



## Research on usability of sulphur polymer composite for corrosion protection of reinforcing steel in concrete

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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. Presented in paper materials, being also the domain of the personal investigations and the methodology are definite. After analyze of the initial results the optimum compositions have been chosen for the experimental research.

Keywords: *corrosion, reinforcing steel, tensile stress, polymeric sulphuric coating, polarization*

### 1. Introduction

The degradation of reinforced concrete may be caused by the corrosion of the reinforcing steel or the concrete or by the simultaneous corrosion of the reinforcing steel and the concrete [2–5]. The considerable porosity of concrete and cracks in or damage to the concrete cover contribute to the diffusion, absorption and adsorption of gases and to the diffusion of the substances dissolved in the pore liquid deep into the concrete. All kinds of aggressive substances from the surrounding environment diffuse into the concrete and directly or indirectly cause the corrosion of the reinforcing steel, which usually ends in the loss of adhesion of the concrete to the steel, manifesting itself in the fracturing, loosening and spalling of the concrete cover [1, 5, 7–9, 13, 17, 23].

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 [18]. Various materials, e.g. polymer epoxy resins [2, 3–5, 7, 19], inhibiting agents (inhibitors) [5, 13, 17, 21, 22], noble metal admixtures [5, 17], or cathodic protection [5, 10–12, 17, 23–25] 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 [6, 13–16, 20].

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 [14].

## 2. Description of investigations

Sulphur polymer composites were investigated in two stages. In the first stage, compositions were fixed and thirty tests 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 [14].

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.

Table 1. Composition of selected sulphur polymer composite [14]

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

Table 2. Experimentally determined properties of sulphur polymer composites [14]

Average bulk density $\rho_{pm}$ [g/cm <sup>3</sup> ]	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 under bending $E_{dm}$ [MPa]	Coefficient of direct elasticity under compression $E_{cm}$ [MPa]
2.10	0.05	$\frac{11.9}{4.9\%}$	$\frac{3.4}{6.1\%}$	$\frac{51.2}{6.2\%}$	0.93	64840	66969

Note: the percentages under the line are coefficients of variation.

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 mm 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.

