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INFLUENCE OF CLIMATIC AGEING ON EROSIWE WEAR KINETICS OF POLYMER NANOCOATINGS

WPLYW STARZENIA KLIMATYCZNEGO NA KINETYKĘ ZUŻYWANIA EROZYJNEGO NANOPOWŁOK POLIMEROWYCH

Key words:

erosion, polyurethane nanocoatings, nanofillers, climatic ageing.

Abstract

The paper presents the results of erosive resistance investigation carried out on three-layer epoxy-polyurethane coating systems of different polyurethane top coat composition. Alumina nanoparticles with a grain size of 20 nm or silica nanoparticles with a grain size of 12 or 20 nm were applied for the top coat modification. Coating systems with top coats modified using silica nanoparticles with the grain size of 12 nm (nanocoatings) revealed the highest erosive resistance, whereas the lowest one was observed in the case of coating systems with unmodified top coats. Lower erosive wear intensity of nanocoatings follows on their relatively high hardness, as well as low surface roughness. Moreover, nanofillers contained in the top coat reduce the development of defects (pores, cracks) in its structure, increasing the erosive resistance of the coatings. Climatic ageing substantially influenced the formation of polyurethane coatings surface topography. Polyurethane coatings modified with nanofillers showed less change in their surface topography than did unmodified coatings. Therefore, the modification of polyurethane top coats with nanofillers decreases their surface susceptibility to destruction.

Słowa kluczowe:

erozja, nanopowłoki poliuretanowe, nanonapełniacze, starzenie klimatyczne.

Streszczenie

W artykule przedstawiono wyniki badań odporności erozyjnej trójwarstwowych epoksydowo-poliuretanowych systemów powłokowych różniących się składem poliuretanowej warstwy nawierzchniowej. Do modyfikacji warstwy nawierzchniowej systemów powłokowych zastosowano nanocząstki tritlenku diglinu (o rozmiarach ziarna $d = 20$ nm) lub nanocząstki krzemionki ($d = 12$ nm, $d = 20$ nm). Najwyższą odporność erozyjną wykazały systemy powłokowe z warstwą nawierzchniową modyfikowaną nanocząstkami krzemionki o rozmiarach ziarna $d = 12$ nm. Natomiast najmniejszą odporność erozyjną obserwowano w przypadku systemów powłokowych z warstwą nawierzchniową niemodyfikowaną. Mniejsza intensywność zużycia erozyjnego nanopowłok wynika z ich relatywnie wysokiej twardości, a także niskiej chropowatości powierzchni. Ponadto nanonapełniacze zawarte w warstwie nawierzchniowej ograniczają powstawanie w ich strukturze wad (porów, pęknięć), powodując zwiększenie ich odporności erozyjnej. Starzenie klimatyczne istotnie wpłynęło na ukształtowanie topografii powierzchni powłok poliuretanowych. Powłoki poliuretanowe modyfikowane nanonapełniaczem wykazały mniejszą zmianę topografii powierzchni, niż powłoki niemodyfikowane. Zastosowanie zatem modyfikacji nawierzchniowych powłok poliuretanowych nanonapełniaczami zmniejsza podatność ich powierzchni na destrukcję.

INTRODUCTION

In environments where erosive particles are characteristic pollutants, erosion is a dominating wear process of polymer protective coatings applied to many technical objects [L. 51, 56]. Coating erosion occurs under impacts of hard particles (in the form of dust, sand,

gravel, lumps of soil, stones, hail, or mud) which are characteristic for a given environment [L. 1, 2]. Surfaces of polymer coatings, worn by the effect of erosion, are susceptible to corrosion development processes.

The intensity of the erosive wear of coatings essentially depends on the surroundings (climatic and environmental), which directly affect elastic, strength,

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and tribological properties of polymer coatings leading to their decrease [L. 4].

The nature of erosive wear processes considerably depend on the physicochemical properties of a polymer coating, as well as erosive particle kind, and especially on its material and shape, speed, and the angle of incidence. Among others, plastic deformation and micro-cutting of a coating's superficial layer are observed after multiple hard particle impacts on the polymer coating surface. As an effect of local material fatigue, breaking away of coating fragments may also occur [L. 3–7].

