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Modification of Ultra-High-Molecular-Weight Polyethylene by Nanostructured B₄C/W Composites under Intensive Mechanical Activation Conditions

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Abstract

Structural transformations of a powder mixture of ultra-high-molecular-weight polyethylene and nanostructured B₄C/W composite were explored by X-ray diffraction, scanning electron microscopy, and FT-IR spectroscopy. The mixture was treated in a high-energy planetary ball mill. It was demonstrated that scaly-shaped polymer composite particles of a 160–400 μm size were generated during mechanical activation. Boron carbide and tungsten particles sized 1–5 and 0.1–0.2 μm, respectively, were evenly distributed therein. The interaction between mixture components during intensive mechanical deformations is accompanied by the crosslinking and decomposition of polymer molecules. As a consequence, there are a decrease in the molecular mass of the polymer and the lack of its extensive oxidative decomposition in this case.

Key words: mechanical activation, mechanocomposites, boron carbide, tungsten, ultra-high-molecular-weight polyethylene, FT-IR spectroscopy

INTRODUCTION

Ultra-high-molecular-weight polyethylene (UHMWPE) is notable for an entirely special combination of properties, such as extremely high viscosity of a notched specimen, superior performance at increased operating speeds, very good sliding properties, incredibly low wear, minor friction losses, very high chemical resistance (acids, alkalis, and aggressive gases), high resistance to cracking, very good noise reduction, and a wide range of applications due to temperature resistance in the range of –200 to 90 °C. Physicochemical

properties of UHMWPE-based materials are determined by the atomic, molecular, and supramolecular structure of this species. The phase state, the dispersion degree of the filler phase, interphase and interactions in the boundary between a single particle and polymer media that considerably affect their distribution in the matrix play a fundamental role [1]. Screens made of UHMWPE-based composites with fillers in the form of boron (or its compounds) and heavy metals (*e.g.* tungsten) are used as efficient protection against neutron and X-ray radiation. Direct use of nanoscale fillers of tungsten and boron carbide is held back by nano-

particle agglomeration, low wettability and weak adhesion of the filler, and also by poor fluidity of the polymer melt due to its high-molecular-weight. From this perspective, the method of formation of composites that is based on the technology of solid-phase deformation mixing is promising.

Both the supramolecular structure of the polymer with a decrease in the molecular weight and molecular composition (without intramolecular bonds breaking) may vary resulting from intensive mechanical activation (MA) of the polymeric compound with fillers [2]. The structural instability of boron carbide does become apparent under conditions of high pressures associated with external loads [3].

The objective of the research was to examine the formation process of the microstructure of UHMWPE/B₄C/W composites under mechanical activation conditions.

EXPERIMENTAL

The B₄C/W composite powder pre-obtained by the mechanochemical alloying of the initial components (B₄C and W) at a 50 : 50 mass ratio was used as a modifier. The average particle size of initial boron carbide (B₄C) and tungsten (PBT grade) powders was 40–60 and 4–6 μm, respectively. Mechanochemical alloying was carried out in an AGO-2 planetary ball mill with a power density of 7 W/g in a protective atmosphere of argon; the processing time was 4 min.

When polymer/B₄C/W composites were generated, UHMWPE powder (GUR 4120 grade manufactured by Ticona GmbH) with a molecular mass of $4 \cdot 10^6$ g/mole and particle size of 100–160 μm was used as a polymer matrix. Composite UHMWPE/B₄C/W powders were produced by the mechanochemical synthesis in a water-cooled Activator 2S planetary ball mill in air. The volume of the drum was 250 cm³, the diameter of steel balls was 9 mm; the loading ball mass was 370 g; the treated sample weight was 40 g; the speed of rotation of the drums around the common axis was ~600 rpm. The processing time was 5, 10, and 25 min.

X-ray measurements were carried out using the D8 Advance diffractometer (Bruker, Germany) operating with radiation of the copper anode (CuK_α). The calculation and refinement of profile and structural parameters were performed by the least squares method with full-profile analysis of X-ray diffraction patterns. Research on mi-

crostructural characteristics (crystallite size, L , microstrain, ϵ) was carried out using the double-Voigt approach. In order to separate the contributions into reflexes broadening *versus* L , the Lorentz function was used, *versus* microstrain ϵ – the Gaussian function.

The microstructure and chemical composition of the resulting composites were investigated by the CamScan 4 scanning electron microscope (Oxford Instruments, England).

Infrared investigations were performed using the Nicolet iS10 FT-IR spectrometer (Thermo Scientific, USA) by the attenuated total reflection method using a diamond crystal in the 4000–400 cm⁻¹ frequency range.

