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Characterization of Polypyrrole–Silver Nanocomposites Prepared in the Presence of Different Dopants

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Received: April 6, 2005; In Final Form: July 4, 2005

Conducting polypyrrole (PPy) powder synthesized by using $\text{FeCl}_3 \times 6 \text{H}_2\text{O}$ and/or $\text{Fe}(\text{NO}_3)_3$ oxidants was impregnated in silver salt solutions. The stability and decomposition of the material was followed by thermogravimetric measurements. The total silver content was determined by atom absorption spectroscopy (ICP-AAS). The heat and electric conductivities of the composites were measured and correlated with the silver content. The incorporated silver was speciated and measured by X-ray diffraction (XRD). The spectra proved that the chemical state of the silver incorporated into the composite depends on the anion used in the polymerization process. In the case of the polymerization in a nitrate ion containing solution, the impregnation leads exclusively to the formation of metallic silver. The size distribution of the AgCl and Ag nanoparticles, determined from transmission electron microscopy (TEM) pictures in the different composites, proves the formation of a rather uniform species below 10 and 7 nm, respectively. The observations can be correlated with the different interactions in the PPy-chloride/nitrate-silver systems. The redox type interaction based conclusions can be considered as a guide during the preparation of other metal-conducting polymer composites.

Introduction

Composite materials are considered to be a group of perspective substances, combining together the different properties of components, leading the way to a new, tunable behavior. During the past decade, a new branch of material science—nanostructured materials—has developed, and the special character of nanosized solid materials has received great attention. Recently, the importance of metal nanoparticles has been summarized in a feature article,¹ emphasizing the photophysical, photochemical, and photocatalytic aspects of the unique electronic and chemical properties of metal nanoparticles, which have drawn the attention of chemists, physicists, biologists, and engineers because of the special opportunities opened by these substances in the development of a new generation of nanodevices. The importance of such composite materials lies in the fact that in these cases, nanometals are dispersed in the matrix of the other component, which ensures their stabilization. Gold nanoparticles have been stabilized in alkane-thiolates² forming self-assembled monolayers of clusters containing ~ 4 nm gold cores. Tetra-octyl-ammonium bromide capped gold nanoparticles exhibited surface binding properties,³ facilitating the formation of ordered arrays of gold nanoparticles. Phosphine-stabilized metal nanoparticles proved to be excellent precursors to specially functionalized nanoparticles⁴ from which blocks possessing well-defined metallic cores can be built. Methods for preparing nanoparticles have extensively enlarged, and various procedures are available in the literature,^{5–7} including new solutions using templates.^{8–9}

A special group of composite materials contains polymers. Electronically conducting polymers are one type of the most perspective materials^{10–13} since under certain conditions they

can endow the composites with a small electric resistance, or—when needed—they can be transformed into the insulating state as well. This family of composites may contain the conducting component either dispersed in inorganic matrix¹⁴ or, vice versa, the conductive organic matrix may incorporate the other phase. Conducting polymer films containing nanodispersed catalytic particles have been patented as a new type of composite materials for technological applications,¹⁵ where the importance of the electrochemical conductance and the retrieval of higher molecular weight poisons have been outlined.

Conducting polymers have been successfully applied as the conducting matrixes of composite materials incorporating TiO_2 ,^{16–17} Fe_2O_3 ,¹⁸ V_2O_5 ,¹⁹ and Fe^{20} particles, but most works give account of the combination of noble metals such as Pd, Au, or Pt.^{21–24} Although conductivity improvement of PPy films by a vacuum deposited silver coating was reported,²⁵ PPy/Ag nanocomposites have received less attention.

Conducting polymers can be easily synthesized by both chemical and electrochemical routes,^{26–27} and preparation of various polymers in both aqueous and nonaqueous solutions has been reported.^{28–31} Our aim was to prepare and characterize silver containing conducting composite materials in the presence of different simple anions as dopants. In this work, preparation and properties of conducting polypyrrole-chloride/ nitrate-nanosized silver composites are reported.

Experimental Procedures

Chemicals were purchased from Aldrich. Pyrrole was freshly distilled under vacuum. $\text{FeCl}_3 \times 6 \text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3$ were used without further purification. All reagents were analytical grade. Water was purified by deionization and reverse osmosis (Milli-Q).