Protective properties of coatings, including a resistance to erosive particles action, in a large extent depend on a kind of applied fillers, and, in particular, on nanofillers. Application of nanofillers to polymer coating (nanocoatings) production enables one to modify their properties in much wider range than in the case of conventional fillers. The introduction of nanofillers to the composition of polymer coatings results in, among others, their tightness increase, as well as resistance to scratching, abrasion, erosion, aggressive media, and the action of climatic factors, UV radiation in particular. Nanocoatings also show thermal stability and increased fire resistance. Admixing paints with copper or silver nanoparticles makes it possible to increase the resistance of polymer coatings to biological corrosion. Modification of polymer coatings compositions with nanofillers improves both their protective and decorative properties through their transparency and increase of colour purity [L. 8–22].

An extremely large specific surface area is a characteristic feature of nanofillers, as well as nanoparticles in general, and usually, it is in the 100–1000 m²/g range. For this reason, they have relatively high surface free energy, which is connected with reactivity and with adsorption and chemisorption as well. High free energy of the surface of nanofiller particles is conducive to its agglomeration. Nanofillers agglomeration has a negative influence on coatings quality, because it leads to a decrease of total filler surface which contacts directly with polymer material. This precludes obtaining coatings of high protective and decorative properties. The highest protective effectiveness may be obtained when nanofillers are dispersed in polymer material into single particles, for example, as a result of ultrasound application in the process of paints (lacquers) mixing. In order to decrease the agglomeration of nanofillers particles, they are coated with a polymer coating, usually made of organosilanes [L. 8, 12, 15, 17, 22].

The following nanofillers are most frequently used for polymer coatings modification: aluminium trioxide, silica, modified layered aluminosilicates, titanium dioxide, calcium carbonate, and carbon black, which was the first nanomaterial used in industry for rubber production at the turn of the 20th century.

The dynamic development of nanotechnology in the area of the production of paints and lacquers contributed to the development of new generation of polymer nanocoating systems of the thickness in the range of 3–30 μm range, while the conventional coating systems are ten times thicker on average. It should be stressed that the mass share of nanofillers in polymer nanocoatings reaches only 3–5%, while the traditional polymer coatings need 20–30% of microfillers to meet similar barrier properties. In this connection, the application of nanofillers for polymer coatings modification leads, in most of cases, to the decrease in the unit cost of protective coatings.

Effective choice of nanofillers, its mass share, as well as its grain shape and size, can increase resistance of coatings to climatic factors and also can decrease their erosive wear intensity [L. 8, 18–21, 28, 29].

METHODICS OF POLYURETHANE TOP COATS EXAMINATION

Materials and samples preparation of polymer top coats

The investigations were made of polyurethane top coats of polymer coatings with three-layer systems consisting of an epoxy primer and interlayer, and polyurethane top coat.

Coating systems were applied on the surface of steel samples (of dimensions 170 × 90 × 1,5 mm) made of S235JR steel. The surface of each steel sample underwent an abrasion process in special tumblers filled with ceramic pins and then, directly before primer coat air-spray application, was degreased with methyl alcohol and dried.

In order to improve top coat erosive resistance, the composition of polyurethane paint was modified with one of three nanofillers. The first and second was silica with a grain size of 12 nm and 20 nm, respectively, while the third was aluminium trioxide (Al₂O₃) with a grain size of 20 nm. The mass share of each nanofiller in the paint was equal to 3%. The surface of nanofiller grains was coated with polymer material preventing their agglomeration. The grains of silica were coated with dimethyldichlorosilane, while the grains of aluminium trioxide were coated with polysiloxane.

The coating systems with top coat made of the modified paint were then subjected to two-stage curing: the first, at a temperature of 20°C for 24 h, and the second at a temperature of 120°C for 0.5 h. Then they were acclimatized for 10 days at a temperature of 20±2°C and a relative humidity of 65±5% (acc.PN-EN-23270: 1993). After acclimatization, such properties of epoxy-polyurethane coating systems like thickness, hardness, and surface roughness were examined.

