

Preparation Method for Noble Metal–Polymer Matrix Nanocomposites

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Abstract—A method is described for the preparation of new nanocomposites based on poly(ethylene terephthalate), poly(vinyl chloride), and polypropylene on the one hand and on noble metals (Ag and Pt) on the other. The method comprises the formation of nanoporous polymer matrices by crazing the polymers with simultaneous incorporation of noble metal precursors (AgNO₃ or H₂PtCl₆) into the matrices. Subsequent in situ reduction of the precursors yields the metal–polymer nanocomposites. Prospects for the practical application of the developed method for the production of metal–polymer nanocomposites are discussed.

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INTRODUCTION

The production of nanocomposites, including those with polymer matrices, comprises the following stages. First, at least one of the components of this composite must be ground to a nanosized state. Second, the components of a system must be mixed to prepare a uniform mixture. Finally, the system thus obtained must be stabilized by any method to avoid spontaneous separation caused by the thermodynamic incompatibility of the components. All these procedures are quite complex physicochemical problems, and their solution encounters substantial difficulties. At present, diverse methods are available for the production of nanocomposites, in particular, those based on polymer matrices. Many of these methods are rather complex and laborious; therefore, they are far from being applied in routine practice [16].

In this work, we used another approach to the production of nanocomposites that differs essentially from the approach formulated above that consists of preliminarily preparing a nanoporous polymer matrix that can subsequently be filled with a second component. If the pore sizes of this matrix are no larger than a few nanometers, the incorporated component will be dispersed in the matrix at the nanosized level; thus, the problem of the nanocomposite preparation will be solved. In this case, the main problems are the preparation of the polymer matrix with nanosized pores and the incorporation of a second component into it.

EXPERIMENTAL

Amorphous nonoriented poly(ethylene terephthalate) (PET) 100- μ m films, 35- μ m nonoriented PET

fibers, commercial 140- μ m isotactic polypropylene (PP) films annealed at 140°C for 2 h, and commercial 180- μ m nonoriented poly(vinyl chloride) (PVC) films were applied in this work.

The aforementioned films and fibers were deformed in the media of specially chosen solutions, i.e., adsorption-active liquids containing precursors of Ag and Pt metal nanoparticles. The effective volume porosities of the films stretched in the liquid media was estimated from the volume increments of the deformed samples.

The amounts of inorganic nanoparticles incorporated into the polymers were determined by two methods, namely, by thermogravimetry from a change in the initial film mass and by thermogravimetry from the mass of a solid residue resulting from the burning of a polymer matrix. The experiments were carried out with a TA4000 thermoanalyzer (Mettler) equipped with a TG50 attachment. The phase composition of the composites was assessed by the large-angle X-ray diffraction method with a DRON-4 diffractometer using the CuK α radiation ($\lambda = 0.154$ nm).

Ultrathin sections were cut from the samples with a diamond knife (ultramicrotome) (Reichert-Jung, Germany) at room temperature. The sections were placed onto copper electron microscopic networks coated with formvar. Samples were examined with a Leo-912, AB Omega electron microscope (K. Zeiss, Germany). In addition, this instrument enables one to measure electron microdiffraction in a specified region of a sample and perform its elemental analysis.

RESULTS AND DISCUSSION

Within the framework of this study, the above-formulated problem will be solved using polymer crazing in liquid adsorption-active media (AAM). Polymer crazing is one of the most typical and specific manifestations of the Reh binder effect [7, 8]. Similarly to the classical case, the features of the Reh binder effect manifest themselves in polymers upon their deformation in AAM. This kind of deformation (stretching) causes the self-dispersion of a solid polymer into the finest aggregates of oriented molecules (fibrils) separated by microvoids with nearly the same sizes. Note that the sizes of fibrils and separating microvoids are ~1–100 nm [9–13], that is, correspond to the phase sizes typical of nanocomposites.

