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# Formation of Composite Polymeric Coatings on Pure Iron

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**Abstract**—We have demonstrated possibility of electrochemical preparation of metal-polymer nanocomposites on pure iron and steel electrodes in the course of electrochemically initiated polymerization of 1-vinyl-1,2,4-triazole accompanied with cathode formation of metals. Silver nanoparticles have been uniformly distributed in the formed polymer matrix. The prepared composites possess excellent thermal stability.

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Composite materials have found numerous applications and therefore have been widely studied [1]. In particular, composite materials containing silver nanoparticles have shown unique properties making them promising for medicine, nanophotonics, and catalysis applications [2–4]. Properties of silver nanoparticles (size, size distribution, stability, etc.) are significantly dependent on the nature of stabilizing polymer matrix as well as on conditions of the nanoparticles formation. Poly(1-vinyl-1,2,4-triazole) has been recognized as new non-toxic ($LD_{50} > 3$ g/kg) water-soluble polymer, efficient stabilizer of nanoparticles of silver and other metals [5, 6].

The preparation of nanosilver-containing composites by using different reducing agents has been discussed in [7]. The composites have been formed by reducing silver nitrate in aqueous solution in the presence of poly(1-vinyl-1,2,4-triazole), the reducing agents tested being sodium borohydride, glucose, and formaldehyde.

In this work we investigated possibility of preparation of metal-polymer composites and coatings onto electrodes made of steel and pure iron by means of electrochemically initiated polymerization of 1-vinyl-1,2,4-triazole accompanied by cathode metals formation.

Electrolysis of aqueous and aqueous ethanol solutions of 1-vinyl-1,2,4-triazole, acrylamide, and their mixture in the presence of $AgNO_3$ (and, in some experiments, KI) gave nanocomposite coatings containing 5–35 wt % of silver; the necessary condition was the presence of peroxide initiator with electroreduction potential close to that of metal formation (–0.6 to 1.2 V with respect to saturated silver chloride electrode), for instance, 4-*tert*-butylperoxy-4-oxobutanoic acid.

Thus prepared nanocomposite electrode coatings became insoluble in water and common organic solvents after drying. Content of silver nanoparticles, their size and size distribution were affected by the monomer nature, current density, and electrode potential.

UV spectra of the composites contained absorption bands at 412 nm (in the case of homopolymer composites, **I**) or 414 nm (copolymer composites, **II**) typical of isolated silver(0) particles of nanodimension [2, 3, 7, 8].

IR spectra of the nanocomposites contained the bands typical of stretching and bending vibrations of triazole cycle in a polymer (3110, 1505, 1275, 1138, 1005, and 661 $cm^{-1}$). In the case of acrylamide copolymers, IR spectra contained the bands assigned to vibrations of amide (1665 $cm^{-1}$) and methylene (1430–1455 and 2930 $cm^{-1}$) groups.

From electron transmission microscopy data (Figs. 1 and 2), the distribution of silver nanoparticles was more uniform in the case of homopolymer composites **I**. The metal nanoparticles size was of 2–8 and 2–12 nm in the cases of nanocomposites **I** and **II**, respectively.

Thermogravimetry data demonstrated excellent thermal stability of the nanocomposites: The decom-

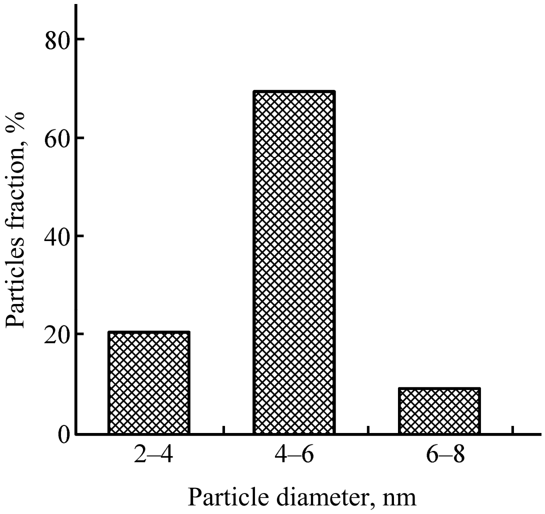

**Fig. 1.** Size distribution of silver particles in composite **I**.

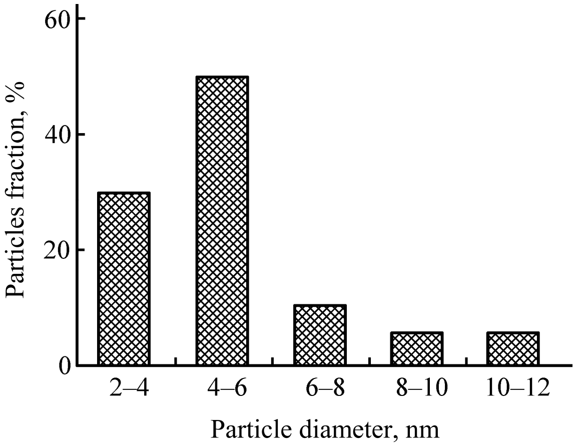

**Fig. 2.** Size distribution of silver particles in composite **II**.

position onset was observed at 255°C (**I**) and 270°C (**II**).

To conclude, the electrochemical synthesis yielded nanocomposites containing silver nanoparticles entrapped into polymer matrix: homopolymer of 1-vinyl-1,2,4-triazole (**I**) or its copolymer with acrylamide (**II**). The particles size distribution was narrow, and they were uniformly dispersed within the polymer matrix.

## EXPERIMENTAL

Electrochemically initiated polymerization was performed in glass electrolyzer without any membrane. IR spectra were registered using the Specord M-80 spectrometer (KBr). Electron absorption spectra were recorded with the Perkin Elmer Lambda 35 UV/VIS spectrophotometer. Silver content in the nanocomposites was determined by elemental analysis and with the Perkin Elmer Analyst 200 atom absorption spectrometer. The nanoparticles distribution was visualized with the Leo 906 E transmission electron microscope. Thermogravimetric analysis was performed using the MOM Paulig–Paulig–Erdei derivatograph at 5 deg/min heating rate.

1-Vinyl-1,2,4-triazole (bp 58–60°C at 10 mm Hg) was prepared as described in [9, 10].

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