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Influence of Mechanical Factors on Surface State of Acrylic Coatings with Nanofillers

Danuta KOTNAROWSKA*

Radom University of Technology, al. Chrobrego 45, 26-600 Radom, Poland

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In the paper, properties of conventional acrylic coatings are compared with those of the same coatings modified with copper nanoparticles. The mass fraction of nanofiller was 3.5 % and the mean diameter of particles did not exceed 66 nm. Modification of acrylic coatings with copper nanoparticles resulted in an increased mechanical wear resistance of the coatings because both erosive wear resistance and scratch resistance increased. This was first of all a result of higher coating hardness (that increased by 7 % as a result of modification), lower coating surface roughness (R_a parameter decreased over three times) as well as higher elasticity modulus of modified coatings.

Keywords: nanofillers, acrylic nanocoatings, copper nanoparticles, erosion, abrasion.

1. INTRODUCTION

Rapid development in the field of nanomaterials testing and manufacturing contributes also to the development of nanofiller manufacturing. This enabled to obtain a new generation of polymeric coatings, of the thickness from the range 3 μm – 30 μm, while traditional coatings are on average ten times thicker [1 – 3]. Polymeric nanocoatings are made of polymer matrix that contains nanofillers (nanopigments). Nanoparticles have at least one characteristic size below 100 nm [2 – 8].

Incorporation of nanofillers in the polymeric coating structure results in increased: barrier properties, thermal stability, fire resistance, transparency and colour purity as well as resistance to organic solvents and in lower coefficient of linear expansion [1 – 9].

Among metal nanofillers applied in coating formulation there are distinguished metal nanoparticles (such as: silver, copper and palladium) or metal compounds (iron oxides, zinc oxide, aluminium oxide, titanium dioxide, zirconium dioxide and calcium carbonate) [3, 8 – 15].

It should be stressed that only 0.5 % – 5 % (mass) of nanofiller suffices for polymeric coating modification while in traditional coatings, nanofiller share must be 20 % – 30 % to obtain the same barrier properties (tightness) [1 – 3, 7].

The paper was intended to present examination results showing positive influence of copper nanoparticles addition to acrylic coating composition resulting in resistance to erosive wear and scratch resistance increase.

2. EXPERIMENTAL

2.1. Examination method of erosive wear of an acrylic coating

The erosive wear examination method employing the testing device, recommended by the Polish Standard PN-76/C-81516, was used. In order to learn the influence of an impact angle of the erosive particle on the wear of an organic coating, the test specimen was mounted in a specially designed specimen holder, which allowed precise setting of the angle of the specimen surface, which was subsequently subjected to testing. The tilt angle α = (30, 45, 60, 75)°. Particles of the granulated alundum of grain size 0.60 mm – 0.71 mm (according to the Polish Standard PN-76/M-59111) were used as the abrasive material. Aluminium trioxide (Al_2O_3) is the main constituent (99 % by weight) of the abrasive while SiO_2, Fe_2O_3, CaO and Na_2O make up its residual part. The mass of one charge of alundum delivered to container 1 was 3.5 kg, while at the end of the test, i. e. when the substrate material was exposed, the charge of alundum was reduced to 0.5 kg.

In order to assess the resistance of the coating to erosive wear the *S*-criterion, calculated from Eq. (1), was used.

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

where *S* is the resistance of polymeric coating to erosive wear *o* (kg /μm), *M* is the mass of erosive particles (kg) and *G* is the coating thickness (μm). The above formula displays the ratio of the coating thickness to the total mass of erosive particles producing the total wear of the coating within the tested area, i. e. generating the exposure of the substrate material in the elliptic shape of the minor diameter of d = 3.6 mm ±0.1 mm.

2.3. Investigation on the scratch resistance of acrylic coatings

Investigation on the scratch resistance of acrylic coatings was carried out with the use of two methods. The first method consisted in scratching the coating with a chisel having a ~1.5 mm broad blade made of H10 sintered carbide (cobalt/tungsten). During testing the chisel was loaded with discs (with step-wise increased mass by 100 g, from 600 g to 2000 g) and moved with constant speed (40 mm/s). A device recommended by the standard PN-65/C-81527 was used in the investigation.