Because the development of these nanoporous structures is only possible when they are continuously filled with an ambient liquid medium, the polymer crazing clears an efficient way to deliver almost any substance into the nanoporous structures being formed [7, 10, 14, 15]. It is obvious that the incorporation of a second component into a nanoporous structure of a crazed polymer automatically leads to the formation of a nanocomposite because the particle size of the second phase thus incorporated cannot exceed the pore size. The third condition, that is, the stabilization of the formed nanostructure, is also easily realized owing to the structural features of crazing. The matter is that, at the initial stages of the polymer deformation in AAM, at low degrees of stretching, a system of interconnected nanosized pores penetrating the whole bulk polymer and continuously filled with an ambient medium spontaneously arises and develops. During subsequent deformation, the nanoporous structure of the crazed polymer evolves in such a way that, at high degrees of stretching in AAM, the structure collapses with a drastic decrease in the effective pore diameter. When any additive is dissolved in AAM, the collapse of the nanoporous structure is accompanied by the mechanical capture (sealing) of the dissolved component in the form of a nanosized inclusion [7, 10, 15]. The aforementioned structural peculiarity of a crazed polymer ensures the stabilization of a nanocomposite being formed and prevents nanoparticles of the second component formed in the crazes, which is incompatible with the polymer, from coalescing because nanoparticle migration is almost impossible in a glassy or crystalline polymer.

In view of the aforesaid, attempts were repeatedly made to apply crazing to the production of diverse nanocomposites. This problem is easiest to solve when a second component incorporated into a polymer is readily soluble in AAM [16, 17] or a melt of the second component itself plays the role of an AAM [18]. Under these conditions, the nanoporous polymer structure being formed in the course of crazing is efficiently filled with the second component, thus leading to the formation of a polymer matrix-based nanocomposite

through simple stretching of a polymer in a properly selected solution of a necessary additive. It is obvious that, in this case, the nanocomposite production can be easily realized as a continuous process, because orientational drawing of films and fibers is widely performed with the application of modern high-performance equipment.

The problem of nanocomposite production is markedly complicated when a second component that is insoluble in AAM is incorporated into a polymer matrix. This situation arises when it is required to distribute metal nanoparticles in a polymer matrix, which is the goal of this work. In this case, the problem of the production of these nanocomposites was also successfully solved with the use of polymer crazing in AAM. Because metals are insoluble in organic media (typical AAM), AAM-soluble precursors had to be incorporated into a polymer with subsequent *in situ* reactions giving rise to the formation of metal nanoparticles immediately in the polymer matrix. In particular, KI was incorporated into a nanoporous polymer structure by means of crazing; then, the product thus prepared was exposed to an AgNO_3 solution to release AgI crystals in the nanopores of the polymer [19]. Subsequent treatment of the obtained material with a photographic developer led to the formation of silver metal crystals in the nanoporous polymer structure.

The interdiffusion method provides another approach to the production of metal–polymer nanocomposites. In this case, a crazed polymer film is placed into a dialysis cell, with aqueous solutions of a metal salt, e.g., AgNO_3 , and NaCl being charged into one and another chambers of the cell [20]. These components diffuse toward one another in the nanoporous crazed polymer matrix, meet inside it, and interact to yield insoluble AgCl. Annealing of the obtained nanocomposite gives rise to the formation of nanosized silver metal immediately in the polymer matrix. When one of the dialysis cell chambers is filled with a solvent of an efficient reducing agent, e.g., sodium borohydride, the metal can be released in nanopores of the crazed polymer in a single stage [21].

The electrochemical production method of metal–polymer nanocomposites may also be mentioned [22]. In this case, a crazed polymer matrix is placed at the cathode of an electrochemical cell filled with a metal salt solution. In the course of the electrochemical reduction, pores in a crazed polymer matrix are primarily filled with a metal with the formation of a metal–polymer nanocomposite.

It must be noted that, although all of the aforementioned procedures yield metal–polymer nanocomposites, from the practical point of view, they have a practical drawback in common. In the two former cases, the rate of the metal phase formation in the polymer matrix is limited by the diffusion of low-molecular-mass components in a solution. Diffusion processes are known to be quite long and are unpromising from a practical point of view. The methods of interdiffusion

and electrochemical precipitation in a polymer matrix are periodic in principle and cannot be realized as continuous high-performance processes.

