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Mechanochemical Preparation of Fe/M/UHMWPE Ternary Composites (M = TiC, HfC, TiB₂, B₄C) under Intense Plastic Deformation

S. A. KOVALEVA¹, V. I. ZHORNIK¹, P. A. VITYAZ¹, T. F. GRIGOREVA², S. V. VOSMERIKOV², N. Z. LYAKHOV²¹Joint Institute of Mechanical Engineering, Belarusian National Academy of Sciences, Minsk, Belarus

E-mail: sveta_kovaleva@tut.by

²Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia

Abstract

Structural changes of ultrahigh-molecular polyethylene (UHMWPE), modified by inorganic mechanocomposites Fe/M (M = TiC, HfC, TiB₂, B₄C) (70 mass %) under intense plastic deformation in a planetary ball mill, were investigated by means of X-ray phase analysis and FTIR spectroscopy. At a short treatment time, the molecular structure of initial UHMWPE is not disturbed, and the change in the shape of powder particles is due to the segmental mobility of macromolecules. The introduction of inorganic mechanocomposites (fillers) into the polymer leads to the formation of a polymer–filler interfacial zone with a branched polymer structure. The crystallinity degree of mechanochemically obtained Fe/M/UHMWPE composites is reduced to 25–40 vol. %, compared to 44 vol. % for initial UHMWPE, depending on the filler nature. No oxidative degradation of the polymer is observed under mechanical treatment.

Keywords: UHMWPE, iron, carbides, titanium boride, mechanical treatment, mechanocomposites, filled polymers

INTRODUCTION

At present, composite polymer materials based on ultra-high molecular weight polyethylene (UHMWPE) with a high filling degree are relevant for the development of efficient protection from multi-factor radiation. Optimization of the combination of mass-size parameters and protective properties of the materials determines attention to the development of coatings and materials based on fine fillers: heavy metals, their carbides and boron compounds [1].

The introduction of fillers into polymers leads to the appearance of a broad range of interactions at the interfaces. The nature of these interactions is substantially dependent on the chemi-

cal properties of filler surface, concentration, dispersity and particle shape, which defines deformation-strength, viscoelastic, thermomechanical properties of the polymer and the filled system in general [2]. An increase in the degree of filler dispersity promotes an increase in the viscosity of the material and deceleration of deformation processes under permanent loading, and the effect is similar to that caused by an increase in filler concentration [2].

The fillers that are necessary to moderate fast and medium-velocity neutrons during elastic scattering are graphite, carbides including boron carbide. To moderate fast neutrons during inelastic scattering and to weaken capture gamma rays, heavy elements are used: tungsten, molyb-

denum, iron. Elements with a high effective cross section such as boron are used to absorb thermal neutrons. Because of this, the promising materials as polymer fillers are composites containing heavy elements, boron, carbides. The composites of this kind were obtained and studied previously [3, 4]. The Fe/TiB₂, Fe/B₄C, Fe/TiC composites synthesized mechanochemically are agglomerates of particles thermally stable up to 800 °C in the atmosphere of argon.

The major technological difficulties in the introduction of fine fillers into polymers are nanoparticle agglomeration, poor wetting with the matrix material due to active adsorption on the surface of various films. A promising method to form composites based on UHMWPE is the technology of solid-phase deformation mixing.

The goal of the present work was to study the effect of the composition of inorganic mechano-composites Fe/TiB₂, Fe/B₄C, Fe/TiC, Fe/HfC on the formation of composite structures with UHMWPE under the conditions of intense plastic deformation in a high-energy planetary ball mill.

EXPERIMENTAL

Materials

Powders used as initial materials included Fe of R-10 grade with particle size 0.2–6.0 μm, TiB₂ of A grade with particle size ≤3 μm, B₄C from Aldrich (CAS: 12069-32-8) with particle size 40–60 μm, TiC with particle size ≤0.1 μm [5], Hf of GFM-1 grade with particle size 0.2–50.0 μm. Hafnium carbide HfC with particle size <0.1 μm was obtained by means of mechanochemical synthesis from a stoichiometric mixture of Hf and C (lamp black). The UHMWPE powder of GUR 4120 grade (manufactured by Ticona GmbH) with molecular mass 4 · 10⁶ g/mol and particle size 100–160 μm was used as the polymer matrix.