In the second method, coatings were scratched with abrasive paper that was moved (with constant speed) along

*Corresponding author. Tel.: +48-606 714 696; fax.: + 48-48-361 76 44.
E-mail address: *d.kotnarowska@pr.radom.pl* (D. Kotnarowska)

the metal specimens coated with investigated coatings. The specific load was constant during testing and was equal 934 Pa. It was applied the 800 A abrasive paper which contained on the surface silicon carbide grains of the size from 20.8 μm to 22.8 μm.

2.3. Preparation of the acrylic coating modified with copper nanoparticles

As acrylic coating microfillers barium sulphate, microtalc and titanium white were used. The mass share of microfillers was 31.5 % and their mean grain diameter did not exceed 35 μm. As nanofiller copper nanoparticles of mean diameter 66 nm were used (Fig. 3). The mass share of nanofiller was 3.5 %.

Before the tests all coating samples were dried and acclimatized at the temperature of 20 °C ±2 °C and at the relative humidity of 65 % ±5 % during10 days. The average thickness of the examined coatings was 189 μm. Copper nanoparticles showed high tendency to agglomeration (Fig. 1). This feature was essentially reduced during mixing process of acrylic paint and high dispersion of nanofiller in acrylic matrix was obtained.

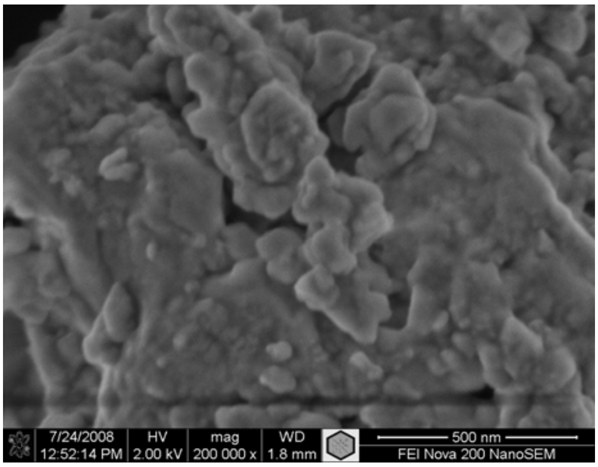


Fig. 1. Morphology of copper nanoparticles

Examination on filler morphology was carried out using Hitachi scanning electron microscope. X-ray spectra of the investigated sample surfaces were obtained using a scanning electron microscope equipped with an energy-dispersive X-ray (EDS) analyser. The spectra testify the copper content in coatings modified with nanofiller.

3. RESULTS AND DISCUSSION

Owing to bigger (about 1000 times) specific surface of copper nanoparticles in comparison with traditional fillers, the stronger adhesive effect occurs between surface of nanofiller particles and acrylic matrix. This feature increases resistance of the coatings to erosive particles action.

Modification of acrylic coating with copper nanoparticles contributed to increase of the coating resistance to erosive wear from 50 % for impact angle $\alpha = 15°$ to 85 % for $\alpha = 80°$ on the average (Fig. 2). This is connected with more effective dumping of energy of alundum particles striking the coating by copper nanoparticles incorporated in the coating [3, 16 – 19].

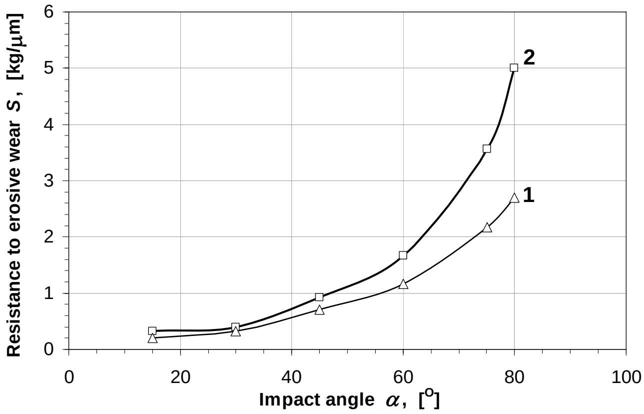


Fig. 2. Resistance to erosive wear of acrylic coatings modified with copper nanoparticles (1 – acrylic coating, 2 – acrylic coating containing 3.5 % copper nanoparticles by weight)

