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ANALYSIS OF POLYURETHANE TOP-COAT DESTRUCTION INFLUENCE ON EROSION KINETICS OF POLYURETHANE-EPOXY COATING SYSTEM

ANALIZA WPŁYWU DESTRUKCJI NAWIERZCHNIOWEJ POWŁOKI POLIURETANOWEJ NA KINETYKĘ EROZJI SYSTEMU POWŁOK POLIURETANOWO-EPOKSYDOWYCH*

The paper presents results of investigations concerning influence of climatic factors and environmental pollution on chemical and physical destruction of polyurethane top coat. In order to increase the operational life of polyurethane coating, its composition was modified by nanoparticles addition of aluminium dioxide (of grain size $d=20$ nm) or silica (of grain size $d=16$ nm), which mass share was 3%. Three-year ageing on climatic station of coating systems samples with such modified top coat as well as with unmodified top coat caused its chemical destruction as FTIR (Fourier-transform infrared spectroscopy) examinations documented relevant increase of carbonyl groups (C=O) content. This fact testified oxidation degree rise of superficial layers which indicated their oxidation resistance decrease. Also oxidation initial temperature decrease of polyurethane coating was revealed using DSC (Differential Scanning Calorimetry). Influence of climatic factors and environmental pollution contributed also to the physical destruction of the coating which caused an increase of its surface roughness and generated craters, etchings and cracks (including the silver cracks). Destruction degree of climatically aged polyurethane coating influenced erosive wear intensity of three-layer polyurethane-epoxy coating system. The lowest chemical and physical destruction under the influence of operational factors as well as the highest hardness revealed the coating systems with polyurethane top coat modified with aluminium dioxide what was the reason that they showed also the lowest erosive wear intensity. On the other hand, aged analogously coating systems with polyurethane top coat modified with silica were marked by comparably bigger destruction than the coating systems modified with aluminium dioxide which was the reason of their erosive wear intensity increase.

Keywords: polyurethane nano top coat, climatic ageing, chemical and physical destruction of a coating, erosion.

W artykule przedstawiono wyniki badań wpływu naturalnych czynników klimatycznych oraz zanieczyszczeń środowiskowych na destrukcję chemiczną i fizyczną nawierzchniowej powłoki poliuretanowej. Celem zwiększenia trwałości eksploatacyjnej powłoki poliuretanowej wprowadzono do jej składu nanocząstki tlenku glinu (o rozmiarze ziarna $d=20$ nm) lub krzemionki (o rozmiarze ziarna $d=16$ nm), których udział masowy wynosił 3,5%. Starzenie próbek systemów powłokowych, zarówno z tak zmodyfikowaną powłoką nawierzchniową, jak i z powłoką nawierzchniową niemodyfikowaną, na stacji klimatycznej w okresie 3 lat spowodowało destrukcję chemiczną powłoki nawierzchniowej. Badania spektroskopowe w podczerwieni (FTIR) udokumentowały bowiem istotne zwiększenie zawartości grup karbonylowych (C=O), świadczące o wzroście stopnia utlenienia warstw nawierzchniowych, co wskazuje na zmniejszenie ich odporności oksydacyjnej. Na podstawie analizy termicznej DSC (różnicowej kalorymetrii skaningowej) ustalono również obniżenie temperatury początku utleniania powłoki poliuretanowej. Oddziaływanie czynników klimatycznych i zanieczyszczeń środowiska przyczyniło się także do destrukcji fizycznej tej powłoki. Skutkowało to wzrostem chropowatości jej powierzchni oraz tworzeniem: kraterów, wytrawień, i pęknięć (w tym pęknięć srebrzystych). Stopień destrukcji starzonej klimatycznie powłoki poliuretanowej miał wpływ na intensywność zużycia erozyjnego trójwarstwowego systemu powłok poliuretanowo-epoksydowych. Najmniejszą destrukcją chemiczną oraz fizyczną pod wpływem czynników eksploatacyjnych oraz najwyższą twardością wyróżniały się systemy powłokowe z poliuretanową warstwą nawierzchniową modyfikowaną tlenkiem glinu, co było przyczyną najniższej intensywności ich zużycia erozyjnego. Natomiast starzone klimatycznie systemy powłokowe z poliuretanową warstwą nawierzchniową modyfikowaną krzemionką charakteryzowały się porównywalnie większą destrukcją, niż systemy powłokowe modyfikowane tlenkiem glinu, co zwiększyło intensywność ich zużycia erozyjnego.

Słowa kluczowe: nawierzchniowa nanopowłoka poliuretanowa, starzenie klimatyczne, destrukcja chemiczna i fizyczna powłoki, erozja.

1. Introduction

Polymer coatings are commonly used in order to protect technical objects surface against destructive action of climatic and environmental factors as well as to improve their visual appearance. Under the influence of above operational factors, a degradation of polymer material occurs, in the form of chemical bonds breaking and crosslinking,

which results in chemical structure and physical properties change [11, 16].

The following kinds of polymer coating wear processes are distinguished [11]: ageing, mechanical, ablational, chemical, thermal, corrosive, and biological. Erosive, tribological (abrasion, scratching) and fatigue wear as well as wear in the form of cracking – all of them are counted to mechanical wear. Cracking may be divided into silver

(*) Tekst artykułu w polskiej wersji językowej dostępny w elektronicznym wydaniu kwartalnika na stronie www.ein.org.pl

cracking, fatigue cracking as well as cracking under the influence of corrosive or residual stresses.

Operational life of polymer coatings in aggressive environment depends considerably on environment state, i.e. temperature, usage conditions variability, concentration of aggressive factor and its movement dynamics. Destruction and degradation degree of polymer coatings significantly depends on ageing factor [16]. Ageing causes degradation of polymer material inducing an increase of carbonyl groups content [5, 11, 12, 16, 39] which usually leads to polymer coatings brittleness growth [10-13].

In fact, operational factors act synergistically on polymer coatings generating intensive development of ageing processes. This leads to coatings destruction and wear contributing to the loss of their protective as well as decorative properties. Ultraviolet radiation influence on polymer coatings is a crucial reason for their decorative properties loss. It leads to generation of superficial silver cracks and surface roughness increase as a result of oxidised layers chipping. This type of destruction causes, in effect, coatings gloss decline as well as their original colour fading and also local discolorations as a result of microbiological corrosion development in niches existing in surface microroughness [14].

Depending on a factor contributing to polymer degradation the following degradation kinds can be distinguished: photodegradation (under the influence of UV radiation), thermodegradation (under the influence of thermal radiation), mechanical degradation (under the influence of mechanical loads), oxidative degradation (under the influence of oxygen), hydrolytic degradation (under the influence of water, acids and alkalis). All above mentioned degradation processes of polymer coatings may occur during their operational use in conditions of climatic and environmental factors action [11].

Degradation processes occurring in coating polymer decline mechanical characteristics of the coatings [11] which leads particularly to the decrease of erosive resistance, tensile and bending strength, abrasive and scratch resistance and to brittleness increase as well. Operational factors contribute also to coatings decorative properties decrease as a result of colour change and shine loss [19].

External factors, contacting with polymer coatings, generate their physical destruction in the following forms: cracks, etchings, craters, blisters, interlayer delaminations, adhesion loss between coatings and a substrate, surface waviness and roughness increase. Therefore, degradation of coating polymer material and destruction of polymer coating both lead to its operational life decrease [11, 19, 24].

Aggressiveness of operational factors increases with environment relative humidity increase. Critical value of relative humidity, which advantages intensive development of electrochemical corrosion, exceeds 75% in clean atmosphere while in polluted declines to 60%. It should be stressed that impurities in the form of solid particles, settled on technical objects surface, create areas of humidity and microorganisms (viruses, bacteria, fungi, algae) condensation [47] which also contributes to electrochemical corrosion development [11].

Type of a resin decides in significant degree about abrasive wear resistance of polymer materials produced of the resin. It was proved by results of experiments carried out by Baier A. and Żółkiewski Sł. [2]. They examined abrasive resistance of laminates produced on epoxy or polyester resin basis. Laminates produced with epoxy resin use revealed higher resistance to abrasion and scratching.

Resistance to wear of polymer materials (protective coatings) depends also on their hardness which usually increases their resistance to abrasion and scratching. Impact of thermal fatigue and ageing on the hardness of polymer-ceramic composites was investigated by the authors of the work [34]. Obtained results confirmed high hardness stability of new silorane composites transferring to its high resistance to abrasive wear comparing with traditional composites.

