Adhesion and mechanical properties of polyanionic cellulose-Al-Zr protective coatings

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Abstract. The paper reports on a new protective coating composed of polyanionic cellulose, Al and micro-additive Zr powders. The work has investigated a structure and phase composition of the composite coating. The study hasn’t revealed any change of chemical composition in components of the overlay when coating and found macro-molecules of the polymer react with oxidic shells of particles due to hydrogen bonding. It has been established that adhesion strength of the coating increases 4 to 15 MPa when modifying an original suspension with zirconium micro-particles of less than 5 μm. The reason adhesion of the coating increases is reported to be agglomerates of Al and Zr fine fractions localized in hollows of the surface to be protected and on “adhesive-base” boundary.

Keywords: coating, adhesion, polyanionic cellulose, Al, Zr.

1. Introduction

To date, researchers have been focused on environmentally friendly materials with functional properties. Composites with a polymer matrix produced of renewable vegetable raw materials are considered to be prospective ones. The most applied of them are water dissolvable cellulose esters – carboxymethyl cellulose, methyl cellulose, ethyl cellulose, and polyanionic cellulose. Traditionally, these polymers are used as stabilizers, thickening and film forming agents [1-8]. Rheological properties of water dissolvable polymers have been studied in detail, so solutions with a certain viscosity and films with sufficient mechanical properties can be synthesized [9]. However, there is little published information on the development and application of protective coatings composed of biopolymers and dispersive metal fillers. Brittleness of biopolymer films and water dissolubility are major setbacks to the use of vegetable polymers.

In our previous research we demonstrated functional coatings could be synthesized with the use of carboxymethyl cellulose and dispersive metal fillers. The study has revealed that dispersion of filling particles and their distribution in the polymer matrix have a significant effect on structure formation in composite systems. It is possible to form composites with certain porosity, varying dimensions of particles to fill systems. The work [10] pointed at generation of orderly located pores in polymer films due to the modification of water-carboxymethyl cellulose-suspensions and Al powder (size < 45 μm) with highly dispersive particles AlOOH. These coatings demonstrated good anti-frictional properties in air when filling pores with solid greases [11]. No cell pores were found provided that the coatings...
were formed using carboxymethyl cellulose suspensions and Al without AlOOH [12]. Aluminum particles were distributed quite homogenously and compactly throughout the polymer matrix. The composites were used as corrosion protective coatings resistant to aggressive organic solvents. Therefore, it is possible to produce materials with certain functional properties applying particles with different chemical characteristics and dispersion as filling agents. This study investigates into a new protective coating composed of polyanionic cellulose and aluminum powder. Rheological characteristics of polyanionic cellulose are more stable than those of carboxymethyl cellulose; moreover, this polymer is a good bonding agent for metallic particles. Zirconium powder with particles below 5 μm was used as a micro-additive component to increase adhesion strength of the coating. Previous research demonstrates that adhesion strength of coatings under consideration increases enormously due to added Zr, making them resistant to concentrated acids, alkalis and organic solvents. According to research data [13-15] Al and Zr improve mechanical and corrosion resistance properties of coatings. Nowadays, it is a burning issue to apply environmentally friendly coatings in order to replace non-ferrous metals through less expensive ferrous ones.

This work aims to get insight into the influence of zirconium powder on adhesion strength of an anticorrosion polyanionic acid – aluminum coating and reveal specifics of structure formation in the composite system under consideration.

2. Materials and Methods

Composite coatings containing purified polyanionic cellulose (a degree of polymerization 500), aluminum powder (produced through spraying of the melt) and a micro-addition of calciothermic zirconium were researched. As a plasticizer we used glycerin to be compatible with simple cellulose esters. SEM-data on powders used are given in Figure 1.

![Figure 1. SEM-data of powders (a) polyanionic acid, (b) Zr, (c) Al, (d) particle-size distribution histogram of Al powder.](image)

The polymer has a fiber structure, in a dry powder fibers are like balls ranging to 900 μm in size. Zr powder contains roundish particles with a size of approximately 5 μm. Al particles are almost spherical ones with dimensions of about 45 μm. The histogram (Figure 1 d) shows data on dispersion of Al powder. A sub-micron fraction (≤0.1 μm) is found in aluminum powder. Peaks in the histogram are particles of approximately 19 μm in size. The biggest particles in the powder are in a range of 37±44 μm, their percentage is 4.5 %.

