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## IMPACT AND ADHESION TESTS OF COMPOSITE POLYMER COATINGS ON STEEL SUBSTRATE

The paper compares the influence of the type and number of composite reinforcement layers on the impact resistance, as well as the effect of the matrix type. Carbon, aramid and carbon-aramid fabrics were tested, and block copolymer styrene-butadiene-styrene and epoxy resin were also tested. In addition to impact tests, investigations were also carried out on the adhesion of the coatings, without reinforcement and with one layer of fabric, to the steel substrate. The highest values of pull-off strength were obtained for the coatings based on the SBS copolymer reinforced with fabrics. In the case of the coatings reinforced with aramid and aramid-carbon fabric, both adhesive and cohesive damage occurred during the pull-off test.

**Keywords:** composites coatings, laminates, impact strength of coatings, pull-off tests

## BADANIA UDARNOŚCI I PRZYPĘCNOŚCI KOMPOZYTOWYCH POWŁOK POLIMEROWYCH NA PODŁOŻU STALOWYM

W pracy porównano wpływ rodzaju oraz ilości warstw wzmocnienia kompozytu na odporność na uderzenia, a także określono wpływ rodzaju osnowy. Przebadano tkaninę węglową, aramidową oraz węglowo-aramidową, a jako osnowę blokowy kopolimer styren - butadien - styren oraz żywicę epoksydową. Oprócz badań udarowych przeprowadzono badania przypięności powłok bez wzmocnienia i z jedną warstwą tkaniny do podłoża stalowego. Największe wartości wytrzymałości na odrywanie uzyskano dla powłok na bazie kopolimeru SBS wzmocnionych tkaninami. W przypadku powłok wzmocnionych tkaniną aramidową i aramidowo-węglową podczas próby odrywania doszło do zniszczenia adhezyjnego i kohezyjnego.

**Słowa kluczowe:** powłoki kompozytowe, laminaty, udarność powłok, badania przypięności

## INTRODUCTION

To date, polymer coatings have been used mainly as anti-corrosion coatings. With the development of industry and advanced technologies, coating-forming polymers are expected to meet increasingly higher requirements and have a number of other advantages besides being protective and aesthetic. Polymeric coatings are divided into protective, decorative and technical due to their function [1]. Protective coatings are effective and very good protection against harmful environmental influences, above all they are resistant to atmospheric, chemical and mechanical factors [2-4]. In order to improve the mechanical properties, the authors reinforced thermoplastic coatings by means of an aramid fabric [5]. Polymeric coatings characterized by high resistance to impact are used mainly in the military industry [6, 7]. The purpose of such coatings is to absorb as much energy as possible from the impact, for example, a bullet fragment [8]. Technical coatings are used to give the material specific mechanical, electrical, thermal properties, etc. These most common coatings possess

improved hardness, abrasion resistance and resistance to high temperatures [9, 10]. Among technical coatings there are also so-called intelligent coatings because they react to the influence of selected exploitation factors, such as heat, solar radiation or microorganisms (viruses, bacteria) [11]. One of such coatings is called a regenerative self-healing coating, which usually contains microcapsules with active chemical compounds that fill up the place of a crack or scratch in the polymer coating after damage [12-16]. The author of work [17] reviewed anti-corrosive coatings with special applications. The topic of coatings has been widely discussed; smart and self-healing coatings for corrosion protection, hydrophobic and superhydrophobic coatings, functional coatings based on modified polymeric and hybrid chemistries, functional coatings for functionalisation and protection of metallic biomaterials.

For the coating to fulfill its functions, a good bond with the substrate is essential. There are many methods to determine the adhesion between coatings and a steel

substrate, such as: knife, peel, hot water immersion, cathodic disbondment, salt spray, pull-off and bending tests [18]. The pull-off method was selected according to the observed tendency of comparing different testing methods to this particular one e.g. the adhesive and cohesive strengths of thermally sprayed coatings were determined by means of the shear test method and the results were compared with the conventional pull-off adhesion test [19]. Pull-off test reliability depends on several factors such as moisture, temperature, the skills of the test operator, curing time and coating thickness [20]. In order to increase the adhesion between the substrate and the coating, proadhesive layers or appropriate preparation of the substrate using mechanical and chemical methods are used. In coatings and composite materials the interaction between the matrix and reinforcement (fibers) is also important. The authors of work [21] studied improved interactions between the coated fibers and resin in composites that were obtained with four types of silica coatings and different organic functional groups.