Synthesis procedure

The UHMWPE composites with Fe/M fillers with a ratio (Fe/M)/UHMWPE = 70 : 30 mass % (M = TiC, HfC, TiB₂, B₄C) were obtained in an AGO-2 high-energy ball planetary mill (Russia) with water cooling in the atmosphere of argon. Vial volume was 250 cm³, ball diameter 5 mm, the mass of loaded balls was 200 g, the portion of the sample under treatment was 10 g, the rate of vial rotation around a common axis was ~1000 r.p.m. Mechanochemical synthesis of Fe/M fillers

with components ratio 50 : 50 mass %, which corresponded to the volume ratio of M in the filler, vol %: TiC 61, HfC 38, TiB₂ 63, B₄C 76, was carried out in the protective atmosphere of argon for 2 min [3, 4], polymer composites with UHMWPE were treated for 0.5 min.

Mechanical treatment (MT) of pure UHMWPE powders was carried out in the AGO-2 planetary ball mill (Russia) under the same conditions for 0.5, 1 and 2 min.

Investigation methods

X-ray structural analysis was carried out with the help of a Bruker Advance D8 diffractometer (Germany) using the characteristic radiation CuK_{α1} (λ = 1.5406 Å). Calculation and refinement of profile and structural parameters were carried out with the help of the least squares method using the full-profile analysis of diffraction patterns. The studies of microstructural characteristics (crystallite size *L* and microstrain ε) were carried out using the double Voigt methodology. Lorentz function was used to separate the contribution into peak broadening from *L*, while the Gaussian function was used for the contribution from ε.

Molecular structures were studied with the help of IR Fourier spectrometer ThermoScientific Nicolet iS10 (USA) by means of disturbed total internal reflection on diamond crystal within the wavenumber range 4000–400 cm⁻¹. Norton-Beer apodization function was average, phase correction was made according to the Mertz method [6].

Crystallinity degree (χ) of UHMWPE was evaluated relying on the ratio of the optical densities *D* of absorption bands at 730 and 720 cm⁻¹ [7] as $\chi = D_{730}/D_{720} \cdot 100 \%$.

The absorption band at 730 cm⁻¹ characterizes *trans*-segments only in the crystalline phase, while the band at 720 cm⁻¹ is composite and corresponds to oscillations in the amorphous-crystalline regions.

RESULTS AND DISCUSSION

It was demonstrated previously [3, 4] that the powders of Fe/TiB₂ and Fe/B₄C mechano-composites form agglomerates up to 50 μm, with the size of separate particles being equal to 0.5–5 μm: Fe/TiB₂ composites are composed of particles 1 to 20 μm in size, Fe/B₄C – 0.5 to 50 μm. The Fe/TiC

and Fe/HfC composites with smaller ($\leq 0.1 \mu\text{m}$) particles form agglomerates with the size within the range 0.5–100 μm .

Initial UHMWPE under the conditions of mechanical treatment

The UHMWPE polymer is an amorphous-crystalline material composed of crystalline folded polymer structures and amorphous regions in which molecular chains remain in the disordered state. Carbon atoms inside the crystalline formations are arranged in the *trans*-zigzag conformation. The crystal structure is represented by the orthorhombic phase with unit cell parameters: $a = 0.74 \text{ nm}$, $b = 0.493 \text{ nm}$, $c = 0.254 \text{ nm}$ [8]. UHMWPE crystallites are oriented mainly along the (110) plane because the reflection corresponding to this plane is much more intensive than others. Crystallite size is $\sim 20 \text{ nm}$ (Fig. 1, curve 1).

The amorphous region of UHMWPE is composed of randomly oriented and straight polymer chains incorporated into two or more neighbouring crystallites at the same time.

Under the impact and shear action implemented in AGO-2, an increase in the integral intensity of the (010) reflection is observed in the diffraction patterns of pure UHMWPE (see Fig. 1, curves 2–4). According to the data reported in [8, 9], this increase is connected with the partial transformation of the orthorhombic crystal cell

into a metastable monoclinic cell, which is again transformed into a more stable orthorhombic modification after thermal treatment at 90–100 °C. With an increase in the time of MT from 1 to 2 min, the crystallite size (L) in UHMWPE slightly increases from 26 to 29 nm.

