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AN INVESTIGATION OF THE INFLUENCE OF CLIMATIC FACTORS ON THE EROSIVE WEAR KINETICS OF POLYMER COATINGS

BADANIE WPŁYWU CZYNNIKÓW KLIMATYCZNYCH NA KINETYKĘ ZUŻYWANIA EROZYJNEGO POWŁOK POLIMEROWYCH

Key words:

erosive resistance, climatic ageing, epoxy nanocoatings

Słowa kluczowe:

odporność erozyjna, starzenie klimatyczne, nanopowłoki epoksydowe

Abstract

The paper presents investigation results concerning the influence of the modification with nanoparticles of silica (of mean grain size 12 nm or 20 nm) or aluminium trioxide (20 nm) of the structure of epoxy coatings on their resistance to climatic factors and the action of erosive particles. Epoxy coatings aged in natural climatic conditions showed an erosive resistance decrease with ageing. The erosive resistance decrease was accompanied by a hardness

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decrease as well as surface roughness increase. The highest resistance to erosive wear after 3 years of ageing revealed coatings modified with aluminium trioxide nanoparticles, while the lowest one showed coatings modified with silica nanoparticles of 12 nm mean grain size. Nanocoatings modified with aluminium trioxide nanoparticles also had the highest resistance to ageing; which was proven by the lowest increase of Ra and Rz surface profile parameter values with time, as well as by a high surface hardness, which was higher than hardness of new unmodified coatings.

INTRODUCTION

Erosion is a dominating wear process of polymer coatings protecting such technical objects as bridges, wharfs, mining facilities, building and agricultural machines, and vehicles chassis. The process of protective coatings' erosive wear occurs as an effect of the impact of erosive particles on the coating surface, which is characteristic for the environment where they are used. The particles are composed of grains of sand, small stones, lumps of soil or coal, etc. Erosion may also be caused by climatic factors such as hailstones, raindrops or strong wind carrying grains of sand (sandstorms) **[L. 1, 2]**.

Presently, intensive development of nanotechnology is observed that allows the production of nanocoatings with structures modified with nanofillers. Among metal nanofillers added to polymer coatings, nanoparticles of metals (silver, copper, and palladium) or metal compounds (iron oxides, zinc oxide, aluminium trioxide, titanium, and zirconium dioxides, and calcium carbonate) are used **[L. 3–5]**. Carbon black, corundum, silica, modified layered aluminosilicates, and glass microspheres are used as non-metallic nanofillers (and microfillers) for polymer coatings modification **[L. 6, 7]**.
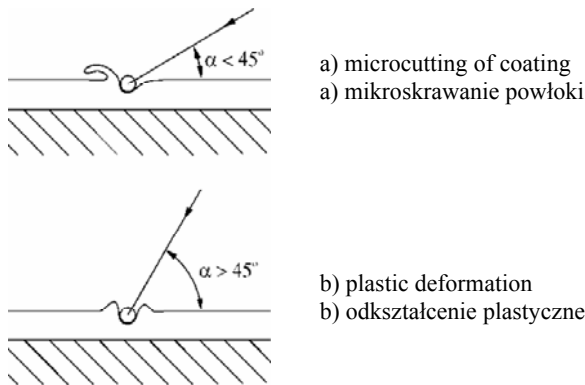
Coatings modified with nanofillers (called nanocoatings) demonstrate increased resistance to abrasion and scratching as well as increased resistance to erosive particles (eroders) action in comparison to coatings not modified with nanofillers. Nanofillers filling pores of different types in the polymer coating's structure improve the coatings tightness as well as thermal stability (fire-resistance, thermal expansion). Due to the modification of polymer coatings with nanofillers, coatings of high aesthetic features are obtained through the increase of their transparency and colour clarity **[L. 3, 4, 6, 7, 10]**.

The kinetics of polymer coatings' erosive wear is conditioned by the type of coating as well as the type of erosive particles and the energy of particles hitting the coating surface, which is determined by their mass (m), velocity (v), and impact angle (α). In the case when α angle is smaller than 45°, the process of microcutting dominates, but when α angle is greater than 45°, the process of coating erosive wear is dominated by plastic deformation. A model of the erosive wear process depending on erosive particles impact angle α are

presented in **Figure 1**, and a model of the distribution of forces acting on the coating at the moment of erosive particle impact is shown in **Fig. 2 [L. 1]**.