Properties of coating systems are also determined by intermediate layer which was documented in the works [18 and 46]. As evidenced

in the work [18], modification of epoxy interlayer with glass microspheres in the system of epoxy coatings increase their resistance to the action of such erosive particles like electro-corundum. Zubieliwicz M. and Królkowska A. in the work [46] documented, on the basis of epoxy-polyurethane coatings examinations, that protection effectiveness of coating systems was determined by degradation degree of epoxy interlayer and the value of stresses generated in it.

Hard particles, characteristic for some kinds of operational environment, hitting surface of polymer coatings with a certain velocity cause their erosion [15, 22]. Authors of works [21, 22, 36, 44] wrote on the basis of their investigations that, in the polymer coatings case, intensity of erosive wear depends on the erosive particles angle of incidence. For acute incidence angles of hard erosive particles, microcutting of coating is a dominating wear process while for incidence angles exceeding 45° plastic deformation of coating dominates. According to carried out investigations, the highest intensity of polymer coatings erosive wear is observed for incidence angle values in the range from 30° to 45°. For this range, microcutting dominates, not fatigue process [22].

Extreme of erosive wear rate characteristic of polymer coating, in dependence on erosive particle incidence angle, is contingent also on coating hardness [22, 44, 45]. In the case of coatings made of elastic polymers, of low elastic modulus, the highest wear rate is observed for acute incidence angles. Moreover, in the work [44] it was showed that friction coefficient increase moves the extreme of erosive wear intensity characteristic in the smaller angle values direction [44]. Investigations made by Zahavi J. [44] proved also high resistance of epoxy composites to erosive action of sand grains. These composites showed semiplastic properties and their wear maximum value occurred for erosive particles incidence angle α values in the range from 45° to 60°. Others examined composites (quartz-polyimide, quartz-polybutadiene) showed wear maximum for incidence angle α values in the range from 75° to 90°. It was stated that the erosion process of the composite material consists of polymer material erosion and fibres of glass filler destruction due to breaking [44]. In the work [45] Zahavi J. presented examination results concerning sand grains (of dimensions in the range from 210 μm to 297 μm) incidence angle on polymer coatings erosive wear. It was determined that examined polyurethane and fluorocarbon coatings revealed maximum wear value for erosive particles incidence angle $\alpha=30^\circ$.

Intensity of polymer coatings erosive wear vitally depends on the stream velocity of erosive particles hitting the coating. The kinetics of polymer coatings erosive wear is also conditioned to a great extent by their thickness [22, 41]. In the frames of the work [22] investigations were made on erosive wear intensity of acrylic coatings comprising from 3 to 10 layers of total thickness from 120 μm to 420 μm . Thickness increase above 240 μm caused resistance of coatings to erosive particles action decrease which was connected with their destruction (cracking) under the influence of stresses arising in too thick coating during drying (curing) process. Influence of acrylic coatings thickness on their erosive wear intensity was also tested by Trezona R.I. and Hutchings I.M. [41]. The tests consisted in silicon carbide (of grain size equal 4.25 μm) erosive action on the 1 to 6-layer coatings of thickness from 12 μm to 184 μm . Determined dependence between coating thickness and its service life, in erosive wear condition, has linearly growing character. In carried out tests which served an assessment of polymer coatings wear kinetics, the total mass of all silicon carbide grains portions had a crucial importance. The method of erosive material (called erodent) exact dosing in examinations of construction materials erosive resistance was presented in the work [32].

Chemical and physical purity of a substrate which polymer coatings are applied on determines their operational life. A range of adhesion forces determining effective bonding of a coating with a substrate surface is of some nanometres order, so this surface should be absolutely impurity-free [48].

When, in natural operational conditions, a polymer coating loses its tightness (e.g. due to cracking or delamination), the electrochemical corrosion develops on metallic substrate. Erosive and corrosive wear processes of just uncovered substrate run by the way of simultaneous development and removing (with erosive particles action) of corrosion products from the substrate surface as the result of cracking, chipping and spalling processes [26].

Acid rains (pH<5.6) are ranked as especially dangerous aggressive media causing polymer coatings destruction [11]. They come into existence as the result of water combining with air gaseous impurities like sulphur dioxide, nitrogen oxides, hydrogen chloride or carbon dioxide which leads to generation of such acids like sulphur, nitric, hydrochloric and carbonic. There are also other dangerous media like salt mist (present in marine climate) as well as brine (sodium chloride water solution of concentration 20% to 25%), commonly used in winter in order to reduce road slipperiness [19].

In the first stage of ageing under the influence of operational factors, the deterioration of polymer coatings decorative properties is observed which consists in colour change as well as gloss decrease. In subsequent stages of coatings operation, their protective effectiveness decreases on account of physical destruction in the form of cracking, layers delamination, blistering, number and volume of pores increase as well as a result of adhesion to the substrate loss [11].

Each type of operational environment factor, acting on a polymer coating, causes usually specific for it cracks which dimensions increase with ageing period elongation [11]. An intensification of polymer coatings surface wear processes strongly depends on ultraviolet radiation which provokes structural defects originating in the coatings like micropores, microcracks and silver cracks. Silver cracking of polymer materials occurs also as a result of tensile stresses. Silver cracking characteristic was presented by Narisawa I. in the work [33]. This type of cracking is the result of such defect generation like empty spaces (pores), microfibrils, and defected macroparticles (oriented in the direction of deforming forces action). In reflected light of an optical microscope, they produce characteristic light reflexions explaining their name [33].

Defects generated in polymer coatings structure under the influence of environmental factors deteriorate their mechanical strength, including resistance to erosion resulting from hard particles hitting [11].

Polymer coating tightness, contingent on its porosity degree, is one of the fundamental criteria of protective function fulfilling by the coating towards the substrate. Pores originate in coatings as a result of ageing processes running in their structure under the influence of climatic (ultraviolet radiation, moisture, heat) and environmental (aggressive media, erosive particles) factors [11, 12, 16, 17]. Essential porosity increase of polymer coatings is caused by the sulphuric acid action. It was proved in the work [12] in which investigation results were presented concerning the influence of sulphuric acid water solutions (3%, 10% and 20%) on epoxy coatings state. Coatings porosity, as well as their surface roughness increase, was observed with the increase of aggressive medium concentration and the period of influencing. The reason of pores generation in polymer coating structure may be also seen in improper execution technique, for instance during drying process [19].

A period of aggressive media migration time in the substrate direction increases with the increase of a number of layers constituting polymer coatings. The probability of capillaries generation as a result of hydrophilic areas joining in multilayer coatings is quite low in comparison with single-layer coatings. This has an impact on delay and intensity decrease of the formation process of paths conducting aggressive media (capillaries). Moreover, capillaries in multilayer coatings have complicated shapes which elongate the way of aggressive media transportation to the substrate protected with the coating. According to the above, application of polymer coating multilayer

systems for technical objects surface protection against the destructive influence of operational environment factors should be considered as effective [11].

An increase of tightness determining polymer coatings protective effectiveness can be also obtained as a result of their structure modification with fillers of different types (organic and inorganic) and especially nanofillers. Coatings improved by nanofillers are called nanocoatings. Nanofillers improve also decorative properties of nanocoatings by their transparency and purity increase. The highest protective effectiveness of nanocoatings is obtained in the case when nanofillers are dispersed in coating forming material into individual nanoparticles, for instance as a result paints (lacquers) ultrasonic mixing. In order to minimise nanofillers particles agglomeration, their surface is covered with a polymer film, usually obtained of organosilanes [38]. Silica, as well as nanosilica, are most frequently applied for polymer coatings modification [3, 4, 6-8, 21, 23, 25, 27-31, 37, 39-43].

Coatings modified with silica addition reveal increased resistance to scratching and abrasion [3, 6, 25]. It was presented in the work [3] by Bauer F. and co-authors who examined acrylate coatings (cured with UV), enforced with nanosilica and microcorundum (containing ~99% of Al₂O₃). These coatings showed substantially higher resistance to scratching and abrasion. The authors of the work [6] found also that polyurethane coatings modified with silica were more resistant to abrasion than unmodified ones. Such coatings revealed also increased gloss and resistance to corrosion. Results of Leder G. and co-authors investigations documented resistance to scratching increase of solvent polymer coatings (cured with UV) containing fumed silica in their composition [25]. It was proved that addition of 5% to 15% fumed silica to polymer coatings composition has essential influence on their resistance to scratching which increased in the range from 10% to 35% [25].

