Electron irradiation resistance of the composite material structure based on ultra-high molecular polyethylene and boron carbide

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Abstract. Effect of electron irradiation on the structural state of a composite material based on ultrahigh molecular weight polyethylene (UHMWPE) and boron carbide particles (B₄C) which is a precursor for functional radiation protection materials has been investigated. Composite powder materials were synthesized from industrially available components by the method of mechanochemical activation under conditions of intense shock-shear deformations. Specimens in the form of 2 mm thick composite powder’s pressed plates were irradiated with 2 MeV electrons in air. Studies of changes in the structural and morphological characteristics of the composite samples were carried out by means of scanning electron microscopy, X-ray diffraction, FTIR spectroscopy and differential scanning calorimetry. Effects of electron irradiation on the structure of the composite as a whole and its components were analysed. The analysis of the obtained data showed the resistance of the composite material with respect to the electron irradiation fluence up to 8·10¹⁴ cm⁻².

1. Introduction

The use of polymeric materials in various industries, such as electronic equipment, radiation medicine, space technology, necessitates the search for materials that are resistant to aggressive external influences of electromagnetic fields [1]. Under the influence of ionizing radiation, a number of reversible and irreversible radiation effects can occur in polymers, destroying their morphology and physical-mechanical properties that violate the performance of the material as a whole [2]. The existing methods of increasing the radiation resistance of polymeric materials to the effects of electromagnetic fields include the synthesis of composites by modifying polymer matrices with radiation-resistant or radiation-absorbing inorganic fillers [3]. Interactions of ionizing radiation with polymer composites induce many competing reactions. The primary interactions of ionizing radiation with polymers include ionization, excitation, free radical formation, and other. The secondary
reactions following the free radical generation include hydrogen abstraction, addition to double bond, recombination (crosslinking or branching), chain scission, oxidation and grafting. From a practical point of view, the most important and beneficial reaction is radiation crosslinking (the formation of cross-links, i.e. the formation of intermolecular bonds). Crosslinking is a chemical process that leads to a formation of a three-dimensional network structure. Radiation crosslinking is a result of recombination of free polymer radicals migrating predominantly in the amorphous regions. Usually, crosslinking and main-chain scission are two competing processes that always occur simultaneously under radiation [4]. If the ratio of the formation of cross-links to the scission of chains is greater than two, crosslinking takes place. These structural changes lead to a significant increase in molecular mass, reduced solubility in organic solvents and improved mechanical, thermal as well as chemical properties, which allows the use of lower-cost commodities or technical polymers instead of costly high-performance polymers.

Commonly used types of electron accelerators are different in energy from medium (0.3-5 MeV) to high energy (5-10 MeV). The penetration capacity of accelerated electrons mainly depends on the acceleration energy and the density of irradiated product. Electrons principle interactions with materials consist of primary electrons from the electron gun and secondary electrons formed in material through the penetration depth. One of the key parameter of the irradiation is the absorbed dose that is the amount of energy of ionizing radiation absorbed by a unit of mass of the processed material. The radiation dose influence on the material is strongly dependent on the choice of the polymer and the composition of the filler particles.

In this work we use industrially available ultra-high molecular weight polyethylene (UHMWPE) as a binding agent and B₄C particles as inorganic filler. The choice of components was determined by their properties. UHMWPE is a polyethylene resin with a high polymerization degree. It’s chemical formula is [–CH₂CH₂–]ₘ. It also has high molecular weight (from 3 to 8·10⁶ g/mol). It is usually semi-crystalline with degrees of crystallinity ranges up to 80% [5,6]. UHMWPE has both the highest abrasion resistance and highest impact strength of any polymeric material. Moreover, UHMWPE has a negligible water absorption, good chemical and corrosion resistance, biocompatibility and stability in the body. Combined with these features, UHMWPE is also an exceptional material for radiation shielding due to its inherent tendency to cross-link upon irradiation, high hydrogen content and high molecular mass. Another concern with radiation shielding material is the effect of atomic oxygen on the degradation of the polymeric material. Boron carbide B₄C has rather low density and is one of the hardest materials with high chemical resistance in various aggressive environments and has a high neutron-capture cross-section [7,8].