In the case of the plastic contact of hard particle with the coating's surface, an increase in the polymer layer hardness results in a decrease in the wear rate. With an increase in the velocity of erosive particles, the erosive wear rate increases, and this dependence has nonlinear nature **[L. 1]**.

Microcutting is a dominating process of polymer coatings' erosive wear at impact angles α of erosive particles in the range (30–50°). However, for erosive particles with impact angles α ≥ 50°, the coating material fatigue is the main reason of erosive wear.

a) microcutting of coating
a) mikroskrawanie powłoki

b) plastic deformation
b) odkształcenie plastyczne

Fig. 1.　A model of erosive particle action on a polymer coating
Rys. 1.　Model oddziaływania cząstki erozyjnej na powłokę polimerową
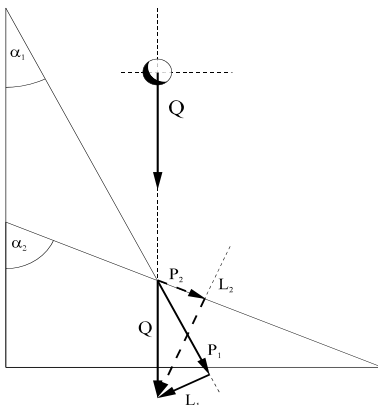
Fig. 2.　Forces acting on the polymer coating at the moment of erosive particle impact
Rys. 2.　Siły działające na powłokę polimerową podczas uderzenia cząstki erozyjnej w jej powierzchnię

The increase in the friction coefficient of the polymer coating–eroder system extremely shifts the characteristics of the coating's erosive wear rate with lower α angles **[L. 1]**.

The intensity of a polymer coating's erosive wear depends on its structure (kind, number, and thickness of layers). If a coating has optimal thickness, not exceeding critical thickness, the erosive wear rate reaches minimal value. It is also promoted by the optimal structure of coating layers (without defects in the form of craters, pores, microcracks) as well as a reduction of the negative influence of the hard substrate **[L. 1]**.

The Intensity of polymer coating's erosive wear increases with an increase of their destruction under the influence of aggressive media **[L. 11, 12]** and climatic factors (especially ultraviolet radiation) **[L. 13]**. An addition of silica **[L. 14–20]** and also aluminium trioxide **[L. 2, 8]** to the composition of polymer coatings advantageously influence their resistance to the action of operational factors (aggressive media, erosive particles, climatic factors).

The resistance of a polymer coating to abrasion is directly proportional to its hardness, tensile strength, elongation at breaking point, and inversely proportional to the friction coefficient of the erosive particle–polymer coating system **[L. 20, 21]**.

METHODS OF INVESTIGATION OF EPOXY COATINGS RESISTANCE TO EROSIVE WEAR

A criterion S $(S = M/G)$ was used for the evaluation of a polymer coating's resistance to erosive wear. The criterion expresses the relation between the total mass of erosive particles (M, [kg]), producing wear of the coating in examined area (i.e. uncovering of substrate fragment, by worn up coating, in the shape of ellipse, which minor axis $d = 3.6 \pm 1$ mm), and the coating thickness (G, [μm]) (acc. PN-76/C-81516).

The erosive material was composed of granulated alundum particles 99A (acc PN-76/M-59111) of particle size 0.6–0.7mm having the main components of silicon dioxide, iron trioxide, calcium oxide, and sodium oxide **(Fig. 2)**.
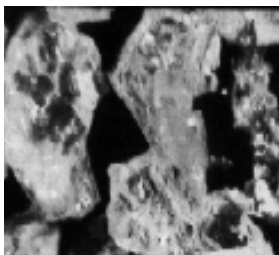
Fig. 3.   Morphology of granulated alundum 99a (MAGNIFICATION 40×)
Rys. 3.   Morfologia elektrokorundu granulowanego 99A (powiększony 40×)

Preparation of samples for examinations

Samples were prepared as four-layer epoxy coatings deposited on a steel substrate by pneumatic spraying. Two undercoat layers were produced of epoxy paint (precoat), while the next layers were made of epoxy exterior paint. The exterior paint (used for modified coating preparation) was modified with one of three following nanofillers: nanoparticles of aluminium oxide (Al_2O_3) – of mean grain diameter equal 20 nm, silica nanoparticles (SiO_2) – of mean grain diameter equal 20 nm or 12 nm. The filler mass share in each epoxy coating was 3.5%. In this way, three types of top layers were prepared.

