

NOVEL POLYMERIC NANOCOMPOSITES ON THE BASE OF AEROCELLULOSE MAKING VIA SUPERCRITICAL CARBON DIOXIDE AND METAL-VAPOR SYNTHESIS

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Abstract

Novel polymeric nanocomposites based on highly porous cellulose (“aerocellulose”) were synthesized via supercritical carbon dioxide and metal-vapor synthesis (MVS). Aerocellulose was prepared from aqueous cellulose/NaOH solutions. Solutions were gelled to obtain shaped three-dimensional objects, then cellulose was regenerated and dried in supercritical conditions using CO₂. The porosity of aerocellulose is higher than 95% with pore sizes distribution from a few tens of nanometers to a few tens of micrometers. The internal specific surface area is around 200–300 m²/g, and density ranges from 0.06 to 0.3 g/cm³, depending on the preparation conditions.

Introduction

A new composites aerocellulose serves a “matrix” for the modification, deposition and stabilization of different functional additives (drugs, conducting polymers, metallic nanoparticles, etc). Nanocomposites were obtained during the introduction of gelatinous cellulose-containing compositions into the reinforcing component with the subsequent effect by supercritical CO₂, which leads to the formation of the highly developed porous structure. As a result nanoporous composites were obtained; they were modified with the drugs (antipyretic, antibacterial and other), conducting polymer (polypyrrole) and also by the nanoparticles of different metals (Au, Ag, Cu, Pd), obtained with the use of MVS. An original procedure for forming the nanostructured materials with the aid of the supercritical medium and MVS was employed.

Experimental

By the modification of sc-CO₂ of the gelatinous cellulose-containing compositions formed the nanoporous polymer, into which with the aid of MVS or sc-CO₂ method were introduced the nanoparticles of Au, Ag, Cu or Pd.

For obtaining the particles of the metals as the reagents the organosols Au and Ag with triethylamine and isopropanol are used. Metals were evaporated in a vacuum of 10⁻⁴ mm Hg: gold (99.99%) from a tungstic rod and silver (99.99%) from a tantalum boat. Isopropanol (99.8% Fluka) was dried and distilled over zeolites in an atmosphere of purified. Before synthesis, it was degassed in a vacuum by the alternation of freeze-defreeze cycles. Metal and isopropanol vapors were simultaneously condensed on the walls of a glass reactor with a volume of 5 l cooled by liquid nitrogen. In typical experiments, the molar reagent metal-to-isopropanol ratio varied within the limits of 1 : 300–500. After the synthesis was terminated, cooling was stopped, cocondensate was heated up until it melted, and the organosol obtained was used to impregnate in vacuum fluoropolymer kept in the Schlenk flask. The excess of the organosol was deleted, and the remaining product was dried in vacuum at 100°C.

Depending on nature of metal and organic reagent are obtained the composite materials with the content of metal from 0.4 to 20 mas.% and the particle size from 3 to 28 nm.

Obtaining of nanoparticle of Ag and Cu in sc-CO₂ conducted by the introduction of complexes 1,5- (cyclooctadiene) - 1,1,1,5,5,5 hexafluoroacetylacetonate of silver or diiminate of copper with that following their reduction in hydrogen. In Fig. 1 and 2 are represented setups.

Analysis of the physical and chemical properties of new composite nanomaterials, type of intermolecular interactions between the metallic nanodimensional systems and matrix is carried out using IR- and UV-spectroscopy, XPS, TEM, etc.

Microscopic studies of nanocomposites were performed on a LEO 912, OMEGA transmission microscope (Zeiss, Germany) and a Hitachi S-520 scanning microscope (Japan). Before scanning samples on a raster electron microscope, the film surface was covered by a 15 nm thick layer of gold (IB-3 Ion Coater, Eiko Engineering, Japan).

Diffraction measurements were performed on Bruker D8 Advance diffractometer ($\lambda[\text{CuK}\alpha]$) = 1.54184 E in the interval of 2θ angles from 2 to 100 with a step of 0.02 and exposition time of 10 s per step at room temperature.

X-ray photoelectron spectra were recorded on a Kratos XSAM800 spectrometer (Great Britain). A magnesium anode with the characteristic radiation energy $\text{MgK}\alpha = 1253.6$ eV was used as an excitation source.