This paper addresses the issues of coatings reinforced with high-strength fiber fabrics - aramid, aramid-carbon and carbon fabric on a steel substrate. The focus was primarily on the impact resistance of these laminates. An important aspect was also to conduct pull-off tests and to examine the effect of coating reinforcement on their adhesion to the substrate. The conducted tests are preliminary and serve primarily to determine the optimal layer thickness and type of reinforcement in polymer coatings applied to a steel substrate.

## EXPERIMENTAL PROCEDURE

### Materials

To manufacture the hybrid coatings used for this paper, the followings materials were used as the reinforcement:

- carbon fabric of a basic weight of 200 g/m<sup>2</sup> and plain weave,
- aramid fabric of a basic weight of 173 g/m<sup>2</sup> and plain weave,
- aramid-carbon fabric of a basic weight of 165 g/m<sup>2</sup> and twill weave. All the fabrics were supplied by Havel Composites.

The matrices used for the first series of laminates were: a two-component epoxy resin Epidian 652 and resin hardener IDA supplied by Organica-Sarzyna and styrene-butadiene-styrene (SBS) copolymer, KRATON® D0243 provided by the Kraton Polymers Company. The steel substrate was made of DP600 steel, which is a Dual Phase steel. The thickness of the substrate was 1.1 mm and the dimensions of the produced sheets were 150 x 150 mm. The steel substrate was pretreated by cleaning in acetone. The roughness was measured with a profilometer by the contact method, determining the arithmetic mean deviation of the roughness profile -  $R_a$

and the roughness height by 10 points -  $R_z$ . For the steel substrate  $R_a$  was 1.45  $\mu\text{m} \pm 0.15$ ,  $R_z$  - 7.37  $\mu\text{m} \pm 0.44$ .

Polymeric coatings without reinforcement were obtained as well as coatings differing in the matrix and number of reinforcement layers, ranging from 1 to 5. Samples based on epoxy resin were produced by the lay-up method, while the samples using the SBS copolymer were made by pressing.

Firstly, SBS granulate was pressed (on an H-type press from Paren) for 3 minutes without load, and then 3 minutes with a load of 2 MPa (at 180°C) to obtain films with a thickness of approx. 500  $\mu\text{m}$ . Next, the films with the fabrics on the steel substrate were pressed with the same pressing parameters as in the case of the plain film. SBS copolymer coatings reinforced with three different fabrics containing a number of layers from 1 to 5 were produced by pressing. Analogous samples were obtained by hand lamination based on the epoxy resin. The manufactured samples were named as follows: EP (epoxy resin), SBS (styrene-butadiene-styrene copolymer) - type of matrix, C (carbon); AC (aramid-carbon); A (aramid) - type of fabric, 1,2,3,4,5 - number of layers of fabric in the substrate.

The thickness of the obtained coatings was measured in accordance with the PN-EN ISO 2808: 2008 standard by means of a magnetic method, Mini Test 730 FH5 by ElectroPhysik using magnetic induction and eddy currents.

### Methodology of studies

Impact resistance tests were carried out according to the guidelines contained in EN ISO 6272-1: 2004 [22]. The tests were carried out using a TQC SP1880-134 device (Fig. 1). The main element of the device is a weight of 2 kg ended with a spherical indenter with a diameter of 20 mm, which is set at the appropriate height on the guide tube. The maximum height of the guide tube from which the weight can be lowered is 1 m. This method determines the minimum height from which the lowered weight will damage the coating.

The adhesion of the obtained coatings was determined in accordance with the PN-EN ISO 4624-2004 standard [23]. This method consists in measuring of the pull-off strength of the coatings on the unit interface. The measure of adhesion of the coating is the smallest stress required to pull-off the weakest boundary layer (adhesive detachment mechanism) or the weakest point of the tested coating system (cohesive detachment mechanism). In order to investigate the adhesion of the obtained coatings, a 20 mm diameter measuring punch was glued to the steel substrate using epoxy glue and pulled off after 24 hours using a DeFelsko PosiTest AT-A (Pull-off adhesion tester). The adhesion tests were carried out on coatings not reinforced with fabrics and on those reinforced with one layer of fabric. The adhesion and impact tests were carried out at room temperature at 45% humidity for the epoxy and SBS coatings.