All coatings used in investigations were produced of epoxy paint cured with polyamide curing agent of ~ 30% stoichiometric mass.

The undercoat was deposited on the surface of steel samples of dimensions $170 \times 90 \times 1.5$ mm made of steel S235JR. The surface of steel samples underwent abrasive treatment (tumbling) with ceramic balls in special barrels.

Before epoxy primer paint application, the steel substrate was degreased with methyl alcohol. After the application of epoxy paint layers (by pneumatic spraying) on steel samples, the coatings underwent drying. Then the epoxy coatings were cured in two stages: at 20°C for 24h, and subsequently at 120°C for 0.5 h. Then the coatings were acclimatized for 10 days at a temperature a $20 \pm 2°C$ and relative humidity $65 \pm 5\%$ (acc. PN-EN 23270: 1993).

Investigations of epoxy coatings properties

Before and after the ageing of epoxy coatings in natural conditions, the measurements of their thickness, hardness, and surface roughness were executed. The measurements of coatings thickness (acc. PN-EN ISO 808:2008) were made using a Mega-Check FE tester. The mean thickness of the four-layer coatings was 163 ± 1 μm, and the total thickness of two layers modified with one of three nanofillers equal 79 ± 1 μm were included in this value. The roughness the coatings were evaluated using the Buchholz method (acc. PN-EN ISO 2815:2004).

Surface roughness parameters Ra and Rz (PN-EN ISO 4287: 1999/A1:2010) of epoxy coatings were measured using a Taylor Hobson interferometric microscope Talysurf CCI. The epoxy coatings were aged for three years under the influence of natural climatic conditions. Hardness and roughness parameters of the examined new ("unaged") and aged epoxy coatings are presented in **Table 1**.

Table 1. The influence of climatic ageing on the properties of epoxy coatings unmodified and modified with nanofillers.

Tabela 1. Wpływ starzenia klimatycznego na własności powłok epoksydowych niemody-fikowanych oraz modyfikowanych nanonapełniaczami

Coating kind	Ageing period	Buchholz hardness H	Roughness parameter Ra	Roughness parameter Rz
	[years]		[µm]	[µm]
EP	0	84	0.24	1.48
3EP	3	80	0.75	5.91
EP-20 Al_2O_3	0	90	0.44	2.57
3EP-20 Al_2O_3	3	85	0.47	2.72
EP-12 SiO_2	0	95	0.84	4.85
3EP-12 SiO_2	3	79	0.99	8.17
EP-20 SiO_2	0	*95*	0.49	3.96
3EP-20 SiO_2	3	85	0.51	3.53

Note: **EP** – unaged epoxy coating; **3EP** – epoxy coating aged for 3 years; **EP-20 Al_2O_3** – unaged epoxy coating modified with aluminium trioxide of grain size 20 nm; **3EP-20 Al_2O_3** – epoxy coating modified with aluminium trioxide of grain size 20 nm, aged for 3 years; **EP-12 SiO_2** – unaged epoxy coating modified with silica nanoparticles of grain size 12 nm; **3EP-12 SiO_2** – epoxy coating modified with silica nanoparticles of grain size 12 nm, aged for 3 years; **EP-20 SiO_2** – unaged epoxy coating modified with silica nanoparticles of grain size 20 nm; **3EP-20 SiO_2** – epoxy coating modified with silica nanoparticles of grain size 20 nm, aged for 3 years.

Epoxy coatings modified with nanoparticles of aluminium trioxide showed considerable stability of surface roughness parameters **(Table 1)**, which determines protective properties (resistance to erosive wear) as well as aesthetic properties (shine durability) of the coatings.

Measurement results **(Table 1)** of the surface roughness of unmodified epoxy coatings document the essential influence of climatic ageing (for 3 years) on the destruction of their surface layers. Roughness parameters Ra and Rz of these coatings increased more than three times as a result of ageing.