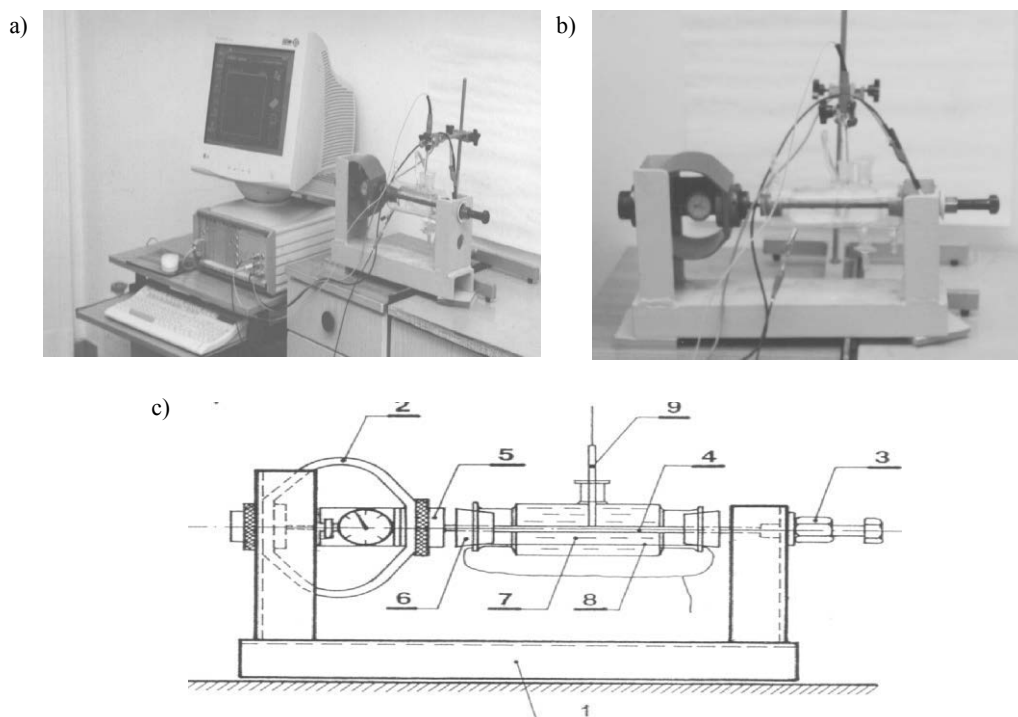


Fig. 1. Device for polarization testing of tensioned rebars: a), b) view of rig, c) schematic of rig (side view), 1 – metal frame, 2 – mechanical dynamometer, 3 – clamping screw, 4 – sample of rebar coated with composite, 5 – dynamometer connector, 6 – rubber stopper, 7 – glass container filled with model pore liquid solution, 8 – platinum wire, 9 – calomel electrode

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.

Polarization investigations of tensioned rebars coated with the sulphur polymer composite were carried out on plain St3S reinforcing steel samples immersed in

a solution modelling the porous liquid in carbonated concrete contaminated with chloride ions. The samples were 10 mm in diameter and 290 mm long. A general view of the polarization test device is shown in Figure 1: a, b, c [10–11, 13–15, 23–25].

### 3. Test results and their analysis

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

Figure 2 shows at what average values of stress  $\sigma_{pm}$  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  $\sigma_{pm}$  (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 3 shows at what average bending stress  $\sigma_{dm}$  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 3, stress  $\sigma_{dm}$  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  $\sigma_{dm}$  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.

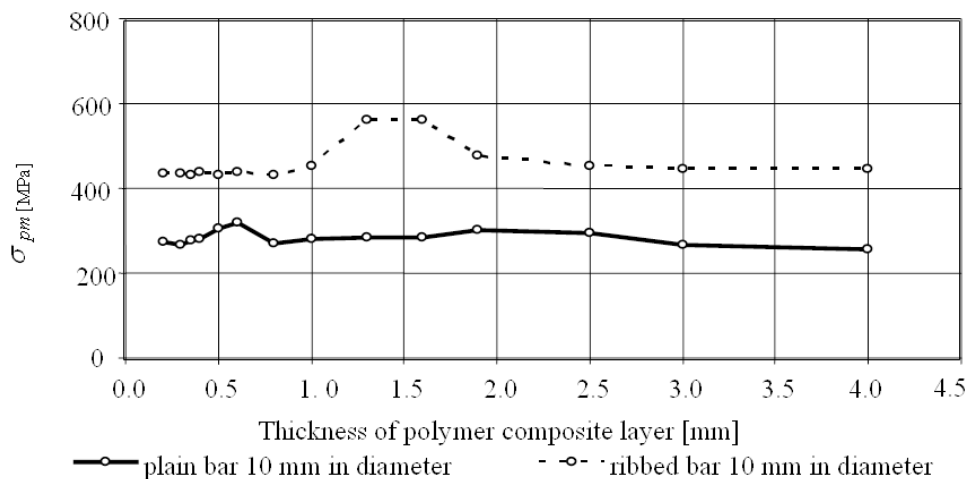


Fig. 2. Average values of stress tensioning rebars 10 mm in diameter, at which sulphur polymer composite layer of different thickness gets unstuck

