Applied Problems of Physics and Mathematics

Technology for the Synthesis of Metal-Filled Nanocomposites Based on Recycled Polymers

Umarov A.V.[1,2], Xamzaev X.[2], Namozova M.[2], Azimov N.[1,2]

[1]University of Tashkent for Applied Sciences, Str. Gavhar 1, Tashkent 100149, Uzbekistan.
[2]Tashkent State Transport University, 1 Temiryo'lchilar Street, Tashkent 100167, Uzbekistan
E-mail:toktogulova.72@mail.ru;

Keywords: Nanocomposite, polyethylene, copper nanoparticles, morphology, cadmium sulfide.
Abstract: The fundamental structural aspects of polymer composite materials, as well as the technology for producing multifunctional polymer composites, are described. The methodology for the synthesis of nanoparticles and their classification is presented in detail. The synthesis approach for metal-filled nanocomposites based on secondary polyethylene is discussed, and the results of studies on the fabrication of novel metal–polymer nanocomposites with copper nanoparticles dispersed in a secondary polyethylene matrix are reported.
Thiourea, when used as a sulfiding agent, forms stoichiometric compounds with metals, which, under thermal treatment, transform into the corresponding metal sulfides [1]. During the sulfiding of metal salts in thiourea-containing solutions, interactions occur leading to the formation of a balanced coordination structure of CdS, enabling the incorporation of sulfur atoms at minimal distances from metal atoms [2].
The synthesis of samples containing CdS nanoparticles based on high-pressure polyethylene (HPPE) was carried out according to procedures described in the literature [3]. In this case, thiourea solutions of the corresponding metals and acetates were used as initial precursors. The obtained nanocomposite powders contained 20% CdS and exhibited a yellow coloration. The synthesized nanocomposites retained the mechanical properties of the polymer matrix, allowing them to be shaped into various forms such as tablets and films.
Composite materials were also produced via the thermal decomposition of copper formate, resulting in copper nanoparticles stabilized within the polyethylene matrix. This approach is particularly effective when polymers are dissolved in organic solvents. However, the limited solubility of polymers reduces the ability to achieve nanoparticles smaller than 30 nm and their uniform distribution. Nevertheless, due to the thermal and mechanical stability of polyethylene, such materials are of significant practical interest. One of the objectives of this study is to improve existing methods for producing polymer composite materials based on HPPE containing copper nanoparticles. Polyethylene is an ideal matrix for stabilizing nanoparticles due to its dielectric properties, stability, low cost, flexibility, and recyclability, and it is one of the first polymers produced in the region.
The advantages of nanomaterials are associated with their low specific weight and the high uniformity of nanoparticle distribution on their surfaces. Composite materials containing copper nanoparticles were obtained by modifying the "Klaspol" method developed by S.P. Gubin and I.D. Kosobudskii [4], which is based on the thermal decomposition of unstable carbonic acid derivatives. Copper diacetate monohydrate $(CH_3COO)_2Cu \cdot H_2O$ was used as the precursor, and the decomposition process was carried out at 300 ± 50 °C in a "high-pressure polyethylene–oil" medium.
A four-neck flask equipped with a stirrer, dropping funnel, thermometer, and condenser was used, with a ratio of 10 parts polyethylene to 100 parts oil. During heating, an intensive reaction occurred, raising the temperature of the synthesis medium. Aqueous copper acetate solution was gradually introduced into the polyethylene–oil mixture using a dropping funnel. Nitrogen gas was applied to ensure the removal of gaseous by-products. The reaction mixture was maintained at synthesis temperature for one hour with continuous stirring. Subsequently, heating was stopped, and the mixture was cooled to room temperature under a nitrogen atmosphere. To prevent nanoparticle aggregation during cooling, ultrasonic dispersion was applied. The product was purified using benzene in a Soxhlet apparatus and dried prior to further analysis.

