

Resistance to Erosive Wear of Epoxy-Polyurethane Coating Modified With Nanofillers

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Abstract

The paper presents results of investigation on the erosive wear kinetics of epoxy-polyurethane coatings modified with alumina or silica nanoparticles, aged climatically for three years. Destruction of coating surface layers due to natural weathering caused a decrease of their erosive wear resistance. Modification of the composition of polyurethane (surface) layer with nanofiller caused the remarkable increase of erosion resistance. Epoxy-polyurethane coatings with nanosilica modified surface layer, showed the highest erosive wear resistance of all investigated coatings.

Keywords: epoxy-polyurethane coating, erosive wear resistance, nanofillers

1. Introduction

A polymer protective coating during its service life in natural conditions is exposed to the action of climatic and environmental factors, that contribute to various types of wear, including erosive wear. The coatings erosive wear process occurs when hard particles (hail, dust, sand, stones, soil lumps etc.) impact their surface. Therefore, erosion is the dominating wear process of polymer protective coatings of agricultural, constructional and mining machines and occurs as a result of erosive particles impacts typical for a given environment (Kotnarowska, 1999a, 2006).

An action of operational factors has a crucial influence on polymer coating surface state. An intensive chemical and physical destruction of superficial layers occurs as the result of aggressive media adsorption on coating surface and due to the action of ultraviolet radiation. Ultraviolet radiation is the dominating factor that causes destruction of polymer coatings used in natural climatic conditions (Kotnarowska, 2006). This contributes to the decrease of resistance to erosive wear of epoxy coatings, first of all due to a significant increase of binding resin brittleness and also to an increase of the coating surface roughness. Also cracks (including silver cracks) generated inside the superficial layers of coating reduce its resistance to erosive wear (Al-Turaif, 2013; Darowicki, Szociński, Schaefer, & Mills, 2011).

Polymeric coatings modified with nanofillers may show better functional properties (higher scratch and abrasion resistance, higher hardness, lower water permeability) than coatings containing microfillers. The effect depends on many factors like, among others, the following: chemical nature of nanofillers, their concentration and level of dispersion in the coating, as well as interaction between filler particles and polymer matrix (Perera, 2004; Chen, Zhou, Chen, & Wu, 2005; Douce, Boilot, Biteau, Scodellaro, & Jimenez, 2004; Zhou, Wu, Sun, & Shen, 2002).

Nowadays, works are carried out concerning size of filler particles as well as their contribution in the polymer matrix influence on the protective properties (Kotnarowska, 2008; Leder, Ladwig, Valter, Frahn, & Meyer, 2002; Wang, Bai, Liu, Wu, & Wong, 2002) and operational durability of polymer coatings (Wang et al., 2011). Usually, the smaller filler particles the bigger their effect on coating properties (Fu, Feng, Lauke, & Mai, 2008; Moloney & Kausch, 1987; Zhou, Lu, Jiang, & Li, 2005; Kotnarowska, 2009).

A modification of the paint composition with nanofiller may lead to improvement of polymer coatings resistance

to scratch, abrasion and to erosive particle impacts. Most frequently metal nanoparticles (aluminium, silver, copper) or metal compounds (zinc oxide, aluminium oxide, titanium dioxide, iron oxides) are used to paints modification. Calcium carbonates, modified layered silicates and carbon nanotubes are used for this purpose as well (Amerio et al., 2008; Bautista, Gonzalez, Gilabert, Ibanez, & Sanz, 2011; Al-Turaif, 2010; Huang, Li, & Yuan, 2001; Oner, Meral, & Nergis, 2013).

Nanofillers have larger specific surface area compared to the conventional fillers which increases their adhesion strength with polymer matrix (Fu et al., 2008; Stojanović et al., 2013). Improved mechanical properties of coatings containing nanofillers result from better conditions for stress propagation inside the coating material. Usually, the stronger physico-chemical bonding between filler particles and polymer matrix is, the easier stress can be transferred through the particle-matrix interfaces and dissipated (Pilotek & Tabellion, 2005).

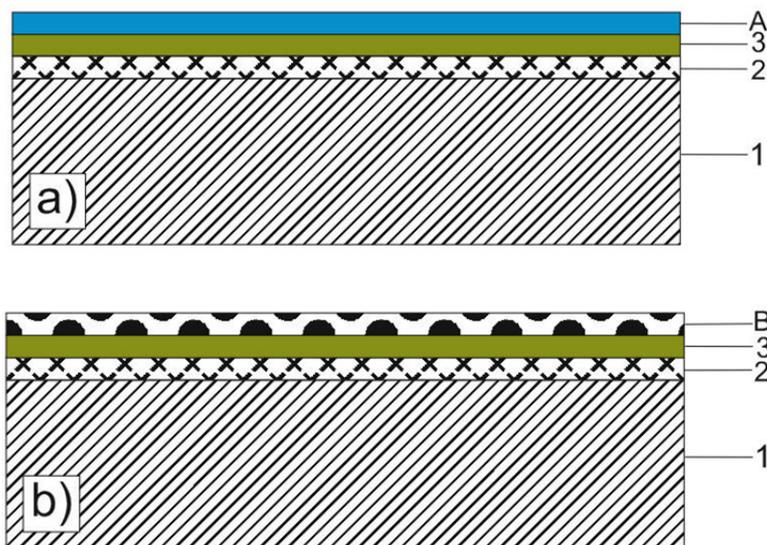
To prevent agglomeration of nanofillers, various methods are applied in the paint formulation process, such as: mechanical or preferably ultrasonic mixing and chemical modification of nanofillers surface. Chemical modification of surfaces of most inorganic nanoparticles (e.g. SiO_2 , Al_2O_3 or ZnO_2) influences their hydrophilic character promoting physical bonding with the paint material as well as facilitating their distribution in the polymer matrix.