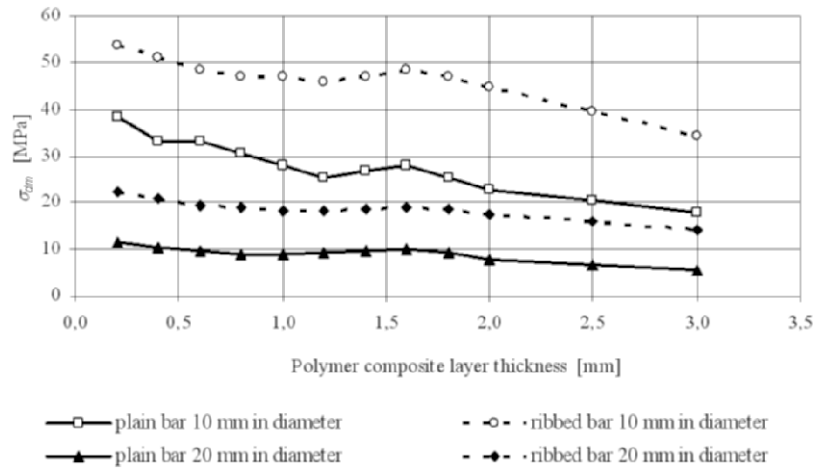


Fig. 3. Average values of stress bending rebars 10 mm and 20 mm in diameter, at which sulphur polymer composite layer of different thickness gets unstuck

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.

### 3.2. Adjacent adhesion of sulphur polymer composite layer to reinforcing bars

The averages values of tangent adhesion  $\tau_{vm}$  of a 1.5 mm thick sulphur polymer composite layer to plain and ribbed rebars 10 mm and 20 mm in diameter are shown in respectively Figure 4.

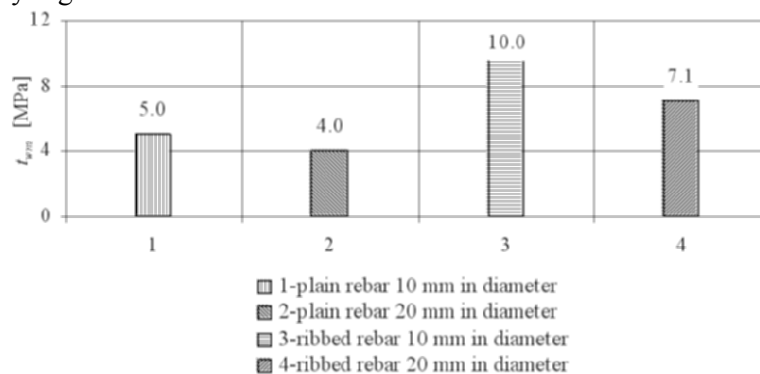


Fig. 4. Average values of adjacent adhesion of 1.5 mm thick sulphur polymer composite to plain and ribbed rebars 10 mm in diameter and 20 mm in diameter

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.

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

The average values of adjacent adhesion  $\tau_{vm}$  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 respectively Figure 5.

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.

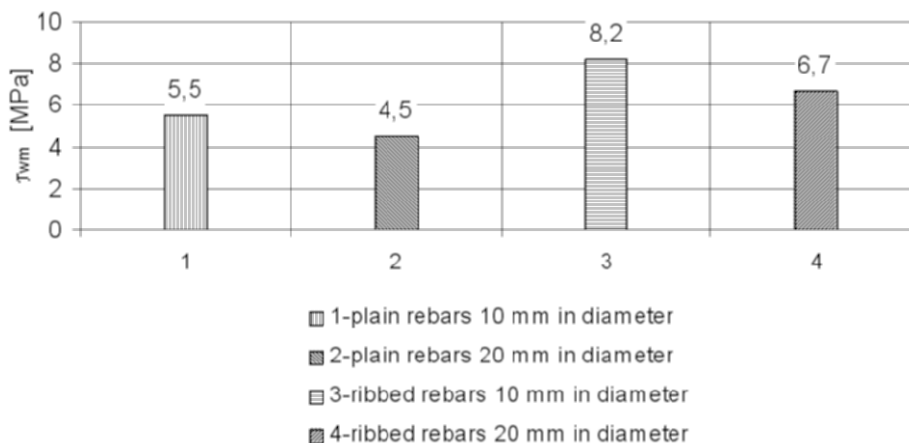


Fig. 5. Average values of tangent adhesion of sulphur polymer composite to plain and ribbed rebars 10 mm in diameter and 20 mm in diameter, being pushed out of composite

### 3.4. Adjacent adhesion of concrete to rebars coated with sulphur polymer composite

The test results for adjacent adhesion  $\tau_{vm}$  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 respectively Figure 6. The results denoted by the digits 1–3 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 7.