These circumstances lead us to search for new ways of producing metal–polymer nanocomposites that would be devoid of the above drawbacks and, hence, the most promising in the practical aspect. Below, we present the results of the studies devoted to the development of methods for the production of new metal–polymer nanocomposites based on PET, PP, and PVC, on the one hand, and noble metals, on the other, as well as the data on the structure and some properties of the nanocomposites. At the same time, the goal of this work is to attempt to develop metal–polymer nanocomposite production methods that would be devoid of the aforementioned drawbacks.

1. PET–Silver Nanocomposites

Silver was chosen because, being incorporated into synthetic and natural polymers, it imparts stable antibacterial and antiputrefaction properties to them. Due to this property of silver, a microorganism-free protective zone arises around silver-containing materials. Commonly, this effect is simply realized by the surface treatment of fibers or fabrics (mainly, based on cellulose and its derivatives) with solutions of silver salts. Due to the presence of active functional groups in macromolecules, silver ions are sorbed in the surface layers of the fabrics and impart them with necessary bactericidal properties. However, this effect turns out to be unstable and short-lived because silver salts are easily desorbed upon washing, which inevitably takes place during textile material service.

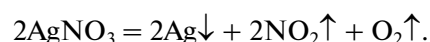
The crazing method makes it possible to incorporate modifiers into bulk polymer that obviously makes it ranking above the surface treatment method in the applied aspect. It is very important that the polymer modification by the crazing method does not require the presence of active functional groups in a polymer. Modifiers are fixed in polymers via the mechanical capture in the structure of a deformed polymer owing to the commensurability of its nanopores and molecular sizes of an incorporated additive [10] rather than through its chemical interaction with active functional groups of the polymer.

Hence, the first problem was the selection of an AAM capable of, on one hand, crazing a modified polymer and, on the other hand, containing a modifier. Therefore, in order to prepare nanocomposites and to incorporate silver into PET films or fibers, they were deformed in a water–alcohol solution of AgNO_3 . The presence of isopropanol ensured PET deformation via the crazing mechanism, thus creating a porous nanostructure filled with the AgNO_3 -containing modifying solution in the polymer. Then, the liquid medium was removed by drying the samples to obtain a PET film (fiber) containing the precursor (AgNO_3),

which was necessary for subsequent silver metal formation in the polymer structure.

The concentration of low molecular compounds incorporated into a crazed polymer is, in the general case, governed by the polymer porosity and the content of a modifier in a solution. PET porosity was close to 50%, and a rise in the AgNO_3 concentration in the solutions from 0.05 to 2.5% increased silver content in nanocomposites from traces to 2.5 wt %.

It is known that silver nitrate can be decomposed to zero-valence silver through both the thermal annealing and irradiation with light. In the free volume, the reaction takes place according to the following scheme:



The time of UV irradiation was preliminarily determined from the depth of film staining. In the course of UV irradiation, the milk-white PET film containing AgNO_3 gradually acquired a brown color, which was obviously related to release of silver metal in its structure.

The fact that, during the UV irradiation of an AgNO_3 -containing film, the chemical reaction yields silver metal is supported by the X-ray diffraction data. The maximum that arises in the diffractogram at $2\theta = 38.2^\circ$ is assigned to the crystalline silver phase.

Previously [10], the structure of crazed polymers was mainly investigated by scanning electron microscopy; however, only transmission electron microscopy data enable one to judge the fine structure of an obtained nanocomposite. In this work, the structural-morphologic experiments were carried out by transmission electron microscopy applying ultrathin sections.

Micrographs of ultrathin sections of a PET nanocomposite containing 2.5 wt % silver are depicted in Fig. 1. The first fact that draws our attention is the nonuniform distribution of the metal over the sample. Figure 1a distinctly demonstrates the alternation of undeformed polymer regions (uniform gray regions) 200–300 nm wide and crazes with uniformly distributed dark inclusions. The boundaries between these regions are quite distinct. Micrographs taken at higher magnifications from the craze regions containing silver particles are illustrated in Figs. 1b and 1c. It is seen that silver particles are almost spherical. Note that, while the average silver content in the polymer matrix is about 2.5 wt %, its local concentration in crazes is noticeably higher because the nondeformed polymer regions contain no silver metal.