2% gel-like water-solution of purified polyanionic cellulose powder, glycerin, and particles of Al and Zr powder were mixed to synthesize coatings. Distilled water was used. The coatings were deposited at a temperature of (40±1)°C. Sample coatings were composed with and without fillers (proportions of components were determined in previous research and given in Table 1).

| Compound | Polyanionic cellulose + glycerin + Al + Zr (g) |
|----------|--------------------------------------------|
| 1        | 100.00+0+0+0                              |
| 2        | 100.00+1.20+0+0                           |
Structural morphology and element composition of coatings deposited on a steel base, physical configuration, dimensions of particles were researched using a SEM-microscope Quanta 200 in spectra of secondary and backscattered electrons. X-ray patterns of coatings were obtained using an X-ray diffraction meter RIGAKY ULTIMA IV in angle 2θ ranging 6° to 100° with an interval 0.02°. Voltage – 40 kV, anode current – 40 mA. Irradiation – CuKα, Kβ. Infrared spectra (IR - spectra) of organic components in composites and polymer powders were registered with the help of a Fourier spectrometer Varian 640 in a range 600–4000 cm⁻¹.

To measure dispersion of metallic powders we used an analyzer MicroTrac Bluwave. Research was carried out using facilities of Platov South-Russian State Polytechnic University. As the anticorrosion material under study is far less strong than a surface to be protected, we explored mechanical characteristics of coatings without the base material. Mechanical strength (σ) and relative strain were determined at axial tension (ε) of coatings deposited on a fluropolymer base according to guidelines [16]. Adhesion strength of coatings on steel 08кп was analyzed using a gluing method [17]. The surface of samples was sandblasted for 5 minutes and degreased with acetone. When testing, a dynamometer PM-4 was used, so a speed of moving gripper along a fixed one was 2.5 mm/min.

3. Results and Discussion

The data on mechanical characteristics and adhesion strength of coatings are given in Table 2. Adhesion strength of polymer films without metallic fillers is low. Mechanical strength of compounds 3 - 4 is quite similar; however, the strength a coating bonds with the surface increases considerably (4 MPa to 15 MPa) provided that zirconium particles are added. Structure and phase composition of coatings were analyzed to find out a reason for higher adhesion strength of a surface to be protected with a coating when introducing zirconium particles. Figure 2 shows side surfaces of deposited coatings. Besides ordered zones some amorphous ones were detected in polyanionic cellulose film (Figure 2 a). There are also cracks; the film is brittle; so its adhesion and mechanical strength is low. An elastic film is formed via adding glycerin, but film-base adhesion drops (Figure 2 b). A coating with Al powder is amorphous, being quite homogenous indeed (Figure 2 c). A fine fraction of Al particles coagulates in a gel-ash polymer medium of the suspension, surrounding quite coarse particles of aluminum. As metallic micro-particles sediment and a solvent – water evaporates; a coating hardens with further tight packaging of aluminum particles in the polymer matrix. Packaging of particles in a composite containing powders Al and Zr is similar (Figure 2 d). Both coarse and fine Al particles are distributed quite homogenously on side surfaces in compounds 3 and 4.

Table 2. Mechanical properties and adhesion strength of coatings.

| Compound | σ (MPa) | ε (%) | Adhesion strength (MPa) |
|----------|---------|-------|------------------------|
| 1        | 9.0     | 10    | 1.0                    |
| 2        | 11.2    | 15    | 0.8                    |
| 3        | 18.0    | 12    | 4.0                    |
| 4        | 19.2    | 10    | 15.0                   |
**Figure 2.** SEM – data of side surfaces of coatings: (a) polyanionic cellulose, (b) polyanionic cellulose + glycerin, (c) polyanionic cellulose + glycerin + Al, (d) polyanionic cellulose + glycerin + Al + Zr.