The erosive wear process of polymer coatings is still not sufficiently recognized, because coating material loss depends on many interrelated factors (Asmatulu, Mahmud, Hille, & Misak, 2011; Kotnarowska, 1999b, 2010b; Kotnarowska, Przerwa, & Wojtyniak, 2011). Therefore, studies on the erosive wear kinetics of polymer coatings should consider the degree of their destruction under the influence of such environmental factors like: acid rains, ultraviolet radiation, mechanical stresses (Barkoula, 2002; Patnaik, Satapathy, Chand, Barkoula, & Biswas, 2010; Kotnarowska, 1997, 2010a).

2. Experimental

2.1 Preparation of Test Samples

Two types of three-layered epoxy-polyurethane coatings were investigated. They were applied by air-spraying on a steel substrate in the form of $160 \times 80 \times 2$ mm plates made of S235JR steel. First two epoxy layers (primer and interlayer) were deposited. Then the surface layer was made of unmodified polyurethane paint (type A) or nanofiller modified polyurethane paint (type B) as it is shown in Figure 1.



Figures 1 (a & b). Scheme of the investigated epoxy-polyurethane coatings: a) unmodified coating, b) modified coating, where: 1 – steel substrate, 2 – primer layer (epoxy), 3 – interlayer (epoxy), A – unmodified polyurethane surface layer, B – nanofiller modified polyurethane surface layer (not to scale)

The steel plates surface were specially prepared by grit blasting (in a special tumbler) with the use of small ceramic bars. Prior to coating application the plates were degreased with ethyl alcohol.

In order to improve the erosive wear resistance (also scratch resistance) the polyurethane paint was modified with alumina nanoparticles Al_2O_3 (of 20 nm grain size) or silica nanoparticles (of 12 nm grain size). The nanofiller content in the paint was 3.5% (by weight). Surfaces of nanofillers particles were chemically modified by manufacturers. The alumina nanoparticles were modified with methoxypropyl acetate using polysiloxane as the carrier whereas hydrophobic silica nanoparticles were modified with dimethyldichlorosilane. To prevent agglomeration of nanofillers paints were mechanically stirred for 18 hours. Moreover, applied nanofillers slow down a sedimentation of other particles (pigments, stabilizers) in coating material increasing its anticorrosive characteristics without a negative influence on decorative properties.

Directly after the paint spraying the samples of epoxy-polyurethane coatings were acclimatized for 10 days at the temperature of $20\text{ }^\circ\text{C}$ and the relative humidity of $65 \pm 5\%$. Then the samples were placed on racks situated in a climatic station on the grounds of Institute of Machines and Vehicles Maintenance in Radom and subjected to ageing in natural climatic factors for three years. The average thickness of three-layer epoxy-polyurethane coatings was $190\text{ }\mu\text{m}$ while the thickness of the polyurethane surface layer was $70\text{ }\mu\text{m}$.

2.2 Erosive Wear Evaluation Methodology

The resistance to erosive wear of the coatings aged for the period of three years was evaluated using the testing device recommended by Polish Standard PN-76/C-81516 (Figure 2).

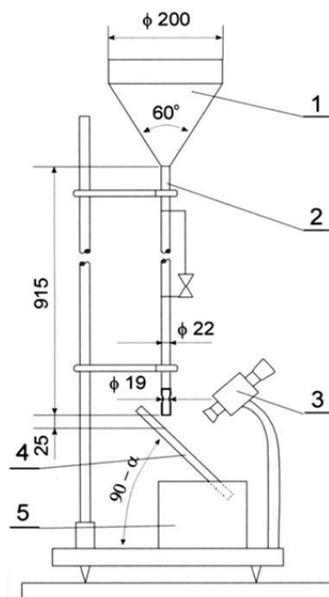


Figure 2. Apparatus for erosive wear of polymer coatings testing, where: 1 – container for erosive material, 2 – pipe transporting erosive material, 3 – optical microscope, 4 – tilting holder for fixing metallic test specimen with examined coating, 5 – container collecting erosive material after the test

Particles of granulated alundum 99A (according to the Polish Standard PN-76/M-59111) of grain number 30 (according to PN-ISO 8486-2) were used as the abrasive material (Figure 3). Alundum grains were of the size $0.60 \div 0.71\text{ mm}$. The main constituent of erosive material was aluminium trioxide (minimum 99%). Other constituents were: silicon dioxide, iron trioxide, calcium oxide and sodium oxide. The erosive particles were poured through the pipe in which they were falling freely from the height of 0.915 m onto the sample surface. The sample with tested epoxy-polyurethane coating was tilted by 45° .