Figure 2 shows the electron diffraction pattern of a PET section containing 2.5 wt % silver. It is distinctly seen that the diffraction pattern represents one distinct diffraction ring. The absence of higher-order maxima is explained by small sizes (about 5 nm) of silver particles in which metal atoms cannot form a lattice with a pronounced long-range order. The interplanar spacing calculated for silver included into the PET matrix

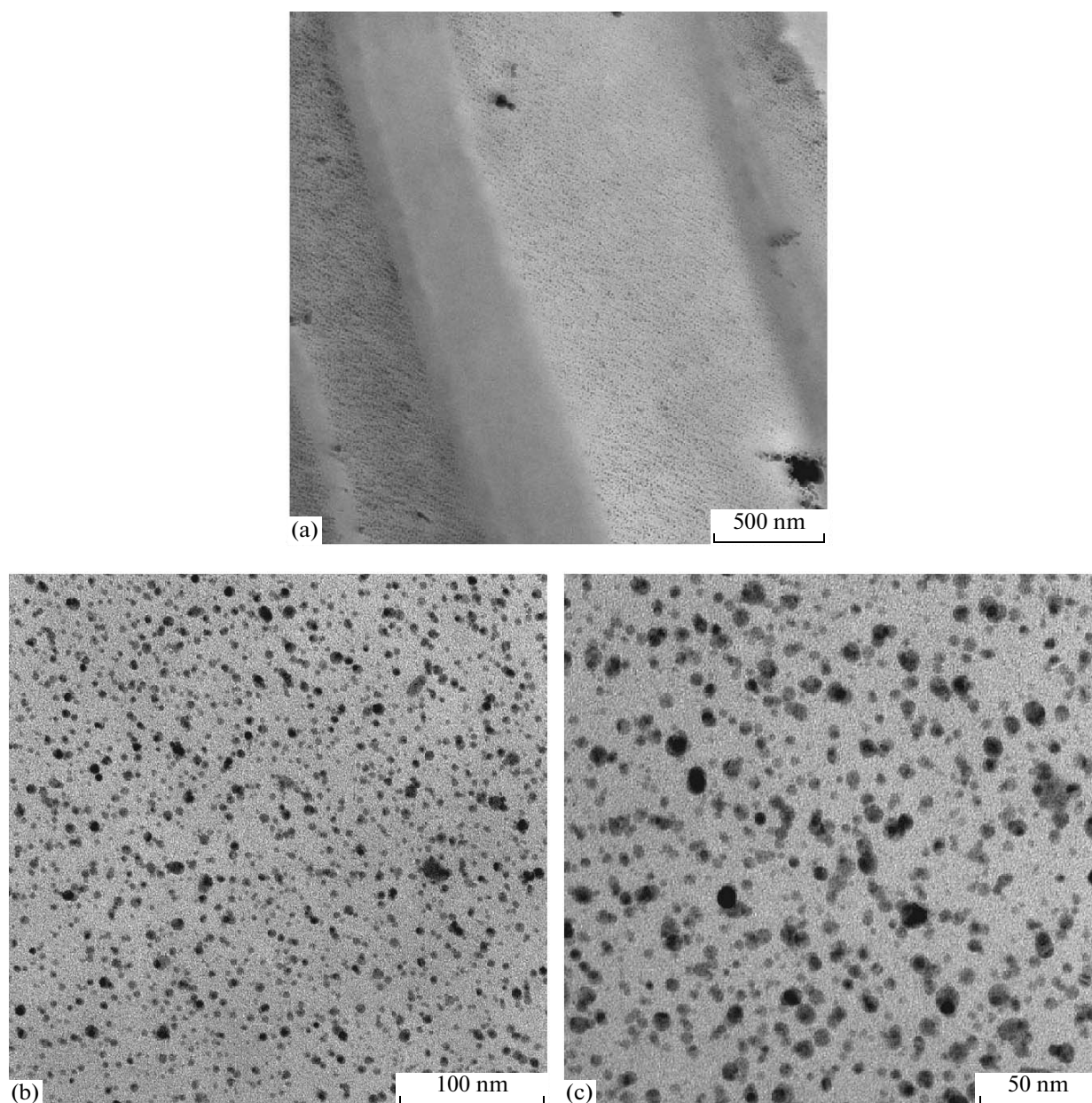


Fig. 1. Micrographs of ultrathin section of PET-silver (2.5 wt %) film taken at different magnifications.

appeared to be 2.355 \AA , which is inherent in the $\{111\}$ reflection plane of silver. The size distribution of silver particles included into the PET film is presented in Fig. 3 as a histogram. It can be seen that the average, smallest, and largest particle diameters are 4.6, about 2, and 8.6 nm, respectively. Thus, based on the example of PET films, it has been shown that the crazing method makes it possible to incorporate rather large amounts of silver metal into the polymer. The prepared nanocomposites are characterized by a high dispersity of the components.

2. *PP–Platinum and PVC–Platinum Nanocomposites*

Platinum-based composites were obtained using PP and PVC films as polymer matrices. Prior to crazing, PP films were annealed at 140°C to transform the polymer into the monocline crystalline modification. In this state, PP is deformed in AAM via the delocalized crazing mechanism, which is characterized by the high uniformity of the nanoporosity development throughout the bulk polymer [23]. In addition to PET, which was considered above, glassy PVC exhibits classical crazing characterized by the structure composed

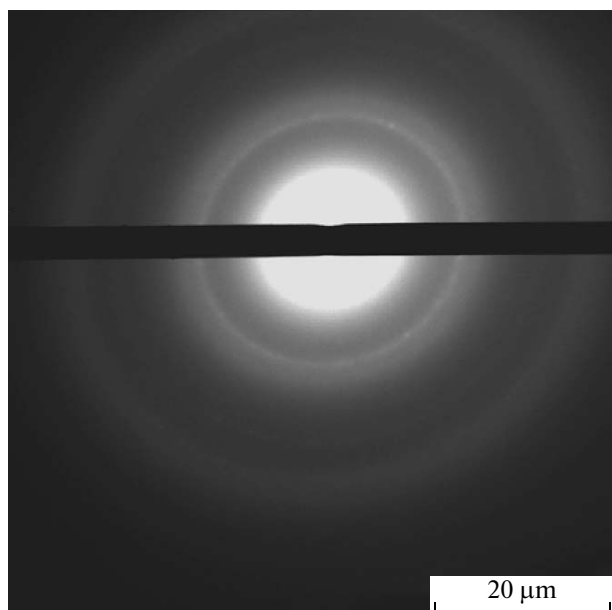