Polypyrrole powder was chemically synthesized through the oxidation of the monomer by $\text{Fe}(\text{III})$ salts (chloride and/or nitrate) in aqueous solutions. The powder obtained was filtered,

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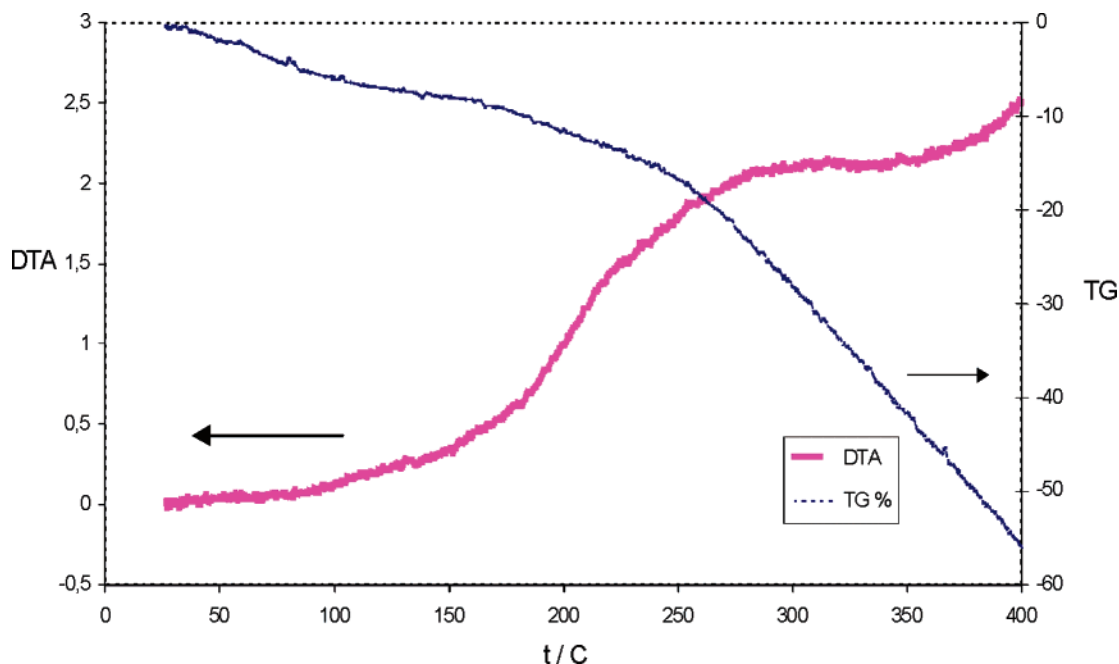


Figure 1. Thermogravimetric curves obtained with a PPy/Cl/Ag powder sample, showing the data in both the TG (dashed) and the DTA (dotted) forms.

washed thoroughly with water to remove ferric or ferrous contamination, and impregnated by stirring the polymeric material in the solutions of silver nitrate solutions ($c = 5 \times 10^{-4}$ to 2×10^{-3} mol/dm³). The decanted solid was dried at 80 °C. The dried powder was used in the XRD and TEM experiments. A part of the substance was dissolved for the elementary analysis, or it was compressed into tablets by applying a pressure of $p = 740$ Mpa for the conductivity measurements.

The silver concentration was determined by the ICP-AAS technique after dissolution in a sulfuric acid–H₂O₂ mixture (pyranina solution). The silver incorporated into the polymer matrix was speciated and measured also by X-ray diffraction (Philips PW-1830 X-ray diffractometer). For irradiation the CuK α line, $\lambda = 0.1542$ nm was applied³² at 40 kV and 30 mA in the range of $2\Theta = 1$ –40°.

Transmission electron microscopy (TEM) was performed using a Philips CM 10, operating at an acceleration voltage of 100 kV. The size distribution of the particles incorporated into the polypyrrole was determined by applying this instrument supplied with Megaview II camera and using the UTHSCSA Image Tool 2.00 computer program.