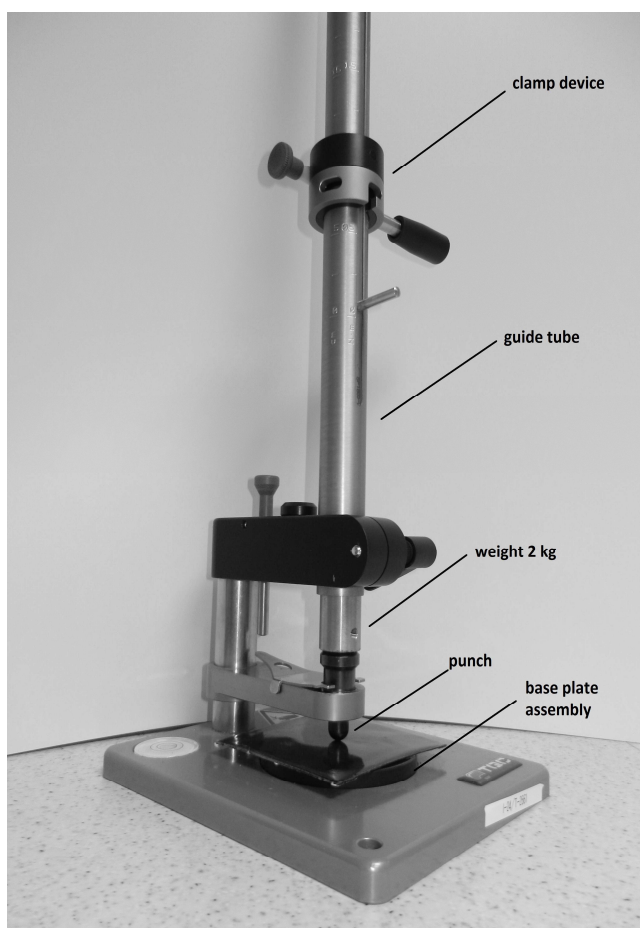


Fig. 1. Device for testing coating impact resistance TQC SPI880-134

Rys. 1. Urządzenie do badania odporności na uderzenia powłok TQC SPI880-134

## STUDY RESULTS

During the impact tests of the plain epoxy coating, the minimum height from which the falling weight

caused mechanical damage could be determined. This height was 45÷50 cm. In the case of the coatings based on the SBS copolymer, no damage was observed after dropping a weight with a mass of 2 kg from maximum height of 1 m. Therefore, the number of impacts, after which the coatings were damaged, was assumed to be the result of impact resistance. The results of the number of impacts followed by tearing of the structure of the reinforced coatings are summarized in Figure 2 for the EP coatings, in Figure 3 for the SBS coatings.

The epoxy coatings reinforced with one layer of fabric cracked after a single impact, while in the SBS coatings, the structure was damaged after the third impact for the carbon fabric, after the fourth impact for the aramid-carbon fabric, and after the seventh-eighth impact for the aramid fabric. With an increase in the number of fabric layers in the coatings, the impact resistance increased. Depending on the type of fabric, the impact resistance was different. The coatings reinforced with aramid fabrics are the most resistant to impact, and the ones reinforced with carbon fabric have the weakest resistance to impact. This result is due to the different properties of carbon and aramid fibers. Carbon fibers are fragile and have a greater Young's modulus  $E$  than aramid fibers. The failure mechanism within the coatings was completely different depending on the matrix. In the epoxy coatings, brittle fracture occurred after a single impact, while in the SBS coatings no damage was observed. For comparison, Figure 4a shows the surface of the EP coating, and Figure 4b the SBS coating reinforced with one layer of aramid fabric. SBS is a polymer belonging to thermoplastic elastomers, while EP is a thermosetting polymer with a spatially cross-linked structure. SBS contains in its composition butadiene, which is classified as rubber, hence the polymer is more resistant to impact than epoxy resin.