Climatic examination methodology of the coating systems with polyurethane top coats

Samples of polyurethane-epoxy systems were aged in natural climatic conditions in climatic station situated in Radom, in UTH Institute of Maintenance of Vehicles and Machines site (Fig. 1). The samples were inclined at 45° to the horizontal and turned south (acc. PN-EN ISO 2810:2005). The maximum ageing period was 42 months.



Fig. 1. Samples of coatings located on racks in climatic station

Rys. 1. Próbkki powłok lakierniczych umiejscowione na stojakach stacji klimatycznej

Physical properties examination methodology of polyurethane top coats

The thickness of polyurethane top coats was examined acc. PN-EN ISO 2808:2008 using Mega Check FE equipment, and their hardness was evaluated on the basis of Buchholz indentation test acc. PN-EN ISO 2815:2004. The thickness of the polyurethane-epoxy coating systems was equal to $175 \pm 1 \mu\text{m}$, while the thickness of polyurethane top coats was equal to $53 \pm 1 \mu\text{m}$.

The examination of the coating's surface roughness was made using interference microscope, Talysurf CCI from Taylor Hobson. This microscope enables the examination of surface roughness, waviness, and shape acc. PN-87/M-04251 and PN-EN ISO 8501-1:2007.

Destruction of aged polyurethane top coats was evaluated on the basis of microscopic examination carried out using Hitachi SU-70 Analytical Field Emission SEM, equipped with an EDS spectrometer from Thermo Scientific.

Method of erosive resistance examination of polyurethane top coats

The examination of the top coat's erosive resistance was executed using the method and the equipment described in Polish standard PN-76/C-81516 (Fig. 2a).

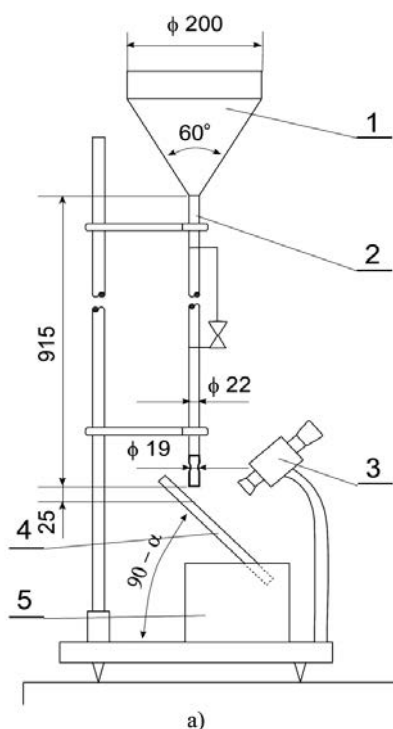
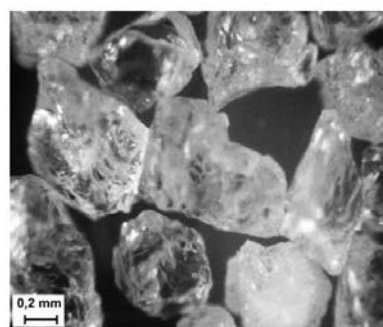
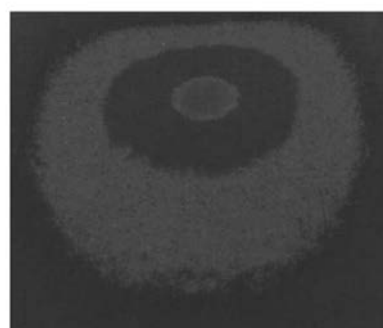


Fig. 2. a) Apparatus for testing erosive wear of polymeric coatings: 1 – container for erosive material; 2 – pipe transporting erosive material; 3 – optical microscope; 4 – rotational holder for fixing metallic test specimen with a polymer coating; 5 – container collecting erosive material after the test; b) morphology of granulated alundum 99A particles; c) wear scar of polyurethane top coat