The heat conductivity of the samples was measured with a stationary calorimeter, developed for this specific case. The thermal contact between the measuring head and the two stabilized heat tanks was established by means of two identical samples. The measuring head contained a thermal sensor and two heating elements. The temperature of the stabilized heating tanks was also measured by the thermal sensor. If we heat the measuring head with an electric power P_H , it will be set to a constant temperature T_H , larger than that of the tanks T_A . By supposing that the heat conductivity of the sample is much smaller than that of the heat tank and the measuring head, the following equation can be used in the stationary state (when T_H is not changing in time any more):

$$2\kappa_x \frac{(T_H - T_A)Q_x}{d_x} = P_H$$

Here, Q_x and d_x are the surface area and thickness of the cylindrical sample, and κ_x is the thermal conductivity.

For the measurement of the electric conductivity the four-point-probe method, a square geometry arrangement has been used. A sine-shaped current was applied through one electrode couple, and the voltage was measured between the other two contacted points. The Fourier spectra of the response have been determined by a specially developed data acquisition system interface on a PC.

Results and Discussion

Before starting the studies on the thermal conductivity, the thermal stability of the samples was controlled. Figure 1 contains the thermogravimetric data of an example of the polypyrrole/chloride/silver composite in both the TG and the DTA forms. As it can be seen, the DTA curve has an inflection point at 200 °C, so the material, just as the polymer itself, is stable until 180–200 °C.

Similar results were obtained both with PPy-nitrate-silver composites and with PPy itself. Thus, the incorporation of silver in this concentration range did not alter the thermal stability of the polymer.

In Figure 2, the thermal and electric conductivities of the polypyrrole and its silver composites are presented versus the analytical concentration in mass % of the noble metal component, the latter obtained from the ICP-AAS measurements. The data are summarized irrespectively of the anion incorporated into the film. The diagram shows that there is no difference between the behavior of the composites containing chloride or nitrate ions. Moreover, the thermal behavior of the polymer is not influenced by the amount of the silver, as this conductivity remains constant in the concentration range studied. As for the electric conductivity, the series of the results exhibits a clearly observable saturation pattern. As polypyrrole is stable in its oxidized, conducting form, the conductivity of the nonimpregnated samples is significant already, but the data indicate that in both types of composites, the silver amount even at these small concentrations has a positive effect on this electric property of the polymer matrix. The oxidized state of the polypyrrole seems to be stabilized by the inorganic component, which might be connected to a redox interaction between the components.

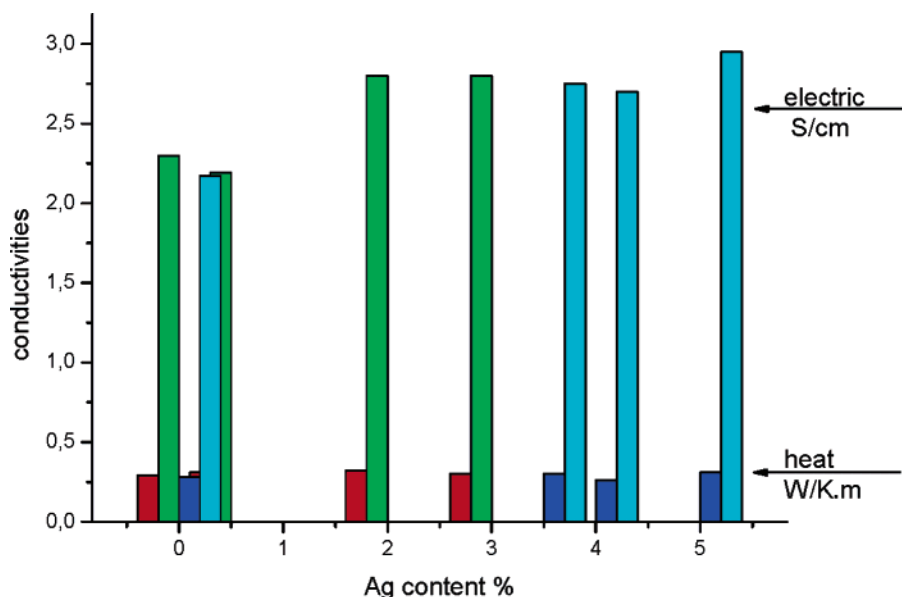


Figure 2. Diagram of the electric and heat conductivities of the composite materials vs the Ag concentration (mass %) determined by the ICP-AAS technique.