RESULTS AND DISCUSSION

The boron carbide/tungsten mechanocomposite was produced in the first step and its microstructure was explored. According to X-ray phase analysis using ICDD PDF-2 (Fig. 1) the composite contains tungsten (SG *Im3m* (229) with crystallite size $L_w \sim 37$ nm and boron carbides B₄C and B₁₀C (*R-3m* (166). Iron (*Im3m* (229) in amounts of ~4 mass % with crystallite sizes $L_{Fe} \sim 8$ nm, appears in the mixture resulting from mechanical processing by milling. Crystallite size (L_{B_4C}) is approximately 46 nm. There were no variations in the structure of tungsten.

When UHMWPE/B₄C/W composite is mechanochemically synthesised within 25 min, the XRD phase composition is not significantly varied. The initial UHMWPE is an amorphous crystalline polymer, wherein the crystal structure is presented by the orthorhombic phase with *Pnma* (62) space group. The intensity of UHMWPE reflections (No 40-1995) is substantially reduced already after 5 min of MA (see Fig. 1), whereas the halo of the amorphous portion of the polymer is not recorded. There is no further fragmentation of tungsten and boron carbide particles during treatment. The crystallite size of tungsten remains unchanged at the 35–37 nm level, whereas that of boron carbide increases to about 60–87 nm (Table 1). There are maximum changes in the structure for iron and boron carbide. The lattice parameter (a) of iron is increased from 2.866 to 2.879 Å, which is likely to be related to the formation of solid solutions.

The quantity of iron in the polymer composite is increased to 5 mass %. B₄C fine structure parameters ($\Delta a = +0.009$ Å; $\Delta c = -0.008$ Å) are

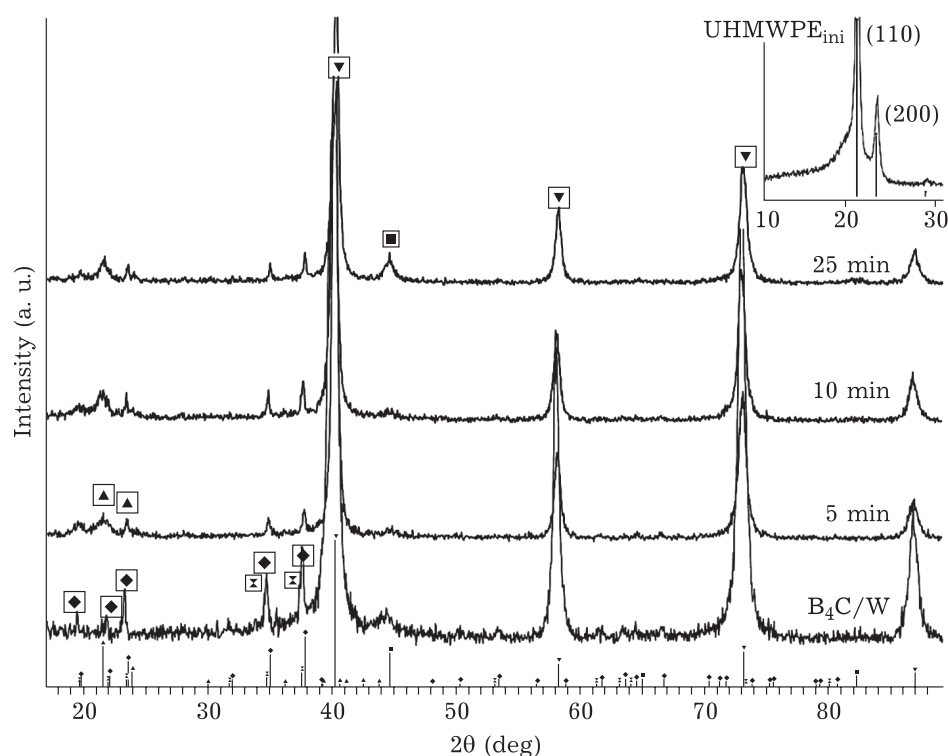


Fig. 1. X-ray-diffraction patterns of initial UHMWPE and B₄C/W, and also UHMWPE/B₄C/W composites generated with mechanical activation time of 5, 10, and 25 min.

changed compared to the No 35-0798 database, probably due to enhanced carbon amount in boron carbide from 18 to 19.6 at. % [3].