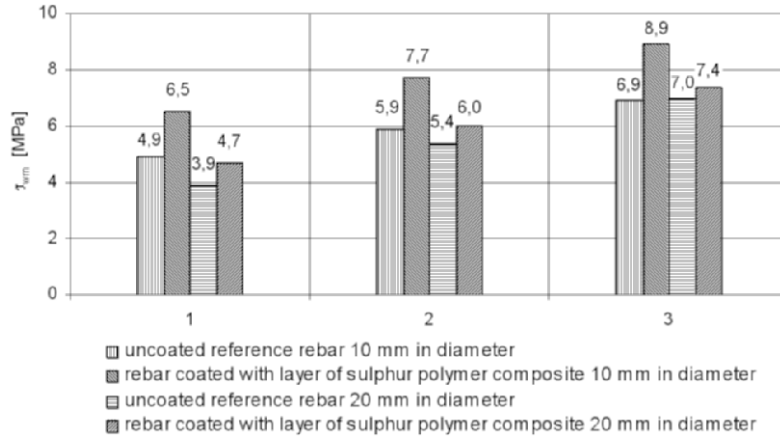


Fig. 6. Average values of adjacent adhesion of ordinary concrete to plain rebars 10 mm in diameter and 20 mm in diameter, coated with 1.5 mm thick layer of sulphur polymer composite, 1 – concrete made using rounded aggregate, 2 – concrete made using crushed basalt aggregate and 3 – concrete made using crushed granite aggregate

For the comparison purposes, Figures 6 and 7 show the adjacent adhesion ( $\tau_{wm}$ ) of ordinary concrete, made using respectively rounded aggregate, crushed basalt aggregate and crushed granite aggregate, to uncoated rebars.

It follows from the results shown in Figures 6 and 7 that in comparison with the uncoated reference rebars, higher values of adjacent adhesion to both plain and ribbed rebars 10 mm 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.

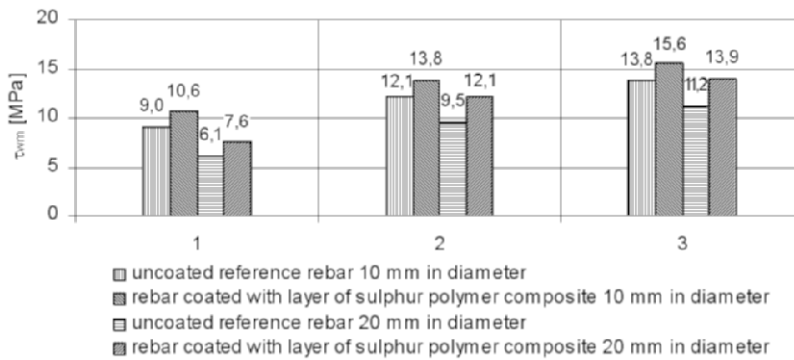


Fig. 7. Average values of adjacent adhesion of ordinary concrete to ribbed rebars 10 mm in diameter and 20 mm in diameter, coated with 1.5 mm thick layer of sulphur composite, 1 – concrete made using rounded aggregate, 2 – concrete made using crushed basalt aggregate, 3 – concrete made using crushed granite aggregate

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.

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

Figure 8 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.