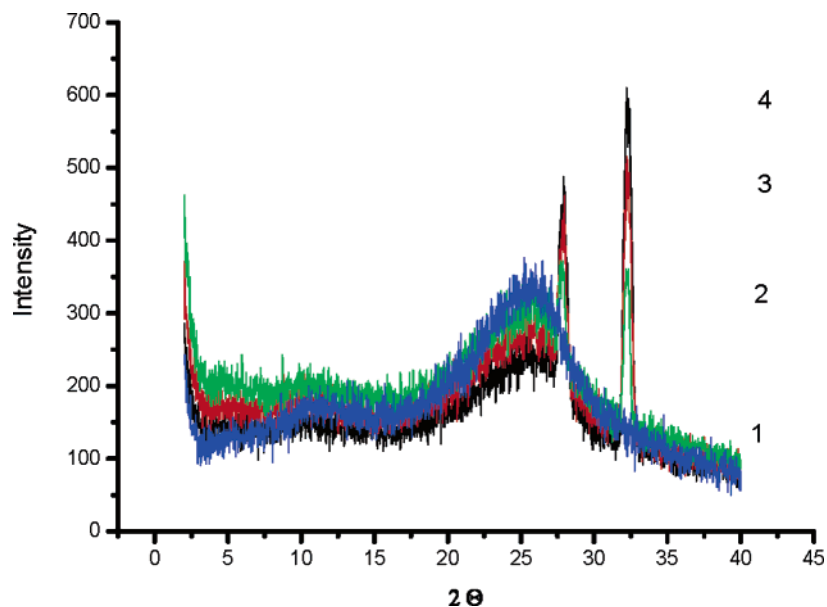


Figure 3. XRD spectra obtained with the PPY/Cl/Ag composites at different silver concentrations. In the case of curve 1, the composite does not contain silver, while the silver content increases from 2 to 4.

The assumption of the redox interaction between the polypyrrole and the impregnating silver salt brings up the question as to what the form and the chemical state of the noble metal are in the composites. To perform this speciation, the X-ray diffraction spectra of the composite materials have been registered. In Figure 3, the spectra obtained with the AgNO_3 impregnated polypyrrole powders, synthesized by FeCl_3 , are presented. The spectra acquired with the composites of different silver content were measured separately; however, the figure—for a better comparison—shows them together. The broad reflection in the range of $2\theta = 15\text{--}35$ indicating a low order of crystallinity has to be attributed to the polypyrrole itself.³³ Beyond this signal, two new excitations have been detected, and both of them increase with the silver concentration. On the basis of their position at $2\theta = 27$ and 32 , these peaks can be identified as the AgCl (111) and (200) signals, respectively. The fact that the silver is present in the form of its chloride salt indicates that it is mainly interacting with the dopant chloride ions.

The XRD measurements of the polymer composites, synthesized by $\text{Fe}(\text{NO}_3)_3$ and prepared by impregnation with AgNO_3 , are shown in Figure 4. In this case, only one peak appears in the spectra, and its position is different from both in Figure 3. From the value of $2\theta = 38$, which is identical with the Ag (111) excitation, the presence of metallic silver can be concluded. Thus, the redox interaction between the two components in the composite material leads to the reduction of the silver ion to metal in this case.

As a next step, the structure of the PPY-silver composites has been studied by taking transmission electron microscope (TEM) pictures. In Figure 5, the records obtained without the metallic component and in its presence can be compared for PPY/ NO_3 . In comparison with panel a, panel b clearly shows the presence of the inorganic component particles in the form of darker spots in the organic matrix.

As for the TEM image obtained with the PPY/Cl/Ag composite, Figure 6 shows the registered image. In all three pictures, the bars show the extent of the enlargement.