The IR spectra of UHMWPE before and after MT contain absorption bands: a doublet (2913 and

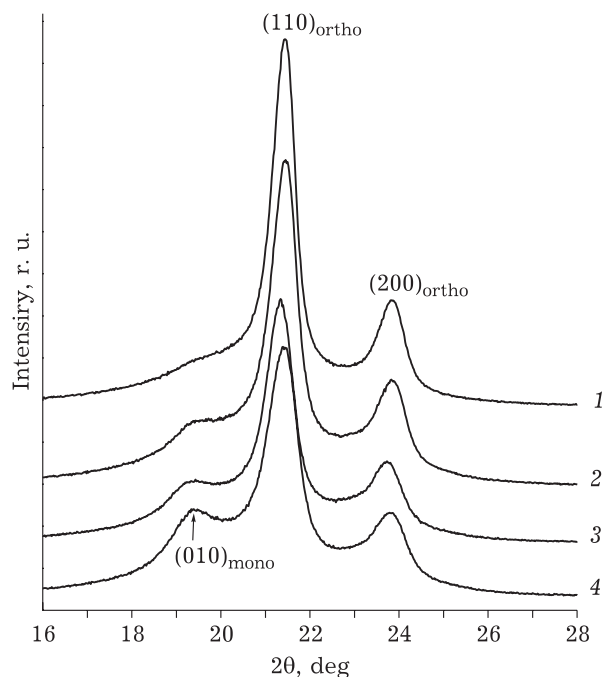


Fig. 1. Diffraction patterns of UHMWPE in the initial state (1) and after mechanical treatment, min: 0.5 (2), 1 (3), 2 (4).

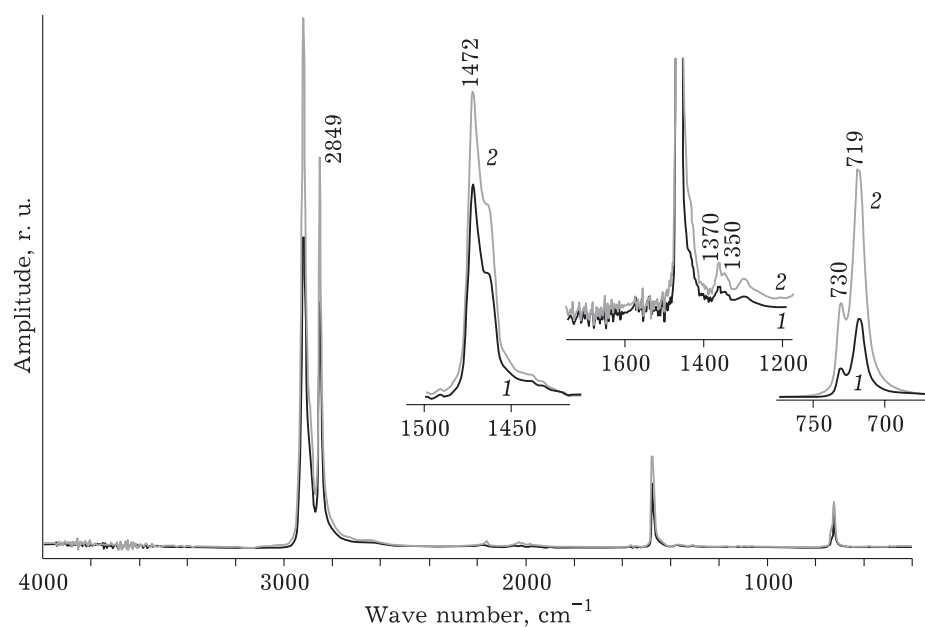


Fig. 2. IR spectra of UHMWPE in the initial state (1) and after mechanical treatment for 2 min (2).

