The Structural State of Ultrahigh-Molecular-Weight Polyethylene in Single-Stage Arc-Discharge Plasma Deposition of Nanoparticles

L. Yu. Fedorov[a, b]*****, **I. V. Karpov**[a, b], **A. V. Ushakov**[a, b], **A. A. Lepeshev**[a, b], **and A. A. Ivanenko**[c]

[a] *Siberian Federal University, Krasnoyarsk, 660041 Russia*
[b] *Krasnoyarsk Research Center, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia*
[c] *Kirensky Institute of Physics, Krasnoyarsk Research Center, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia*
*e-mail: fedorov.krsk@gmail.com
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Abstract—We present the results of a study of the structural state of ultrahigh-molecular-weight polyethylene (morphology, X-ray-diffraction patterns, IR spectra) obtained in a single technological cycle combining the synthesis of nanoparticles and their deposition onto the surface of polymer microgranules. Technological conditions for the preservation of the initial state of ultrahigh-molecular-weight polyethylene are found for its presence in the zone of thermal action of the plasma flow. Mechanisms of degradation of the polymer are discussed.

One of the advantages of the synthesis of nanoparticles by vacuum arc deposition [1] is the possibility to create hybrid materials, semifinished products, and nanocomposites with metal-containing compounds using a single-stage process. Metal, ceramic, polymer, or carbon matrices can be used as the base.

When creating composite materials (CMs) based on polymers, regardless of the technology used, two important factors stand out. One is the need for determining the type of the modifying component and its optimal concentrations, which is related to the requirements for the surface activity of polymer microgranules. It is necessary to avoid the formation of a monolayer of the modifier, which prevents further sintering of the composite. Another factor is the prevention of destructive effects that may occur under thermal exposure because of local overheating of the polymer due to its low thermal conductivity.

In this paper, we focus on the analysis of degradation changes in ultrahigh-molecular-weight polyethylene (UHMWPE) in a single-stage process for depositing a CuO nanomodifier on a powder surface. A number of studies have been devoted to changes in the molecular structure of the polymer after treatments of various types. Most of their results are focused on the effect of mechanical activation of UHMWPE powders on the formation of a supramolecular structure [2, 3] or on the effects of polymer processing by radiation, electron [4], or laser [5] irradiation. In [6, 7], structural changes in UHMWPE after surface modification by plasma are discussed. However, in the synthesis and deposition of oxide nanoparticles, the situation is aggravated by the presence of molecular oxygen in the chamber, which creates conditions favorable to thermal-oxidative degradation of the polymer.

The features of the technology for the synthesis of CuO nanoparticles are discussed in detail in [1, 8]. Powder materials of initial UHMWPE (GUR 4120) and samples with CuO nanoparticles deposited on the surface of microgranules (semifinished composite materials) with variable sputtering time are investigated. The modes for depositing nanoparticles are presented in Table 1, and the main parameters of the arc discharge (current 90 A, chamber pressure 60 Pa, ratio of the Ar : O_2 gas mixture 80 : 20%) remained unchanged. In depositing nanoparticles, UHMWPE powder was placed on a rotating ($\omega = 10$ min^{-1}) stainless-steel dish 300 mm in diameter in a plane lying 100 mm below the cathode plane, while the distance from the edge of the dish to the end of the cathode was 300 mm. To confirm that there were qualitative changes in the IR-spectra and X-ray-diffraction patterns, caused by the long-term effect of temperature, a control sample of "overheated" UHMWPE powder (sample 6) was prepared.