To produce composite compounds, we apply method of mechanical activation (MA) of heterogeneous mixtures of powdered UHMWPE with B₄C. MA is a well-known powder processing technique that allows to synthesize homogeneous composite material starting from elemental powder mixtures and involves repeated welding, fracturing, and re-welding of powder particles in a high-energy ball mill [9]. This technique is widely applied to metallic systems, but recently has been studied in blending polymers when combination of shearing, extension, fracturing and cold-welding of polymeric powder may induce chain scission or hydrogen abstraction and, consequently, free radical formation.

The purpose of this work was to study the effect of different irradiation doses of an accelerated electrons on the structural state of composites (100–x)UHMWPE/xB₄C (x = 70, 50 wt.%) synthesized as precursor for radiation protection functional material.

2. Experimental

2.1. Specimens preparation

Composite samples of UHMWPE/B₄C (50:50 wt.% and 30:70 wt.%) have been synthesized mechanochemically in AGO-2 in Ar vial using industrial powdered B₄C and UHMWPE (Ticona GmbH). The volume of a milling drum was 250 cm³. Steel balls of 5 mm diameter with total mass 200
g were used to achieve the ball-to-powder ratio 20:1. The drum rotation speed was 1000 rpm. During milling, the drum was cooled with flowing water. The mixture milling time was 2 min. To prevent surface oxidation, specimens were kept in a mill under argon for several hours. Then powders were pressed with Portable Press in special mold (P5 Ton) into disc plates with 3 mm diameter and 2 mm thickness.

2.2. Irradiation condition
Irradiation of specimens was performed under industrial conditions (normal atmosphere and at the room temperature) at electron accelerator U-10 of IMET RAS (2 MeV energy and normal distribution of the electron beam flux over the beam cross section) with a radiation fluence ranging from 0 to 8·10¹⁴ cm⁻². The distance of the specimen plate from the irradiation source was 20 cm. The illumination area completely covered the entire sample with electron fluence nonuniformity less than 10%.

2.3. Experimental methods

2.3.1. X-ray diffraction (XRD)
XRD data was collected using PANalytical Empyrean powder diffractometer equipped with a PIXcel 3D detector (Bragg-Brentano geometry, Cu Kα-radiation, Ni filter). HighScore (PAnalytical) software and ICDD PDF2 databases [10] were used for phase identification.

2.3.2. Scanning electron microscopy (SEM)
For collection of scanning electron microscopy (SEM) data, specimens’ powders were dusted on a carbon duct tape. Sputtering of Au particles (~200 nm) has been performed to avoid charging decrease sample damage due to electron beam and increase resolution. Images were recorded using FEI Quanta 3D FEG microscope with secondary electrons signal.

2.3.3. Differential Scanning Calorimetry (DSC)
The composites were investigated by DSC using a Perkin Elmer DSC8000 differential scanning calorimeter operating under argon flow. Samples were sealed in corundum pans. A heating rate of 20°C/min was used to heated the samples from room temperature (25°C) up to 200°C followed subsequent cooling with the same rate. Tm (melting temperature) was determined from the position of the peak maximum. The melting enthalpy of each sample was obtained from the area under the melting peaks. The crystallinity degree was calculated by dividing the melting enthalpy of the samples by the melting enthalpy of UHMWPE 100% crystalline (299 J/g) [11]. Since the specimens contain polymer and boron carbide particles, the reinforcement mass had to be subtracted from the total. Therefore, the levels of crystallinity of UHMWP/B₄C composites were determined according to [12]

\[ \chi_{dsc} = \frac{\Delta H_c}{\Delta H_m^0(1-x)} \times 100\% \]

where \( \chi_{dsc} \) is the degree of crystallinity (%), \( \Delta H_c \) is obtained by the melting peak area, \( \Delta H_m^0 \) is the melting enthalpy of UHMWPE with 100% crystalline, and \( x \) is particles weight fraction.