Composite UHMWPE/B₄C/W particles with prevailing sizes of 160–400 μm are generated already in the initial step of MA. When mechanical

TABLE 1

Microstructural parameters of UHMWPE/B₄C/W mechanocomposite phases

Parameters	B ₄ C/W			
	Initial	After MA, min		
		5	10	25
B₄C				
<i>a</i> , Å	5.604	5.608	5.608	5.609
<i>c</i> , Å	12.104	12.099	12.079	12.078
<i>L</i> , nm	46	67	87	60
ε _G	0.2949	0.6004	0.4002	0.2778
α-Fe				
<i>a</i> , Å	2.866	2.879	2.874	2.873
<i>L</i> , nm	8	57	26	17
ε _G	–	0.01	0.01	1.1032
W				
<i>a</i> , Å	3.166	3.167	3.166	3.166
<i>L</i> , nm	37	37	36	35
ε _G	0.4083	0.5607	0.447	0.4398

activation time is increased, the size of composite particles is slightly enhanced due to plastic deformation processes. According to scanning microscopy data, there is no grinding of the used B₄C/W modifier particles upon MA up to 25 min (Fig. 2 and 3). A size of 1–5 μm for boron carbide particles remains unchanged, whereas tungsten and iron species of 0.1–0.2 μm and less than 0.08 μm sizes, respectively, are distributed in a polymer matrix.

Composite UHMWPE/B₄C/W particles with prevailing sizes of 160–400 μm are generated already in the initial step of MA. When mechanical activation time is increased, the size of composite particles is slightly enhanced due to plastic deformation processes. According to scanning microscopy data, there is no grinding of the used B₄C/W modifier particles upon MA up to 25 min (see. Fig. 2 and 3). A size of 1–5 μm for boron carbide particles remains unchanged, whereas tungsten and iron species of 0.1–0.2 μm and less than 0.08 μm sizes, respectively, are distributed in a polymer matrix.

Figure 4 gives IR data for chemical bonds in B₄C/W and UHMWPE/B₄C/W composites obtained at different mechanical activation time. There are characteristic absorption bands of boron carbide in the 1600–700 cm⁻¹ wavelength range [4]. After MA, the spectrum of B₄C/W

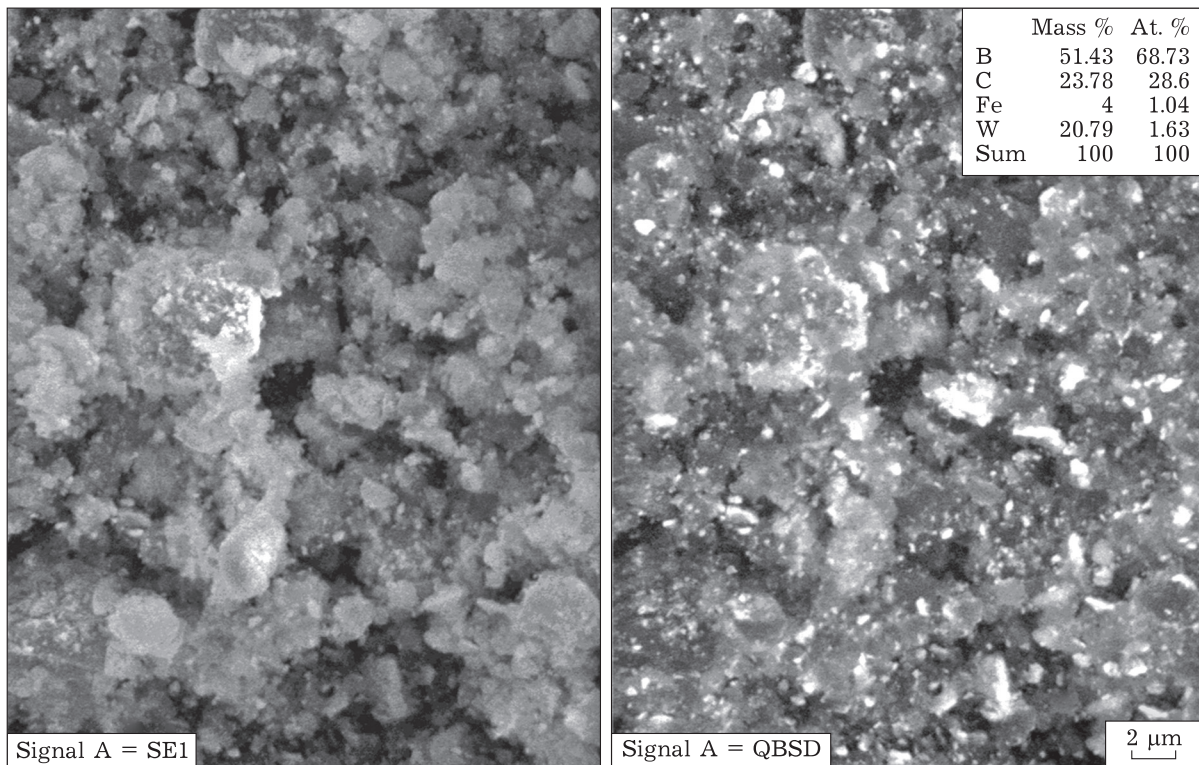


Fig. 2. Composite B_4C/W . The light areas in the BSP image correspond to W and Fe particles.