Silica addition improves also polymer coatings resistance to erosion what Malaki M. and co-authors demonstrated in the work [30]. They investigated properties of polyurethane-epoxy composites, which were reinforced with silica nanoparticles, and stated that nanosilica addition significantly improved adhesive strength and microhardness of examined nanocomposites. Suraj M. and others [29] used nanosilica (of grain size 20 nm) for their modification to improve mechanical properties of polymer coatings. The coatings modified with nanofillers of mass share equal 3.50%, 6.74%, 9.75%, 15.17% were investigated. The improvement of mechanical properties (like tensile strength, elasticity, relative elongation at break) was obtained for nanosilica mass share equal 9.75% [29]. Chen G. and co-authors [5] enhanced mechanical properties of waterborne polyurethane coatings as a result of their composition modification with starch nanocrystals. They obtained coatings of increased cross-linking degree which advantageously affected their mechanical properties i.e. Young's modulus and tensile strength.

Nanofillers found also application in polymer topcoats, as introduction of nanofillers to these coatings composition does not affect their transparency, what was shown by the authors of the works [7, 8, 27, 39]. Barna E. and others [7] examined polyurethane coatings, modified with nanosilica of grain size below 100 nm and mass share up to 23%, obtaining highly transparent composite coatings. Lin B. and co-authors [27] examined polyurethane-acrylic coatings modified with nanosilica which grains were covered with silane film. Thanks to the modification the coatings were transparent and cracks free. Investigations in natural conditions revealed high resistance to soiling [27]. The authors of the work [39] showed that coumarin (for modification of nanosilica particles surface) added to polyurethane coatings composition beneficially influenced on their optical transparency. What more, coumarin diol assured total blocking of UV radiation which is beneficial in these coatings application for protection of such surfaces on which quality UV radiation influences negatively. Introduction of

modified nanosilica, as well as photo-induced cross-linking process, increased hydrophobicity of such obtained nanocomposites.

The authors of the works [6, 31] stated corrosive resistance increase of polymer coatings as a result of their modification with nanofillers. Matin E. and co-authors [31] examined epoxy coatings modified with nanosilica (of particles coated with polysiloxane anti-agglomeration agent) of grain size 20 nm and mass share from 3% to 6%. The most advantageous influence of nanosilica on the coatings corrosive resistance (during tests in salt mist for the period of 240 h) was detected for 5% mass share. In this case, the lowest development of corrosion was observed in the zone of the cross cut made on the coating surface during cross cut adhesion test. Moreover, microscopic examinations proved lower hydrolytic degradation, resulting from the coating tightening with this filler.

Modification of polymer coatings with nanofillers influences advantageously also on their thermal stability what was showed in the works [8, 37, 39, 40]. In the frames of the work [37], nanosilica of grain size 7 nm and mass share up to 3% was used for acrylate coatings composition modification. The nanosilica caused the substantial increase in thermal stability as the decomposition temperature (T_{dec}) value of these coatings increased by 40°C compared with unmodified coatings. The glass transition temperature T_g value increased by 10°C for nanosilica mass share 1%. For higher nanosilica concentrations, the increase of glass transition temperature value was slightly lower. The authors of the work [39] obtained thermal stability of the polyurethane coating improvement following the introduction to its composition of nanosilica particles coated with the film of a substance obtained from the coumarin. Su J. and co-authors [40], in order to increase the thermal stability of polymer coatings, modified their composition with the addition of nanosilica (of grain size from 80 nm to 120 nm) coated with polystyrene film which assured good dispersibility of the nanofiller in the paint. The addition of nanosilica improved also mechanical properties of the nanocoatings causing the increase of Young's modulus and tensile strength (in the case when the mass share of nanosilica was equal 10%), as well as elongation at break value increase (in the case when the mass share of nanosilica was up to 5%).

The content of silica nanoparticles in polymer coatings leads also the increase of polymer cross-linking degree which was shown in the work [4]. Bauer F. and co-authors investigated modified acrylate-epoxy coatings containing from 5% to 30% of nanosilica. These coatings revealed higher cross-linking density and hardness (pencil) than unmodified ones. However, the higher nanosilica content caused their brittleness increase which transferred into a gloss and coatings resistance to scratching decrease [4]. On the other hand, in the work [5] it was shown that the 2.5% (wt) nanosilica addition to the polyurethane coatings composition increased their cross-linking degree, improving thereby coatings adhesion, evaluated on the grounds of the cross-cut adhesion test.

Nanoparticles of aluminium trioxide (Al_2O_3) are frequently used for modification of polymer coatings structure [7, 23, 42]. Such type of nanofiller introduction to polymer coatings structure improves their mechanical properties as well as the tightness [7, 41]. Gorlu S. and others [7] investigated epoxy coatings with addition of (1, 2.5 and 3.5)% (wt) Al_2O_3 particles (coated with polymer film), of diameter below 100 nm. Investigation results showed that Al_2O_3 nanoparticles significantly improved erosive resistance of such epoxy nanocoatings. What more, the nanoparticles reduced permeability of water through the coatings and, in this connection, their resistance to hydrolytic degradation [7]. High resistance to corrosion showed oxysilane coatings, modified with Al_2O_3 nanoparticles, which were investigated in salt spray and also using linear voltammetry (LVA) and electrochemical impedance spectroscopy (EIS) in 0.05 M solution of NaCl, which was described in the work [23]. Wang Y. and co-authors documented in the work [42] that polymer coatings containing from 5% to 20%

(wt) Al_2O_3 nanoparticles showed increased resistance to scratching and abrasion in comparison to unmodified ones. The improvement resulted from high hardness of Al_2O_3 nanoparticles dispersed homogeneously in the coatings structure.

Nanofillers application in polymer coatings reduces their porosity which effectively influences barrier properties of such obtained nanocoatings [20, 35]. In the work [20] it was shown that copper nanoparticles of 66 nm grain size and 3.5% wt share, used for epoxy coatings modification, contributed to decrease pores volume in them (evaluated using mercury porosimetry method) by 32%. Beneficial changes of nanocoatings physical properties obtained in this way contributed to these coatings erosive resistance increase [21].

To modify paints (lacquers), of which protective-decorative polymer coatings are produced, to their composition are introduced nanoparticles of the following substances: zinc oxide [28], titanium dioxide [8, 38], calcium carbonate or carbon black [9, 35]. Nanoparticles of minimum size introduction to polymer coatings structure do not decrease their transparency. The authors of the work [28] obtained this effect introducing ZnO nanoparticles (of 3-5 nm size and share 1-15% wt) to the structure of transparent methacrylate coatings. What more, composite coatings containing more than 7% of ZnO absorbed UV radiation (of wave length below 350 nm) which testified their ability to screen this type of radiation.

Properties of polymer coatings depend also strongly on paint mixing way, influencing dispersion degree of nanoparticles, which was documented by Xiong M. and co-authors in the work [43]. They applied the high shear mixing technique obtaining in this way good dispersing of silica nanoparticles in polymer composition which resulted in increase of coatings tensile strength as well as glass transition temperature (T_g) of acrylic material.

Nanotechnology advancement [35] in the area of paints and lacquers production in last ten years contributed to the development of new generation polymer coating systems which thickness was of 3-30 μm order whereas the conventional coating systems are, on average, ten times thicker. It should be stressed that in the technology of polymer nanocoatings constituting the mass share of nanoparticles is in the range from 3% to 5%. In order to obtain similar barrier properties in the case of traditional coating, the mass share of microfiller should be in the range from 20% to 30%. In this connection it can be stated that nanofillers application to polymer coatings modification leads now, in the most of cases, to decrease of coating materials consumption which, in the effect, decreases environmental pollution as well as cuts back material costs. Through the optimal choice of a nanofiller kind and its volume share as well as its grains shape and size one can increase coatings resistance to the influence of such factors like climatic (moisture, solar radiation) and environmental (aggressive media, erosive particles, microorganisms). Polymer nanocoatings, due to their particular properties, possess higher operational life resulting from their higher resistance to climatic and environmental factors action in comparison to traditional coatings. Moreover, they have better aesthetical values [6, 7, 9, 35].

The modification with nanofillers use is often applied to polyurethane coatings which, even as unmodified, reveal high resistance to climatic factors action; especially they are highly resistant to ultraviolet radiation. The aim of polyurethane coatings modification with addition of nanofillers is their tightness enhancement which transfers to their protective efficiency increase as a result of their resistance to mechanical and corrosive loads growth [5, 6, 27, 29, 39, 46].