The morphology and elemental composition of the nanocomposites were investigated using a scanning electron microscope (SEM) EVO MA 10 (Carl Zeiss, Germany) equipped with an energy-dispersive X-ray spectroscopy (EDS) system. This technique enables the analysis of all chemical elements starting from boron. The phase composition of the obtained materials was studied using X-ray diffraction (XRD) analysis. Powder samples were analyzed using a Panalytical B.V. diffractometer (Netherlands) with CuK radiation ($\lambda(K\alpha 1)$ = 1.54060 Å, $\lambda(K\alpha 2)$ = 1.54443 Å, $\lambda(K\beta 1)$ = 1.39225 Å). Measurements were conducted in the angular range of 5.0038° to 84.9928° (2θ) with a step size of 0.0130° and a counting time of 97.92 s per step. Data analysis was performed using X'Pert HighScore Plus software.
As a result of the study, metal–polymer nanocomposites with copper nanoparticles uniformly distributed within a polyethylene matrix were successfully synthesized.

$$Cu(COOCH_3)_2 \cdot H_2O \rightarrow Cu(COOCH_3)_2 + H_2O \qquad (1)$$

$$2Cu(COOCH_3)_2 \rightarrow 2Cu + 3CH_3COOH + CO_2 + C \qquad (2)$$

The first stage is primarily associated with the removal of hydration water from $Cu(CH_3COO)_2 \cdot H_2O$. According to thermogravimetric and differential thermal analyses reported by researchers [4], this stage proceeds up to 120 °C, and all endothermic peaks observed within this temperature range are attributed to the evaporation of hydration water.

The second stage involves the decomposition of $Cu(CH_3COO)_2$, which begins at approximately 120 °C and is completed at around 300 °C. In particular, endothermic peaks observed at 134 °C and 145 °C correspond to the decomposition of copper acetate.

However, under our experimental conditions, all processes occur simultaneously at a temperature of 300 °C. It should be noted that, at the initial stage, the evaporation of the aqueous precursor solution is energetically favorable. Following the complete or localized evaporation of water within the system, the loss of water continues during the crystallization stage.

References:

1. Krupa, I., Novák, I., & Chodák, I. (2004). Electrically and thermally conductive polyethylene/graphite composites and their mechanical properties. *Synthetic Metals*, 145, 245–252.
2. Monte, A.F.G., Dantas, N.O., Morais, P.C., & Rabelo, D. (2006). Synthesis and characterisation of CdS nanoparticles in a mesoporous copolymer template. *Brazilian Journal of Physics*, 36(2A), 427–429.
3. Khanna, P.K., Gokhale, R.R., Subbarao, V.S., Singh, N., Jun, K.W., & Das, B.K. (2005). Synthesis and optical properties of CdS/PVA nanocomposites. *Materials Chemistry and Physics*, 94, 454–459.
4. Ushakov, H.M., Kosobudskiy, I.D., Yurkov, G.Yu., Gubin, S.P., Zapsis, K.V., Kochubey, V.I., & Ulzutuev, A.N. (2005). New composite nanomaterials with controlled properties for radio engineering and electronics. *Radiotekhnika*, 10, 105–108.
5. Umarov, A.V., Abdurakhmanov, U., Khamzayev, H.E., Kattaev, N.T., & Tozhiboev, A.G. (2019). Synthesis and structural investigations of metal-containing nanocomposites based on polyethylene. *Zeitschrift für Naturforschung A*, 74(3), 183–187.
6. Umarov, A.V., Yokubov, B.E., Abdurakhmanov, U., & Khamzaev, X.E. (2017). Influence of filler particle size on the dielectric conductivity of metal–polymer composites. *Compositional Materials Journal*, 4, 16–18.
7. Umarov, A.V., & Khamzaev, X.E. (2019). Structural investigation of polyethylene-based metal-filled nanocomposite polymers. *Journal of Composite Materials*, 3, 45–48.
8. Umarov, A.V., Abdurakhmanov, U., & Khamzaev, X.E. (2017). Structural studies of nanocomposite materials based on polyethylene. In: *Proceedings of the Republican Scientific and Technical Conference "Modern Technologies for the Production and Processing of Composite and Nanocomposite Materials"* (pp. 183–185). Tashkent.
9. Umarov, A.V., & Khamzaev, Kh.E. (2020). Temperature dependence of the heat capacity of polymer compositions with metal oxide fillers. In: *Proceedings of the XV International Conference "Physics of Dielectrics"* (pp. 2315–2318). St. Petersburg, Russia.