Fig. 2. Electron diffraction pattern of ultrathin section of PET-silver film.

of alternating regions of nanoporous (crazed) and monolithic material [10].

Chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was applied as a metal-containing precursor, which was dissolved in an isopropanol–water mixture (water content of 10 wt %). This mixture served as an AAM in which, on the one hand, H_2PtCl_6 (~5%) was dissolved and, on the other hand, both chosen polymers were efficiently crazed. Because pure H_2PtCl_6 per se could not be

decomposed to yield platinum metal upon the annealing in the polymer matrices, a reducing agent (glucose) was added to the crazing solution in a ratio of 1 : 1.5, mol/mol, with respect to H_2PtCl_6 .

In order to elucidate the principle feasibility of reducing H_2PtCl_6 with glucose to obtain platinum metal, preliminarily this reaction was realized by heating a mixture of these components at 110°C for 20 min. A black compound thus formed was analyzed by the X-ray scattering and transmission electron microscopy methods. Figure 4 illustrates the electron micrograph of a platinum metal preparation obtained by the aforementioned method. It is distinctly seen that the thermal treatment and the interaction of H_2PtCl_6 with the reducing agent result in the formation of platinum metal nanoparticles with sizes of 3–4 nm. The X-ray scattering data attest to an amorphous state of the metal phase (the absence of crystal reflections). A further thermal treatment of the mixture of the above components at $\sim 700\text{--}800^\circ\text{C}$ causes organic phase burning, which yields a black powder whose diffractogram confirms the formation of platinum metal ($2\theta = 39.8^\circ$ and 46.3°). The crystallite size estimated from the reflection half-width (the Scherrer equation) is ~ 40 nm.