It should be noticed that the initial roughness of climatically unaged modified coatings was higher than were those without nanofillers. This was due to the creation of globules by nanoparticles of filler, which have not been atomized during the mixing of epoxy coating. However, roughness parameters of modified coatings showed better stability with the lapse of time. This was probably due to the improved tightness of these coatings and their increased resistance to UV radiation action **[L. 21]**.

After three years of climatic ageing of epoxy coatings, the highest hardness was retained in coatings modified with aluminium trioxide or silica with a grain

size equal 20 nm. Their hardness was 6% higher than the hardness of aged epoxy coatings **(Table 1)**.

Climatic ageing of coatings caused the disappearance of adhesive joints between the epoxy material and surface of fillers and pigments, which facilitated the chipping of coating surface. This resulted in the formation of different types of craters and grooves on the coating surface, which is documented in the images made with SEM **(Fig. 4)**.
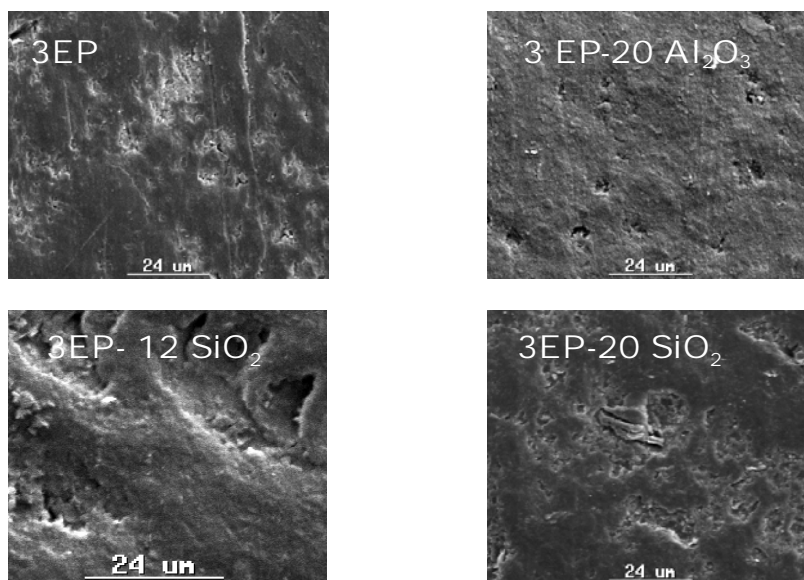
Fig. 4.   Morphology of epoxy coating's surface after 3 years of ageing
Rys. 4.   Morfologia powierzchni powłok epoksydowych starzonych w ciągu 3 lat

INVESTIGATION RESULTS CONCERNING THE EROSIVE RESISTANCE OF EPOXY COATINGS

The results of investigations testify that coatings modification with nanofillers caused an increase in their erosive resistance. As a result of the coatings modification with aluminium trioxide nanoparticles, their erosive resistance increased by ~ 13%, and the erosive resistance of coatings modified with silica nanoparticles of grain size 20 nm increased by 10%; however, the erosive resistance of coatings containing silica nanoparticles of grain size 12 nm increased by only 1%. The erosive resistance of epoxy coatings aged in natural climatic conditions decreased. The highest resistance to erosive wear after three-year ageing was demonstrated by coatings modified with nanoparticles of aluminium trioxide. In this case, the coating's erosive resistance decreased by ~ 33%. However, the erosive resistance of epoxy coatings modified with silica nanoparticles of grain size 20 nm decreased by ~ 37%, and the resistance of

coatings containing silica nanoparticles of grain size 12 nm decreased by ~ 49%. It should be underlined that the erosive resistance of unmodified coatings decreased by 43%.