The evaluation of another parameter of the supramolecular structure of polymers — the parameter of intra-chain cooperativity of melting (\( \nu \)), the physical meaning of which is that it determines the minimum sequence of \( \nu \) repeating units in the chain, passing as a whole from the crystallite to the minimized state of the statistical coil in the melt [13], was carried out according to the formula

\[ \nu = 2R(T_{max})/\Delta T\Delta H^0 \]

where \( R \) stands for gas constant. The dimensionless parameter is expressed by the number of CH₂ groups in the trans-region of the polymer chain, simultaneously participating in the melting act. When \( \nu \) is multiplied by the length of the C–C single bond, this parameter \( L = \nu h \) (\( h = 0.124 \) nm) can be compared with the parameters of the supramolecular structure, including the dimensions of the lamellar formations. The thickness of the lamellar crystals known to be of the order of 21 nm [14].
2.3.4. Fourier Transform Infrared Spectroscopy (FTIR)

IR studies were performed using a Nicolet iS10 FTIR spectrometer (Thermo Scientific, USA) by the method of impaired total internal reflection on a diamond crystal in the frequency range of 4000-400 cm$^{-1}$. Spectra analysis has been made using average function of apodization of Norton-Bearer and Merz method for phase correction. The degree of crystallinity $X_{ir}$ in UHMWPE was determined using the ratio of optical densities of absorption bands of the crystalline and amorphous phases (730 cm$^{-1}$ and 720 cm$^{-1}$ respectively $[15])$

$$X_{ir} = \frac{D_k}{D_a},$$

where $D_k$ and $D_a$ are the optical density of the absorption bands of the crystalline and amorphous phases, respectively.

3. Experimental results and discussion

X-ray diffraction pattern of initial UHMWPE powder shown on figure 1a clearly indicate the semicrystalline structure for this type of polymer. Several peaks corresponding to orthorhombic structure (Oh) at $2\theta$ approximately 21.5°, corresponding to (110) plane and $d$ spacing of 4.13 Å, and at 23.9° corresponding to (200) plane and $d$ spacing of 3.72 Å on the broad halo of amorphous phase are most evident. A weak intensity of the monoclinic (110) peak (M) at $d$ spacing of approximately 4.55 Å or a Cu $K\alpha$ diffraction 2$\theta$ of approximately 19.5° is also present. The amorphous phase in UHMWPE is a collection of entangled disordered chains. The crystalline region is a collection of chains that are fully organized into an orthorhombic lattice. The orthorhombic cell in UHMWPE is most common, each of its axes having a different length while the angles made by adjoining faces are all 90° $[5]$. Monoclinic is a metastable phase formed from orthorhombic cells under elongation and deformation conditions $[16]$. It may be present to a small extent in commercial samples, from 5 to 10% $[17]$. Temperatures in excess of 60-70°C cause it to revert to the orthorhombic form $[5]$.

Commercial B$_4$C powder (figure 1b) in addition to the main phase of hexagonal structure with the parameters $a = 5.600$ Å and $c = 12.086$ Å contained impurity (9-15%) of boron carbide with other stoichiometry like boron carbide with variable structure corresponds to $B_{10.5}C - B_{4.0}C$. Comparing the X-ray diffraction patterns of an initial UHMWPE/B$_4$C composite with irradiated UHMWPE/B$_4$C (figure 2) one we didn’t reveal any differences in phase compositions. The main phase of the material was a boron carbide but because the very high hardness of B$_4$C the additional amount of iron containing phase ($\alpha$-Fe(C)) has been detected on XRD pattern as a result of grind from the walls of the mill.

The DSC heating and cooling curves of the composite samples irradiated with different dose are displayed in figure 3. The melting peak area of the DSC curves increases with the decrease of the cooling rate due to the higher crystalline content of the UHMWPE. This behavior can be better observed in Table 1, where the melting enthalpy $\Delta H$ (or melting peak area) is used to obtain the crystallinity percentage of UHMWP/B$_4$C composites via dose value.

In addition to the alteration in the area, two other differences in the DSC-curves observed. Firstly, it is observed that the melting temperature changes (increases) with the dose, which indicates that the solid polymer has better ordered crystallites. Secondly, composite initial state consisted of several sub-molecular structures with slightly different melting temperature. This structure was formed during mechanical activation of UHMWPE with B$_4$C. Several steps of melting observed in the DSC curves suggesting the presence of several different ordering of the crystallites correlate with XRD data according to which stable and metastable crystalline polymer phases and amorphous one have been determined. Cooling of the sample with the same rate leads to the merging of the maxima into one as a result of the transformation of the metastable phase and return to the equilibrium state.

After electron irradiation there is only a single broad peak with the temperature maximum around 142°C. It means that irradiation stimulated transformation of mechanically synthesized metastable state of the polymer to the another one, changing its sub-molecular structure.

