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# Structure and Tribological Properties of Polytetrafluoroethylene Nanocomposite Coatings Formed from Active Gas Phase

**Alexander Aleksandrovich ROGACHEV[1, 3*], Maxim Anatolievich YARMOLENKO[1], Alexander Vladimirovich ROGACHEV[2], Sigitas TAMULEVIČIUS[3], Igoris PROSYCEVAS[3]**

[1]*Belarusian State University of Transport, Kirov Str. 34, Gomel, 246653, Belarus*
[2]*Francisk Scorina Gomel State University, Sovetskaya Str. 104, Gomel, 246019, Belarus*
[3]*Institute of Physical Electronics, Kaunas University of Technology, Savanorių 271, LT-50131 Kaunas, Lithuania.*

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Surface morphology and structure of micro- and nanocomposite polymer-polymer (polytetrafluoroethylene and polyurethane) and metal-polymer (polytetrafluoroethylene and copper or iron) coatings obtained by vacuum plasma method were investigated. The influence of coating composition and deposition conditions onto coating properties and structure were analyzed. The peculiarities of deposition of nanocomposite polymer-polymer and metallopolymer coatings structure and properties of formed surface layers were determined. It was shown that the polymer-polymer coating presents a fine-grained micro- and nanocomposite binary mechanical mixture of the modified components. Additional activation of the dispersion products leads to the formation polymer-polymer and metal-polymer coatings with excellent tribological properties.

*Keywords*: nanocomposite coating, morphology, attenuated total reflection, tribological properties.

## 1. INTRODUCTION

Thin polymer based micro- and nanocomposite coatings obtained by vacuum methods demonstrate unique properties enabling possibilities to solve different technical problems including dressing and coloration of fiber-fabric materials, growth of 0.1 μm – 5.0 μm films with a low coefficient of friction and high wear resistance, and preparation of thin-film recording systems [1 – 3].

The properties of these nanocomposite coatings are known to be dependent on various structural factors, e. g, form, concentration, and size distribution of the embedded nanoparticles as well as molecular structure of polymeric matrix [2 – 6]. The methods with competitive growth of polymer and metal clusters permit in large range to change listed factors and properties of nanocomposite coatings. On the other hand, methods of deposition of composite coating based on evaporation (sputtering) from several sources and subsequent precipitation of the complex compound vapours on substrates are technologically complicated [4 – 6].

Due to simple and efficient technique, generation of active gas phase by electron beam from the combined dispersion of initial materials is perspective technology. This method is the most effective one, especially for deposition of coatings with complex structure and composition. Electron beam impacts on polymer surface and evaporation of polymer chains leads to the formation of numerous active particles in gas flow. Polymer layers obtained from the active gas flow have excellent mechanical and electrophysical properties [7]. Additional activation of particles in the gas flow can be performed by means of glow discharge excitation.

The main goal of the present work is investigation of structure and tribological properties of micro- and nanocomposite polymer-polymer and polymer-metal coatings deposited from the active gas phase under the conditions of additional plasma activation.

## 2. EXPERIMENTAL

Morphology, structure and tribological properties of polytetrafluoroethylene (PTFE), polyurethane (PU) coatings containing different nature polymer (or metal) of nanosize particles were investigated. The coating was performed from the active gas phase formed by electron beam dispersion of mixture of the initial materials, polymer and applicable metal-containing compound in vacuum. The concentration of metal in the composite coating was varied changing mass fraction of metal in the bombarded target (up to 17 %).

The conditions and regimes of deposition were described in [8]. Typical deposition rate of the coating was 5 nm/s – 10 nm/s and the final thickness of the deposited films was 500 nm. Activation of the volatile products was performed in a glow discharge. The discharge parameters were 1500 V and 20 mA – 60 mA. The silicon wafers, surface of butadiene-nitryl rubbers and aluminium-plated polyethylene terephthalate films were used as the substrates.

Surface morphology of the coatings was investigated by atomic force microscopy with “Nanotop-203” measuring system. Scanning of the surface was executed in a tapping mode. An additional mathematical analysis of the cluster formation images was carried out. The cutting-plane method and cluster labelling were employed to plot the distribution of islets over the area $n(S)$ and to calculate fractal dimensionality by the area-perimeter algorithm proposed by Feder [9]. Characteristic section with the maximum number of isolated clusters not touching the image boundary was chosen for analysis. Scanning electron microscopy (Hitachi S-806 device) was employed

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[*] Corresponding author. Tel.: +375-293-583274; fax: +375-232-555416. E-mail address: *rogachev78@mail.ru* (A. Rogachev)

to investigate the morphology of formed coatings. Fracture of the coatings was carried out in liquid nitrogen.