Rys. 2. a) Urządzenie do badania zużycia erozyjnego powłoki polimerowej: (1 – pojemnik na materiał erozyjny; 2 – rura transportująca materiał erozyjny; 3 – mikroskop; 4 – uchwyt obrotowy do mocowania próbki metalowej z powłoką polimerową; 5 – pojemnik zbierający przesypany materiał erozyjny); b) morfologia elektrokorundu granulowanego 99A; c) ślad przetarcia powłoki poliuretanowej



b)



c)

The method consist in subjecting a coating to the action of successive portions, 3.5 kg, of erosive particles, which are poured into Container 1 (Figs. 2a and 2b), where they freely fall on the coating sample, inclined at an angle of 45° in relation to the stream direction from the height of 1 m. The examination is continued until the wear of the top coat is observed. Then the portion of erosive particles is reduced to 0.5 kg, and the examination is continued to the moment when in the top coat elliptic wear scar occurs of a minor diameter $\varphi = 3.6$ mm (Fig. 2c). The portion of erosive material is replaced with new material after each hundred applications.

As erosive material alundum 99A (acc. PN-76/M-59111) of grain no. 30 (acc. PN-ISO 8486-2:1998) (Fig. 2b) is used in this method. Aluminium trioxide is the main constituent of alundum (99% min.), while silicon dioxide, iron trioxide, calcium oxide, and sodium oxide are other constituents.

An index S was used for the evaluation of the polymer coating's resistance to erosive wear, which expresses the relation between the total mass of erosive particles (M), producing wear of the coating in the examined area, and the coating thickness (G).

$$S = \frac{M}{G} \quad (1)$$

where

- S – erosive resistance, kg/μm;
- M – erosive particles mass, kg;
- G – mean thickness of examined coating, μm.

The reciprocal of the S index is called the intensity (I) of polymer coating erosive wear.

EROSIVE RESISTANCE EVALUATION OF POLYURETHANE NANO TOP COATS AGED CLIMATICALLY

Climate ageing of polyurethane-epoxy coating systems had a significant impact on the erosive wear intensity increase of polyurethane top coats. Erosive resistance characteristics of polyurethane nanocoatings are presented in Fig. 3.

Table 1. Trend line equations and coefficient of determination R^2 values of polyurethane top coats erosive resistance characteristics

Tabela 1. Równania linii trendu i wartości współczynnika determinacji R^2 charakterystyk odporności erozyjnej nawierzchniowych powłok poliuretanowych

No.	Coating type	Trend line equations	Coefficient of determination R^2
1	PUR-SiO ₂ – 12	$y = -0,078x + 0,892$	0,995
2	PUR-Al ₂ O ₃ – 20	$y = -0,062x + 0,734$	0,956
3	PUR-SiO ₂ – 20	$y = -0,063x + 0,684$	0,995
4	PUR	$y = -0,076x + 0,674$	0,971

The highest erosive resistance was revealed by the polyurethane coating modified with silica with a grain size of 12 nm. An increase of silica grain size up to 20 nm caused its erosive resistance to decrease. On the other hand, modification of the polyurethane top coat with aluminium trioxide nanoparticles with a grain size of 20 nm resulted in higher erosive resistance than in the case of using nano-silica of the same grain size. The lowest erosive resistance was observed for unmodified polyurethane coatings, both unaged and climatically aged (Fig. 3).

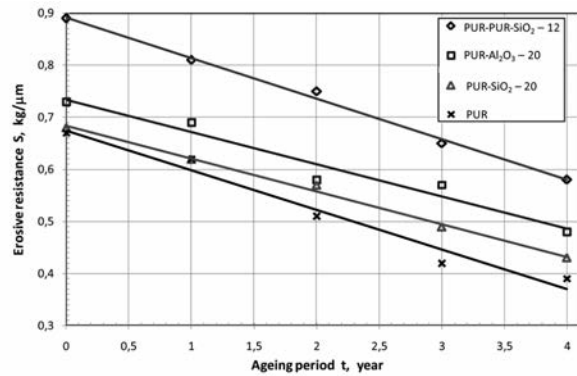


Fig. 3. Erosive resistance of polyurethane top coats: PUR-SiO₂ – 12 – polyurethane top coat modified with nanoparticles of silica, with a grain size of $d = 12$ nm; PUR-Al₂O₃ – 20 – polyurethane top coat modified with nanoparticles of aluminium trioxide, $d = 20$ nm; PUR-SiO₂ – 20 – polyurethane top coat modified with nanoparticles of silica; $d = 20$ nm; PUR – unmodified polyurethane coating