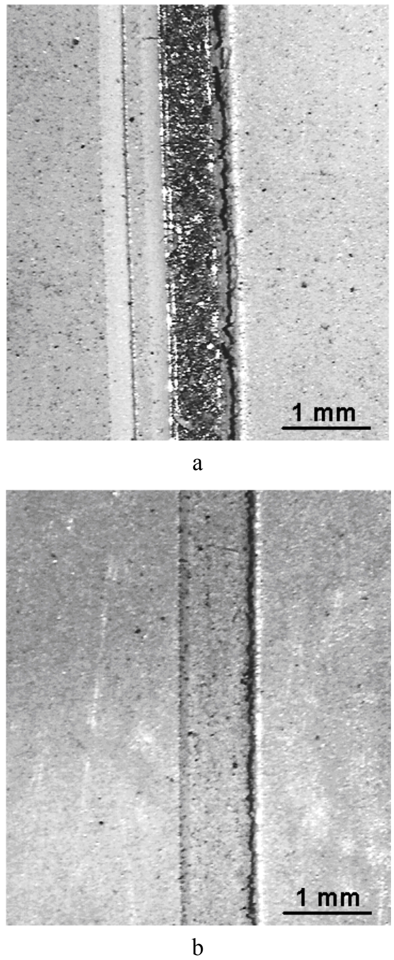
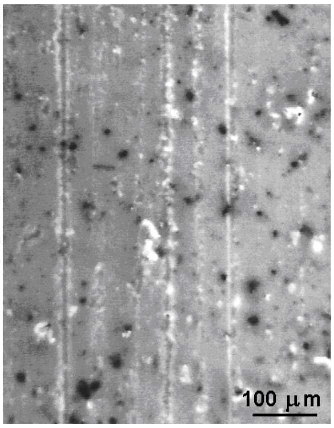


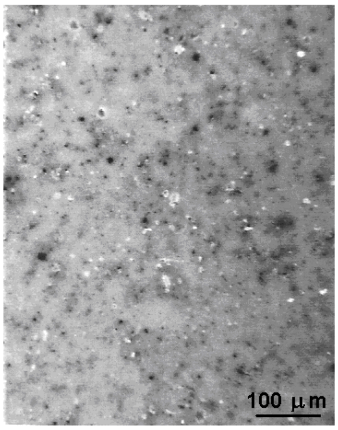
Fig. 3. Surface of the unmodified acrylic coating (a) and the one modified with copper nanoparticles (b) after scratch test with the use of a chisel made of H10 sintered carbide (cobalt/tungsten)

Results of investigation of the scratch resistance show that copper modified acrylic coatings are more resistant to scratch than traditional acrylic coatings. For instance, while scratching the coating with a chisel (loaded with weights having the total mass of 2 kg) it was observed only a superficial scratch on the acrylic coatings modified with nanoparticles while acrylic coating without nanofiller shoved the scratch up to the steel substrate just at the load of 1.5 kg (Fig. 3).

After the test of scratch resistance with the use of abrasive paper, the coating modified with nanofiller did not show any signs of scratching. On the modified coating surface there were observed parallel scratches being a result of silicon carbide grains action during the contact of abrasive paper with the investigated coating (Fig. 4).



a



b

Fig. 4. Surface of the unmodified acrylic coating (a) and the one modified with copper nanoparticles (b) after scratch test with the use of 800 A abrasive paper (containing silicon carbide grains)

Investigation on the acrylic coatings carried out with the use of dynamic-mechanical thermal analysis (DMA) proved an elasticity increase (below $T = 30$ °C) of coatings modified with copper nanoparticles what is evidenced by higher modulus of elasticity E' (Fig. 5). It was also observed an increase of glass transition temperature T_g of the modified acrylic material, what results in higher thermal stability [14].

