Pull-off strength and abrasion resistance of anti-corrosive polymer and composite coatings

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Abstract: The paper aims at presenting the results of pull-off strength and abrasion resistance tests for anti-corrosive coatings on steel substrates. It contains the measured data on the thickness of manufactured coatings in the function of the applied amount of abrasive material. Three polymeric coatings were subjected for testing: chlorinated rubber, oil-phthalic and alkyd. The analogous studies were repeated for composite coatings with alumina α-Al₂O₃ filler and subsequently also for the aged (72 h, –19°C) systems. For the pull-off tests, the damage analysis of samples after failure was performed. The highest pull-off strength’s values for the produced coatings were obtained for the alkyd one. Concerning the abrasion resistance it can be stated that, the addition of a filler significantly improves the system’s durability, while the aging process causes its deterioration.

Keywords: anti-corrosive; coatings; abrasion resistance; pull-off strength; composites; polymers.


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1 Introduction

More than 90% of technical devices are covered with protective coatings, mainly for their protection against corrosion. According to Kotnarowska and Wojtyniak, 2007 losses caused by corrosion in the world account for 2–5% of gross domestic product, in Western Europe 1.3–3%, while in Poland – 6–10%. As the technology develops, the emphasis is put not only on the anti-corrosive properties of protective coatings, but also on their mechanical properties, primarily resistance to abrasion, scratches, impacts, bending, peeling and physical properties such as adhesion to the substrate or ecological, health and decorative issues what is described by Yeh and Chang (2008), Chattopadhyay and Raju (2007) and Przerwa (2010). Polymeric coatings are commonly used to protect various surfaces against the negative effects of ambient factors, due to their high durability, good adhesion to most substrates, ease of application and renovation and low manufacturing costs. They are applied on various types of substrates including metals, concrete, wood, plastics and ceramics. Technical coatings are used to ensure the material to possess the desired mechanical, electrical and thermal properties, i.e., in coatings with improved hardness, abrasion resistance or resistance to high temperatures as was presented by Hallman et al. (2012) and Zhang et al. (2011). Among technical coatings, also the ‘smart’ coatings can be distinguished, which properties change according to the selected exploitation factors, such as: solar radiation or microorganisms exposition that was tested by Balagna (2012). An interesting example of such coatings can be the ‘self-healing’ coating, that have the ability to regenerate due to the microcapsules with active chemical compounds contained in their composition, which fill the damaged place after cracking or scratching of the polymer coating (Huang et al., 2012; Moynot et al., 2018; Nesterova et al., 2012; Hua et al., 2013; Bolimowski et al., 2017). Montemor (2014) presented the work reviewing the anti-corrosive coatings with special application. The topic of coatings has been widely discussed especially for: smart and self-healing coatings for corrosion protection, hydrophobic and superhydrophobic coatings, functional coatings based on modified polymeric and hybrid chemistries. Polymeric coatings make up over 80% of all coatings that are used in the protection of various types of surfaces, practically in all branches of industry. Among the most commonly used the following should be mentioned (Kotnarowska, 2007):

- Alkyd coatings – produced on the basis of polyester resins, obtained as a result of polycondensation of glycerol, phthalic acid or phthalic anhydride, due to what are also referred to as ‘phthalic’. Often modified with unsaturated fatty acids. Coatings obtained from alkyd resins are characterised by good resistance to aggressive media, atmospheric agents, solvents and water. They show good anti-corrosion properties (Kotnarowska and Wojtyniak, 2007; Kotnarowska, 2007).

- Chlorinated rubber coatings – obtained on the basis of chlorinated natural rubber. They are resistant to acids, alkalis and water. Intended for corrosion protection of surfaces used in heavily polluted environment. Not resistant to solvents, vegetable and animal fats. They have low aesthetic qualities due to the tendency to chalk, yellowing and poorly maintain gloss (Kotnarowska and Wojtyniak, 2007; Kotnarowska, 2007).
For a coating to fulfil its function, a good adhesion between it and the substrate is one of the most crucial factors. The methods of quality evaluation of such connections include: knife, peel, hot water immersion, cathodic disbondment, salt spray, pull-off and bending tests were distinguished in works of Vaca-Cortes et al. (1998) and Dmitruk et al. (2017).

This paper examines the abrasion resistance and the pull-off strength of selected polymer coatings (chlorinated rubber, phthalic and alkyd) in pure form and with the addition of a filler – applied on the same type of steel substrate (steel sheet DC01). Manufactured coatings were tested also after 72 h of aging. The main purpose of the presented research was to identify coatings with the highest durability of exploitation. Among the possible application of such coatings the following are foreseen: machine covers or metal elements in the construction of machines and devices.