Rys. 3. Odporność erozyjna nawierzchniowych powłok poliuretanowych: PUR-SiO₂ – 12 – powłoka poliuretanowa modyfikowana nanocząstkami krzemionki o rozmiarze $d = 12$ nm; PUR-Al₂O₃ – 20 – powłoka poliuretanowa modyfikowana nanocząstkami tritlenku diglinu o $d = 12$ nm; PUR-SiO₂ – 20 – powłoka poliuretanowa modyfikowana nanocząstkami krzemionki o $d = 12$ nm; PUR – powłoka poliuretanowa niemodyfikowana

Characteristics of polyurethane coatings erosive resistance are described with straight lines (Table 1).

Destruction of the coating's surface under the influence of climatic factors caused an erosive resistance decline of polyurethane coatings. The following defects

were detected on the surface of aged coatings: blisters (Fig. 4.2), etchings, cracks (Fig. 5.1), and silver cracks in this number (Fig. 5.2).

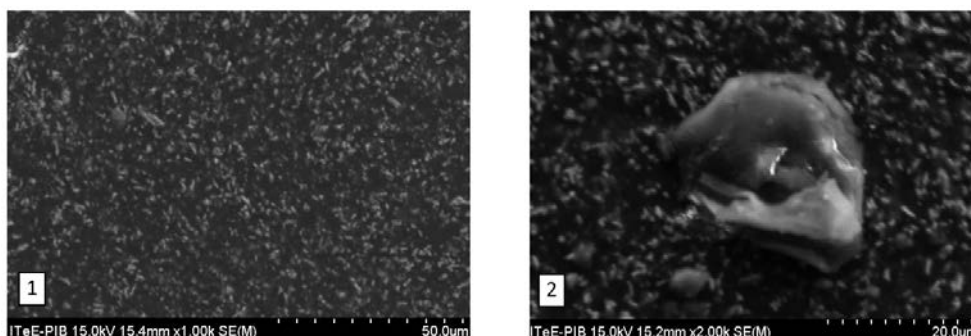


Fig. 4. Surface morphology of polyurethane top coat modified with silica nanoparticles with the grain size of 12 nm (1 – unaged coating, 2 – coating aged climatically for 3 years)

Rys. 4. Morfologia powierzchni nawierzchniowej powłoki poliuretanowej modyfikowanej nanocząstkami krzemionki o rozmiarach ziarna $d = 12$ nm (1 – powłoka niestarzona, 2 – powłoka starzona klimatycznie w okresie 3 lat)

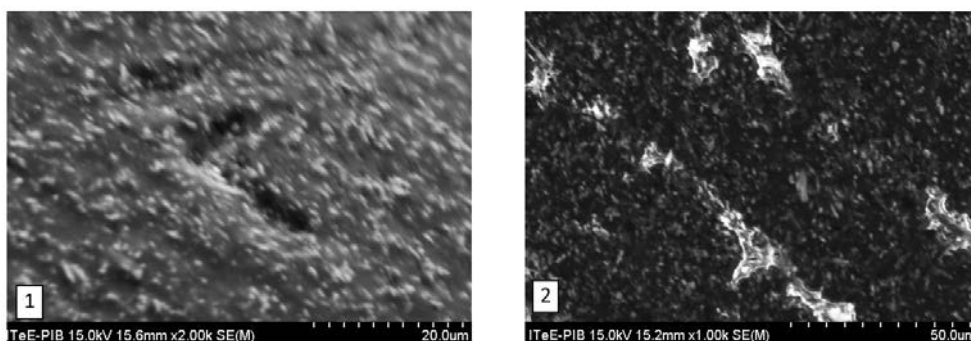


Fig. 5. Influence of climatic ageing for 3 years on surface destruction of polyurethane coating modified with silica nanoparticles with the grain size of 12 nm (1 – etchings in surface layer, 2 – superficial silver cracks)