The obtained samples of semifinished composite materials were externally distinguished by the degree of coloring. The morphological features of the materials are presented in Fig. 1. The initial UHMWPE is a powder with particles of irregular shape and 50–150 μm in size. After processing in the reaction chamber and deposition of nanoparticles on it, the structure

Mode of deposition of CuO nanoparticles

Sample	Description	Mode
0	Initial (unfilled) UHMWPE	−
1	Filling corresponds to processing for 10 min	Continuously
2	Filling corresponds to processing for 20 min	Continuously
3	Filling corresponds to processing for 30 min	Continuously
4	Filling corresponds to processing for 40 min	20 min *Dep* → 10 min *P* → 20 min *Dep*
5	Filling corresponds to processing for 60 min	20 min *Dep* → 10 min *P* → 20 min *Dep* → 10 min *P* → 20 min *Dep*
6	Overheated UHMWPE	Temperature 320°C, $\tau = 60$ min

Dep, deposition; *P*, pause. During pauses, the processed powder is not removed from the chamber and the supply of the gas mixture is not stopped.

of the polymer does not undergo any visible changes. There are no microgranules melted or damaged by the action of low-temperature plasma. One can note that there is a characteristic distribution of nanodispersed particles over the surface of polymer microgranules. They are distributed in a uniform "cobweb" of agglomerates of variable thickness over the entire surface of the microparticles, leaving some regions of the polymer "open."

At the same time, sample 6 of UHMWPE powder is characterized by marked melting, spheroidization, and coagulation of individual microgranules. Although the powder has only external signs of melting, there is no reason to believe that it does not melt completely. The temperature in the experiment reached 320°C, a value that considerably exceeds the melting point of UHMWPE, which lower than 140°C. Obviously, the high viscosity of the UHMWPE melt, coupled with the experimental conditions (reduced pressure of ~100 Pa in the vacuum chamber), prevents spreading of the molten powders. Therefore, they practically retain their original shape and, to a certain extent, appearance during subsequent crystallization. However, changes in the structure of such particles, as shown below, are significant. Such changes are caused by intense thermal destruction with a significant decrease in molecular weight.

The results of X-ray-phase analysis of the samples are shown in Fig. 2. The reflections of the crystalline orthorhombic polyethylene subcell with the orientation of the crystallites predominantly along the (110) plane at $2\theta \sim 21.54°$ and (200) at $2\theta \sim 23.85°$ are clearly seen in the diffraction patterns. The observed changes in peak (110) for the overheated UHMWPE (sample 6) can probably be explained by the transformation as a result of heating of the metastable monoclinic phase present in the initial UHMWPE at $2\theta \sim 19.5°$ and superimposed on the main peak of the orthorhombic phase. This conclusion is based on the results described in [9], in which the conditions for the formation, existence, and detection of the monoclinic phase in UHMWPE powders are discussed. The con-

ditions for the recrystallization of previously melted UHMWPE powders (sample 6) contribute to the crystallization of the polymer in the orthorhombic phase, as a smooth rate of temperature decrease favors the relaxation of the passage molecules of amorphous regions, reducing the stress at the crystallites formed.

The X-ray patterns of sample 6 show a decrease in the intensity of the main reflections, as well as some of their displacement, narrowing, and a visible decrease in the amorphous component. It should be noted that, for sample 6, only the very fact of qualitative changes in its indices after the exposure to temperature was interesting, as well as a comparison of the experimental data with those for sample 5, for which, as was supposed, such changes could occur.

In the diffraction pattern of a sample containing a nanodispersed filler, we could not separate the phases of the CuO nanoparticles themselves against the background of the high-intensity main peaks of UHMWPE. The changes in the diffraction pattern of semifinished composite material (sample 5) are insignificant in comparison with those detected for the initial UHMWPE (sample 0), which indicates the absence of destructive phenomena in the processing of the polymer in the reaction chamber.

Textures were not detected in the X-ray patterns of any samples under study, as X-ray studies were carried out only for samples of powder materials and it is not possible to detect with a high degree of probability the preferential orientation of the crystallites.