2 Experimental methods and materials

Three types of enamels based on chlorinated rubber, oil-phthalic and alkyd were used for the tests. These are diluent enamels characterised by fast drying time. Selected products are available commercially and can be characterised by anti-corrosion properties and good resistance to mechanical factors. An additional selection criterion was also the adaptation of the enamel for direct application to the metal surface without the need to use a separate undercoat layer. Table 1 contains basic technical data for selected products.

Table 1 Characteristics of coating-forming materials

<table>
<thead>
<tr>
<th>Basis</th>
<th>Density [g/cm³]</th>
<th>Chemical composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorinated rubber</td>
<td>1.013</td>
<td>xylene, ethylbenzene, n-butyl acetate, 2-butanone oxime, 2-ethylhexanoic acid, zirconium salt, bisphenol A, diglycidyl ether resin, cobalt bis (2-ethylhexanoate), (methyl-2-methoxyethoxy) propanol, 2-butoxyethanol</td>
</tr>
<tr>
<td>Oil-phthalic</td>
<td>1.200</td>
<td>hydrocarbons, C9-C11, n-alkenes, iso-olefins, cyclics, &lt;2% compounds, butane-2-one oxime, acetone, cobalt bis(2-ethylhexanoate), zinc bis (2-ethylhexanoate), (methyl 2-methoxyethoxy) propanol</td>
</tr>
<tr>
<td>Alkyd</td>
<td>1.200</td>
<td>hydrocarbons, C9-C11, n-alkanes, isoalkanes, cyclic, &lt;2% aromatic hydrocarbons, acrylic amine, cobalt bis (2-ethylhexanoate), ethyl methyl ketone oxime</td>
</tr>
</tbody>
</table>


Al₂O₃ alumina filler in the form of powdered alumina α-Al₂O₃, grain size from 5 to 10 μm and purity of about 99.5% was also used in the conducted tests. The enamels were mixed with the filler maintaining the 1:1 mass ratio. Alumina α-Al₂O₃ is a mineral powder characterised by very high hardness – 9 on the Mohs scale. It increases the overall hardness of the coating and, as a result, also affects its mechanical properties. Polymeric coatings were applied to the substrate in the form of a sheet of thickness 1.0
mm and dimensions 10 × 10 cm made of DC01 constructional steel (PN-EN 10127-1). It is a low carbon steel (C-0.12%, Mn-0.6%) intended for cold forming, mainly used as a substrate for varnish products. Table 2 presents the chemical and mechanical parameters of DC01 steel.

Table 2  Mechanical properties of DC01 steel

<table>
<thead>
<tr>
<th>Steel type</th>
<th>Yield point Re max. [MPa]</th>
<th>Tensile strength Rm min/max [MPa]</th>
<th>Ductility A80 min. [%]</th>
<th>Vicker’s hardness [HV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC01</td>
<td>280</td>
<td>270–410</td>
<td>28</td>
<td>105</td>
</tr>
</tbody>
</table>


Before applying the coatings, substrates were cleaned with abrasive paper and degreased with acetone. The coatings were thoroughly mixed before application and then carefully applied by hand. The finished coatings were allowed to dry for 48 hours.

Coating thickness measurements were carried out using the ElektroPhysik meter MiniTest 730 with a measuring range from 0 to 2,500 μm and accuracy ± (1.5 μm + 0.75%) of the measurement value ([http://somet.pl/pdf/3/Minitest720_730_740_PL.pdf](http://somet.pl/pdf/3/Minitest720_730_740_PL.pdf); PN-EN-ISO 2808, 2008).

The pull-off adhesion tests for the produced coatings were carried out according to the (PN-EN ISO 4624, 2004) standards by Posi test AT. The Posi test AT pull-off adhesion tester allows the evaluation of pull-off strength of a coating by determining the greatest load it can bear before detaching. Breaking points, demonstrated by fractured surfaces, occur along the weakest plane within the system consisting of a dolly, glue, coating and substrate.

Abrasion testing of coatings was carried out in accordance with PN-76/C-81516. The abrasive material used in the test is alumina 99A according to PN-76/M-59111 in which the grain size is from 0.6 to 0.71 mm. The test is carried out on a standard abrasion tester and consists of subjecting of the coating to the stream of abrasive in 3.5 kg portions by pouring it into the funnel and free fall for 1 metre onto the substrate. This process is repeated for initial coating abrasion. After noticing the visibility of the substrate the portions of the abrasive material should be reduced to 0.5 kg and the test should be continued until an elliptical hole of 3.6–3.7 mm is formed within the coating.

