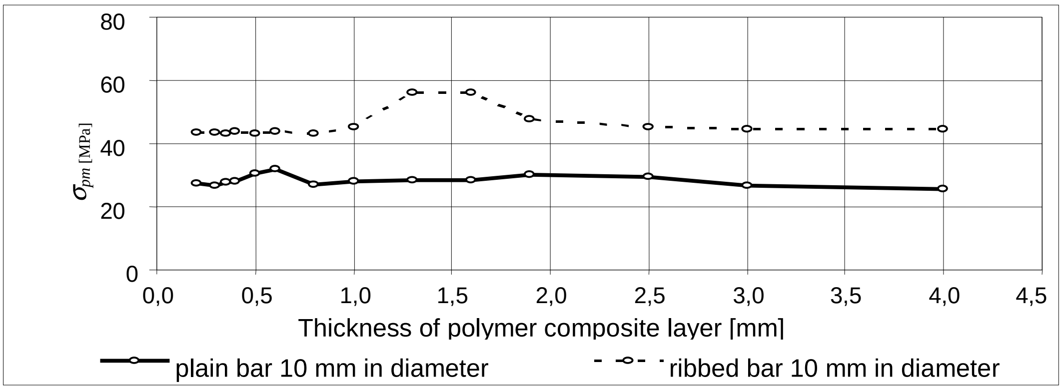

Fig. 1. Average values of stress tensioning rebars 10 mm in diameter, at which sulphur polymer composite layer of different thickness gets unstuck

Rys. 1. Wartości średnie naprężenia rozciągającego pręty zbrojeniowe o średnicy 10 mm, przy których następuje odspojenie warstwy o różnej grubości polimerowego kompozytu siarkowego

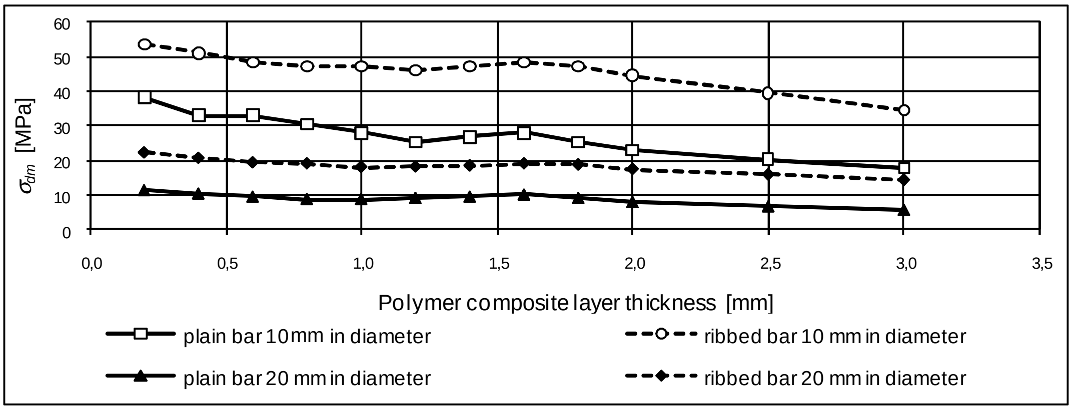

Fig. 2. Average values of stress bending rebars 10 and 20 mm in diameter, at which sulphur polymer composite layer of different thickness gets unstuck

Rys. 2. Wartości średnie naprężenia zginającego pręty zbrojeniowe o średnicy 10 i 20 mm, przy których następuje odspojenie warstwy o różnej grubości polimerowego kompozytu siarkowego

Adjacent adhesion of sulphur polymer composite layer to reinforcing bars

The averages values of tangent adhesion τ_{wm} of a 1.5 mm thick sulphur polymer composite layer to plain and ribbed rebars 10 and 20 mm in diameter are shown in Figure 3.

According to the test results, the adjacent adhesion of a 1.5 mm thick sulphur polymer composite layer to the ribbed rebars is twice higher than that to the plain rebars of the same diameter. It is also higher than in the case of the smaller diameter rebars, regardless of whether they are plain or ribbed.