Rys. 5. Wpływ starzenia klimatycznego w okresie 3 lat na destrukcję powierzchni powłoki poliuretanowej modyfikowanej nanocząstkami krzemionki o rozmiarach ziarna $d = 12$ nm (1 – wytrawienia w warstwie nawierzchniowej, 2 – powierzchniowe pęknięcia srebrzyste)

The addition of nanofillers resulted in a increase in the Buchholz hardness of polyurethane coatings. It was connected with the high hardness (acc. Mohs scale) of the nanofillers, since aluminium dioxide (alundum) hardness is equal to 9 and silica hardness is equal to 7. Ordinary fillers, commonly used in polymer paints, have hardness lower than alundum and silica. For example, the Mohs hardness of iron dioxide (haematite) is in the

5.5–6.5 order, of barium sulphate, it is equal to 2, and of microtalc, it is equal to 1.

Climatic ageing in three-year period caused the Buchholz hardness of the polyurethane coating to decline. The biggest decline (by 24%) was observed in the case of unmodified polyurethane coatings; whereas, coatings modified with nanofillers presented a high stability of their hardness (Table 2).

Table 2. Buchholz hardness of polyurethane top coats (acc. PN-EN ISO 2815:2003)

Tabela 2. Twardość (wg Buchholza) nawierzchniowych powłok poliuretanowych (wg PN-EN ISO 2815:2003)

No.	Coating type	Hardness of unmodified coatings	Hardness of coatings aged climatically in the period of 3 years	Decrease of coating hardness after ageing period [%]
1	PUR-SiO ₂ – 12	94	89	5
2	PUR-Al ₂ O ₃ – 20	91	85	7
3	PUR-SiO ₂ – 20	87	79	9
4	PUR	80	69	24

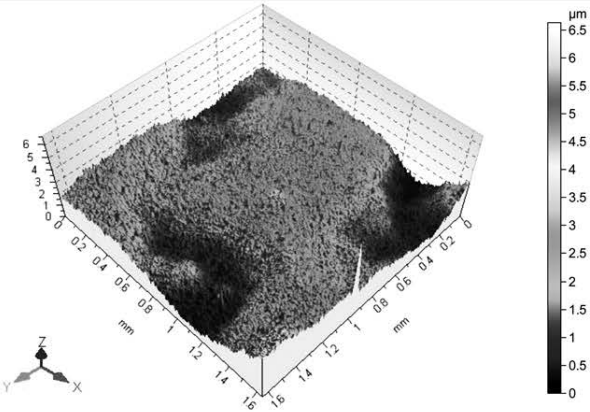
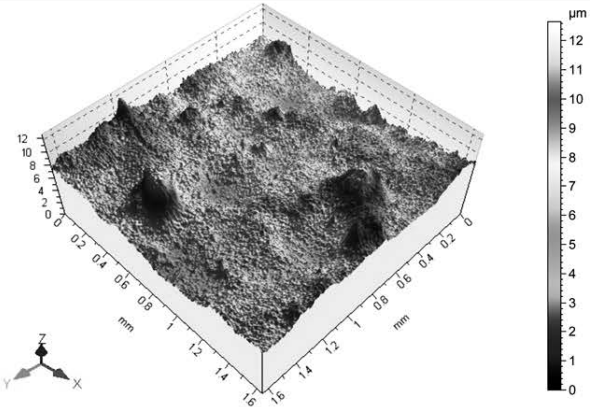
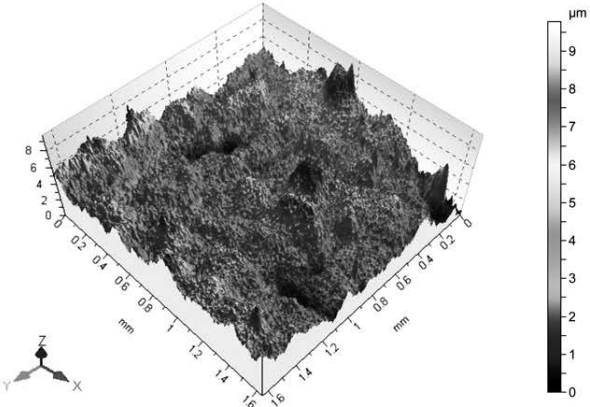
Climatic ageing meaningfully influence surface topography configuration of polyurethane coatings (**Table 3**). Polyurethane coatings modified with nanofiller showed lesser change in surface topography than unmodified coatings, because the modification of polyurethane top coats with nanofillers decreases their susceptibility to surface destruction.