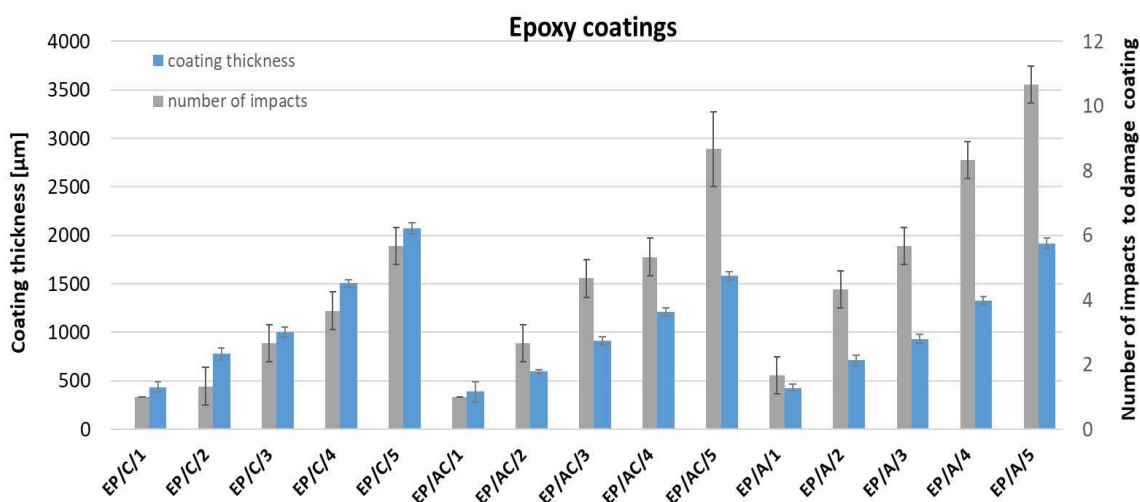


Fig. 2. Number of impacts leading to complete destruction of epoxy coatings reinforced with fabrics and their average thickness

Rys. 2. Liczba uderzeń prowadząca do całkowitego zniszczenia powłok epoksydowych wzmocnionych tkaninami oraz ich średnia grubość

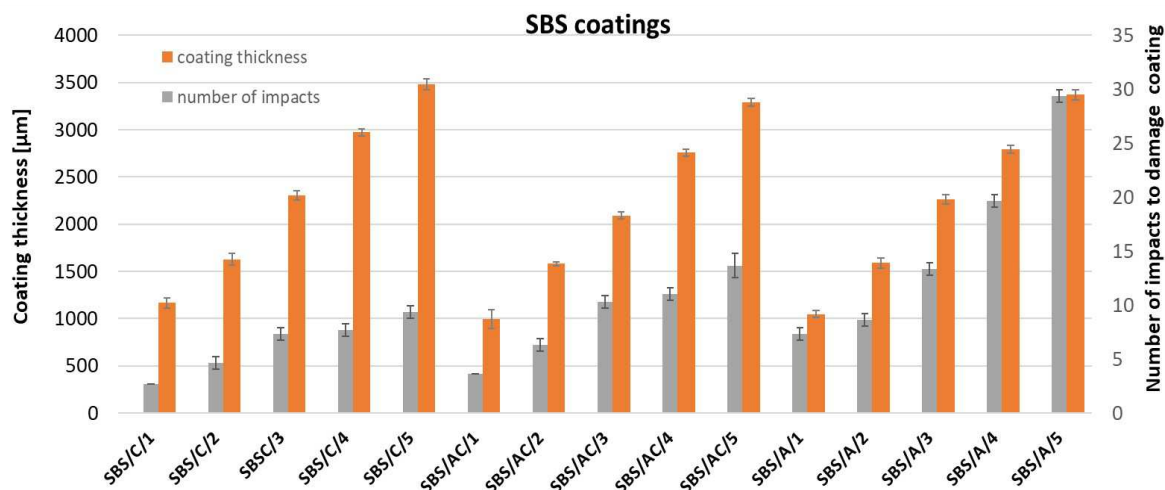


Fig. 3. Number of impacts leading to complete destruction of SBS coatings reinforced with fabrics and their average thickness

Rys. 3. Liczba uderzeń prowadząca do całkowitego zniszczenia powłok SBS wzmocnionych tkaninami oraz ich średnia grubość