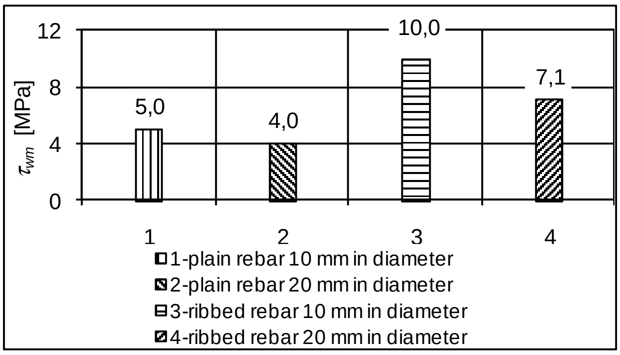

Fig. 3. Average values of adjacent adhesion of 1.5 mm thick sulphur polymer composite to plain and ribbed rebars 10 mm in diameter and 20 mm in diameter

Rys. 3. Wartości średnie przyczepności stycznej warstwy polimerowego kompozytu siarkowego o grubości 1,5 mm do prętów zbrojeniowych gładkich i żebrowanych o średnicy 10 i 20 mm

Adjacent adhesion of sulphur polymer composite to rebars in pushed-out test

The average values of adjacent adhesion τ_{wm} of the sulphur polymer composite to plain and ribbed rebars 10 mm in diameter in the push-out test and the same results for rebars 20 mm in diameter are shown in Figure 4.

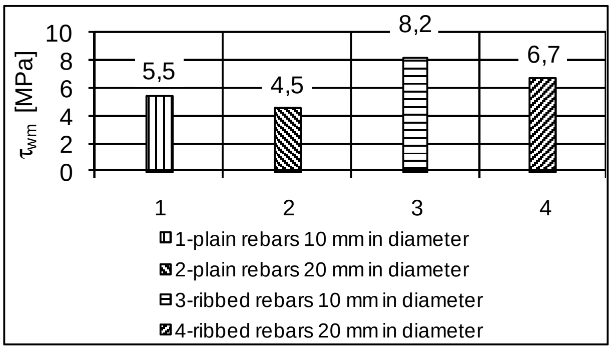

Fig. 4. Average values of tangent adhesion of sulphur polymer composite to plain and ribbed rebars 10 mm in diameter and 20 mm in diameter, being pushed out of composite

Rys. 4. Wartości średnie przyczepności stycznej polimerowego kompozytu siarkowego do prętów zbrojeniowych gładkich i żebrowanych, wypychanych z tego kompozytu, o średnicy 10 i 20 mm

According to the test results, the average values of adjacent adhesion of the composite to the ribbed rebars are much higher than those for the plain rebars. They are also higher for the smaller diameter (10 mm) rebars as compared to the 20 mm diameter rebars, regardless of whether they are plain or ribbed.

Adjacent adhesion of concrete to rebars coated with sulphur polymer composite

The test results for adjacent adhesion τ_{wm} of ordinary concrete to plain rebars 10 mm in diameter, coated with a 1.5 mm thick layer and to plain rebars 20 mm in diameter are shown in Figure. 5. The results denoted by the digits 1, 2 and 3 are for ordinary concrete made using respectively rounded aggregate, crushed basalt aggregate and crushed granite aggregate. The average values of this adjacent adhesion to rebars 10 mm in diameter and 20 mm in diameter, coated with a 1.5 mm thick layer of the sulphur polymer composite are shown in Figure 6.

For comparison purposes, Figures 5 and 6 show the adjacent adhesion (τ_{wm}) of ordinary concrete: made using respectively rounded aggregate, crushed basalt aggregate and crushed granite aggregate, to uncoated rebars.

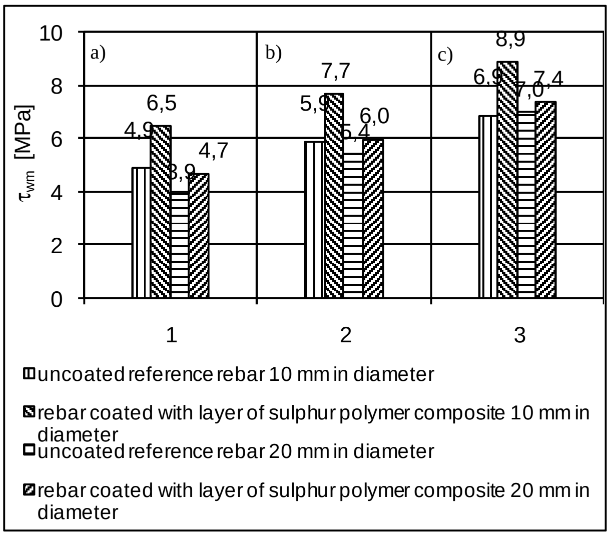

Fig. 5. Average values of adjacent adhesion of ordinary concrete to plain rebars 10 mm in diameter and 20 mm in diameter, coated with 1.5 mm thick layer of sulphur polymer composite, a) concrete made using rounded aggregate, b) concrete made using crushed basalt aggregate and c) concrete made using crushed granite aggregate

Rys. 5. Wartości średnie przyczepności stycznej betonu zwykłego do prętów zbrojeniowych gładkich o średnicy 10 i 20 mm, pokrytych warstwą kompozytu siarkowego o grubości 1,5 mm: a) beton wykonany z użyciem kruszywa otoczakowego, b) beton wykonany z użyciem kruszywa łamanego bazaltowego, c) beton wykonany z użyciem kruszywa łamanego granitowego

It follows from the results shown in Figures 5 and 6 that in comparison with the uncoated reference rebars, higher values of adjacent adhesion to both plain and ribbed rebars 10 m and 20 mm in diameter are obtained when the rebars are coated with a layer of the sulphur polymer composite. Then the adhesion values are in a range of 4.7÷15.6 MPa depending on the kind of aggregate used, the rebar diameter and the grade of the rebar steel.