Niches appearing in aged top coats (**Table 3**) increase the susceptibility of coatings to biological corrosion, because moisture and organic impurities accumulate in them that favour the development of

such microorganisms, e.g., viruses, bacteria, and fungi. Products of their metabolism cause the destruction of coatings in the form of craters and etchings, which decrease the coating's protective effectiveness. The appearance of the coating deteriorates as a result of original gloss and colour loss. Moreover, discolorations occur in the sites of biological corrosion development, which is observed especially in the first period of the coating's destruction under the influence of microorganisms [L. 32].

Table 3. Topography of polyurethane coating surface

Tabela 3. Topografia powierzchni powłoki poliuretanowej

Kind of polyurethane coating	Ageing period [year]	Surface topography
Unmodified coating	0	
Unmodified coating	3	
Coating modified with silica nanoparticles (grain size $d = 12$ nm)	3	

Ageing of polyurethane coatings in natural climatic conditions contributed to the increase of their surface roughness. The polyurethane coating modified with silica with a grain size of 20 nm showed a Ra parameter value twice as high as other coatings. The reason of its relatively high surface roughness may be seen in agglomerates forming by silica nanoparticles. This testifies to the uneven distribution of nanofiller grains in the polyurethane coating. It should be noticed that climatic ageing of polyurethane coatings modified with silica with a grain size of 20 nm did not influence its surface roughness parameter Ra. In the case of the ageing of other polyurethane coatings Ra parameter, they increased by about 20% (Fig. 6).

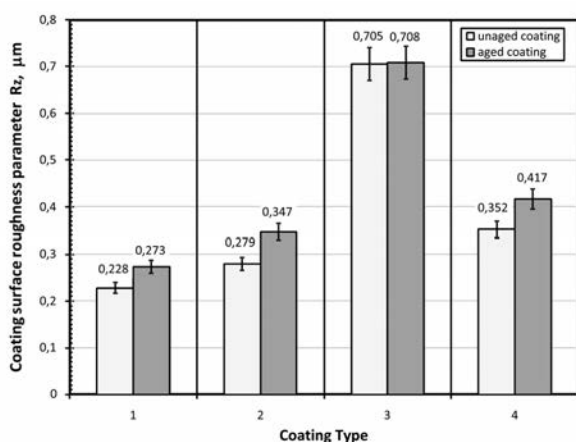


Fig. 6. Influence of climatic ageing for 3 years on Ra parameter value of polyurethane coating surface (1 – PUR-SiO₂ – 12, 2 – PUR-Al₂O₃ – 20, 3 – PUR-SiO₂ – 20, 4 – PUR)

Rys. 6. Wpływ starzenia klimatycznego w okresie 3 lat na wartość parametru Ra chropowatości powierzchni powłoki poliuretanowej: (1 – PUR-SiO₂ – 12, 2 – PUR-Al₂O₃ – 20, 3 – PUR-SiO₂ – 20, 4 – PUR)

In the case of the climatically aged coatings, the lowest increase (by 70%) of the Rz parameter was observed for coatings modified with silica with a grain size of 20 nm (Fig. 7), whereas the highest increase (by 90%) of Rz parameter was observed for coatings modified with aluminium trioxide. These coatings demonstrated chipping of nanofiller agglomerates from the nanocoating's superficial layers.

The increases of Ra and Rz roughness parameters of polyurethane coatings (Figs. 6 and 7) result from the coating's constituents chipping from their superficial layers as a result of an increase in brittleness. The brittleness of coatings increases primarily due to the oxidation of polyurethane material under the influence of ultraviolet radiation coming from the sun [L. 1, 22].