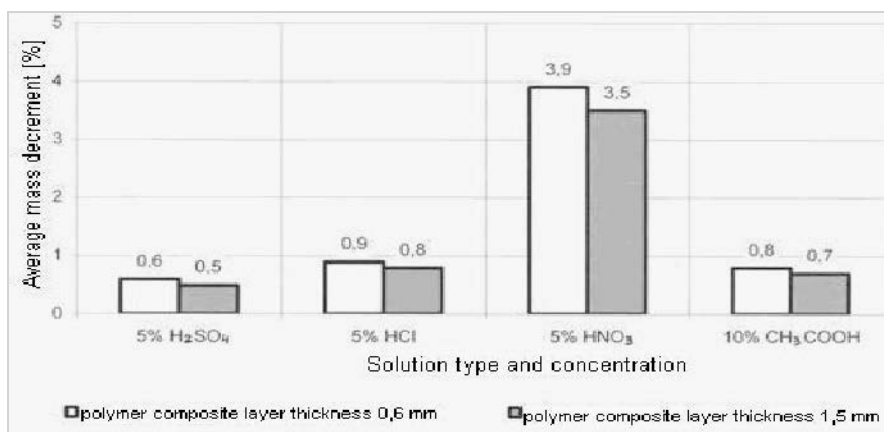


Fig. 8. Average mass loss (in %) for plain rebars 10 mm in diameter, coated with layer of sulphur polymer composite, stored in aqueous solutions of acids for 1 year

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 9 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 mm 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%.

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 10. According to the figure, the average mass loss for the rebars stored in: a 10% solution of NaCl, a 10%



solution of  $(\text{NH}_4)_2\text{SO}_4$ , a 10% solution of  $\text{CaCl}_2$ , a 10% solution of  $\text{K}_2\text{CO}_3$  and a 10% solution of  $\text{CaCO}_3$  is slight, being in a range of 0.1–0.7%.

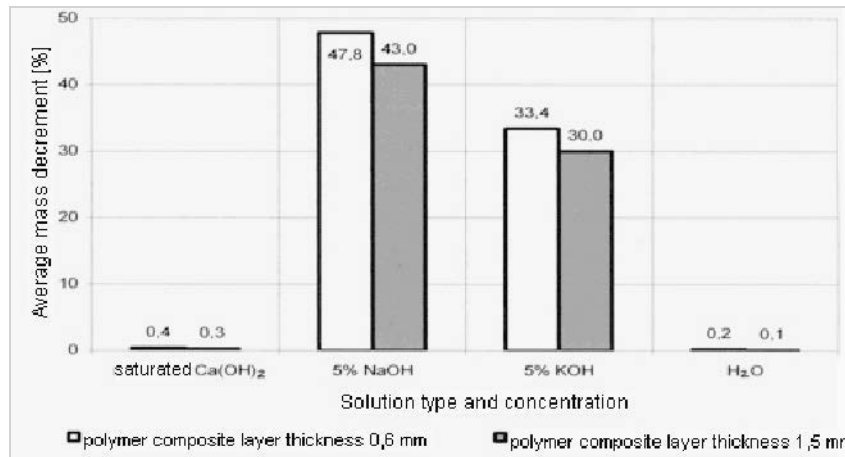


Fig. 9. Average mass loss [%] for plain rebars 10 mm in diameter, coated with layer of sulphur polymer composite, stored in aqueous solutions of hydroxides and in water for 1 year

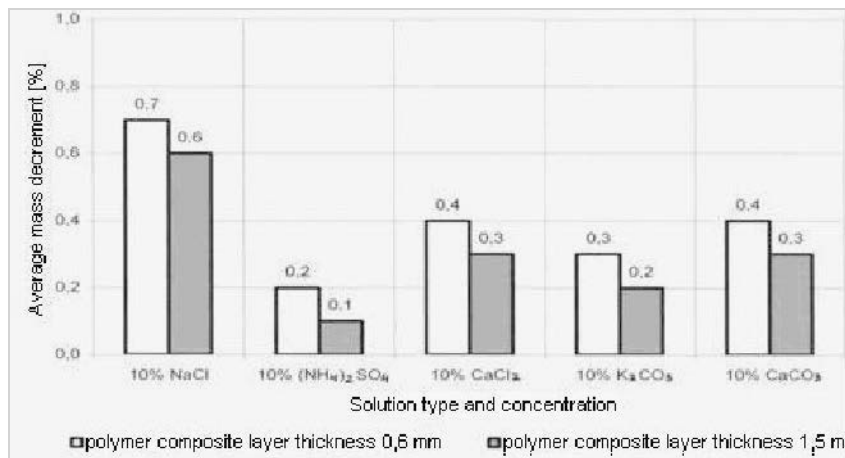


Fig. 10. Average mass loss for plain rebars 10 mm in diameter, coated with layer of sulphur polymer composite, stored in aqueous solutions of salts for 1 year

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  $\text{HNO}_3$  – 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.