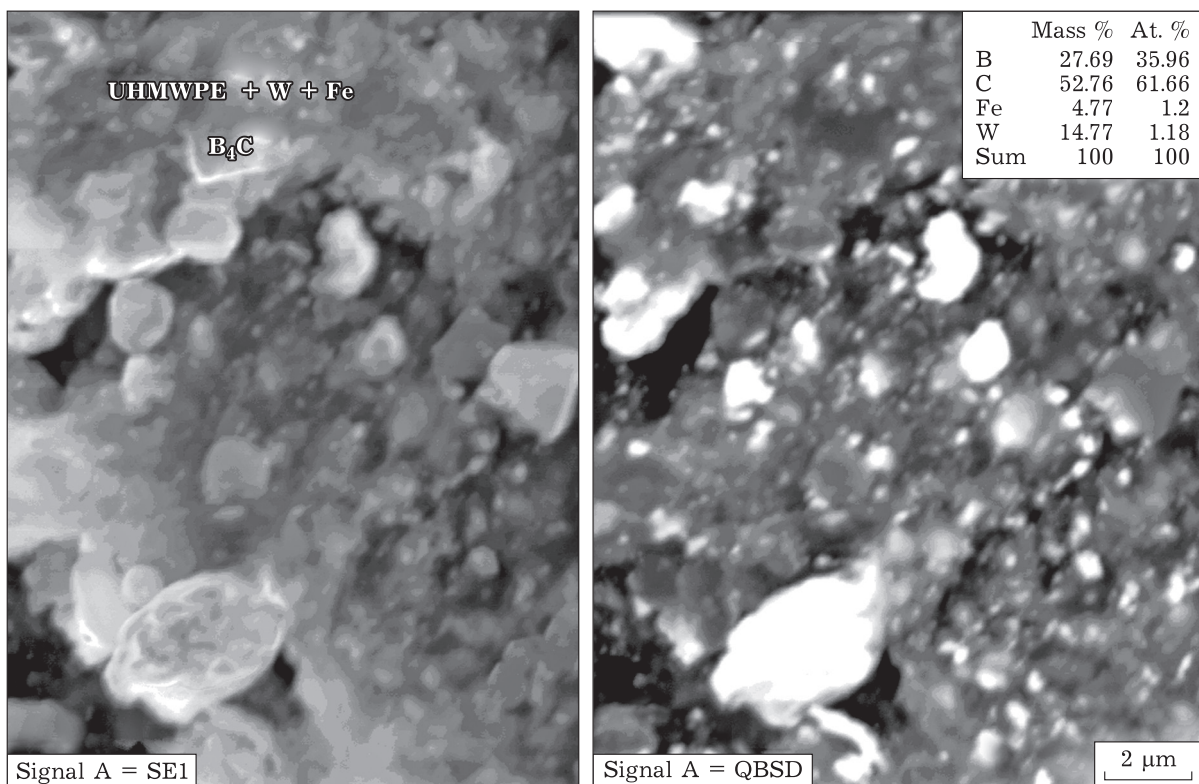


Fig. 3. UHMWPE/ B_4C/W composite generated during mechanical activation (MA) within 25 min.