Thus, the preliminary study indicates that during the annealing in the region of 110°C (i.e., in the temperature range where both selected polymers remain in the solid aggregate state), the chemical interaction in the mixture of H_2PtCl_6 with the chosen reducing agent (glucose) indeed takes place to yield zerovalence platinum, seemingly according to the following scheme:

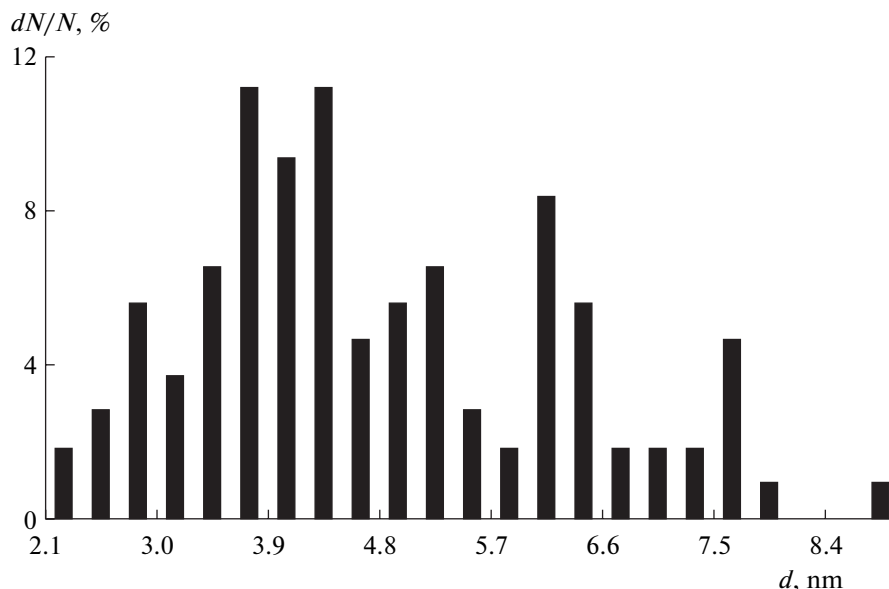


Fig. 3. Size distribution of silver particles included into PET matrix.

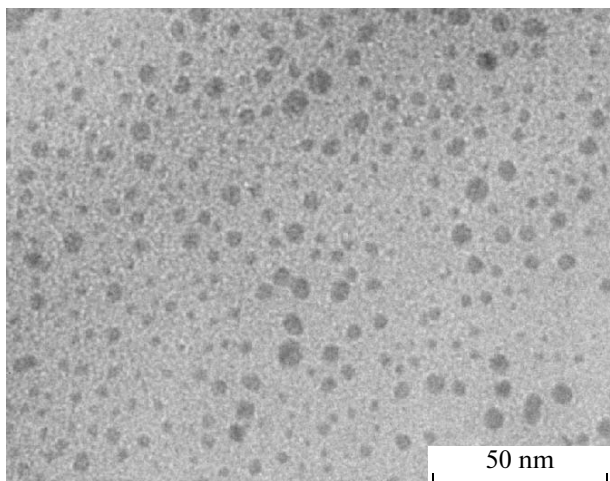
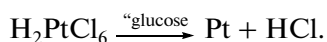


Fig. 4. Micrograph of platinum nanoparticles. See text for explanations.



Further, the PP and PVC films were stretched in a water-alcohol solution of the aforementioned H_2PtCl_6 –glucose mixture, and the samples thus prepared were withdrawn from the solution, dried until the solvent was completely removed, and heated at 110–120°C for 40–50 min. As a result of this thermal treatment, PP-based composites acquired a uniform black color, although the obtained films were transparent in the transmitted light. As might be expected, PVC-based

compositions exhibited densely located alternating dark (crazes filled with platinum metal) and light strips.