The surface area of porous FPMs after modification processing measured by the Brunauer-Emmett-Teller (BET) method

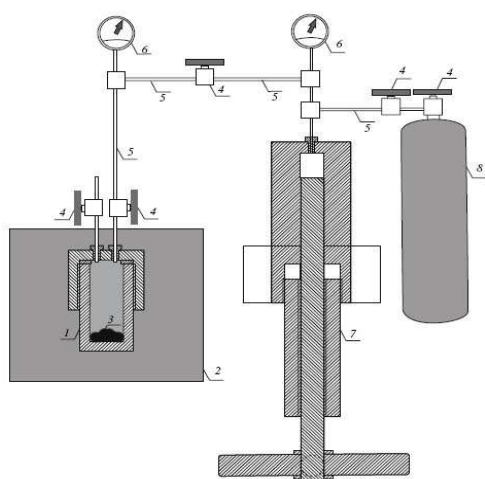


Fig. 1. Experimental setup for the making of aerocellulose and synthesis of metal-containing nanoparticles in sc-CO₂:

- (1) autoclave,
- (2) liquid thermostat,
- (3) reaction mixture,
- (4) valves,
- (5) capillaries,
- (6) pressure gages,
- (7) hand pressure generator,
- (8) CO₂ cylinder.

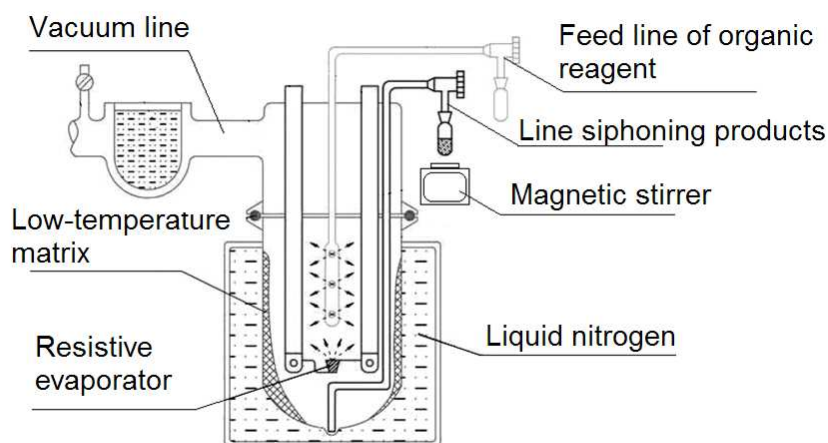


Fig. 2. Schematic diagram of the reactor of the metal-vapor synthesis.

Results and Discussion

As the example in Fig. 3a is depicted microphotography of system Ag /“aerocellulose”, while to Fig. 3b of system Cu /“aerocellulose”, obtained with the use sc-CO₂.

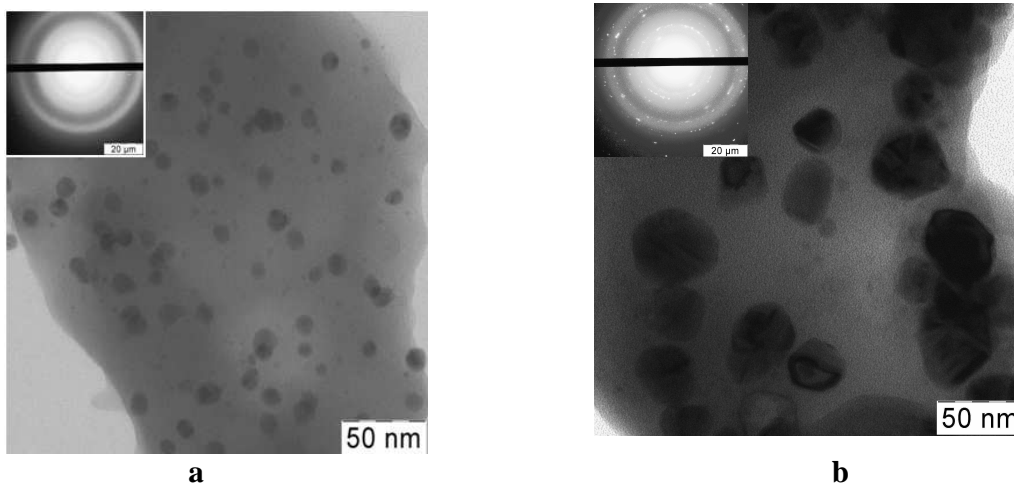


Fig. 3. PEM microphoto of the structure of systems obtained with the use sc-CO₂.
(a) Ag /“aerocellulose”;
(b) Cu /“aerocellulose”.

TEM data show that the nanoparticles of silver in aerocellulose are evenly distributed and they have sizes the close to 10 nm, while nanoparticles of copper have larger spread along the sizes: from 2 to 40 nm, that it is possible to explain by the larger lability of precursor with its impregnation into aerocellulose.