2. Research methodics

2.1. Materials and samples preparation

The aim of presented in the paper investigations was an analysis of top coat destruction influence on erosive wear kinetics of whole

coating system, protecting steel substrate. The three-layer polymer coating systems were investigated which consisted of epoxy primer layer, epoxy interlayer and polyurethane top coat. The coats were applied using air-spray method on steel plates of dimensions 160 x 80 x 2 mm, made of steel S235JR sheet. Steel plates surface was cleaned in special abrasive tumbling barrels filled with ceramic pins. Immediately before coats application, steel plates surface was degreased.

In order to improve the top coat resistance to operational factors, the polyurethane paint composition was modified using one of two nanofillers. Silica (silicon dioxide, SiO_2) of grain size $d=16$ nm was the first one and alumina (aluminium dioxide Al_2O_3) of grain size $d=20$ nm was the second one. The mass share of each kind of filler in the coating was 3.5%. Prior to nanofiller introduction to the polyurethane paint, a polymer film was applied on the surface of nanofiller grains to protect them against agglomeration. The grains of silica were coated with dimetyldichlorosilane and the grains of alumina were coated with polysiloxane.

The coatings were cured in two stages – for 24 h at 20°C and then for 0.5 h at 120°C . After application, polyurethane-epoxy coating systems underwent acclimatisation for 10 days at temperature $20 \pm 2^\circ\text{C}$ in environment of relative humidity $65 \pm 5\%$ (acc. PN-EN 23270:1993). After acclimatisation preliminary examinations of such coating systems properties like thickness, hardness and surface roughness.

2.2. Ageing of polyurethane-epoxy coatings on the climatic station

The samples of polyurethane-epoxy coating systems were aged in natural climatic conditions at climatic station situated on the site of Institute of Vehicles and Machines Maintenance, University of Technology and Humanities in Radom. The steel plates with examined coatings were inclined at an angle of 45° and turned south (acc. PN-EN ISO 2810:2005). Maximum period of climatic ageing was 3 years.

2.3. Methodics of polyurethane-epoxy coatings examination

Examined coatings thickness was measured using apparatus Mega-Check FE (of List-magnetik) according to the standard PN-EN ISO 2808:2008. Coatings hardness was evaluated by the Buchholz method according to standard PN-EN ISO 2815:2004.

A state of coatings surface was analysed grounding on R_a and R_z parameters of surface roughness and on surface topography images. Examinations were made using interferometric microscope Talysurf CC of Taylor Hobson which enabled optical surface roughness measurements. Coating surface roughness was evaluated according to the standards PN-M-04251:1987 and PN-EN ISO 8501-1:2008 requirements.

Physical destruction of aged polyurethane coatings (top coats) was examined using Hitachi FE-SEM SU-70. The microscope was equipped with energy-dispersive *x-ray* spectrometer of Thermo Scientific enabling qualitative evaluation of chemical composition changes in polyurethane top coats (to $1 \mu\text{m}$ depth), generated by ageing processes.

Destruction analysis of polyurethane top coats chemical structure, following ageing at climatic station, was carried out on the basis of IR spectrophotometry using Jasco FT/TR 6200 apparatus. This apparatus was controlled by a computer with the help of the Spectra Manager programme enabling also graphical and mathematical processing of spectra. Spectra were recorded applying reflectance method using single-reflection ATR accessory of IR spectral range $\nu=(4000-600) \text{ cm}^{-1}$ and 4 cm^{-1} resolution.

Polyurethane top coats oxidation stability, assessed on the basis of oxidation onset temperature (OOT) value which determined their thermal resistance, was examined using LABSystem SETARAM TG-DTA/ DSC apparatus. The measurements were carried by dynamic

method at linear temperature rise, in oxygen atmosphere. Polyurethane material samples were heated in platinum melting pot starting from 20°C and ending at 400°C temperature, at velocity $10^\circ\text{C}/\text{min}$ and oxygen flow rate $60 \text{ ml}/\text{min}$. The mass of each sample was $3.0 \pm 0.5 \text{ mg}$. On the basis of obtained DSC curves, the extrapolated OOT of polyurethane material was determined. The measurement conditions were the same for all polyurethane coating samples which enabled comparison of determined DSC characteristics.

Erosive wear process of polyurethane-epoxy coating system was investigated with an apparatus described in the polish standard PN-76/C-81516. The erosive wear test consists in coating sample subjecting to the action of successive 3.5 kg electrocorundum portions falling freely through the pipe of 19 mm output internal diameter, from the height of 1 m. The coating sample was inclined at an angle of 45° to the steel pipe vertical axis. The criterion of the erosive wear was defined as obtaining of elliptic wear scar on coating system (eroded by falling electrocorundum grains up to the steel substrate surface) of minor diameter $d=3,6 \pm 0,1 \text{ mm}$. Following each 100 time-use, the 3.3 kg portion of erosive material was replaced with a new one.

In above method of coating systems erosive wear investigation, the noble electrocorundum 99A (acc. PN-76/M-59111) of grain no. 30 (acc. PN-ISO 8486-2:1998) was used. The grain size was in the range from 0.6 mm to 0.71 mm. Aluminium oxide is the main constituent of electrocorundum (minimum 99%) while the others are as follows: silicon dioxide, iron trioxide, calcium oxide and sodium oxide. In order to evaluate the erosive wear intensity of polyurethane-epoxy coating systems under the influence of electrocorundum grains impacts, the index I , [$\mu\text{m}/\text{kg}$] was taken. It is defined as the ratio between the initial thickness (G , [μm]) of the coating system and the total mass (M , [kg]) of erosive particles producing its erosive wear in the examined area, according to the above criterion.

2.4. Chemical composition analysis of polyurethane top coats

Chemical composition of polyurethane top coats, been included in examined coating systems composition, was determined with the help of EDS X-ray microanalyser which was SEM equipped with. Obtained results are presented in X-ray spectrographs below (Figs 1-3).

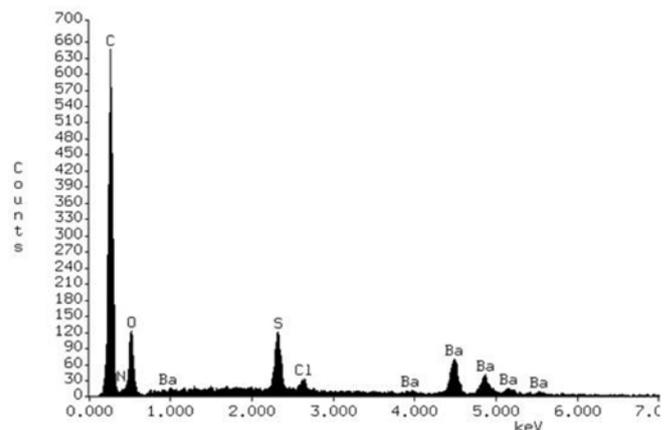


Fig. 1. X-ray spectrum of unmodified polyurethane top coat (EDS-SEM)

3. Results presentation and discussion

Carried out investigations proved beneficial influence of aluminium oxide nanoparticles addition to polyurethane coatings structure on their resistance to climatic ageing. On the other hand, modification of polyurethane coatings with silica nanoparticles worsened resistance of the coatings to ageing which was documented by FTIR (Figs 4-6) and (Figs 7-12) DSC examinations.

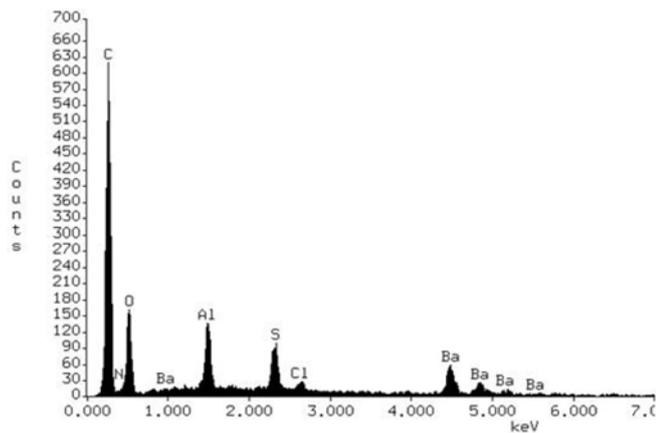


Fig. 2. X-ray spectrum of polyurethane top coat modified with aluminium oxide nanoparticles (EDS-SEM)

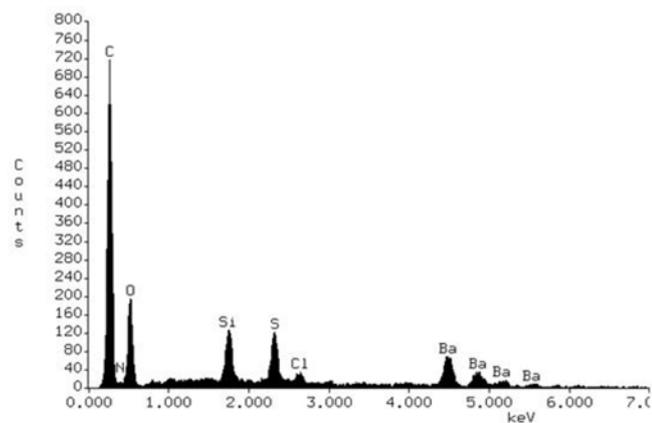


Fig. 3. X-ray spectrum of polyurethane top coat modified with silica nanoparticles (EDS-SEM)

FTIR examinations of coating systems with polyurethane top coat, which were aged at the climatic station for 3 years, documented changes in chemical structure of the top coat layer.