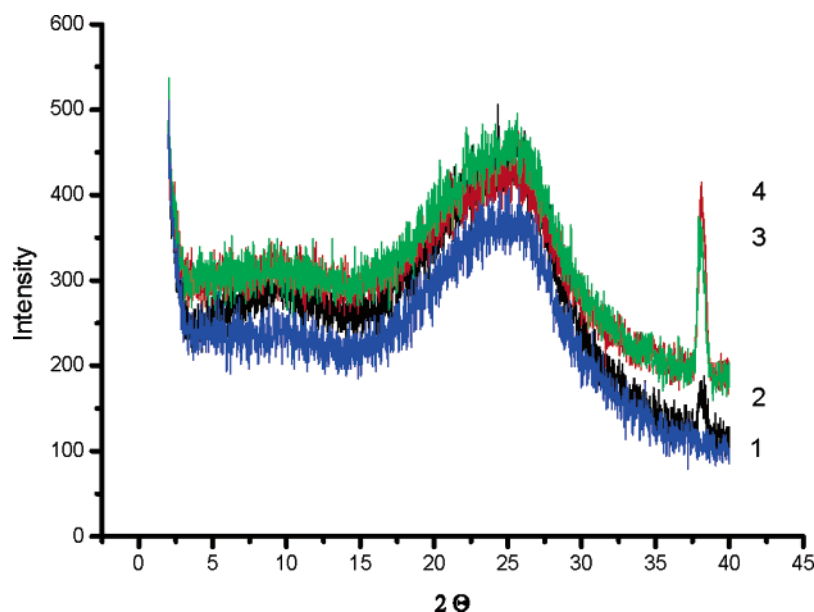


Figure 4. XRD spectra registered with the PPy/NO₃/Ag composites. Curve 1 is obtained with the nonimpregnated material, while the concentration of silver increases from 2 to 4.

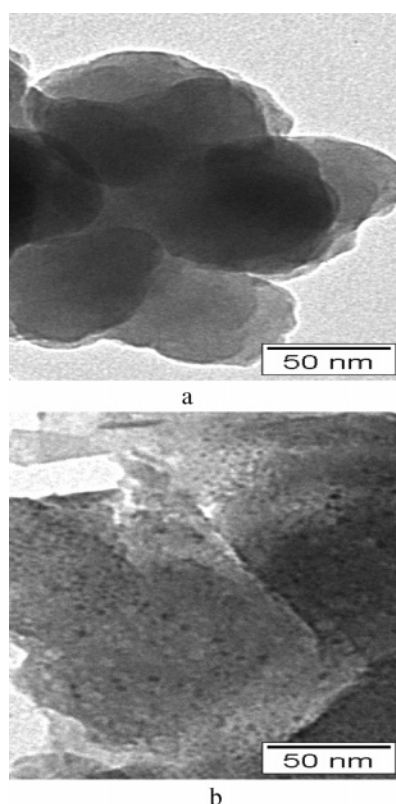


Figure 5. TEM pictures of the PPy/NO₃ polymers. (a) Before the impregnation and (b) after the impregnation. The bars indicate a size of 50 nm.

By applying the special UTHSCSA Image Tool 2.00 particle finder and size determination software, the data in Figure 7 have been received for the size distribution in the polypyrrole/chloride/silver composite. The results exhibit that the size of the largest particles is 9–10 nm and that the distribution can be characterized by one maximum at 4–5 nm. On this basis, we may state that this PPy/AgCl composite contains the inorganic component in the nanosize range, and the size distribution of the nanocomposite is rather uniform.

In the case of the composite obtained in the presence of nitrate ions, the TEM picture shows an even more uniform distribution

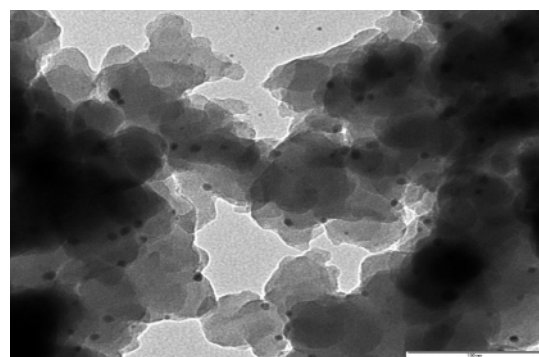


Figure 6. TEM picture registered with the PPy/chloride/silver composite. The bar indicates a size of 100 nm.