The Pt nanophase contents in PP and PVC were ~3.3 and 1.2%, respectively. The sizes of Pt particles in PP- and PVC-based composites were ~2–3 and 10–30 nm, respectively. According to the electron diffraction data, in the prepared materials, platinum nanoparticles are amorphous, seemingly, because of their small sizes. The electron microscopy data on the ultrathin sections of the examined materials (Fig. 5) provide adequate information on the structure of the obtained nanocomposites.

Thus, it can be concluded that crazing can in fact be used to produce new metal–polymer nanocomposites, including those based on noble metals. It must be noted that, from a technological point of view, the developed procedure basically comprises only two operations, namely, the stretching of a polymer in an AAM containing a necessary precursor (the incorporation of a metal compound into a bulk polymer) and the annealing of a prepared material (metal isolation into a separated nanophase). This circumstance causes this procedure to rank above those developed previously [18–21] because both the stretching of polymer films and fibers and the annealing are easy to implement in a continuous high-performance regime and can underly new technology for the production of nanocomposites based on noble metals and polymers.

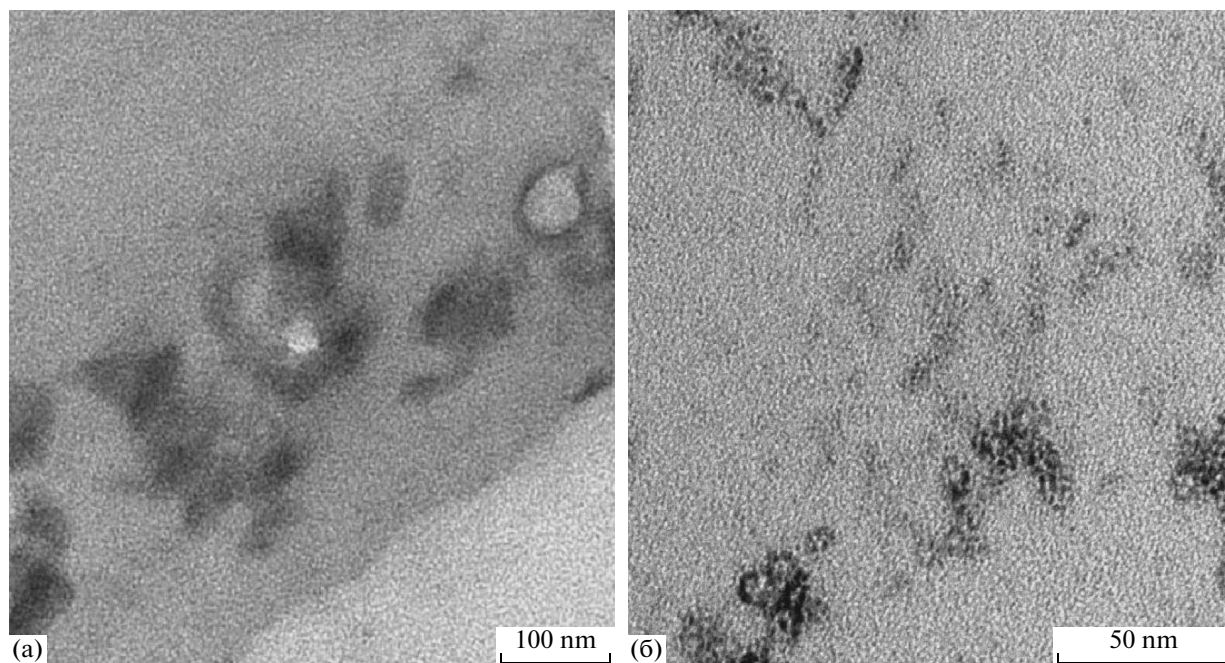


Fig. 5. Micrographs of ultrathin sections of (a) PVC and (b) PP containing platinum nanoparticles.

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