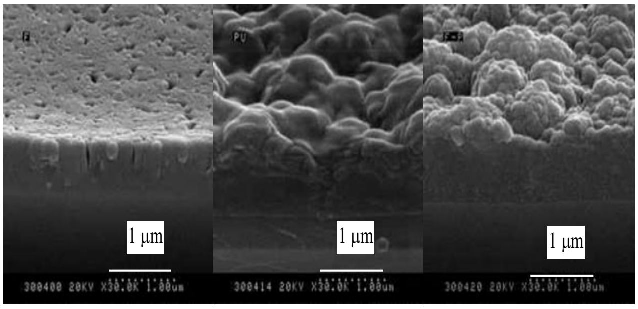
The molecular structure of the coatings was studied by FTIR-spectroscopy using a VERTEX-70 spectrometer and an attachment for the attenuated total reflection (ATR).

Tribological tests were performed using a microtribometer operating in a sphere-plate friction scheme. The ball of 6 mm in diameter made of 100 CR 6 steel served as the indenter. Speed of the indenter during the friction measurement was $3.3{\cdot}10^{-6}$ m/s, normal component of the force was 0.2 N.

## 3. RESULTS AND DISCUSSION

### 3.1. Nanocomposite polymer-polymer coatings

It is established that structure and properties of the composite coating are different from those of homogenous coatings. Fig. 1 shows the SEM images of the coating surfaces and corresponding profiles. As one can see, the PTFE coating surface has low roughness but it contains micropores that are approximately of 0.15 µm size. Formation of these pores is a result of polymer phase synthesis under the conditions of active particle deficiency. Structural elements with normal orientation to the surface are well visible in the profiles of coating. The PU coating has a developed structure. It contains globular micro elements of about 0.1 µm size. These formations have no evident orientation.



a b c

**Fig. 1.** SEM images (fracture) of coatings: a – PTFE, b – PU, c – PTFE-PU

Co-dispersion of PTFE and PU leads to the formation of coating that can be described as a nanosized polymer mixture. On the SEM images of profiles and surfaces of the composite coating one can see both morphological elements that are typical for the structures of homogenous coatings. It means that the composite coating structure can be considered as a mechanical mixture of homogenous polymer nanoparticles.

Vacuum deposition of thin polymer coatings is an effective way to produce surfaces with the lower friction coefficient. According to the obtained results, polymer coating nature and structure, have a strong influence on friction properties of the coating (Fig. 2). Mainly adhesion mechanism of friction in the test conditions used was detected. As shown in Fig. 2, the composite coatings PTFE-PU have much lower and more stable friction coefficient versus number of cycles as compared to the single PTFE or PU polymer coating.

The SEM image of a friction path shows the smoothing of the nanocomposite coating surface morphology (Fig. 3). No cracks were detected in the composite coating after the abrasion. Such coatings are worn without peeling or scuffing. Friction of the homogenous polymer coatings leads to the destruction of coating already after 60 – 70 cycles of abrasion.

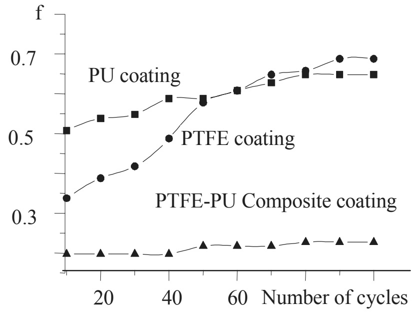
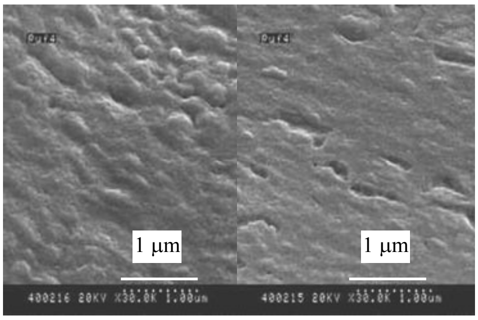


**Fig. 2.** Variation of the friction coefficient (*f*) versus the number of friction cycles



a b

**Fig. 3.** SEM images of the friction surface of PTFE-PU coatings after: a – 300 cycles of friction; b – 1000 cycles of friction

The IR-spectra of composite coatings PTFE-PU formed with the additional plasma activation have all absorptions bands typical for PU and PTFE (Fig. 4), i. e. they can be considered as a superposition of two IR-spectra of PTFE and PU.