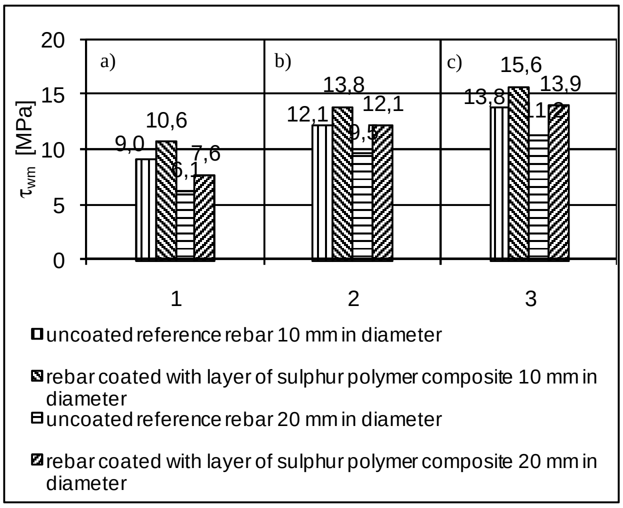

Fig. 6. Average values of adjacent adhesion of ordinary concrete to ribbed rebars 10 mm in diameter and 20 mm in diameter, coated with 1.5 mm thick layer of sulphur composite, a) concrete made using rounded aggregate, b) concrete made using crushed basalt aggregate, c) concrete made using crushed granite aggregate

Rys. 6. Wartości średnie przyczepności stycznej betonu zwykłego do prętów zbrojeniowych żebrowanych o średnicy 10 i 20 mm, pokrytych warstwą kompozytu siarkowego o grubości 1,5 mm: a) beton wykonany z użyciem kruszywa otoczakowego, b) beton wykonany z użyciem kruszywa łamanego bazaltowego, c) beton wykonany z użyciem kruszywa łamanego granitowego

Therefore it can be concluded that a 1.5 mm thick layer of sulphur polymer composite applied to plain and ribbed rebars of different diameters does not reduce their adjacent adhesion to concrete.

Mass loss of plain rebars in aqueous solutions of acids, hydroxides and salts and in water

Figure 7 shows the average mass loss (in %) for plain rebars 10 mm in diameter, coated with a 0.6 mm and 1.5 mm thick layer of sulphur polymer composite, immersed in acid aqueous solutions for 1 year. According to the figure, the average mass loss for plain rebars coated with the composite and stored in 5% solutions of H_2SO_4 and HCl and in a 10% solution of CH_3COOH is small - below 0.9%. Whereas in a 5% solution of HNO_3 the average mass loss for the rebars is larger, amounting to respectively 3.5 and 3.9%, depending on the protective layer thickness. One should note that the loss in the mass of the rebars coated with the tested composite only to a small degree depend on the thickness of the coating.

Figure 8 shows the mass loss for rebars 10 mm in diameter, stored in aqueous solutions of hydroxides and in water. According to the figure, the average mass loss for the rebars, coated with a 0.6 and 1.5 mm thick layer of the sulphur polymer composite, stored in a saturated solution of $Ca(OH)_2$ and in H_2O, is negligible, being in a range of 0.1÷0.4%. Whereas in both a 5% solution of NaOH and a 5% solution of KOH this loss is very large, amounting to respectively 47.8% and 30.0%.

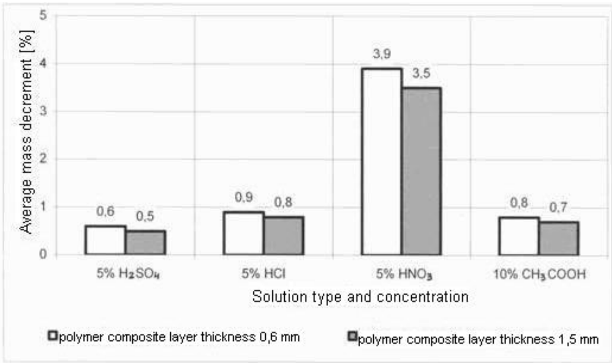

Fig. 7. Average mass loss (in %) for plain rebars 10 mm in diameter, coated with layer of sulphur polymer composite, stored in aqueous solutions of acids for 1 year