Analysis of IR spectra obtained for aged climatically polyurethane top coats (modified and unmodified) showed intensity increase of bands with peaks of wavenumbers $\nu=(1727, 1685, 1523, 1241) \text{ cm}^{-1}$ (Figs 4-6). The band with peak $\nu=1727 \text{ cm}^{-1}$ represents stretching (valence) vibrations of carbonyl groups. An increase of this band intensity demonstrates ageing oxidation development of the polyurethane top coat [5, 39].

As a result of 3-year climatic ageing of coating systems with unmodified polyurethane top coat, carbonyl group band intensity in this coat increased two times (Fig. 4). Only 1.5 times increase of this band intensity was noticed in the case of climate aged top coat modified with aluminium oxide (Al_2O_3) nanoparticles (Fig. 5). Intensity of the corresponding band in aged climatically polyurethane top coat modified with silica (SiO_2) nanoparticles increased more than two times (Fig. 6).

Thus climatic ageing of coating systems with polyurethane top coat caused the greatest increase of carbonyl group band intensity in the case of top coat modified with silica which attested the highest oxidation degree of this coating. The reason should be seen in the lower tightness [20, 35] of coatings modified with silica (having tendency to agglomeration) which conduce to accumulation in them of aggressive media, accelerating a development of ageing processes [12]. Due to mentioned tendency of this nanofiller to agglomeration, existing in the coating nanopores cannot be efficiently filled. This causes also coatings hydrolytic degradation increase [7]. Moreover, in the case of conducting paths generation (as an effect of pores connecting),

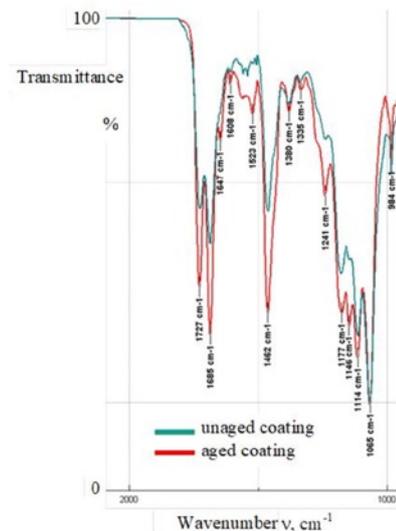


Fig. 4. FTIR spectra of unmodified polyurethane top coat, unaged and aged climatically for 3 years

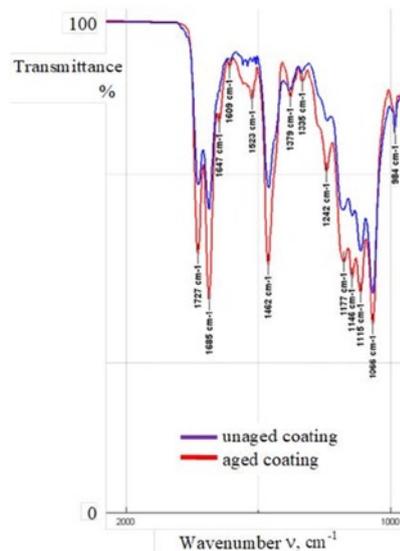


Fig. 5. FTIR spectra of polyurethane top coat, modified with aluminium dioxide nanoparticles, unaged and aged climatically for 3 years

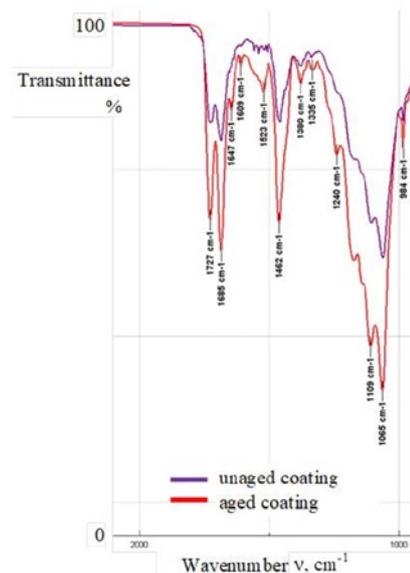


Fig. 6. FTIR spectra of polyurethane top coat, modified with silica nanoparticles, unaged and aged climatically for 3 years

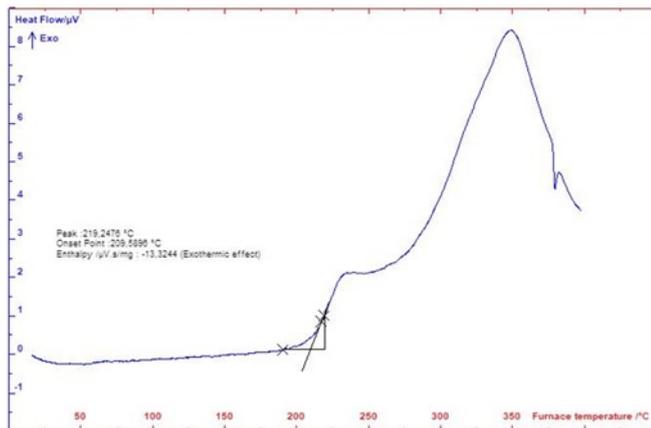


Fig. 7. DSC curve of unaged and unmodified polyurethane top coat

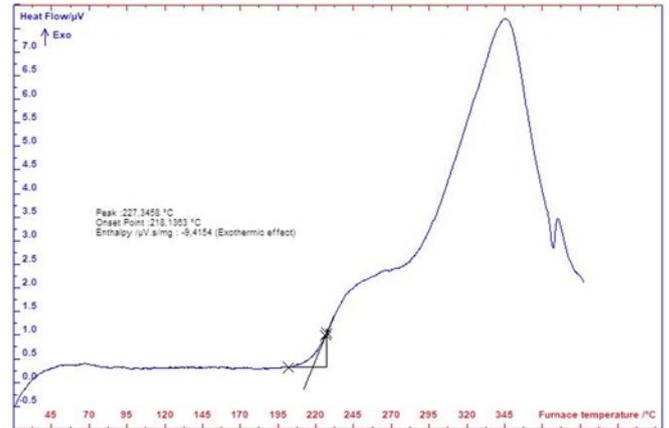


Fig. 9. DSC curve of unaged polyurethane top coat modified with silica nanoparticles

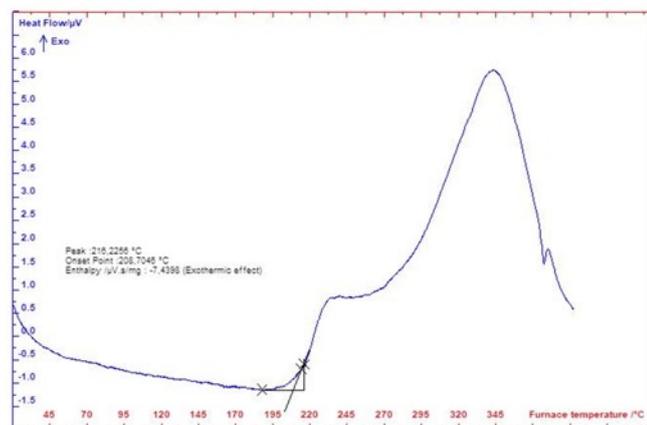


Fig. 8. DSC curve of unaged polyurethane top coat modified with aluminium dioxide nanoparticles