Figure 3 a shows IR–spectra of polyanionic cellulose powder and Al-Zr coating. Spectra are almost identical in a range 3400-3800 cm⁻¹. An absorption band in a range 3350-3200 cm⁻¹ is in line with a valence fluctuating band of OH – group. This band for sample Al-Zr coating is more intensive than that for polyanionic cellulose sample. A band in range 1590 cm⁻¹ identified in spectra corresponds with a group C=O for intermolecular hydrogen bonding. An absorption band tends towards lower frequencies because a hydroxyl group contributes to the formation of intermolecular hydrogen bonds [18]. This frequency for polyanionic cellulose sample is 3380 cm⁻¹, and for a coating 3275 cm⁻¹, respectively. The increase in intensity of absorption band for a group OH (3290 cm⁻¹) in a spectrum of the coating and dropping intensity of absorption band 1592 cm⁻¹ for a group C=O as compared with a spectrum of powder polyanionic cellulose point at hydrogen bonding between active hydroxyl macromolecule groups and Al and Zr oxidic shells. A set of bands in a range 1350-700 cm⁻¹ is an individual parameter for each substance [19]. They are nearly the same for polyanionic cellulose and a composite coating. The study on spectra revealed no transformation in a polymer matrix; chemical bonds are not formed between components of a coating.

X-ray pattern of Al-Zr coating (Figure 3 b) demonstrates diffraction peaks corresponding with peaks of a face-centered Al cubic cell (space group Fm3m) and reflexes similar to a six-sided tightly packed Zr cell (space group P63/mmc). A phase composition of original metallic fillers is constant when coating. Al and Zr oxides are not registered, probably, because of their low concentration in the coating.

**Figure 3.** (a) IR-spectra of polyanionic cellulose powder (1) and a composite polyanionic cellulose+Al+Zr+glycerin (2), (b) X-ray pattern of a composite polyanionic cellulose+Al+Zr+glycerin; element composition of the surface in a composite (polyanionic cellulose + glycerin + Al + Zr): (c) formed in air, (d) deposited on the base.

Infrared spectroscopy and X-ray phase analysis haven’t revealed any changes in phase composition of original components in the process of coating deposition.

The distribution of metallic particles on the contact edge “base – coating”, and the way they fill up defects in the surface have a strong effect on adhesion strength of the composite. There are coarse
particles in Al powder and also particles with a size similar to that of Zr particles (< 5 μm). Aluminum and zirconium particles have quite a similar spherical physical configuration. It is difficult to identify these particles using SEM methods. Therefore, we explored element composition in air-deposited Al and Zr compounds and that of a steel surface (Figure 3 c, d). According to the data of electron spectroscopy there is potassium, chlorine in the coating, so formation of NaCl is possible. This is not in contradiction with a traditional approach to the synthesis of highly purified polyanionic cellulose. NaCl is a secondary product in etherification reaction, when polyanionic cellulose is synthesized [18]. Producing highly-purified polyanionic cellulose NaCl is removed from the main substance by a solvent. A purified powder of polyanionic cellulose used in the study contains around 0.5% NaCl, as required in technical standards of the powder. The concentration of NaCl in the coating is low, so an X-ray pattern demonstrates no NaCl reflexes. A surface to contact with air contains Al (Figure 3, c). Al and Zr were detected on the surface close to the base (Figure 3, d). Therefore, Zr particles, a density of which exceeds that of Al, localize largely on the contact «base – coating» when they sediment. A peak-to-hollow distance in the surface under study (steel 08кп) ranges to 10 μm, so macro-roughness is registered. As Zr particles are mainly on the contact surface, adhesion strength of a coating with Zr increases, since hollows in a metallic base are filled up better with Zr particles. A coating-steel boundary consists of agglomerates formed due to sticking of Al and Zr particles in the coating and space. Agglomerates of fine Al and Zr fractions in the surface hollows and on the edge “adhesive – base” are like spanning elements, so adhesion increases due to mechanical bonding.

Resistance of compounds 3 and 4 was also checked, they are resistant to organic solvents, polyester varnishes, and quite stable to concentrated acids and alkalis.

4. Conclusions

To sum up, a new protective coating composed of polyanionic cellulose, Al and Zr powders is developed. A structure and phase composition of the composite coating has been investigated using methods of SEM and X-ray phase analysis and infrared spectroscopy. The study hasn’t revealed any change of chemical composition in components of the overlay when coating. Macro-molecules of the polymer react with oxidic shells of particles due to hydrogen bonding. It has been shown that aluminum particles are packed tightly in a polymer matrix when hardening. Agglomerates of fine aluminum and zirconium fractions in the surface hollows and on the edge “adhesive – base” are like spanning elements, improving adhesion due to mechanical bonding.

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