The abrasiveness of the coating can be calculated as the ratio of the weight of the abrasive material applied to the average thickness of the tested coating which has been removed. It is calculated from the following formula (1):

\[
S = \frac{M}{G} \tag{1}
\]

where

- \(M\) weight of the abrasive material applied [kg]
- \(G\) average thickness of the removed coating [μm].

The thickness of the coating at the area of abrasion was measured after each transfer of abrasive material. The tests for unfilled and filled samples were carried out for an inclination angle of 45°. An aging process was also carried out for 72 h at –19°C. The results presented in the diagrams show the drop in coating thickness with the measured
measurement error values, depending on the amount of abrasive material being poured. The abrasion resistances for the produced coatings were calculated and listed in Table 3.

3 Results and discussion

Substrates painted with enamels without the addition of a filler are characterised by a very delicate gloss and relatively small roughness. The measured coating thicknesses showed that the coatings were applied evenly as the thickness difference in the whole area was negligible. In the case of composite coatings with the addition of a filler, a significant increase in the roughness and thickness in relation to the unreinforced coatings is noticeable.

Figure 1 View of the examined surfaces (dolly and substrate) after pull-off strength test (see online version for colours)

Samples of sole enamels after performed pull-off strength test are shown in Figure 1. As one might notice, the nature of failures is mainly adhesive. Only in the case of chlorinated rubber coating the observed damage seems to consist of a mixture of adhesive-cohesive mechanism. Pull-off strength values are gathered in Figure 2. As was predicted in studies presented by Kordzangeneh et al. (2017) and Zheng and Myers (2013), the alkyd coating exhibit the highest pull-off strength, as it is already readily applied as a protective film on metal surfaces, both in its pure or filler reinforced form. In future works, the thickness of the applied coatings can be also adjusted, because the increasing thickness of the coating affects the pull-off strength as it promotes the cohesive type of the failure. Moreover, for further adhesion enhancement the substrate surface pretreatment can be applied. Development of the steel specific surfaces via mechanical roughening or chemical processing can lead to the improvement of mechanical adhesion (Rudawska, 2013; Dayss et al., 1999; Li et al., 2004; McCafferty, 2002; Ge et al., 2003). As was reported earlier, also such processes as anodisation, micro-arc oxidation (Li et al., 2014) or plasma activation (Reicher et al., 2015) could lead to the enhancement in adhesion of coating to the substrate. Nevertheless, in the previous work of Dmitruk et al. (2017) it was found that the best outcomes of pull-off strength were obtained for the pretreatment method in which the substrates were only degreased with acetone instead of sandblasting, both for reinforced and unreinforced coatings. This is the reason why for the purpose of the presented preliminary study substrates were only...
cleaned and degreased. Last but not least, in the future work, more advanced application methods could be used such as spray coating or thermal spray coating (Bendikiene et al., 2017 and Hafiz et al., 2014).

Figures 3 and 4 showing the damaged area of chlorinated rubber and alkyd coatings are similar. The oil-phthalic coating (Figure 5) has not been removed as uniformly as the others as there are visible traces of the remaining coating on the substrate surface. Since the steel substrate is porous and full of irregularities, the filler addition has a beneficial influence on coating’s strength, because its particles penetrate the surface and promote the mechanical adhesion.

**Figure 2** Pull-off strength according to the coating material (see online version for colours)

![Figure 2](image)

**Figure 3** View of the damaged area of chlorinated rubber samples after the abrasion resistance tests, (a) unreinforced sample (b) sample reinforced with alumina $\alpha$-Al$_2$O$_3$ filler (c) reinforced sample after aging process (72 h, $-19^\circ$C) (see online version for colours)

![Figure 3](image)

**Figure 4** View of the damaged area of alkyd samples after the abrasion resistance tests, (a) unreinforced sample (b) sample reinforced with alumina $\alpha$-Al$_2$O$_3$ filler (c) reinforced sample after aging process (72 h, $-19^\circ$C) (see online version for colours)

![Figure 4](image)

The thickness drop for coatings without a filler at an inclination angle of 45° for three different coating types varies quite significantly. For a chlorinated rubber coating (Figure 6), the change in the thickness of the coating depending on the amount of material to be poured up to the appearance of a visible metal surface is almost linear.
However, for oil-phthalic and alkyd coatings (Figures 7–8) this mechanism is slightly different. Change in the thickness of the oil-phthalic coating at the beginning has a linear course, but then the decrease can be approximated exponentially. The graph for the alkyd coating is comparable to the graph for the oil-and-phthalic coating, but in this case the break in the linearity of the approximation occurs after pouring of 91 kg of the abrasive material.

