Synthesis and Structural Investigations of Metal-Containing Nanocomposites Based on Polyethylene

Abstract: Copper-containing nanoparticles in a high-pressure polyethylene matrix were prepared by thermal decomposition of copper acetate. An electron microscopic study of the morphology and an X-ray diffraction analysis of the phase composition of a nanocomposite were carried out. It was shown that the dispersed phase essentially consisted of metallic copper nanoparticles with a size of 33.94 nm.

Keywords: Metal-Containing Nanocomposite; Polyethylene; Thermal Decomposition.

1 Introduction

In modern science and technology, use of terms such as nanotechnology, nanochemistry, nanophysics, nanophase, nanohybrid, nanocrystalline and nanoporous materials, nanostructures, nanocrystals and nanoscale design have become common [1]. This demonstrates their special place of application in science, as for example in chemistry with catalytic and sensory systems. Nanocomposites with their newly found complex properties, which were previously unknown in physics, are being used for the creation of nanomaterials in electronics and the conversion of radiation of various energies. Nanometallurgy, laser processing of metal surfaces and similar processes are promising in nanoscale materials science, particularly in nanotechnology of advanced metallic materials.

In [2], a scheme illustrates the main stages of the transformation of a single atom into a block metal through cluster, nanoscale and colloidal particles (‘active metals’). Small j-nuclear particles characterised by nanometric dimensions of structural morphological elements and ultra-fine powders occupy an intermediate position between clusters and block metals.

At present, composites with nanostructured morphology of individual elements are of great interest in the field of materials development. Nanosized dispersed systems play an important role in developing methods for the creation of nanomaterials. Due to its unique properties, ultra-dispersed media based on metal polymers are widely used in radio and optoelectronics as magnetic [3], electrically conductive [4] and optical media [5]. Moreover, depending on the filling density of the dielectric matrix by metal nanoparticles, in particular iron, electrophysical and optical properties of metal-polymeric nanocomposites, changes can be observed in several instances with the manifestation of quantum-size effects [6].

The unique properties of nanoscale disperse systems are associated with the features of the individual nanoparticles. The collective behaviour in the ensemble and the commensurability of the nanoparticle sizes shows the correlation between the scales of any implemented physical processes and the turn of different dimensional effects. The small particles are characterised by nanosized structural morphological elements; nanoscale systems occupy intermediate positions between atoms (clusters) and massive metals.

Nanocrystalline metals exhibit remarkable mechanical properties, such as high strength and hardness. However, due to their high internal boundary area and high interfacial energy, they are susceptible to grain growth under thermal or mechanical stress, which worsens their excellent properties. Impurities of elements with small atomic dimensions (e.g. C, S, P), which are divided into boundaries by the block and reduce mobility or driving force, usually stabilise the nanometre-sized grain structure. However, these elements generally lower the strength of the boundary, especially at higher temperatures.
Metal nanocomposites consisting of immiscible metals, as for example Cu and Co, can overcome these problems [7]. As conventional synthesis routes cannot produce these composites, new methods are needed, including mechanical alloying and electrochemical deposition. Here, super-saturated solid solutions can be obtained in a wide range of concentrations.

The following annealing of kindling can be used for decomposition of a solid solution, for example processing spinoidal decomposition and obtaining metal nanocomposite. Due to non-mixture elements and generally bad mutual diffusion, these structures are both mechanically and thermally very stable. The physical and chemical properties of both the original components and the composite itself change substantially in the metal-polymeric nanocomposites. This is due to the fact that the size of the polymer and metal particles decreases. The share of the interfacial component contrastingly increases, which makes it possible to influence the electrophysical physico-mechanical and chemical parameters of the material and, consequently, the creation of new materials with the desired functional characteristics [8].

For functional purposes, the composites are conditionally subdivided into structural, insulating and magnetodielectric composites. Moreover, it is necessary to distinguish classes of materials for ensuring electromagnetic compatibility with regard to radio-transparent, radio-absorbing and shielding properties.

Due to the combination of their properties, the composites based on metal-containing nanoparticles in a polymer matrix are promising for application, especially for electromagnetic compatibility, interference protection, radio masking and protection of biological objects from electromagnetic radiation.

However, despite a large number of polymer nanocomposite materials being created, technological advancements for obtaining structures and properties were not sufficiently studied yet. This necessitates a complex study of the inter-relation between the type and nature of the components to be explored and should include interphase interactions, reaction modes and mechanical and functional properties of the materials.