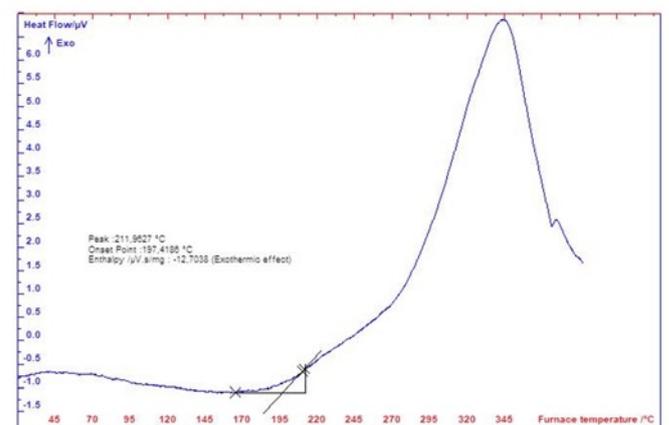


Fig. 10. DSC curve of unmodified polyurethane top coat aged climatically for 3 years

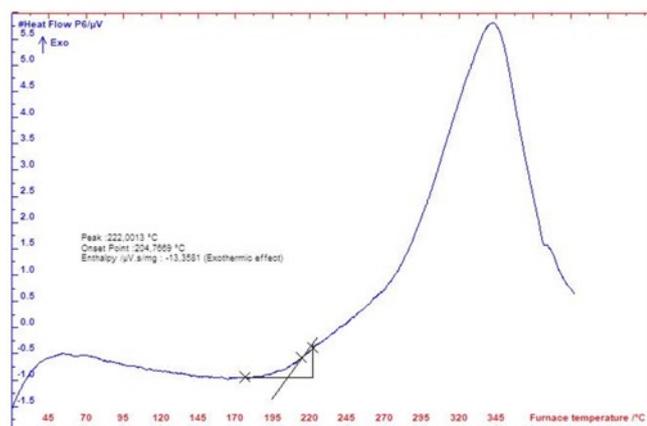


Fig. 11. DSC curve of polyurethane top coat modified with aluminium dioxide nanoparticles, aged climatically for 3 years

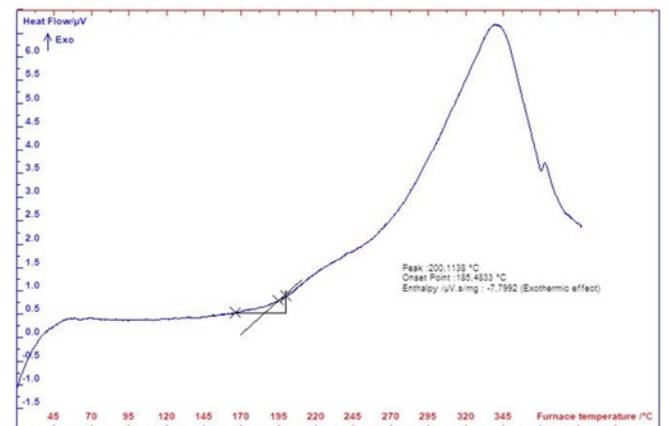


Fig. 12. DSC curve of polyurethane top coat modified with silica nanoparticles, aged climatically for 3 years

aggressive media migrating to the substrate may cause undercoating corrosion development, contributing to coating delamination [11].

Ageing changes in chemical structure of polyurethane top coats influenced value of their oxidation onset temperature (OOT). Oxidation resistance of these coatings was determined with the help of the thermal analysis method using differential scanning calorimetry (DSC). Oxidation onset temperature was determined on the basis of obtained DSC curves course (Figs 7-12). Higher value of oxidation

onset temperature in the case of coatings modified with nanofillers proved their higher oxidation resistance [8, 37, 39, 40].

Polymer nanocoatings show higher thermal resistance than unmodified ones due to their higher value of thermal destruction temperature [39]. It was observed in the case of a coating modified with aluminium oxide which oxidation onset temperature value increased by 4% (Figs 7 and 8). Destruction processes development in aged climatically polyurethane top coats caused the decrease of oxidation onset temperature value by 6% (Figs 7 and 10) in the case of

the unmodified coating, by 6% in the case of the coating modified with aluminium oxide nanoparticles (Figs 8 and 11), and by 11% in the case of the coating modified with silica nanoparticles (Figs 9 and 12). According to this, the greatest negative ageing effects, proved by oxidation onset temperature decrease, were observed in the case of the coating modified with silica nanoparticles. This coating revealed also the higher increment of carbonyl groups band intensity. For this reason, the coating modified with nanosilica underwent the strongest chemical destruction under the influence of operational factors.

Examinations of the polyurethane top coats surface state carried out using SEM document that as ageing period increases the coats destruction degree increases too (Figs 13-16). As a result of climatic ageing, fillers and pigments particles chipped from these coatings surface (Figs 14a and 15a). Also some etchings (Fig. 14), craters (Fig. 15) and microcracks (Fig. 16) originated on the surface. Superficial microcracks in the form parallel strips probably formed silver cracks zones, occurring as a result of UV radiation destructive action (Fig. 16a) [12, 13, 21].

Damaging climatic factors influence on the state of coating system surface was substantially constrained in the wake of polyurethane top coat composition modification with nanofillers. Nanofiller particles suspended in polyurethane material form a barrier limiting a development of microcracks. The smallest physical destruction of the coatings was observed in the case of the modification with aluminium oxide nanoparticles which reduced their oxidation degree (Figs 5 and 11) decreasing thereby susceptibility to coating constituents chipping from superficial layers [11].

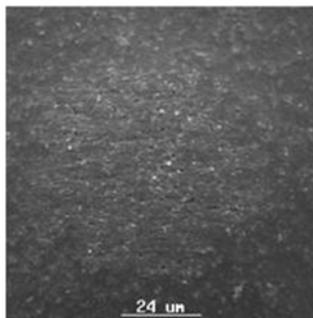


Fig. 13. Polyurethane top coat unmodified and unaged (SEM)

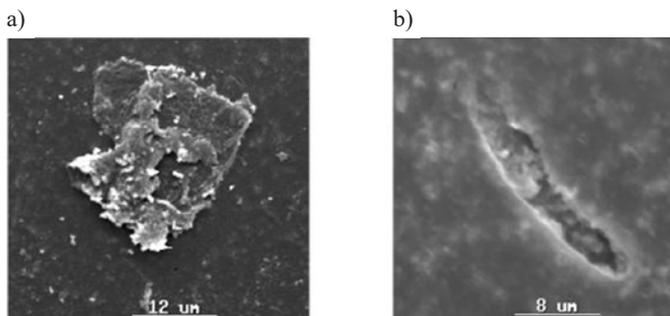


Fig. 14. Destruction of unmodified polyurethane top coat aged climatically for 3 years (SEM)

Introduction of hard particles like nanosilica [3, 6, 25] or aluminium dioxide [42] to polymer coatings composition increases their hardness as the silica hardness in the Mohs scale is equal 7 and aluminium oxide 9. This is the reason of increase of such coatings resistance to abrasive wear [30, 42] and erosion [7]. Among examined coatings, the highest hardness revealed polyurethane top coat modified with aluminium oxide (Fig. 17).

Coating systems climatic ageing for 3 years caused hardness decrease of polyurethane top coats. The most significant hardness decrease (by 24%) was observed in the case of unmodified coatings.