**Figure 5** View of the damaged area of oil-phthalic samples after the abrasion resistance tests, (a) unreinforced sample (b) sample reinforced with alumina $\alpha$-$\text{Al}_2\text{O}_3$ filler (c) reinforced sample after aging process (72 h, $-19^\circ\text{C}$) (see online version for colours)

**Figure 6** Dependence of the thickness of the chlorinated rubber coating from the amount of poured abrasive material

**Figure 7** Dependence of the thickness of the oil-phthalic coating from the amount of poured abrasive material
The highest abrasiveness for the angle of 45° was observed for coatings with the addition of alumina. This is due to the physicochemical properties of the filler, which is a hard and wear-resistant material and its mass content in the entire coating is 50%. The involvement of Al₂O₃ filler increases the abrasion resistance more than four times in each system in comparison to the sole enamel. Highly improved adhesion and as a consequence the corrosion resistance is gained due to the small dimensions of the alumina particles and their high specific surface. The content of reinforcement also is properly chosen as the enhancement is observed. In the case of higher reinforcement to matrix ratio, the overall performance of the system could be deteriorated as it could lead to restricted dispersion and forming of agglomerates.

The same coatings subjected to the aging process in each of the three cases achieved lower abrasion results, what may be related to the increase in the brittleness during the aging process which could result in micro-cracks in the coating and deterioration of its mechanical properties. Moreover, materials subjected to low temperatures tends to shrink, which could cause a decrease in the elasticity of the coating material and thus influence the energy absorption of falling abrasive grains. Nevertheless, the most durable reinforced composite coating both before and after the aging process remains the alkyd one.

### Table 3  Calculated abrasiveness for tested coating systems

<table>
<thead>
<tr>
<th>No.</th>
<th>Coating type</th>
<th>Inclination angle</th>
<th>Filler</th>
<th>Aging parameters</th>
<th>Abrasiveness S [kg/μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chlorinated rubber</td>
<td>45°</td>
<td>-</td>
<td>-</td>
<td>1.22</td>
</tr>
<tr>
<td>2</td>
<td>Chlorinated rubber</td>
<td>45°</td>
<td>α-Al₂O₃</td>
<td>-</td>
<td>3.63</td>
</tr>
<tr>
<td>3</td>
<td>Chlorinated rubber</td>
<td>45°</td>
<td>α-Al₂O₃</td>
<td>72 h, –19°C</td>
<td>2.92</td>
</tr>
<tr>
<td>4</td>
<td>Oil-phthalic</td>
<td>45°</td>
<td>-</td>
<td>-</td>
<td>0.98</td>
</tr>
<tr>
<td>5</td>
<td>Oil-phthalic</td>
<td>45°</td>
<td>α-Al₂O₃</td>
<td>-</td>
<td>3.42</td>
</tr>
<tr>
<td>6</td>
<td>Oil-phthalic</td>
<td>45°</td>
<td>α-Al₂O₃</td>
<td>72 h, –19°C</td>
<td>3.15</td>
</tr>
<tr>
<td>7</td>
<td>Alkyd</td>
<td>45°</td>
<td>-</td>
<td>-</td>
<td>1.45</td>
</tr>
<tr>
<td>8</td>
<td>Alkyd</td>
<td>45°</td>
<td>α-Al₂O₃</td>
<td>-</td>
<td>3.80</td>
</tr>
<tr>
<td>9</td>
<td>Alkyd</td>
<td>45°</td>
<td>α-Al₂O₃</td>
<td>72 h, –19°C</td>
<td>3.30</td>
</tr>
</tbody>
</table>
The calculated values of abrasiveness for each coating system are presented in Table 3.

4 Conclusions

Coatings of three polymer matrices (chlorinated rubber, oil-phthalic and alkyd) were deposited on steel substrates in the unfilled or reinforced with alumina filler form. Manufactured pure coatings were subjected to pull-off strength test. The most durable coating in comparison to chlorinated rubber (0.79 MPa) and oil-phthalic (1.44 MPa) was the alkyd one with the pull-off strength of 1.74 MPa. Both unfilled and filled samples were as well subjected to the abrasion resistance tests. Also, in this case, the alkyd one exhibited the highest values among the unreinforced coatings, as it lasted more than 115 kg of poured abrasive material until the final failure. The abrasiveness values for filled, unfilled and aged alkyd coating equalled 1.45, 3.80, and 3.30 kg/μm, while for the chlorinated rubber and oil-phthalic coatings it was, respectively: 1.22, 3.63, and 2.92 kg/μm and 0.98, 3.42, and 3.15 kg/μm. For each system the abrasion resistance for composite coatings was enhanced more than four-times in comparison to the pure ones. The proposed methodology is thought to be truly valuable as it allows the reliable anti-corrosive polymer and composite coating systems to be applied in simple and cost-effective way.

References


Pull-off strength and abrasion resistance of anti-corrosive polymer


Websites