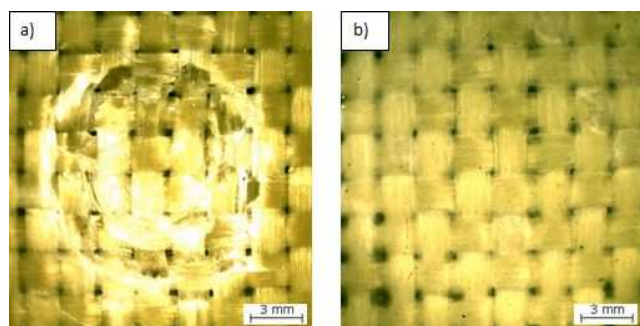


Fig. 4. Coatings: a) epoxy, b) SBS copolymer reinforced with one layer of aramid fabric after one impact

Rys. 4. Powłoki: a) epoksydowe, b) z kopolimeru SBS wzmocnione jedną warstwą tkaniny aramidowej po jednokrotnym uderzeniu

By analyzing the obtained data, it is not possible to state conclusively the linear relationship between the thickness of the composite coatings and their resistance to impact. The SBS copolymer coatings reinforced with 5 layers of fabrics were destroyed on average after 29 impacts, and those with four layers after 20 impacts.

The adhesion of the epoxy coatings (EP) and SBS copolymer coatings as well as both coatings reinforced with one layer of carbon cloth (EP/C and SBS/C),

aramid-carbon fabric (EP/AC and SBS/AC) and aramid fabric (EP/A and SBS/A) was analyzed. The results of the measurements are summarized in Figure 5. For the coatings based on SBS with aramid and aramid-carbon fabric, the obtained values were applied depending on the type of damage after the adhesion test. In the abbreviations SBS/AC-k, SBS/AC-a, SBS/A-k, SBS/A-k means k - cohesive detachment, a - adhesive detachment.

When comparing the results for both coatings, SBS copolymer coatings are characterized by a significantly higher pull-off strength. For coatings based on SBS reinforced with aramid fabric, higher pull-off strength values were obtained than for those reinforced with aramid-carbon fabric. On the other hand, epoxy coatings reinforced with carbon fabric have a higher pull-off strength than the same coatings with aramid and aramid-carbon fabric. During the pull-off tests, various types of mechanical damage to the coatings were observed, in the epoxy samples without reinforcement and with the reinforcement, detachment of the coatings from the steel substrate occurred (adhesive pull-off). Figure 6 shows photos of the epoxy reinforced fabric after separation from the steel substrate.

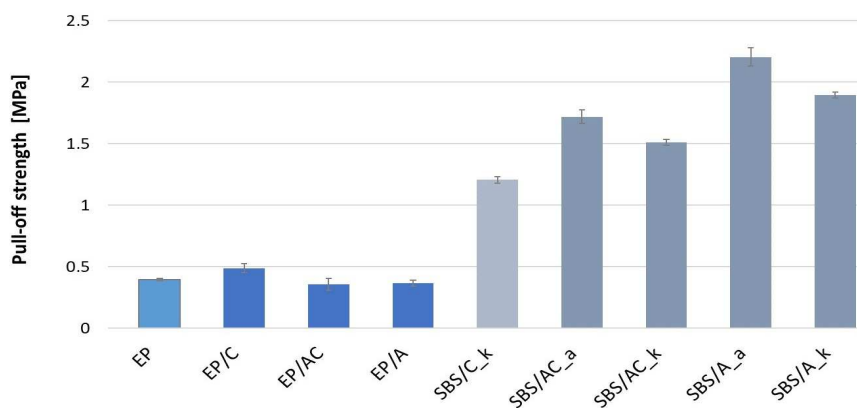


Fig. 5. Pull-off strength according to the series of samples

Rys. 5. Wytrzymałość na odrywanie serii próbek





Fig. 6. Epoxy coating after pull-off test: a) with aramid fabric, b) with aramid-carbon fabric, c) with carbon fabric

Rys. 6. Powłoki epoksydowe po oderwaniu: a) z tkaniną aramidową, b) z tkaniną aramidowo-węglową, c) z tkaniną węglową

In the coatings based on the SBS copolymer reinforced with the carbon fabric, there was cohesive detachment in the coating between the polymer layer and the carbon fabric (Fig. 7).

In the coatings based on the SBS copolymer reinforced with aramid and aramid-carbon fabric, there were two types of damage, cohesive (detachment of the fabric from the matrix) and adhesive (detachment of the coating from the substrate). In Figure 8a-b samples with aramid and aramid-carbon fabric are shown after the adhesion tests.