Figure 3. Morphology of alundum particles

The initial mass of one charge of alundum was 3.5 kg. When the first signs of coating wear up to the substrate material appeared, the mass of one alundum charge was reduced to 0.5 kg. The pouring of abrasive material was continued until the area of exposed substrate achieved the shape of ellipse of minor diameter equal $d = 3.6 \pm 0.1$ mm. The tests were carried out at the temperature of 20 ± 2 °C and the relative humidity of $65 \pm 5\%$.

The resistance to erosive wear of epoxy-polyurethane coatings was evaluated applying the criterion S according to Equation (1). It expresses a proportion of the total mass M of erosive particles which erode the coating (generating normative coating wear) to the coating thickness G (1):

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

where: S - erosive wear resistance, [kg/ μm]; M - mass of erosive particles, [kg]; G - average coating thickness, [μm].

3. Results and Discussion

The action of climatic factors caused cracking of polyurethane superficial layers of epoxy-polyurethane coatings and increasing of their porosity. Whereas adhesion loss between particles of fillers and polyurethane material caused their chipping from the coating superficial layer contributing to the increase of its roughness. It resulted in decrease of the resistance to erosive wear of testing epoxy-polyurethane coatings.

In order to describe a time evolution of the resistance to erosive wear of epoxy and polyurethane coatings, a phenomenological expression $S(t)$ consisting of exponential and Gaussian terms was introduced (2). First of them describes a continuous (long-term) process of coating destruction and its nature represents progressive propagation of silver cracks. The second component of Equation (2), which is the Gaussian function, models a periodic process of coating resistance to erosive wear increase as the result of coatings hardening and roughness decrease during the climatic ageing. The explicit form of $S(t)$ expression is following:

$$S(t) = A_e e^{-\frac{t}{T_e}} + A_G e^{-\frac{(t-T_G)^2}{2\Delta T_G^2}}, \quad (2)$$

where: A_e – is an amplitude of exponential process, T_e – a time constant of exponential process, A_G – amplitude of Gaussian-type evolution, T_G – its characteristic time, and ΔT_G – a time spread of Gaussian changes.

The time characteristics of the erosive wear resistance of epoxy-polyurethane coatings are presented in Figure 4.

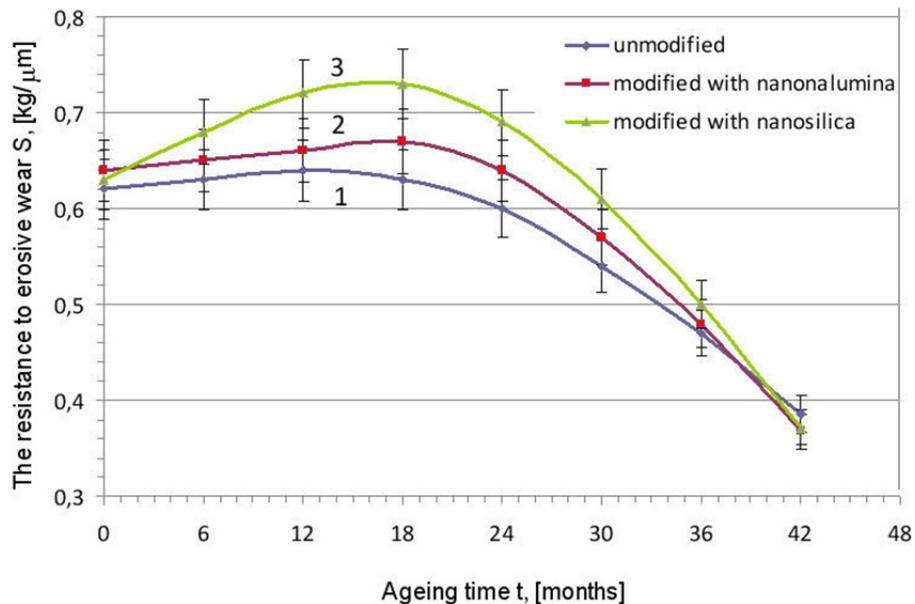


Figure 4. The resistance to erosive wear of epoxy-polyurethane coatings as a function of time, where: 1 – unmodified epoxy -polyurethane coating, 2 – epoxy-polyurethane coating with nanoalumina modified surface layer, 3 – epoxy-polyurethane coating with nanosilica modified surface layer

4. Conclusions

(1) Modification of polyurethane superficial layer of epoxy-polyurethane coating with nanofiller (silica as well as alumina) caused erosive resistance increase of epoxy-polyurethane coatings aged climatically, especially during the period from 6 to 30 months. The epoxy-polyurethane coating with superficial layer modified with silica nanoparticles exhibited the highest erosive resistance

(2) The increase of coating erosive resistance was caused by higher hardness of modified coatings as well as by lower roughness of their surface layers in comparison with unmodified coatings. Moreover, nanofillers filled pores existing inside the coatings and effectively suppressed development of cracks arising in the coating as the result of ageing.

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