In Fig.4 are presented microphotography the system, obtained by the method of MVS. It is evident that the nanoparticles are present in the surface layer of aerocellulose in the form of aggregates with average size of 10 nm. This fact apparently can be explained by the charging of nanoparticles during carrying out of synthesis.

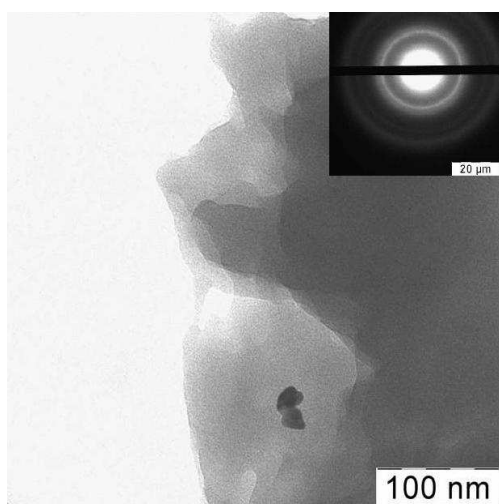


Fig. 4. TEM microphoto of the silver-containing aerocellulose obtained by the method of MVS.

In Fig. 5 is represented the diffractogram of system silver/aerocellulose. The size of the nanoparticles of metals was calculated with the aid of the specific routine. In particular for silver it comprised order 16 nm, which correlates well with the data of PEM. It was also revealed, that the

introduction of the nanoparticles of metals led to a certain reduction in the value of the index of crystallinity, i.e., to the disordering of the structure of aerocellulose.

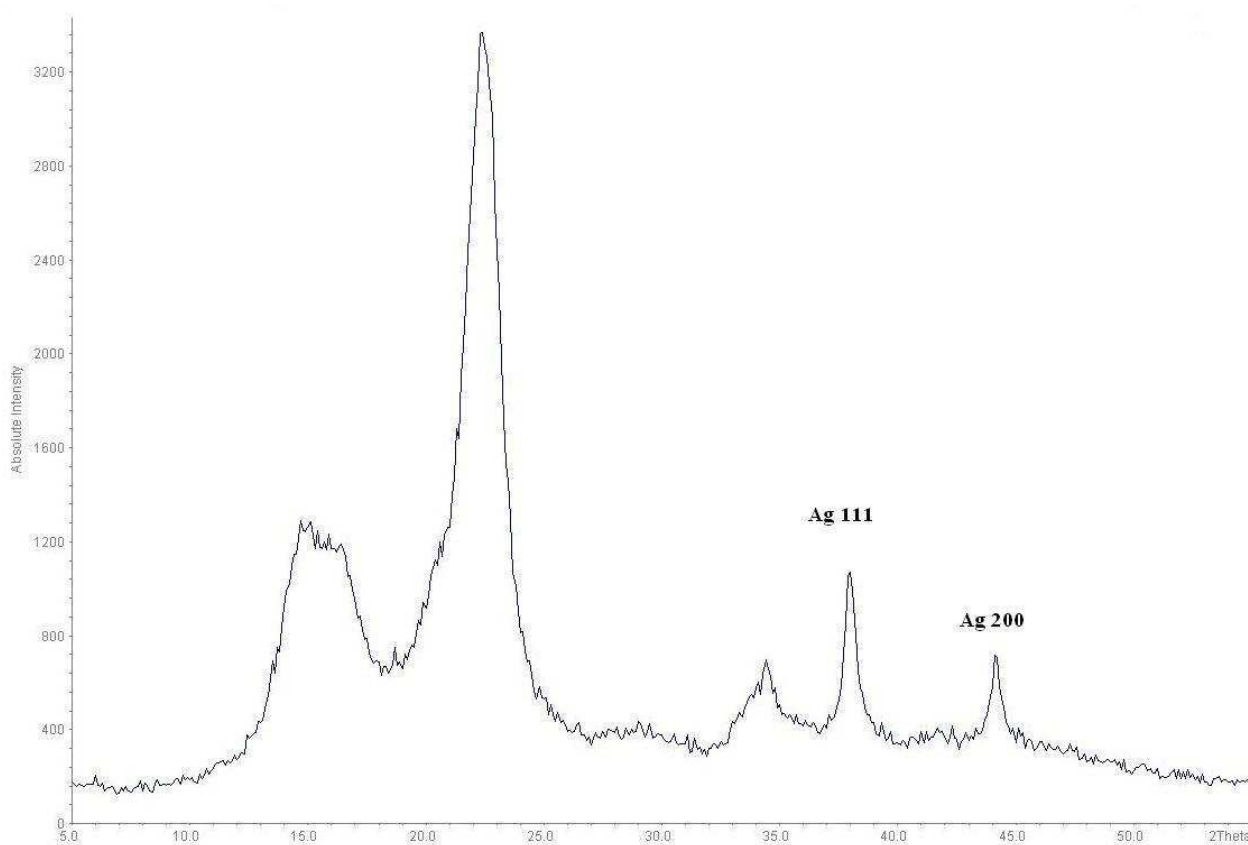


Fig. 5. The diffractogram of silver/aerocellulose system.