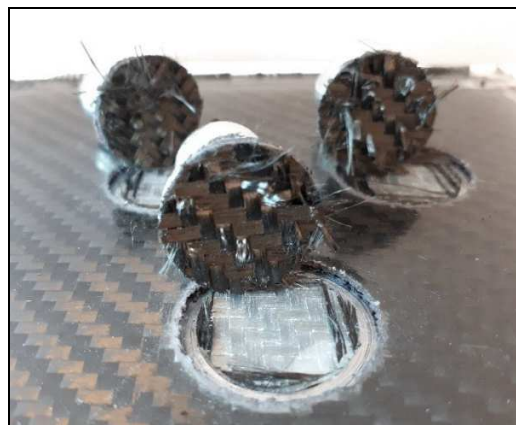


Fig. 7. Cohesive detachment in SBS coating reinforced with carbon fabric

Rys. 7. Oderwanie kohezyjne w powłoce SBS wzmocnioną tkaniną węglową

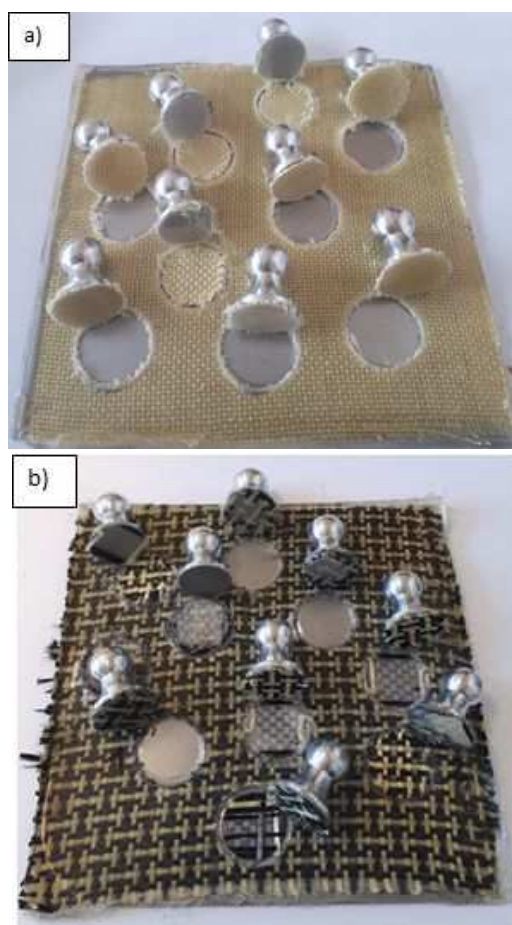


Fig. 8. SBS coating after pull-off test: a) with aramid fabric, b) with aramid-carbon fabric

Rys. 8. Powłoki SBS po oderwaniu: a) z tkaniną aramidową, b) z tkaniną aramidowo-węglową

## CONCLUSIONS

The impact resistance of epoxy resin and SBS copolymer coatings was tested. The smallest resistance to impact was exhibited by the epoxy coatings, which after impact with a weight of 2 kg from a height of 45÷50 cm, undergo breakage. In the coatings not rein-

forced with SBS, after damage from a maximum height of 1 m, no damage was observed. Studies were carried out on coatings reinforced with: carbon, aramid and aramid-carbon fabrics with the number of layers varying from 1 to 5. As a result of the test the number of strokes with an impactor with the energy of 19.62 J was chosen. For both the epoxy and SBS copolymer coatings the best results were obtained by the aramid fabric-reinforced ones.

Adhesion of the coatings to the steel substrate was also determined. Unreinforced coatings and those reinforced with one layer of fabric were tested. For the coatings with the SBS copolymer, over four times better pull-off strength values were obtained than by the epoxy coatings. In the epoxy coatings reinforced with fabrics, the type of detachment was adhesive, while in the coatings based on SBS with different fabrics, two types of detachment were observed, both adhesive and cohesive ones.