DSC curve for the sample after highest irradiation dose has a completely different profile (figure 3f). The appearance of the several maxima in that case may be the indicator of polymer structure degradation and stitching. As seen from the result of calculation (Table 1) the value of polymer crystallinity is increasing.
Figure 1. XRD patterns: $a$ — initial UHMWPE; $b$ — $B_4C$ initial; $c$, $d$ — MA 50UHMWPE.

Figure 2. XRD patterns of MA composites: $a$ — initial 50UHMWPE/50$B_4C$; $b$ — 5 s irradiated 50UHMWPE/50$B_4C$; $c$ — 15 s irradiated 50UHMWPE/50$B_4C$; $d$ — initial 30UHMWPE/70$B_4C$; $e$ — 30 s irradiated 30UHMWPE/70$B_4C$; $f$ — 90 s irradiated 30UHMWPE/70$B_4C$.

Table 1. The results of DSC analysis of samples. $T_{onset}$, $T_{max}$, $T_{end}$ — the beginning, maxima and the end temperature of melting process, $\Delta H$ — melting enthalpy, $\nu$ — parameter of intra-chain cooperativity of melting, $\chi_{ir}$ — crystallinity by DSC, $X_{ir}$ — crystallinity by IR.

| Sample | Irradiation time | Dose, $10^{14}$ cm$^{-2}$ | $T_{onset}$, $^\circ$C | $T_{max}$, $^\circ$C | $T_{end}$, $^\circ$C | $\Delta H$, $^\circ$C | $\nu$ | $L$ | $\chi_{ir}$, % | $X_{ir}$, % |
|--------|-----------------|--------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------|-----|----------------|----------------|
| 50/50  | 0               | 0                        | 109                     | 143                     | 169                     | 60                      | 180   | 22  | 73             | 78             |
|        | 5 s             | 0.443                    | 126                     | 142                     | 163                     | 37                      | 300   | 37  | 76             | 80             |
|        | 30 s            | 2.66                     | 128                     | 140                     | 163                     | 35                      | 310   | 38  | 75             | 79             |
| 30/70  | 0               | 0                        | 109                     | 143                     | 169                     | 60                      | 200   | 24  | 72             | 63             |
|        | 15 s            | 1.33                     | 126                     | 142                     | 163                     | 37                      | 310   | 38  | 85             | 64             |
|        | 90 s            | 7.97                     | 130                     | 156                     | 170                     | 40                      | 340   | 42  | 90             | 67             |

An extremely informative method for identifying the effects of polymer degradation, the appearance of radicals and oxidation is IR-spectroscopy. The features of the IR-spectra reflect the effects of irradiation on the structural state. FTIR spectroscopy estimates the presence and the amount of double bonds and of oxidation products in a polymer. The IR spectrum of the initial UHMWPE (figure 4) in general has specific vibration characteristics of the molecules in the amorphous-crystalline state with absorption bands (2913 cm$^{-1}$ and 2846 cm$^{-1}$), responsible for the symmetric and
asymmetric stretching vibrations C–H, (1472 cm⁻¹ and 1463 cm⁻¹), responsible for the deformation vibrations C–H, and bands corresponding to pendulum oscillations of CH₂-groups (730 cm⁻¹ and 720 cm⁻¹) the trans segments only in the crystalline phase. The 720 cm⁻¹ band is complex and corresponds to the pendulum oscillations of the CH₂ groups in the amorphous-crystalline regions.

Depending on the structure of UHMWPE in the range of 1450-1475 cm⁻¹, the absorption bands of the methylene groups of the corresponding crystalline, intermediate, and amorphous parts of polyethylene can be identified as follows: 1473 and 1462 cm⁻¹ — δ-vibrations of the trans-methylene groups with two different types of symmetry in the crystalline region; 1471, 1468.5 and 1464 cm⁻¹ are assigned to bands of mixed δ oscillations of gauche and trans-methylene groups in the intermediate region; 1466 cm⁻¹ are assigned to the band of δ vibrations of gauche methylene groups and 1456 cm⁻¹ — asymmetric deformation vibrations of methyl groups in the amorphous region [18].