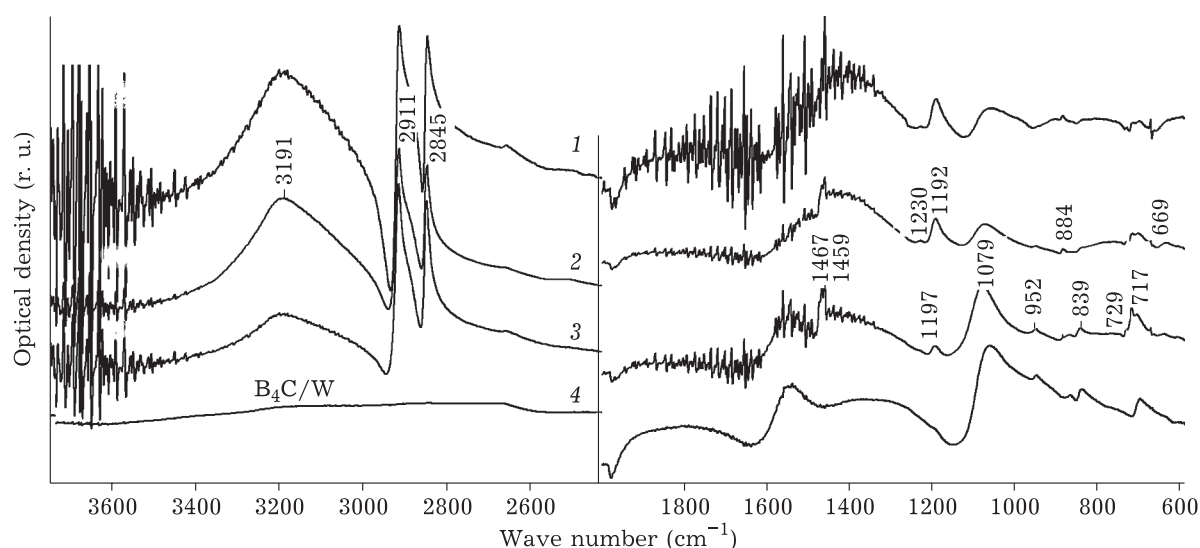


Fig. 4. FT-IR spectra of composite UHMWPE/B₄C/W particles obtained at different mechanical activation (MA) times: 1 is B₄C, W, 2–4 are mechanically activated within 5 (2), 10 (3), and 25 min (4).

composite contains bands for boron carbide with the following main frequencies, cm⁻¹: 1560 (ν_{as} C–B–C), 1430, 1194 (shoulder), 1058 (ν_{as} C–B₃), 946 (ν_s C–B₃), 866, 837, and 695 (ν_1 B12). Carbon content in boron carbide has an effect on the position of absorption bands of the B–C bond. A shift of peaks to the low-frequency region upon MA is due to the reduced carbon content in boron carbide and the appearance of the B_{6.5}C phase enriched with boron. The band near ~1600 cm⁻¹ is assigned to asymmetric stretching vibrations (ν_a) of C–B–C in B_{4.3}C composition, whereas the band at ~1450 cm⁻¹ appears in more boron-rich B_{6.5}C composites as new modes occurring upon the stretching and bending of bonds that contain a carbon atom in the central node of B–C–B or C–C–C [3].

Upon the co-processing of B₄C/W composite and the polymer, absorption bands of boron carbide are shifted towards the high-frequency range, which corresponds to the increased carbon content in boron carbide until the B₄C stoichiometry. The clear absorption peak with the maximum near 1194 cm⁻¹ is related to B–C bond vibrations. The former usually appears in polycrystalline boron carbide samples.

The whole series of spectra have absorption bands typical for UHMWPE, such as a doublet (2913 and 2846 cm⁻¹) responsible for symmetric and asymmetric stretching C–H vibrations (1468 and 1458 cm⁻¹) corresponding to bending C–H vibrations and crystallinity bands (730 and 719 cm⁻¹).

Nevertheless, their intensity is significantly reduced already in 5 min of treatment, and the shape is widened, yielding a low-frequency shoulder, apparently because of extra intermolecular hydrogen bonds that are generated resulting from deformation (the formation of cross linkages). When treatment time is increased to 10 and 25 min, polyethylene crystallinity bands (730 and 719 cm⁻¹) disappear, which may be related to the distortion of the conformational regularity of macromolecules. The appearance of absorption bands near 883 and 1420 cm⁻¹ after mechanical activation within 10 and 25 min, respectively, is driven by planar δ -vibrations of terminal methylene RR'C=CH₂ moieties [5]. Presumably, an increase in their intensity is due to the cleavage of molecular chains and hence to a reduction in polymer molecular mass. The appearance and an increase of band intensities in the 3000–3300 cm⁻¹ range indicate the formation of oxidic B–OH bonds, as deformation processing was carried out in air, its humidity might be reaching 70 %. There are no additional bands that would point to generating oxygenated products of thermal oxidation of polymers in the 1600–1800 cm⁻¹ IR spectral range.

CONCLUSION

In such a way, the co-processing of ultra-high-molecular-weight polyethylene (UHMWPE) and B₄C/W mechanocomposite in a planetary mill results in the formation of scaly-shaped polymer

composite particles. The latter are evenly distributed in the polymer matrix of boron carbide and tungsten particles sized 1–5 and 0.1–0.2 μm , respectively. As a consequence, fine texture parameters of boron carbide (B_4C) are changed. The main possible results of the interaction between the polymer matrix and modifier disperse powders upon mechanical activation is crosslinking, in other words, the formation of cross-linked compounds and decomposition of the polymer decreasing its molecular mass.

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