2849 cm⁻¹) related to symmetric and asymmetric stretching vibrations $\nu(\text{CH}_2)$; a doublet (1472 and 1463 cm⁻¹) corresponding to the bending scissoring vibrations of *trans*-methylene groups $\delta(\text{CH}_2)$; 730 and 720 cm⁻¹, related to pendular vibrations $\rho(\text{CH}_2)$ [10] (Fig. 2). In addition, other absorption bands may be identified in the IR spectra of UHMWPE within the region of bending vibrations 1450–1475 cm⁻¹, in particular, the bands related to methylene groups that are assigned to the intermediate (transient) and amorphous parts [11]: 1) bands at 1471, 1468 and 1464 cm⁻¹ – to the mixed δ -vibrations of methylene groups of *gauche*- (convolute) and *trans*- (extended) rotational isomers in the intermediate region; 2) 1466 cm⁻¹ – to δ -vibrations of methylene groups of *gauche*-isomers in the amorphous region, and 3) 1456 cm⁻¹ – to the mixed disordered δ -vibrations of methylene chains of *gauche*- and *trans*-isomers in the amorphous region.

The bands related to the amorphous phase of UHMWPE also include those at 1370, 1350 and 1303 cm⁻¹, two former bands are conformation-sensitive and correspond to *trans*- and *gauche*-rotational isomers, respectively [12].

Taking into account the dependence of the viscoelastic behaviour of the polymer on the speed and time of deformation, we may assume that in the case of a short high-speed pulsed mechanical action the UHMWPE powder behaves mainly as an elastic body. Deformation in the structure of globule is connected with the

segmental mobility of molecules, leading to a decrease in intermolecular distances in accordance to the applied strain field, which results in the general increase in the intensity of absorption bands in the IR spectra, and particle shape changes from globular to scaly. The energy in the chosen MT modes is insufficient to break C–C bonds [13] but sufficient to bring about partial changes of the supramolecular structure of the polymer. The degree of UHMWPE crystallinity after MT increases insignificantly from 40 to 44 vol. %.

Composite powders UHMWPE/70 mass % filler

The introduction of dispersed Fe/M fillers into the polymer during MT has a more substantial effect on the transformation of polymer structure. Even after intense MT of the mixtures of UHMWPE with dispersed fillers for 0.5 min, the IR spectra (Fig. 3) exhibit a decrease in the intensity of absorption bands corresponding to the vibrations of CH₂ groups, and the shift of these bands to lower frequencies occurs. The shape of bands changes, with the elevation of the baseline level, which may point to the deformation of molecules and the strengthening of intermolecular interactions. The most substantial decrease in absorption intensity is characteristic for the mixture with Fe/B₄C filler, and the least one – for Fe/HfC, which is defined by the volume fraction of filler particles.