Analysis of the IR spectra (Fig. 3) of the samples of both pure UHMWPE and UHMWPE subjected to different processing times indicates the presence and coincidence of all the main peaks at characteristic frequencies: bands at 2917 and 2848 cm^{-1} responsible for asymmetric and symmetric stretching vibrations of C−H bonds, respectively; a doublet in the region of 1472−1462 cm^{-1} caused by bending vibrations of CH$_2$ groups; and a doublet at 730−717 cm^{-1} characteristic of rocking vibrations of CH$_2$ groups. The obtained experimental spectra are in good agreement with both
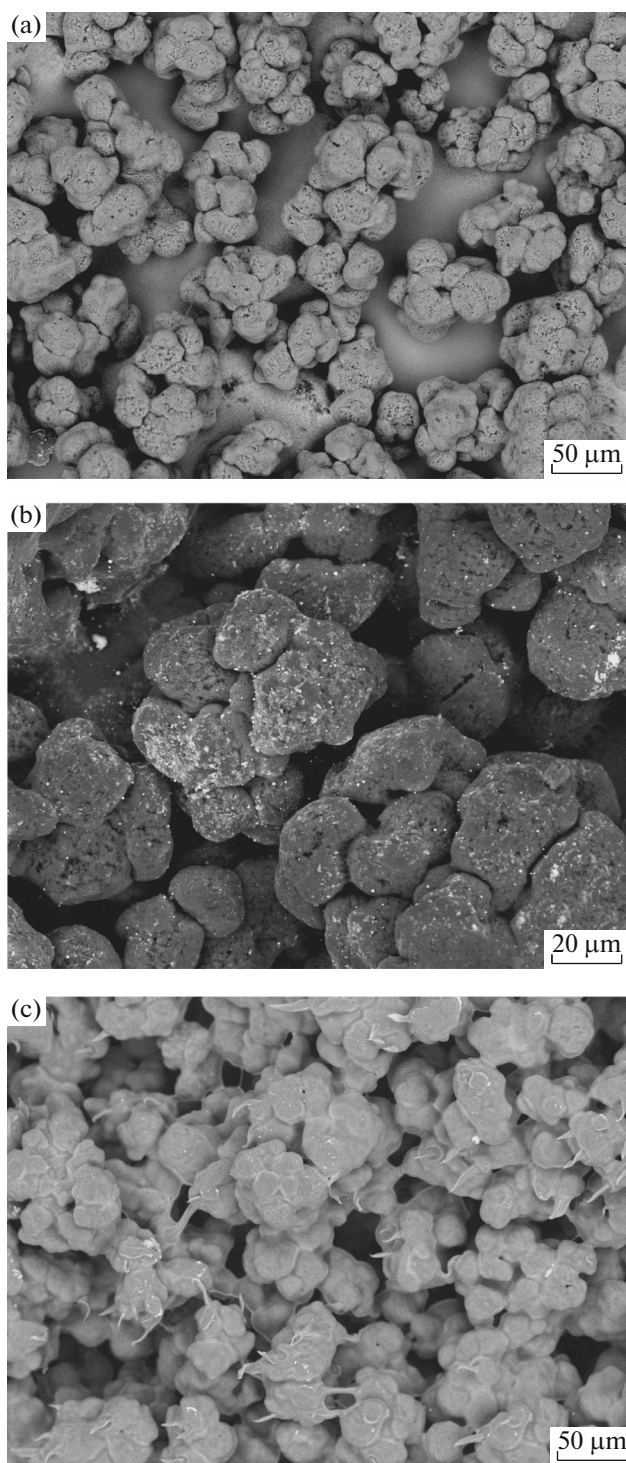
Fig. 1. Scanning-electron-microscopy images of (a) microgranules of original UHMWPE, (b) microgranules with precipitated CuO nanoparticles at a total processing time of 60 min, and (c) microgranules subjected to overheating. The SEM images were recorded using a Hitachi TM-3000 microscope.
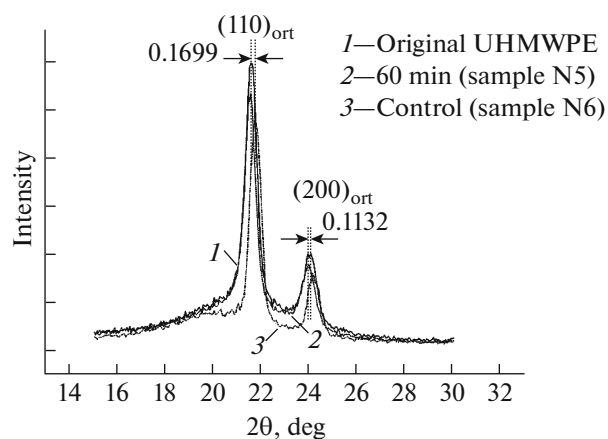
Fig. 2. Fragment of X-ray-diffraction patterns of (*1*) original UHMWPE, (*2*) a sample obtained at a processing time of 60 min, and (*3*) overheated UHMWPE. The X-ray-diffraction pattern of sample 5 (*2*) coincides with the X-ray-diffraction pattern for the original sample (*1*). Diffraction patterns were recorded using a Bruker D8 diffractometer.