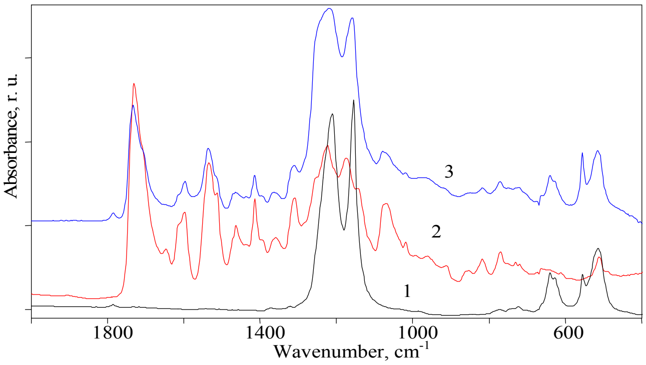


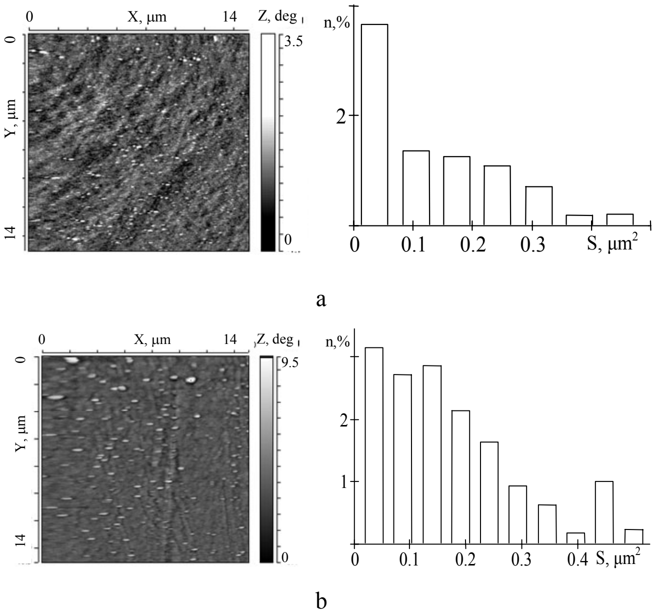
**Fig. 4.** IR-spectra of the coatings: 1 – PTFE coatings; 2 – PU coatings; 3 – composite PTFE + PU coatings

Analysis of the results of FTIR investigations allows one to assure that the composite PTFE-PU layers correspond to a fine-grained micro- and nanocomposite binary mechanical mixture of the modified components (Figs. 1 and 4).

In this way, the composite PTFE-PU layer combines high antifriction properties of PTFE as well as wear-resistance of PU and the best uses in friction unit [10].

## 3.2. Metal-polymer nanocomposite coatings

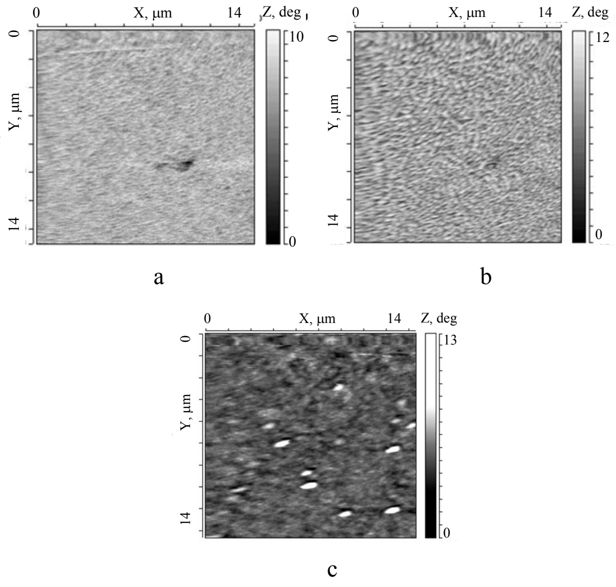
The structure of PTFE nanocomposite coatings containing metal (iron) can be considered as a polymer matrix and uniformly distributed metal particles of 100 nm – 200 nm size. According to our analysis, these coatings are continuous with effective thickness higher than 3 nm. This fact can be related to the influence of metal particles onto adsorption and polymerization processes. Well-ordered areas of polymer near the metal particles can be observed on the phase contrast AFM images after the surface etching in a glow discharge plasma (Fig. 5). The size of ordered polymer areas around the metal particles is about 200 nm – 300 nm for the PTFE-Fe coating.



a

b

**Fig. 5.** Phase contrast AFM images of PTFE-Fe coatings and distribution of metal particles versus surface area: a – as deposited, b – after glow discharge etching



a

b

c

**Fig. 6.** Phase contrast AFM images of PTFE-Fe coatings: a – pure PTFE, b – 8 % Fe, c – 17 % Fe

Morphology of the coating surface depends on the metal concentration. One can see that roughness of the surface increases with the increasing of the metal concentration and typical dimensions of the metallic particle vary as well (Fig. 6).