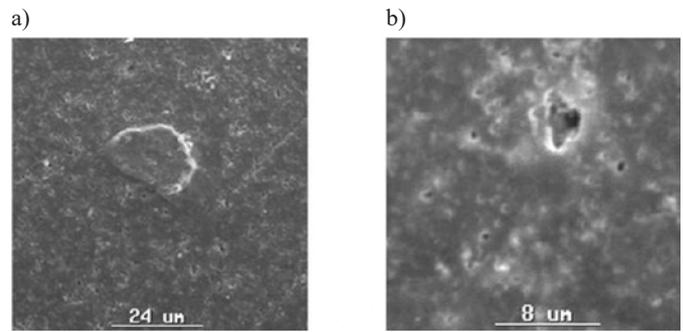


Fig. 15. Destruction of polyurethane top coat modified with aluminium oxide nanoparticles, aged climatically for 3 years (SEM)

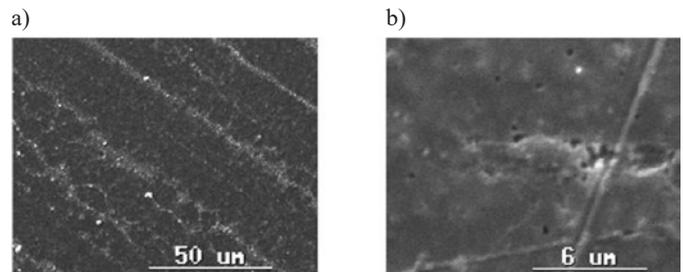


Fig. 16. Destruction of polyurethane top coat modified with silica nanoparticles, aged climatically for 3 years (SEM)

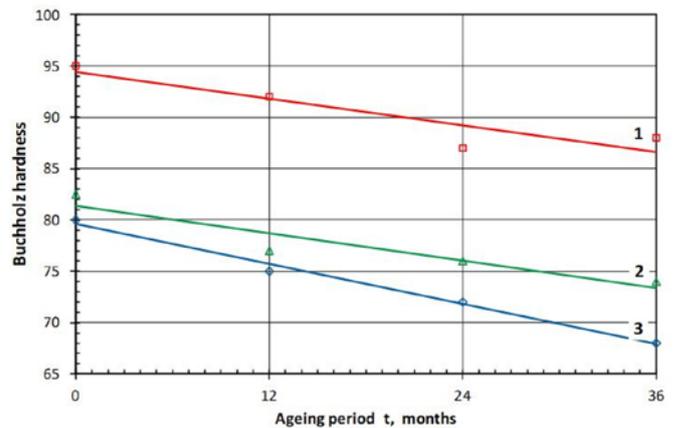


Fig. 17. Climatic ageing influence on Buchholz hardness of polyurethane-epoxy coating system. Top coat type: 1 – polyurethane top coat modified with aluminium oxide nanoparticles (PUR-Al₂O₃), 2 – polyurethane top coat modified with silica nanoparticles (PUR-SiO₂), 3 – unmodified polyurethane top coat (PUR)

Coatings modified with nanofillers revealed higher hardness stability which decreased by 11% in the case of the coating modified with silica and by 7% in the case of the coating modified with aluminium oxide (Fig. 17).

Nanoparticles of fillers, included in polymer (polyurethane) top coats, fill microruggednesses of substrate surface decreasing coatings surface roughness [11, 20]. In carried out investigations, a roughness

Table 1. Trend line equations and coefficient of determination R² values of polyurethane-epoxy coatings hardness characteristics

No.	Coating type	Mathematical model	Coefficient of determination R ²
1.	PUR-Al ₂ O ₃	y = -0.2208x + 81.35	0.885
2.	PUR-SiO ₂	y = -0.325x + 79.6	0.991
3.	PUR	y = -0.2167x + 94.4	0.824

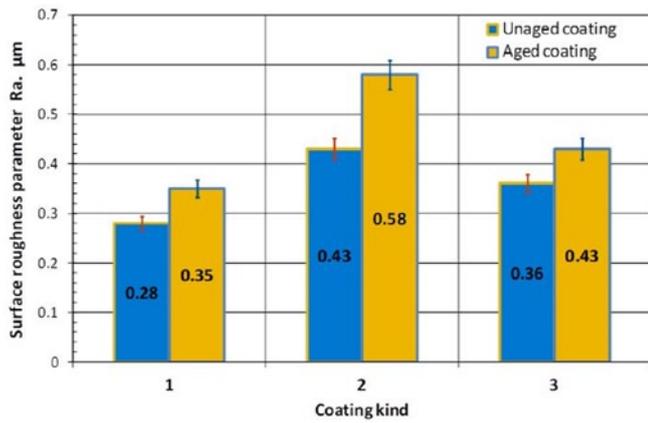


Fig. 18. Influence of 3-year ageing on Ra roughness parameter of polyurethane top coats surface. Top coat type: 1 – polyurethane top coat modified with aluminium oxide nanoparticles (PUR- Al_2O_3), 2 – polyurethane top coat modified with silica nanoparticles (PUR- SiO_2), 3 – unmodified polyurethane top coat (PUR)

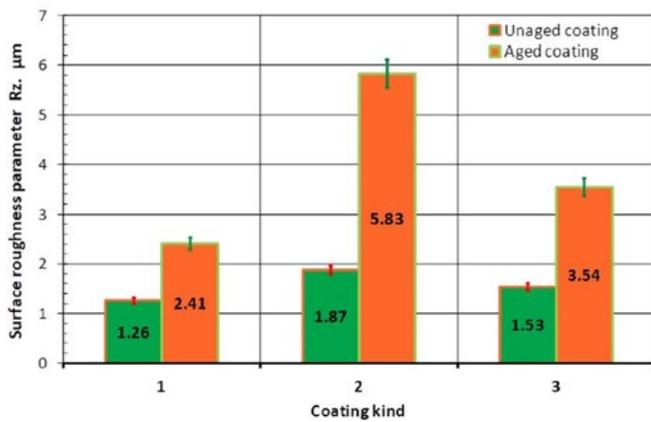


Fig. 19. Influence of 3-year ageing on Rz roughness parameter of polyurethane top coats surface. Top coat type: 1 – polyurethane top coat modified with aluminium oxide nanoparticles (PUR- Al_2O_3), 2 – polyurethane top coat modified with silica nanoparticles (PUR- SiO_2), 3 – unmodified polyurethane top coat (PUR)

decrease, assessed with Ra and Rz parameters (comparing to the unmodified coating), showed the coatings modified with aluminium oxide (Figs 18 and 19), both unaged and aged climatically for 3 years.

The lowest values of Ra and Rz roughness parameters revealed the coating modified with aluminium oxide nanoparticles, both unaged and aged climatically for 3 years. On the other hand, the highest values of these parameters showed the coating modified with nano-silica, both unaged and aged climatically for 3 years (Figs 18 and 19). As it was showed before, this kind of coatings had higher susceptibility to ageing due to nanofillers particles agglomeration which was caused by the improper coating of the nanoparticles with the silane (dimetyldichlorosilane) film. Probably not each of nanofiller grains were fully coated with the silane film which increase their susceptibility to agglomeration [7].

Operational factors influence generates most of all a destruction of polymer coatings superficial layers which leads to their components (fillers and pigments) chipping as a result of adhesion loss between them and the coating resin [16, 19, 48]. This brings the change of coatings surface topography which was proved by interferometric examinations of aged climatically polyurethane coatings, made using Talysurf CCI microscope ((Figs 20-22). The smallest changes in to-

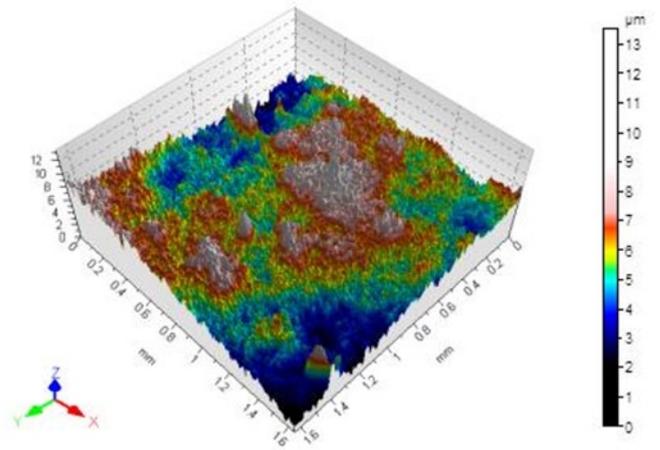


Fig. 20. Surface topography of unmodified polyurethane top coat aged for 3 years

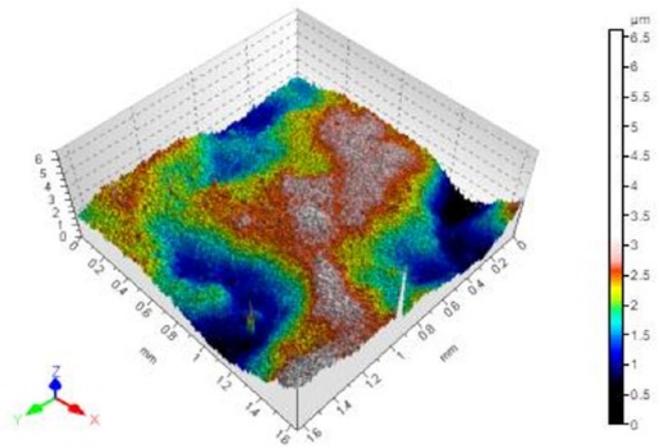


Fig. 21. Surface topography of polyurethane top coat modified with aluminium dioxide nanoparticles, aged for 3 years