Oxidised layers revealed an adhesion loss of polyurethane material from the surface of fillers and pigment particles [L. 30, 31]. The subsequent stage of the polyurethane coating's destruction consisted

in the release of particles of fillers and pigments from superficial layers of the examined polyurethane-epoxy coating systems. In consequence, this phenomenon had a substantial influence on the increase of the surface roughness parameters of polyurethane-epoxy coatings aged climatically. It should be stressed that addition of nanosilica with a grain size of 12 nm, as well as addition of aluminium dioxide, reduced the destruction of the polyurethane coating's superficial layers, which decreased the loss of the coating's constituents.

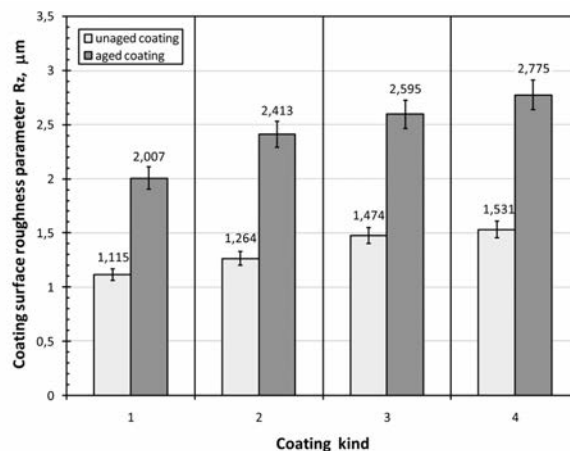


Fig. 7. Influence of climatic ageing for 3 years on Rz parameter value of polyurethane coating surface (1 – PUR-SiO₂ – 12, 2 – PUR-Al₂O₃ – 20, 3 – PUR-SiO₂ – 20, 4 – PUR)

Rys. 7. Wpływ starzenia klimatycznego w okresie 3 lat na wartość parametru Rz chropowatości powierzchni powłoki poliuretanowej (1 – PUR-SiO₂ – 12, 2 – PUR-Al₂O₃ – 20, 3 – PUR-SiO₂ – 20, 4 – PUR)

CONSLUSIONS

1. Climatic ageing of polyurethane top coats essentially influenced their erosive wear kinetics. With an increase of the ageing period, the intensity of coatings erosive wear increased too. It was caused by the destruction of the coating's surface in the form of cracking and blistering, as well as craters and etchings formation, as a result of chipping of the coating's constituents. It caused a surface roughness increase of the polyurethane coatings, evaluated on the basis of Ra and Rz parameters.
2. Polyurethane top coat's erosive resistance was enhanced by their composition modification with the addition of nanofiller of a 3% mass share, e.g., silica (with a grain size of 12 nm or 20 nm) or aluminium trioxide (with a grain size of 20 nm). Nanoparticle content in the superficial layer caused the hardness increase of modified coatings, as well as a decrease of their surface roughness.
3. The highest erosive resistance was gained by polyurethane top coat modified with silica with a grain

size of 12 nm. The increase of silica grain size to 20 nm induced a decrease of the coating's erosive resistance which was connected with higher surface roughness caused by filler nanoparticles' agglomeration. Application of aluminium trioxide nanoparticles with a grain size of 20 nm for the polyurethane top coat modification contributed to achieve higher erosive resistance than in the case of silica nanoparticle application of the same grain size. It is probably connected with higher hardness of aluminium trioxide nanoparticles than silica nanoparticles, which transfers to the hardness of polyurethane top coats modified with these fillers application.

4. The lowest erosive resistance was revealed by the unmodified polyurethane top coat, aged climatically,

as well as unaged. These coatings showed a higher surface roughness among the examined samples. In the case of unmodified coatings, the biggest development of the observed surface destruction was caused by climatic ageing (in the form of craters, etchings, and cracks).

5. Climate ageing significantly influenced the surface topography configuration of polyurethane top coats. Polyurethane coats modified with nanofillers revealed lower surface topography change than unmodified coats. This leads to the conclusion that the modification of polyurethane top coats with nanofillers decreases their surface susceptibility to destruction.

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