the calculated data do not exceed 1% and are within the instrumental error of the spectrometer. For the samples after the nanoparticle deposition procedure, no changes in the spectra are observed compared to the original UHMWPE spectrum, in contrast to the control sample (sample 6), for which such changes are significant.

A characteristic feature of the spectrum of the UHMWPE sample subjected to overheating is the enhancement of the transmission bands at 3430 and 1630 cm^{-1}, which are responsible for the vibrations of hydroxyl OH groups with a simultaneous decrease in the peak intensity of the stretching C$-$H and deformation vibrations of CH$_2$ groups. This and some intensification of the C$-$O$-$C line in the region of 1100 cm^{-1} can apparently be explained as being due to the breakdown of the hydrocarbon chains of the UHMWPE macromolecules to form the $-$OH and C$-$O bonds. To a lesser extent, this is expressed in the spectra of samples with deposited nanoparticles, which confirms the retention of the structure of initial UHMWPE during processing. A larger increase in the intensity of C$-$O lines for the sample treated for 30 min compared to the sample processed for 60 min can be explained as being due to the nanoparticle-deposition mode: 30-min treatment was carried out continuously, and the 60-min mode included 20-min deposition cycles with pauses. Thus, the limitation of the continuous effect of plasma is determined.

Semifinished nanocomposite products of the UHMWPE$-$copper-oxide system were obtained, and the features of their morphology, structure, and chemical structure were studied. X-ray diffraction and IR spectroscopy were used to determine limitation in the continuous deposition of copper-oxide nanoparti-

the theoretical calculated data for the orthorhombic polyethylene subcell (indicated by the lines in Fig. 3) and the published data [2, 4]. The discrepancies with
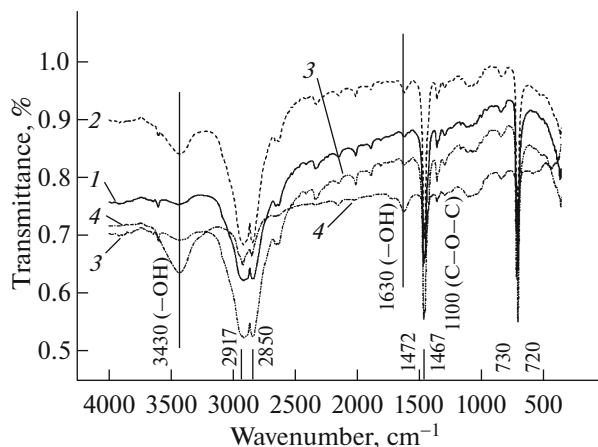
Fig. 3. IR-transmission spectra of (*1*) original UHMWPE, semifinished composite materials with the processing time of (*2*) 30 and (*3*) 60 min, and (*4*) overheated UHMWPE. The lines denote the calculated data for the corresponding bands of the orthorhombic polyethylene subcell; the experimental values are given in the text. Spectra were obtained using a Vertex 80V vacuum Fourier spectrometer (Bruker).

cles on UHMWPE powder, which is 20 min at the set parameters. UHMWPE powder, both before and after the treatment, exhibits pronounced reflections from the orthorhombic subcell and a characteristic set of absorption bands in the IR spectra. Exceeding the continuous processing time leads to the occurrence of thermal-oxidative destruction of the polymer and affects the nature of its IR spectra.

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