Fractal analysis of the topography AFM images shows a nonmonotonic character of the fractal dimension. The fractal dimensions have a maximum at 8 % of metal-organic compound concentration. The analysis of phase contrast AFM images indicates the formation of compact cluster structures with lower fractal dimension while the concentration of metal particles is increased. It is related to the volume structuring processes that is a result coalescence of metal nanoparticles.

The IR spectra of copper containing PTFE coating (8 % Cu) have several low intensity absorption bands at 1750 $cm^{-1}$ ÷ 1400 $cm^{-1}$, which indicate the formation of copper-organic chemical compounds [11].

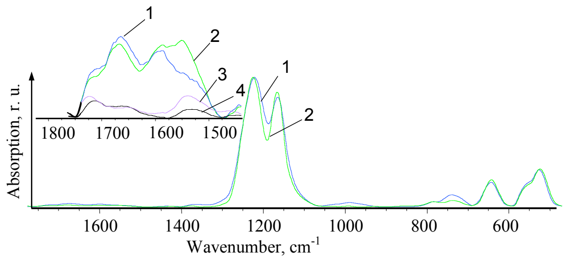


**Fig. 7.** Infrared spectra of the vacuum coatings: 1 – 8 % copper containing PTFE* coating; 2 – 8 % copper containing PTFE coating; 3 –PTFE coating; 4 –PTFE*
*deposited in additional activation condition

We have also observed the decrease of order sensitive bands at 516 $cm^{-1}$ and 640 $cm^{-1}$ and amorphous sensitive band at 740 $cm^{-1}$ in IR spectra of copper containing PTFE coatings deposited at additional plasma activation condition (Table 1). The variations of IR spectra indicate the chemical interaction between the electron beam dispersion products of PTFE and copper. The copper particles may be the centres of polymer phase structuring.

**Table 1.** Variation of relative optical density ($A/A_{1152}$) of IR absorption bands of the Cu containing PTFE coatings

| Coating | Wavenumber, $cm^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | 516 | 625 | 638 | 720 | 740 | 516/740 |
| PTFE | 0.36 | 0.045 | 0.084 | 0.029 | 0.0068 | 52.99 |
| PTFE* | 0.38 | 0.049 | 0.096 | 0.030 | 0.014 | 27.98 |
| PTFE-8 % Cu | 0.37 | 0.049 | 0.089 | 0.027 | 0.0074 | 49.83 |
| PTFE-8 % Cu* | 0.40 | 0.052 | 0.10 | 0.034 | 0.011 | 35.50 |

*deposited in additional activation condition.

The tribological properties of composite PTFE-Cu coatings were tested during the abrasion of butadiene-nitryl rubbers, that were modified with the coatings produced using glow discharge plasma activation. After $10^4$ cycles no crack and carry-over the coatings out of friction area, were detected, i. e. the coatings demonstrate the increased of wear-resistance [12].

## 4. CONCLUSIONS

The method of obtaining micro- and nanocomposite polymer-polymer and metal-containing polymer coatings has been elaborated. Complex research has been conducted onto the morphology, structure and tribological properties of composite coatings. Thin nanocomposite polymer coatings (PU-PTFE, PTFE-Fe, PTFE-Cu) have a developed morphology. The structure of coatings depends greatly on deposition parameters and conditions.

The composite polymer-polymer PTFE-PU layers correspond to a fine-grained micro- and nanocomposite binary mechanical mixture of the modified components.

The concentration of filling metal influences on the roughness, fractal dimension of the composite coatings as well as on the cross-linking polymeric matrix and defines number of metal clusters, their size and pattern of spacing. The metal clusters activate the process of polymer phase nucleation and are the centres of polymer phase structuring.

Additional activation of the volatile products leads to the formation of more continuous coatings with high mechanical properties. It is established that the best tribological characteristics are obtained when micro- and nanocomposite coatings (PTFE-PU, PTFE-Cu) are applied to the surface of butadiene-nitryl rubbers in the active gaseous phase, i. e. when the dispersion products are activated in the glow discharge plasma.

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