Similar results as for the 10 mm diameter rebars were obtained for the 20 mm diameter rebars [14].

### 3.6. Polarization investigations of tensioned rebars coated with sulphur polymer composite

Figure 11 shows corrosion rate  $H_t$  versus time (in a time interval of 3–168 hours) at a constant rebar tensile stress  $\sigma_a$  of 194.5 MPa. The rebars are plain rebars 10 mm in diameter, coated with a 0.5 mm and 1.5 mm thick layer of the sulphur polymer composite, immersed in a solution modelling the pore liquid in carbonated concrete contaminated with chloride ions.

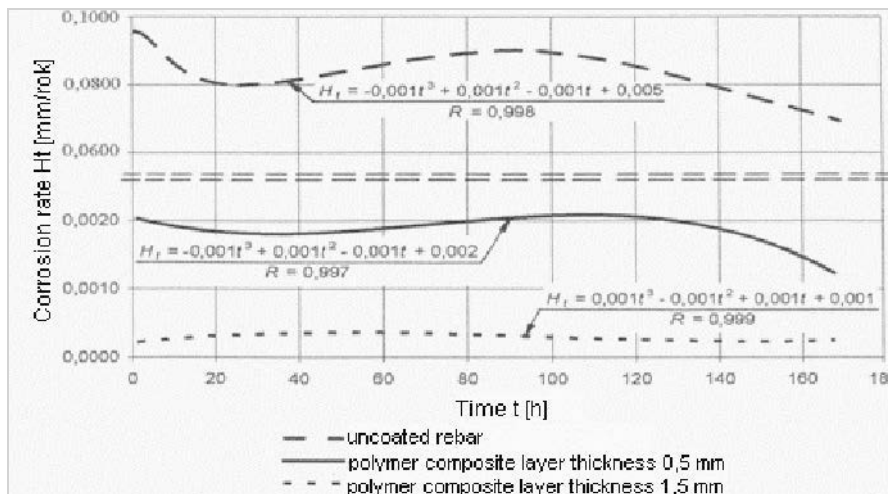


Fig. 11. Corrosion rate versus time at constant tensile stress  $\sigma_a = 194.5$  MPa for plain rebars 10 mm in diameter, coated with sulphur polymer composite and for uncoated rebars

According to the figure, after a tensile stress ( $\sigma_a$ ) of 194.5 MPa is reached, the corrosion rate ( $H_t$ ) changes in a time interval of 3–168 hours as follows: it increases initially and after 90 hours from the beginning of the test it starts decreasing, amounting to about 0.0010 mm/year after 168 hours. It is lower in the case of the rebars coated with a 1.5 mm thick layer of the sulphur polymer composite. At this layer thickness, the corrosion rate is only very slightly dependent on time and on the increasing tensile stress in the rebars. Within the test time interval it remained at an almost constant level of 0.000186–0.000242 mm/year. As the figure shows, the corrosion rate for the uncoated rebars is by three orders of magnitude higher. The corrosion rate over time is described by the equations given in Figure 11.

The very low, nearly constant corrosion rate in the case of the rebars coated with a 1.5 mm thick layer of the sulphur polymer composite is beneficial. Therefore such a layer can be considered as contributing to the protection of the reinforcing steel against corrosion in the solution modelling the porous liquid in carbonated concrete contaminated with chloride ions.

Figure 12 shows the dependence between stationary potential  $E_o$ , time and tensile strength for the tested rebars coated with a 0.5 mm and 1.5 mm thick layer of the sulphur polymer composite. For comparison purposes, stationary potential  $E_o$  in similar uncoated rebars is shown. The dependencies are described by the included equations.