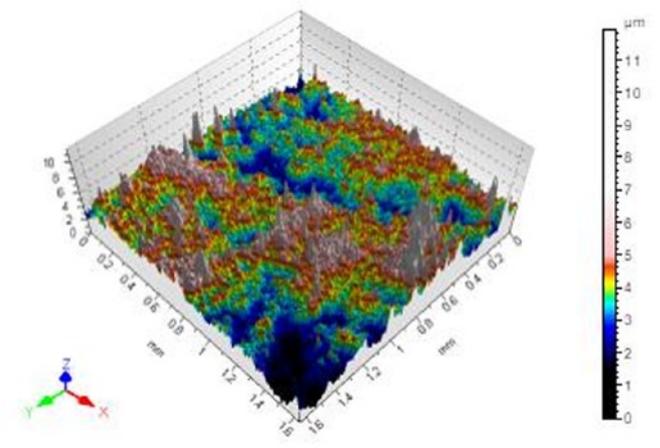


Fig. 22. Surface topography of polyurethane top coat modified with silica nanoparticles, aged for 3 years

pography of aged coatings surface were observed in the case of coatings modified with aluminium dioxide as these coatings showed the highest oxidation resistance (Figs 5 and 11) [37]. The coatings modified with silica revealed the strongest changes in surface topography which confirms the thesis about this filler inclination to globules

forming. Moreover, these coatings were the most susceptible to their components chipping from superficial layers (Fig. 22).

Modification of polymer coatings with nanofillers beneficially influences erosive resistance of the coatings obtained in this way [7] which is the result of: their porosity decrease [35], their structure reinforcement [4] and their superficial layer hardness increase [4, 5]. It was confirmed by investigations of erosive wear kinetics, carried out on polyurethane-epoxy coatings, which showed that modification of polyurethane top coat with silica or aluminium oxide nanoparticles resulted in erosive resistance increase of 3-layer system of polyurethane-epoxy coatings (Fig. 23). It was also stated that polyurethane top coat destruction degree influenced erosive wear intensity of 3-layer polyurethane-epoxy coatings system. The coating system with the top coat modified with aluminium oxide manifested the lowest destruction under the influence of operational factors which resulted in the lowest intensity of erosive wear [22]. On the other hand, aged climatically the coating system with the top coat modified with silica presented bigger destruction and in this connection higher intensity of erosive wear than the system with the top coat modified with aluminium oxide. This type of coating was harder than unmodified one and this fact in large extent resulted in higher resistance to erosion of the whole coating system [7]. What more, hard particles of the nanofiller (suspended in elastic polyurethane material) effectively dump an energy of erosive particles (corundum) hitting the modified coating which also conduces to its erosive resistance increase [18].

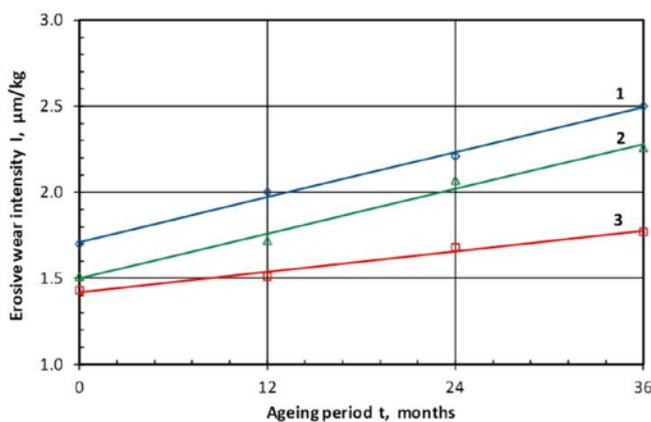


Fig. 23. Erosive wear intensity of polyurethane-epoxy coating system. Top coat type:
1 – unmodified polyurethane top coat (PUR)
2 – polyurethane top coat modified with silica nanoparticles (PUR-SiO₂)
3 – polyurethane top coat modified with aluminium oxide nanoparticles (PUR-Al₂O₃),

Table 2. Trend line equations and coefficient of determination R² values of polyurethane top coats erosive resistance characteristics

No.	Coating type	Mathematical model	Coefficient of determination R ²
1.	PUR	$y = 0.0218x + 1.711$	0.9957
2.	PUR-SiO ₂	$y = 0.0217x + 1.5$	0.9866
3.	PUR-Al ₂ O ₃	$y = 0.0099x + 1.419$	0.9797

4. Conclusions

Ageing of polyurethane epoxy coating systems (situated at the climatic station) for 3-year period caused chemical destruction of polyurethane top coats. It was documented by results of spectroscopic examinations in infrared (FTIR) which revealed intensity rise of carbonyl group (C=O) band in polyurethane material testifying oxidation

degree increase of superficial layers. As a consequence of climatic ageing, intensity of carbonyl group band increased 2 times in the case of unmodified polyurethane coatings and more than 1.5 times in the case of polyurethane coatings modified with aluminium oxide nanoparticles. On the other hand Polyurethane coatings modified with silica nanoparticles showed more than 2.5 times increase of carbonyl group band intensity. Therefore polyurethane top coats modified with aluminium oxide nanoparticles demonstrated therefore the highest resistance to ageing oxidation.

Increase of carbonyl group band intensity testifies ageing oxidation development in polyurethane top coats increasing their brittleness. Coatings brittleness increases, first of all, under the influence of such climatic factor like ultraviolet radiation of the solar radiation origin.

An oxidised coating forming material loses adhesion to fillers and pigments grains surface which as a result chip from the top coats structure contributing to the value increase of surface roughness parameters Ra and Rz.

In the microroughness niches, both existing originally and forming as a result of ageing on coating surface, microorganisms embed conducing to biological corrosion of coatings. Microorganisms, developing on coatings surface and especially in all kind of cavities as well as products of their metabolic conversion, cause generation of pits (etchings) and craters reaching even metal substrate. These craters, forming paths conducting aggressive media, lead to electrochemical corrosion development. In the case of the aged coating modified with aluminium oxide nanoparticles of grain size $d=20$ nm, the lowest changes of Rz as well as Ra parameters were observed. The highest increase of Rz parameter value was noticed in the case of the coating modified with nanosilica of grain size $d=16$ nm.

Development of destruction processes in aged climatically polyurethane top coats contributed to the oxidation onset temperature decrease of coating forming material (determined on DSC curve basis) by 6% in the case of polyurethane unmodified coatings, by 6% in the case of polyurethane coatings modified with aluminium oxide nanoparticles and by 11% in the case of polyurethane coatings modified with silica nanoparticles. Thermal resistance decrease influences mechanical strength of coatings during their frictional contact with co-operating elements, for example during coating contact with erosive particles. Moreover, the oxidation degree of aged coatings superficial layers influences a value of their hardness decrease. The coatings modified with aluminium oxide revealed the highest hardness and the lowest oxidation degree (the lowest content of carbonyl groups) while the unmodified coatings showed the lowest hardness and the highest oxidation degree.

SEM investigation of coatings surface state documented polyurethane top coats destruction signs, developing with ageing period increase, like: etchings, craters, microcracks and silver cracks. The significant change in aged coatings surface topography revealed also investigation made with interferometric microscope use. It results from the topography images of aged coatings surface that the highest resistance to ageing reveals the polyurethane coating modified with aluminium oxide nanoparticles while the lowest reveals the coating modified with silica nanoparticles which is connected with its bigger susceptibility to ageing oxidation inducing chipping of coating components.

Modification of polyurethane top coat with nanofiller (aluminium oxide or silica) caused the increase of its resistance to erosive particles influence. Destruction degree of the aged climatically polyurethane coating influenced erosive wear intensity of the 3-layer polyurethane-epoxy coating system. The system with the top coat modified with aluminium dioxide distinguished itself by the lowest chemical and physical destruction under the influence of operational factors. What more, this system featured the highest hardness and thermal resistance among the all examined which had effect in its the lowest intensity of erosive wear. On the other hand, aged in the

same way the coating system with the top coat modified with silica showed comparatively bigger destruction than the system with the top coat modified with aluminium dioxide which contributed to its higher erosive wear intensity.

The results of presented investigations demonstrate that modification of polyurethane top coats with aluminium oxide (of 20 nm grain size) influences more effectively on operational properties improve-

ment of the whole 3-layer polyurethane-epoxy coating system than modification with silica (of 16 nm grain size). The coating system with polyurethane top coat modified with aluminium oxide shows the highest operational life of all examined in conditions characterised by such disadvantageous elements like climatic factors, acid rains, heat or erosive particles.

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