Trend curves of examined epoxy coatings are presented in **Figure 5** and mathematical models describing these curves are showed in **Table 2**.
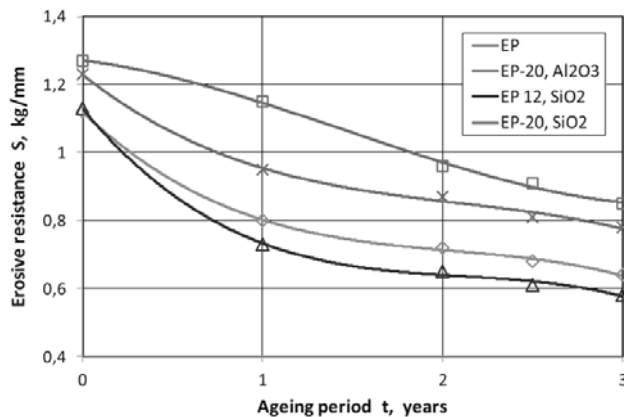
Fig. 5.   Erosive resistance trend curves of examined epoxy coatings
Rys. 5.   Krzywe trendu odporności erozyjnej badanych powłok epoksydowych

Table 2. Mathematical models describing trend curves of epoxy coatings erosive resistance
Tabela 2. Modele matematyczne opisujące przebieg krzywych trendu odporności erozyjnej powłok epoksydowych

No.	Coating kind	Equation of trend line	Coefficient of determination R^2
1.	EP	$y = -0.0358x^3 + 0.2215x^2 - 0.503x + 1.1195$	0.9993
2.	EP-20 Al_2O_3	$y = 0.0182x^3 - 0.0799x^2 - 0.0626x + 1.2707$	0.9977
3.	EP-12 SiO_2	$y = -0.0452x^3 + 0.2865x^2 - 0.6371x + 1.1293$	0.9987
4.	EP-20 SiO_2	$y = -0.0268x^3 + 0.1688x^2 - 0.4167x + 1.2291$	0.9968

CONCLUSIONS

1. Modification of coatings with nanofillers causes an increase in their erosive resistance. Moreover, all the unmodified epoxy coatings aged in natural climatic conditions demonstrated lower erosive resistance than the modified coatings. The highest resistance to erosive wear after three-year's of ageing were demonstrated by the coatings modified with nanoparticles of aluminium trioxide, while the coatings modified with silica nanoparticles of grain size 12 nm demonstrated the lowest resistance.

2. The low erosive resistance of the coatings modified with silica nanoparticles of grain size 12 nm was caused by the significant tendency of this filler to form globules (in comparison to silica nanoparticles of grain size 20 nm). The probable reason for this phenomenon was the insufficient quantity of the epoxy resin to cover each filler grain.

3. The decrease in the coating's erosive resistance was caused by their hardness reduction and surface roughness increase. After a three-year period of climatic ageing, the highest hardness was retained by the coating modified with nanoparticles of aluminium trioxide. These coatings also showed the lowest values of Ra and Rz roughness parameters. Additionally, the coatings modified with aluminium trioxide nanoparticles demonstrated the lowest destruction of their surface. For this reason, they revealed the highest resistance to the action of erosive particles.

4. Climatic ageing of the coatings caused the destruction of adhesive joints between the epoxy material and surface of fillers and pigment grains, which chipped from the coating surface for this reason. This led to coating surface destruction in the form of craters and grooves of different sizes.

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Streszczenie

W artykule przedstawiono wyniki badań wpływu modyfikacji struktury powłok epoksydowych nanocząstkami krzemionki (o średnim rozmiarze ziarna 12 nm lub 20 nm) lub tritlenku aluminium (20 nm) na ich odporność na oddziaływanie czynników klimatycznych oraz cząstek erozyjnych.

Powłoki epoksydowe starzone w naturalnych warunkach klimatycznych charakteryzowało zmniejszanie ich odporności erozyjnej w miarę upływu okresu ich starzenia. Obniżeniu odporności erozyjnej powłok towarzyszyło zmniejszenie twardości oraz zwiększeniem chropowatości ich powierzchni. Największą odporność na zużycie erozyjne, po trzyletnim okresie starzenia, wykazały powłoki modyfikowane nanocząstkami tritlenku aluminium, zaś najmniejszą powłoki modyfikowane nanocząstkami krzemionki o średnim rozmiarze ziarna 12 nm. Nanopowłoki modyfikowane nanocząstkami tritlenku aluminium cechowały się również najwyższą odpornością na starzenie, ponieważ stwierdzono najmniejszy przyrost, w miarę upływu czasy starzenia, wartości parametrów (Ra i Rz) profilu chropowatości powierzchni, a także wysoką twardość, która była wyższa niż niestarzonych powłok niemodyfikowanych.