## REFERENCES

- [1] Kotnarowska D., Wojtyniak M., Metody badań jakości powłok ochronnych, Wydawnictwo Politechniki Radomskiej, Radom 2010.
- [2] Yeh J-M., Chang K-C., Polymer/layered silicate nanocomposite anticorrosive coatings, *Journal of Industrial and Engineering Chemistry* 2008, 14, 275-291.
- [3] Chattopadhyay D.K., Raju K.V.S.N., Structural engineering of polyurethane coatings for high performance applications, *Progress in Polymer Science* 2007, 32, 352-418.
- [4] Przerwa M., Wpływ czynników klimatycznych na stan powierzchni powłok poliuretanowych i epoksydowych, TRANSCOMP - XIV International Conference Computer Systems Aided Science, Industry and Transport, Logistyka 2010, 6, 2811-2817.
- [5] Mayer P., Pach J., Udarność kompozytowych powłok z tkaniną aramidową na podłożu stalowym, *Interdisciplinary Journal of Engineering Sciences* 2016, 4, 1, 6-10.
- [6] Tekalur S.A., Shukla A., Shivakumar K., Blast resistance of polyurea based layered composite materials, *Composite Structures* 2008, 84, 271-281.
- [7] Xue L., Mock W., Belytschko T., Penetration of DH-36 plates with and without polyurea coating, *Mechanics of Material* 2010, 942, 81-103.
- [8] Roland C.M., Fragiadakis D., Gamache R.M., Elastomer-stell laminate armor, *Composite Structures* 2010, 92, 1059-1064.
- [9] Hallmann L., Ulmer P., Mreusser E., Hanmerle C., Effect of blasting pressure, abrasive particle size and grade on phase transformation and morphological change of dental zirconia surface, *Surface & Coatings Technology* 2012, 206, 4293-4302.
- [10] Zhang T., Bao Y., Gawne D.T., Mason P., Effect of a moving flame on the temperature of polymer coatings and substrates, *Progress in Organic Coatings* 2011, 70, 45-51.
- [11] Balagna C. et al., Antibacterial coating on polymer for space application, *Materials Chemistry and Physics* 2012, 135, 714-722.
- [12] Huang M., Zhang H., Yang J., Synthesis of organic silane microcapsules for self-healing corrosion resistant polymer coatings, *Corrosion Science* 2012, 65, 561-566.
- [13] Moynot V., Gonzalez S., Kittle J., Self-healing coatings: An alternative route for anticorrosion protection, *Progress in Organic Coatings* 2018, 63, 307-315.
- [14] Nesterova T., Johansen K., Pedersen L., Kill S., Microcapsule-based self-healing anticorrosive coatings: Capsule size, coating formulation, and exposure testing, *Progress in Organic Coatings* 2012, 75, 309-318.
- [15] Hua Z., Hongxia W., Haitao N., Gestos A., Tong L., Robust, self-healing superamphiphobic fabrics prepared by two-step coating of fluoro-containing polymer, fluoroalkyl silane, and modified silica nanoparticles, *Advanced Functional Materials* 2013, 23, 1664-1670.
- [16] Bolimowski P.A., Kozera R., Kozera P., Boczkowska A., Charpy impact tests of epoxy matrix filled with poly(urea-formaldehyde) microcapsules for self-healing applications, *Composites Theory and Practice* 2017, 17, 4, 206-210.
- [17] Montemor M.F., Functional and smart coatings for corrosion protection: A review of recent advances, *Surface and Coatings Technology* 2014, 258, 17-37.
- [18] Vaca-Cortes E., Lorenzo M.A., Irsa J.O., et al., Adhesion testing of epoxy coating; 1998. (Research Report no. 1256-6).
- [19] Siegmann S., Dvorak M., Grutzner H., et al., Shear testing for characterizing the adhesive and cohesive coating strength without the need of adhesives. *Proceedings of ITSC 2005 thermal spray connects: explore its surfacing potential!* 2005, 823-829.
- [20] Baek Y.H., Chung M.K., Son S.M., et al., Reliability on coating pull-off adhesion strength test. *Corrosion Conference and Expo 2009*, 1-10.
- [21] Szczurek A., Barcikowski M., Leluk K., Babiarczuk B., Kaleta J., Krzak J., Improvement of interaction in a composite structure by using a sol-gel functional coating on carbon fibers, *Materials* 2017, 10, 1-15.
- [22] PN-EN ISO 6272-1:2011 - Studies of sudden deformation (impact resistance). Part 1: Testing with a falling weight, indenter with a large surface area.
- [23] PN-EN ISO 4624:2016-05. Paints and varnishes - pull-off test for adhesion.