In order to create nanomaterials with given characteristics, it is necessary to establish a connection between the methods and conditions of synthesis of these objects and their properties. Majority of technologies create nanoparticles with a complex structure, which often cannot be determined by using any type of standard (e.g. X-ray phase) analysis.

To solve this problem, it is necessary to perform a study using various methods that allow us to compare information about the local and volumetric properties of nanostructures.

The aim of this work is to obtain a composite material consisting of copper-containing nanoparticles localised in the high-pressure polyethylene matrix, and then to study its complexity using numerous experimental techniques, such as transmission electron microscopy and X-ray phase analysis.

2 Experimental Part

Samples of copper-containing composite materials were prepared according to what is known as the ‘caspol’ method, developed by Gubin et al. [9]. This method is based on the thermal decomposition of unstable carboxylic acids. The starting compound (precursor) was used as a single-water copper ((CH₃COO)₂Cu·H₂O) diacetate whose decomposition was carried out at \( t = 300\, ^\circ\text{C} \pm 5\, ^\circ\text{C} \) in the medium 'high pressure polyethylene (HDPE) – oil'. To achieve this, 10 g of polyethylene and 100 ml of oil were placed in a four-necked flask. A stirrer, a dropping funnel, a thermometer and a condenser were part of the equipment. The reaction mixture was heated to the synthesis temperature (300 °C) under an atmosphere of nitrogen gas with vigorous stirring. Subsequently, whilst maintaining a constant temperature, an aqueous solution of copper acetate was introduced drop-wise into the transparent mixture of oil with polyethylene by means of a dropping funnel. The rate of delivery of the solution was 15 ml/h. The rate of supply of nitrogen gas was controlled in such a way so as to ensure the rapid removal of gaseous products from the reactor. After the addition of the total copper acetate solution, the reaction mixture was held for 1 h at the synthesis temperature, maintaining vigorous stirring. The heat was then turned off and the reaction mixture was cooled to room temperature under a nitrogenic atmosphere. After washing the samples with benzene oil, they were dried and stored in a Soxhlet apparatus until they solidified in the air.

The morphology of the supramolecular structure of nanocomposites and their elemental composition were studied using a scanning electron microscope (SEM) EVO MA 10 (Carl Zeiss, Germany) and a microanalytical system for the energy dispersive X-ray (EDX) microanalysis of INCA Energy (Oxford Instruments, UK) for all chemical elements, starting with boron.

The X-ray phase analysis method was used for studying the phase composition of the obtained material. Samples were examined using a powder diffractometer Empyrean firm of Pananalytical B.V (Almelo,
Netherlands) (CuKα). The wavelength of the copper radiation is \( \lambda(K\alpha_1) = 1.54060\ \text{Å} \), \( \lambda(K\alpha_2) = 1.54443\ \text{Å} \), \( \lambda(K\beta_1) = 1.39225\ \text{Å} \). The survey was carried out at angles \( 2\theta \) from 5.0038° to 84.9928° at the measurement step \(-0.0130\ (°2\theta)\) and the measurement time corresponded to \(-97.9200\ \text{s/step}\). The phases were identified using the XpertHighscore Plus program (Malvern Panalytical, Malvern, UK).

3 Results and Discussion

As a result of the investigations, new metal-polymeric nanocomposites were obtained. These were copper particles dispersed in a polyethylene polymer matrix.

According to the findings of [10–14], the decomposition of the precursor (copper acetate monohydrate) proceeds in several stages based on the following scheme:

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\begin{align*}
\text{Cu(COOCH}_3\text{)}_2 \cdot \text{H}_2\text{O} & \rightarrow \text{Cu(COOCH}_3\text{)}_2 + \text{H}_2\text{O} \quad (1) \\
2\text{Cu(COOCH}_3\text{)}_2 & \rightarrow 2\text{Cu} + 3\text{CH}_3\text{COOH} + \text{CO}_2 + \text{C} \quad (2)
\end{align*}
\]

The first stage is mainly due to the liberation of hydration water from Cu(COOCH\(_3\))\(_2\) ⋅ H\(_2\)O. Japanese scientists showed, by a thermogravimetric and differential-thermal analysis [10], that up to 120 °C all endothermic peaks in this temperature range are caused by the evaporation of hydration water. The decomposition of Cu(COOCH\(_3\))\(_2\) begins at 120 °C and ends at \( \sim 300 \) °C. In particular, the endothermic peaks at 134 °C and 145 °C correspond to the decomposition of copper acetate [10].