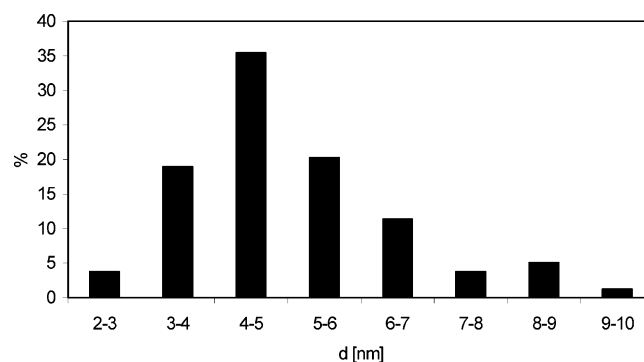


Figure 7. Size distribution of the AgCl nanoparticles in the polypyrrole composite (from Figure 6).

of the nanoparticles. By applying the computer program for the data of the TEM picture in Figure 5b, the largest silver particles in the composite have been identified as 6–7 nm. The sharp maximum of the distribution in Figure 8 proves that the average size of the nanometal particles is even smaller, about 3 nm.

Conclusions

On the basis of the results, we may state that silver containing nanocomposite polymer materials can be successfully prepared by using a rather simple impregnation method. The chemical state of the incorporating silver depends first of all on the nature

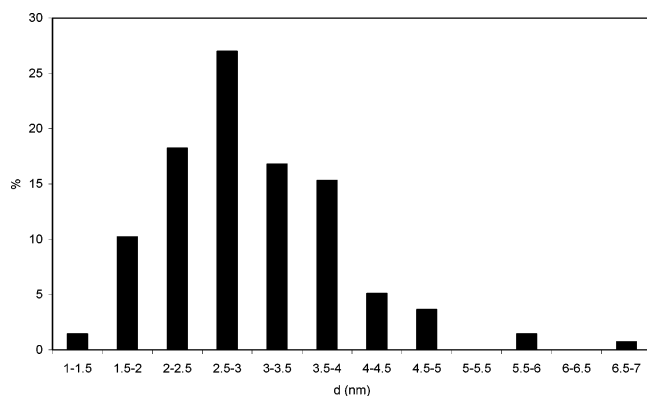
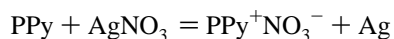


Figure 8. Size distribution of the Ag metallic nanoparticles in the composite obtained in the presence of nitrate ions (from Figure 5b).

of the anion, present in the polymerization solution. In the case of when FeCl_3 is applied as an oxidant, the form of the silver in the composite material is exclusively AgCl. The result of the same preparation procedure is basically different when pyrrole is polymerized by $\text{Fe}(\text{NO}_3)_3$ (i.e., the solution does not contain anions strongly interacting with silver ions). In this case, the composite is a metal conducting polymer nanocomposite, as proved by the XRD spectra. On the basis of this experimental fact, we may come to the conclusion that silver directly interacts with nonoxidized segments within the polymer.

Since the conductance of the polypyrrole prior to impregnation is 2.2–2.3 S/cm, the polymer is in the oxidized state without the interaction with silver nitrate. The value is the same for both types of the materials, independently of the anion present during the synthesis. It means that anions are there within the substance to compensate the positive charges along the chains and that the oxidation state of the polymers does not depend on the anion.

After the impregnation, the conductance increased a little bit and reached a saturation level with the increase in the silver content in both cases. In PPY/ NO_3 , the XRD data evidenced the metallic form of the silver, which could be easily interpreted by assuming a redox reaction between the polymer and the silver ions, as



However, the similar conductance increase has not been accompanied by silver(0) formation in the case of PPY/Cl, and it is difficult to give an established interpretation. A more complex interaction might be assumed, leading to some NO_3^- -PPy $^{\delta+}$ -Cl $^-$ -Ag $^{\delta+}$ adduct, where silver is much more associated with the chloride ion and polypyrrole is meanly doped by nitrate. This assumption needs further verification in the future.

These results may be applied in the preparation and application of conducting polymer-silver composites as new electrodes, where the catalytic activity of the nanosize metal component wired electrically through the conducting matrix can be utilized. On the other hand, the successful simple preparation procedure is assumed to be applicable in other cases and can be considered as a general route that leads to a redox interaction based conducting polymer-noble metal nanocomposites. The effect of the character of the anions—reflecting the priority of different

interactions—can be used as a guide during the preparation of further metal incorporating conducting polymer composites with tunable properties.

Acknowledgment. This work has been sponsored by the Hungarian National Scientific Research Fund (OTKA T042539) and the National Research and Development Program (NKFP 3/012/2001).

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