In Fig. 6 are represented the data of TGA and DTA of the samples of initial and modified by the nanoparticles of the metals aerocellulose. As can be seen, the oxidation of nanocomposites on the basis of copper flows more effectively. The peak of decomposition (exoeffect) is displaced into the region of low temperatures. At the same time significant mass remainder is observed for the composites of silver.

In argon all processes are passed identically. All differences observed in the course of the process are apparently connected with the reactions of the oxidation products of metals with the cellulose.

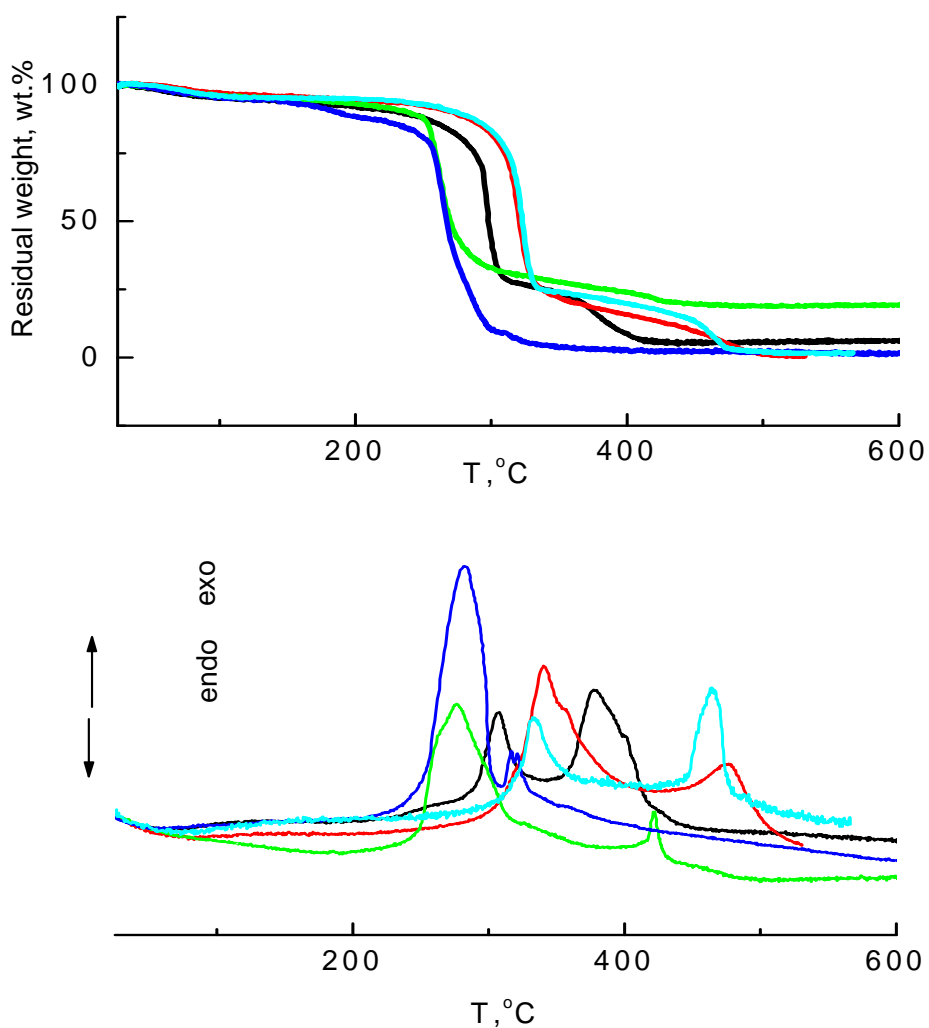


Fig. 6. Data of TGA and DTA for the samples of aerocellulose and its nanocomposites with the metals.

Initial aerocellulose - light- of green;
 System of nickel /aerocellulose - black;
 System of palladium /aerocellulose - red;
 System of silver/ aerocellulose - green;
 System of copper/ aerocellulose - dark-blue.

Conclusions

The executed studies make it possible to obtain new functional hybrid nanomaterials for different applications.

Acknowledgments

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