According to the test results, once tensile strength  $\sigma_a$  of 194.5 MPa is reached in the rebars, a slight increase in stationary potential over time is observed. In the case of a 1.5 mm layer, potential  $E_o$  remains constant (close to 0 mV) in the whole test period. It also remains constant for the uncoated reference rebars, but at a level much different from 0 mV.

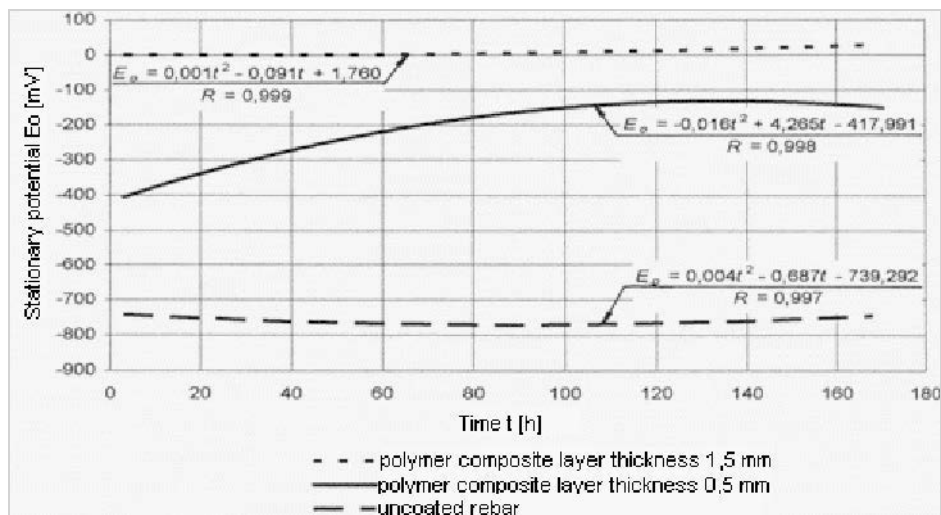


Fig. 12. Stationary potential versus time and constant tensile stress  $\sigma_a = 194.5$  MPa for plain rebars 10 mm in diameter, coated with sulphur polymer composite and for uncoated rebars

#### 4. Conclusions

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  $\text{HNO}_3$  and  $\text{KOH}$  and  $\text{NaOH}$ .

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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#### **Badania przydatności polimerowego kompozytu siarkowego do ochrony przed korozją stali zbrojeniowej w żelbecie**

W pracy przedstawiono rezultaty badań doświadczalnych i analiz wykazujących przydatność polimerowych kompozytów siarkowych do ochrony przed korozją stali zbrojeniowej.

Dokonano przeglądu literatury, między innymi w zakresie wybranych zastosowań polimerowych kompozytów siarkowych w budownictwie, metod i sposobów powierzchniowej ochrony przed korozją stali zbrojeniowej i betonu, a także metod i sposobów oceny szczelności warstw zabezpieczających te materiały przed korozją.

Sprecyzowano także zakres badań własnych i stosowanej metodyki. Przeprowadzono badania wstępne obejmujące ustalenie składów i warunków wytwarzania oraz zbadano podstawowe własności fizyczne i mechaniczne wytworzonych próbnych polimerowych kompozytów siarkowych. Dokonano analizy uzyskanych rezultatów badań wstępnych i wytypowano polimerowy kompozyt siarkowy, spośród próbnych, do dalszych badań zasadniczych.

Przeprowadzono badania zasadnicze dla wybranego, spośród próbnych, polimerowego kompozytu siarkowego, w tym: zbadano przyczepność do prętów zbrojeniowych gładkich i żebranych, określono ubytki masy zarówno kompozytów, jak i prętów zbrojeniowych, pokrytych warstwą kompozytów i przechowywanych w roztworach wodnych kwasów, wodorotlenków i soli oraz w wodzie, wykonano badania polaryzacyjne dla prętów zbrojeniowych pokrytych i nie pokrytych taką warstwą. Wykazano przydatność polimerowych kompozytów siarkowych do powierzchniowej ochrony przed korozją stali zbrojeniowej.