All processes proceeded simultaneously at a temperature of 300 °C under the conditions of our experiment.

It should be noted that in the case of using an aqueous solution of a precursor, it is energetically advantageous, in the preliminary stage, to evaporate the water (the solvent of the precursor). After the evaporation of water in the system as a whole, or locally in separate areas, a loss of crystallisation water can be observed. Figure 1 shows the electron microscopic morphology and EDX spectrum of copper-containing nanocomposite obtained based on HDPE + 20 wt % Cu.

Figure 1 shows the formation of dispersed particles of micron size. However, smaller particles of the nanometer level are difficult to discern in SEM images.

As followed from the data presented on the EDX spectrum, the obtained nanocomposite contains a sufficiently high amount of copper, which in turn attests to the success of the synthesis result. It should be noted that there is no peak in the spectrum (Fig. 1b) that corresponds to the oxygen atom, which can be explained by the lack of air access. The absence of oxygen in the composition of the composite is an indication for a dispersed system as a result of the complete decomposition of the precursor, accompanied by the restoration of copper to an atomic neutral state (\( \text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0 \)) [15].

Thermal stability of the polymer decreases with increase in the percentage of 5–20 µm metal particles introduced into the polymer [16].

It should be noted that copper particles in nanocomposites are distributed almost uniformly throughout the volume without the formation of large agglomerates or crystals (Fig. 2). The copper particles are well separated and almost uniform in size.

From the visual analysis of the SEM image and the map of copper particle distribution, it becomes evident that the dispersed phase has a spherical or spheroidal shape. It can also be visually assumed that the particle inhomogeneity coefficient is close to unity in size. Figure 3 shows an X-ray diffraction chart of a copper-containing composite.

The X-ray diffraction analysis of the obtained samples demonstrates that diffraction patterns induce the reflections at different values of 2\( \theta \). There is a strong

Figure 1: Electron microscopic morphology (a) and energy-dispersive X-ray (EDX) spectrum (b) of a copper-containing nanocomposite.
intense peak at $2\theta = 43.1727^\circ$, which corresponds to $d_{hkl} = 2.09376 \ \text{Å}$. According to the ICSD card, this indicator $d_{hkl}$ equals Cu (111). The results of X-ray diffraction analysis show (Fig. 3) that copper binary compounds with sulphur stoichiometric (Cu$_2$S) and non-stoichiometric compositions (Cu$_{1.8}$S, Cu$_{31}$S$_{16}$) were formed, in addition to atomic copper. The formation of copper sulphides in the nanocomposite was probably due to an additional reaction of copper ion restoration due to the impurity of sulphur and/or its derivatives, present in industrial oil.

It is possible to estimate the size of the structural elements (particles, crystallites, coherent scattering blocks, etc.) via X-ray phase analysis [17].

The particle size is determined from the integral width of the diffraction peaks in accordance with the Debye-Scherer formula [18]:

$$d = \frac{K\lambda}{\beta \cos \theta}$$

where $d$ is the average crystal size; $K$ is the dimensionless particle shape factor (Scherrer constant); $\lambda$ is the wavelength of X-ray radiation; $\beta$ is the width of the reflex at half-height, expressed in radians; and $\theta$ is the diffraction angle (Bragg angle).

The coefficient $K$ can take different values, depending on the shape of the particles. For example, for spherical particles, $K$ is usually taken to be 0.9. For crystallites of a cubic form, for instance, the Scherrer constant can be calculated for each reflex by the following formula:

$$K = \frac{6|h|^3}{\sqrt{h^2 + k^2 + l^2(6h^2 - 2|hk| + |kl| - 2|hl|)}}.$$

where $h$, $k$ and $l$ are Miller indices.

For the Cu (111) structural element, the particle size is $d = 33.94$ nm. However, this value differs significantly from the visually detected particle sizes of the dispersed phase. Therefore, it can be assumed that each particle consists of several individual crystallites (regions with different orientations).

### 4 Conclusion

Spherical nanoparticles of copper isolated from one another are obtained in the matrix of high-pressure polyethylene. This is achieved through thermal decomposition of copper acetate. For the material LDPE + 20 wt % Cu, the main phase is uniformly distributed metallic copper with a particle size of 33.94 nm and small admixtures of copper binary compounds with Cu$_2$S and nonstoichiometric composition (Cu$_{1.8}$S, Cu$_{31}$S$_{16}$).
References