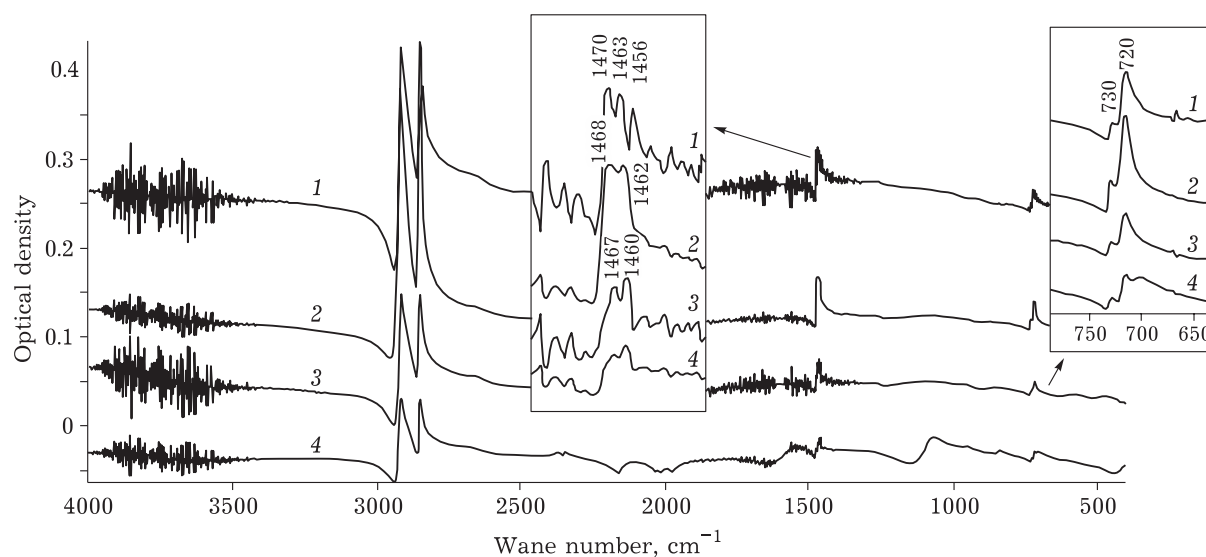


Fig. 3. IR spectra of UHMWPE/70 mass % Fe/M composites obtained after MT for 0.5 min, M = TiC (1), HfC (2), TiB₂ (3), B₄C (4).

In the region of scissoring deformation vibrations of CH_2 groups, we observe the shifts characteristic of the formation of straight chains with the mixed vibrations of the crystalline and amorphous regions (see Fig. 3). It may be assumed that these regions are due to interfacial zones around filler particles.

A decrease in the degree of polymer crystallinity allows us to assume that the deformation of the polymer with the filler involves the straightening of the regions of UHMWPE chains incorporated in crystallites. In the case of Fe/TiC filler, the band at 1456 cm^{-1} points to an increase in the fraction of disordered δ -vibrations of *gauche*- and *trans*-methylene chains in the amorphous region. An increase in the amount of straight chains is also characteristic of Fe/TiB₂ filler. The highest crystallinity degree (38 %) is exhibited by UHMWPE with Fe/B₄C filler, though the volume concentration of B₄C (76 vol. %) in the filler exceeds the content of TiB₂ and TiC by a factor of 1.2. The degree of UHMWPE/Fe/TiB₂ and UHMWPE/Fe/TiC crystallinity is 34 and 25 %, respectively. The lowest volume concentration in the filler is that of HfC (38 vol. %), however, the degree of crystallinity of UHMWPE/Fe/HfC is not high (32 %).

Conformation-sensitive bands at 1370 and 1350 cm^{-1} are not manifested in the spectra of composites (see Fig. 3), which may be due to the distribution of dispersed particles exactly in disordered regions. According to literature data, these bands disappear when filler content is 50 mass % [14].

An increase in the amount of the amorphous phase may point to the formation of a branched (or pseudo-grid) spatial structure of the interfacial zone. The nodes of branching in the grid may be amorphous clusters composed of more ordered fragments of UHMWPE macromolecules on the surface of filler particles. The formation of the branched structure of the interfacial zone will promote an increase in the temperature of its segmental relaxation, which may be much higher than the temperature of polymer melting [15].

A decrease in the crystallinity degree and the high degree of interlacing of macromolecules that bind lamellar nodes with each other will also provide a decrease in the plastic properties of the polymer [16]. The period of chain relaxation is longer than the time of chain rearrangement, which causes deceleration of the dislocation of a chain as a whole. Under these conditions, the

accumulation of highly elastic deformation dominates.

An increase in the intensity of bands within the ranges 3500 – 3800 and 1600 – 1700 cm^{-1} is characteristic of mechanocomposites, which points to the formation of adsorbed hydroxyl OH groups.

We did not detect any additional bands in the IR spectra within the range 1600 – 1800 cm^{-1} which would point to the formation of polymer oxidation products.

CONCLUSION

Mechanical treatment of initial UHMWPE for up to 2 min does not cause substantial changes in its molecular structure, while the change in the shape of polymer powder particles proceeds due to the compression of the molecular grid connected with the segmental mobility of macromolecules. The particles change their morphology from globular to scaly.

Mechanochemical introduction of inorganic mechanocomposites Fe/M (M = TiC, HfC, TiB₂, B₄C) (70 mass %) into the polymer promotes the formation of an interfacial polymer–filler zone with the grid-like spatial structure of the polymer, with the arrangement of polymer particles in disordered regions, which causes a decrease in the segmental mobility of molecules. The crystallinity degree of filled polymer powders decreases to 25–40 vol. % depending on filler nature.

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