The influence of ionizing radiation on ultra-high molecular weight polyethylene (UHMWPE) should rise to both the formation of radicals and of stable products [19]. The primary effect is the random scissioning of C–C and C–H bonds. The scissioning of a C–H bond should give vinylene double bonds, trans-vinylene double bonds, H-radicals, and secondary alkyl macroradicals in both the crystalline and in the amorphous phase of the polymer. The trans-vinylene yield can be quantified using infrared spectroscopy by monitoring the absorbance band at 965 cm⁻¹.

Typical peaks of boron carbide B₄C lie in the wavenumber region of 1600–700 cm⁻¹ [20]. So, the main frequencies of boron carbide are: 1560 cm⁻¹ (νa C–B–C), 1430 cm⁻¹, 1058 (νa C–B₃) cm⁻¹, 946 (νs C–B₃) cm⁻¹, 866, 837 and 695 cm⁻¹ (ν₁ B₂). The carbon content of the carbide affects the position of the absorption bands of the C–B bond. The shift of the peaks to the low-frequency region is due to a decrease in the amount of carbon in boron carbide and the appearance of a phase enriched in boron B₆.5C. The band ~1560 cm⁻¹ is attributed to asymmetric stretching vibrations νa C–B–C in the structure of compound B₄.3C, and the appearance of the band ~1450 cm⁻¹ takes place in the more

![Figure 3. DSC heating and cooling curves for UHWMPE (a), mechanosynthesized UHMWPE/B₄C composite (b), 5 s electron irradiated UHMWPE/B₄C composite (c), 15 s irradiated composite (d) and 90 s irradiated composite (e).](image-url)
boron-rich compositions $\text{B}_6\text{C}$ as new modes arise during stretching and bending of bonds that contain a carbon atom in the central mode of the B–C–B or C–C–C [8].

Figure 4. IR-spectra of MA 50UHMWPE/50B$_4$C composite ($a$, $b$) in initial state ($1$), irradiated with 2 MeV electrons in duration 5 s ($2$); 15 s ($3$); MA 30UHMWPE/70B$_4$C composite ($c$, $d$) in initial state ($1$) and irradiated in duration of 30 s ($2$) and 90 s ($3$).

Figure 4 shows the absorbance spectra of the irradiated 50UHMWPE/50B$_4$C and 30UHMWPE/70B$_4$C. With an increase in the duration of irradiation of samples the absorption bands appear in the range of 3500–3800 cm$^{-1}$, which are responsible for the vibrations of hydroxyl OH$^-$ groups, that may indicate an increase in their adsorption capacity. Significant changes in the structure of the polymer and carbide do not occur, as seen from the figure for studied mutual boron carbide and UHMWPE composite concentrations and irradiation dose for a duration of up to 90 s. At irradiation dose obtained by the sample at 90 s peak at the 965 cm$^{-1}$ is clearly present indicating the trans-vinylene double bonds yield.

Calculation of the UHMWPE crystallinity $X_c$ from the IR-spectra analysis (Table 1) let us conclude that its crystallinity degree is slightly smaller in composite with higher B$_4$C content. Then, the irradiation dose increase also promotes an increase in the UHMWPE crystallinity degree. That, presumably, is caused by stitching processes. Increasing crystallinity means increasing density.

The SEM images shown in the figures $5a$-$d$ demonstrate the morphological features of the studied samples. Boron carbide particles have a pronounced interface with the polymer, indicating that the formation of sufficiently strong bonds between the various components of the powder composition does not occur. These SEM images of polymer part of the composite (figures $5e$-$g$) appear very similar in structure morphology up to high irradiation dose (figure $5h$). However, looking closely at the fracture image of figure $5h$ the structure becomes more damaged due to effect of crosslinking and shows different morphologies with stretched molecules and pore cracks in different regions of the samples.
Figure 5. SEM images with different resolutions of MA 50UHMWPE/50B4C composite (a) irradiated 5 s (b) and 30 s (c) and MA 30UHMWPE/70B4C irradiated 90 s (d) and corresponding polymer part of the samples (e–h)

4. Conclusion
The dose influence of 2 MeV electron irradiation on the structure of new mechanically synthesized composite material have been investigated. The experimental data obtained with X-ray diffraction, SEM, differential scanning calorimetry and FTIR spectroscopy let us to reveal the relatively good resistance of material to electron irradiation at the air up to ~8·10^{14} cm^{-2}. Higher doses promote the appearing of signs of UHMWPE structure transformation to crosslinked network structure with an increase in the polymer crystallinity degree.

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