Rys. 7. Średni procentowy ubytek masy prętów zbrojeniowych gładkich o średnicy 10 mm, pokrytych warstwą polimerowego kompozytu siarkowego, przechowywanych w roztworach wodnych kwasów przez okres 1 roku

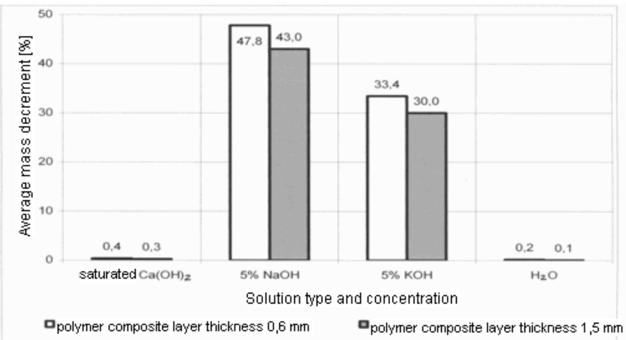

Fig. 8. Average mass loss (in %) for plain rebars 10 mm in diameter, coated with layer of sulphur polymer composite, stored in aqueous solutions of hydroxides and in water for 1 year

Rys. 8. Średni procentowy ubytek masy prętów zbrojeniowych gładkich o średnicy 10 mm, pokrytych warstwą polimerowego kompozytu siarkowego, przechowywanych w roztworach wodnych wodorotlenków i w wodzie przez okres 1 roku

The average mass loss for rebars 10 mm in diameter, coated with the composite and stored in aqueous solutions of salts are shown in Figure 9. According to the figure, the average mass loss for the rebars stored in: a 10% solution of NaCl, a 10% solution of $(NH_4)_2SO_4$, a 10% solution of $CaCl_2$, a 10% solution of K_2CO_3 and a 10% solution of $CaCO_3$ is slight, being in a range of 0.1÷0.7%.

The investigations have shown that after storage in aqueous solutions of acids, hydroxides and salts and in water the loss in the mass of plain reinforcing bars coated with a layer of the sulphur polymer composite depends mainly on the type of the environment and to a lesser degree on the thickness of the coating. For example, for the 1.5 mm thick sulphur polymer composite layer the largest loss in the mass of the rebars was recorded in a 5% solution of HNO_3 - 3.9% and in 5% solutions of hydroxides KOH and NaOH - 30% and 43%, respectively. The smallest loss in the mass of the rebars, i.e. 0.1%, was recorded in water.

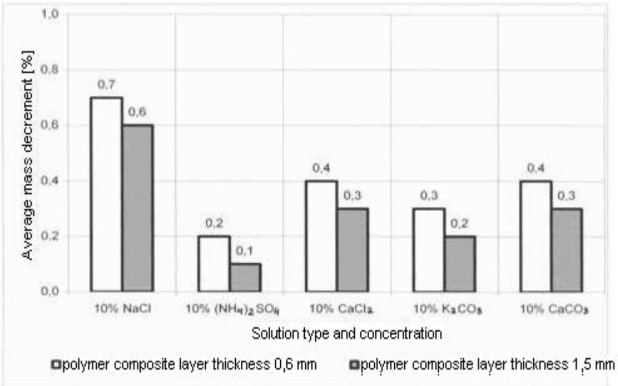

Fig. 9. Average mass loss for plain rebars 10 mm in diameter, coated with layer of sulphur polymer composite, stored in aqueous solutions of salts for 1 year

Rys. 9. Średni procentowy ubytek masy prętów zbrojeniowych gładkich o średnicy 10 mm, pokrytych warstwą polimerowego kompozytu siarkowego, przechowywanych w roztworach wodnych soli przez okres 1 roku

Similar results as for the 10 mm diameter rebars were obtained for the 20 mm diameter rebars [4].

CONCLUSION

It can be concluded from the test results that the tested sulphur polymer composite can provide surface corrosion protection to the reinforcing steel in concrete. Sulphur composites have not been applied for this purpose before.

The tests have shown that a proper thickness of the sulphur polymer composite and the type of surrounding corrosion environment are important factors here. One can conclude that the optimum thickness of the sulphur polymer composite layer should be 1.5 mm and the reinforcing steel protected with this composite should not be used in aqueous solutions of HNO_3 and KOH and NaOH.

The authors are aware that although the range of the tests carried out so far is quite wide, still further tests are needed to ultimately determine the suitability of the sulphur polymer composite for the surface protection of the reinforcing steel in concrete against corrosion. Also a simple and practical technology of applying this material to the surface of reinforcing steel needs to be developed.

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