Hardness (according to the Buchholz method, PN-EN ISO 2815:2000) of the coating modified with nanofillers increased by 7 %. Coating surface roughness, expressed by the R_a parameter, decreased by 78 %. However, R_z parameter decreased by 81 % and coating waviness W_t – by 10 %. This contributed to coating gloss increase. Reduction of microcavities on the coating surface reduces also coating susceptibility to biological corrosion. Both modified coating hardness increase and their surface roughness decrease result in increase resistance of such coatings to the action of mechanical factors. For instance, polymeric coating containing nanofillers (nanopigments) demonstrate increased scratch resistance [1, 15].

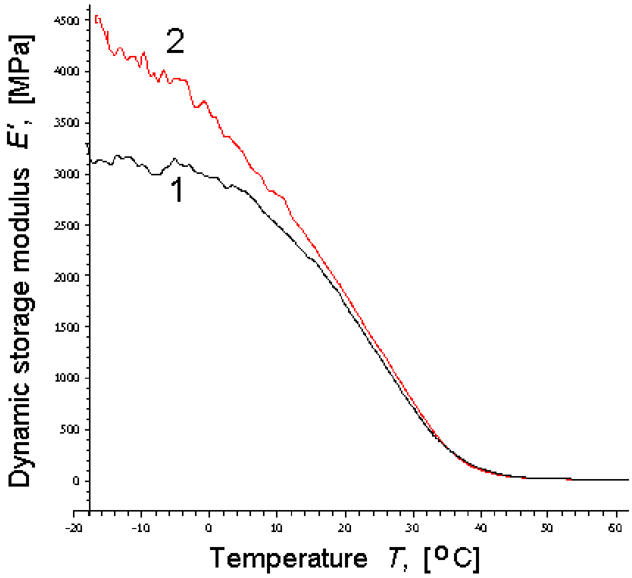


Fig. 5. Dynamic storage modulus E' of acrylic coatings (1) and acrylic coatings modified with copper nanoparticles (2)

Investigation carried out with the use of nitrogen porosimetry revealed also the influence of copper nanoparticles on the modified coating porosity decrease because the specific volume of coating pores decreased by 29 %. It results in decreased probability of generation of paths conducting aggressive media to the metal substrate what, in turn, delays corrosion process development on this substrate [7].

4. CONCLUSIONS

1. Modification of acrylic coatings with copper nanoparticles resulted in an increase of their mechanical wear resistance. Both resistance to erosive wear and scratch resistance increased. This was first of all a result of higher coating hardness (that increased by 7 % as a result of modification), lower coating surface roughness (R_a parameter decreased over three times). Moreover it was influenced by higher elasticity modulus and cumulative volume of pores decrease (by 29 %) of acrylic coatings modified with copper nanoparticles.
2. It was stated that the higher impact angle (α) of erosive particles, the stronger influence of nanofiller on the erosive wear resistance increase. This is connected with more effective dumping of energy of alundum particles striking the coating by copper nanoparticles incorporated in the coating volume. Modification of acrylic coating with copper nanoparticles contributed to increase of the coating resistance to erosive wear from 25 % for impact angle $\alpha = 30°$ to 65 % for $\alpha = 75°$on the average. For an impact angle $\alpha = 30°$ and below, the erosion process is dominated by shearing.
3. Results of investigation of acrylic coating scratch resistance show much higher resistance of the coatings modified with copper nanoparticles than the unmodified ones. For instance, while testing the scratch resistance with a chisel loaded with weights, having the total mass of 2 kg, only a superficial scratch on the acrylic coatings modified with copper

nanoparticles was observed while acrylic coatings without nanofiller shoved scratches up to the steel substrate on a significant surface of contact with the chisel just at the load of 1.5 kg.

4. In connection with the above results, acrylic coatings modified with copper nanoparticles should be widely applied as protective-decorative coatings of car bodies. Polymeric nanocoatings should also be applied in environments characterised by intensive action of erosive particles (dust, sand, stones and soil clods) to protect mining, constructional and agriculture machines.

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