



Influence of ultrasonic treatment on mechanical and electro-physical characteristics of UHMWPE/MWCNT composites

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ABSTRACT

The influence of ultrasonic treatment on the strength and dielectric properties of composites based on ultra-high molecular weight polyethylene (UHMWPE) and multi-walled carbon nanotubes (MWCNT) is studied. It is revealed that the ultrasonic treatment of composite melt at 130 °C results in the uniform distribution of nanotubes in the UHMWPE matrix, an increase in the degree of composite crystallinity by 10%, an increase in abrasion resistance by 37%, an increase in elongation at rupture by a factor of 2. The change in the physical and mechanical properties of the composite is caused by the change in the polymer matrix structure, taking place as a result of ultrasonic action, and does not depend on the presence of nanotubes in the polymer matrix.

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1. Introduction

As science and technology are developing, more and more polymers appear that can successfully replace metals. One of these polymers is ultra-high molecular weight polyethylene (UHMWPE). It is widely used in various engineering products, medicine, and agriculture [1–3]. This material has high wear resistance, resistance to shock loads and to most aggressive environments; ice and wet bulk materials do not freeze to it. The world production of UHMWPE is constantly growing, and any improvement in certain properties will inevitably extend its application range. UHMWPE is unique in its ability to maintain toughness even at ultralow temperatures. This is urgent in connection with the development of the Northern territories. The most important property of UHMWPE is radio transparency in the entire range of microwave radiation. Due to this, UHMWPE can be used as a protective shield for radar and communication antennas. Based on UHMWPE, microwave filters can be created. For this purpose, composites with a specific arrangement of conductive particles in them are necessary.

The best studied way to change the properties of UHMWPE is the introduction of various fillers into UHMWPE [4–8]. However, the influence of the introduced particles on strength characteristics is ambiguous [5–7].

A composite with high dielectric permittivity (DP) can be obtained depending on DP of the introduced particles and their concentration [9–11]. Introducing electrically conductive carbon nanotubes (CNTs) into polymers, it is possible to obtain a composite with high conductivity and large dielectric loss tangent, as well as a dielectric with an increased dielectric constant and a low dielectric loss tangent [12–14]. To increase the strength properties of polymer composite, a high interphase interaction between the matrix and nanotubes and the uniform distribution of CNTs in the bulk are required [15]. Otherwise, CNT clusters will become stress concentrators that degrade the material strength. It remains unknown why the interphase interaction between hydrophobic UHMWPE and hydrophilic multi-walled carbon nanotubes (MWCNT) leads to composite strengthening. No results of any successful production of UHMWPE and MWCNT composites with high strength properties, high DP and low dielectric losses are known. Among the reported methods for producing UHMWPE-based composites with nanoparticle inclusions, the method of components

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mixing in a solution is the most versatile and effective one [16]. The degree of uniformity of MWCNT distribution in UHMWPE matrix can be determined by DP value and dielectric loss tangent ($tg\delta$) in the microwave radiation range.

The objective of this work is to study the influence of ultrasonic action on the strength, electrical and physical properties of UHMWPE composite with MWCNT.

2. Experiments

The samples of initial UHMWPE and composites with the addition of 1% MWCNT were produced by introducing MWCNT into UHMWPE and mixing the components in xylene at 90 °C in an AGO-2M high-energy planetary mill at the rotation speed of 1000 rpm for 10 min (composite UHMWPE/MWCNT 90 °C); and by ultrasonic treatment (US) in the Volna generator with the intensity of 100 W/cm² for 20 min at 130 °C (sample UHMWPE/MWCNT 130 °C and sample UHMWPE/US 130 °C without MWCNT). After filtration and vacuum drying, the samples for testing were prepared by hot pressing at a pressure of 6 MPa and temperature of 160 °C.

The electrical and physical properties were studied in the frequency range from 100 Hz to 100 MHz by means of impedance measurement using the E5061B vector network analyzer (Agilent Technology) [17]. For measurements, thin indium electrodes were used with a negligible transition resistance. The studied samples had the shape of disks with a diameter of 16 mm and a thickness of 1 mm.

The tensile strength characteristics of the material were measured with an Inspekt Table Blue 5kN installation from Hegewald & Peschke (Germany). The tensile rate was 500 mm/min. The samples were shaped as strips 60 × 3 × 2 mm in size. At least three measurements were carried out for each type of material; the results were averaged.

The composites were tested for abrasion resistance when sliding over a renewable surface using the MZ-4060 tester according to State Standard 23509–79. Sandpaper with a grain size of 160–200 μm was used as an abrasive. The normal force pressing the sample to the drum was 10 MPa. The mass loss during abrasion was determined by the difference in the sample weight before and after testing. Weighing accuracy was ± 1 mg. The relative abrasion (Δ) of the composites was determined according to the formula

$$\Delta = \frac{(m_1 - m_2)}{m_1} 100\%, \quad (1)$$

where m_1 is the mass loss when the original UHMWPE is worn; m_2 is the mass loss when the composite is worn. To determine the state of the sandpaper abrasive ability, control testing of a pure UHMWPE sample was performed every five tests. If the mass loss was reduced by more than 10%, the sandpaper was replaced with a new one. The test samples were 16 mm in diameter and 6 ± 0.5 mm thick.

The surface of the samples after the abrasion test was examined using Hitachi TM3000 Benchtop Scanning Electron Microscope (Japan). Differential scanning calorimetry (DSC) of the test samples was performed with a 204 F1 Phoenix device (“Netzsch”, Germany) in accordance with the ASTM d3418–15 method in argon (flow rate

30 ml/min) in closed aluminum crucibles. The samples were removed using the melting-crystallization-melting program in the temperature range from 25 °C to 160 °C at a rate of 10 °C/min. Melting temperatures and enthalpies were determined from the data of the second melting. The degree of polyethylene crystallinity X was calculated according to the formula

$$X = \frac{\Delta H_m}{\Delta H_0} 100\% \quad (2)$$

where ΔH_m is the melting enthalpy of the sample calculated from the area under the endothermic melting peak, ΔH_0 is the melting enthalpy of the polymer with a crystallinity degree of 100% [18]. The structure of the samples was studied by means of X-ray Powder Diffraction (XRD) at Station 2 of the Siberian Synchrotron and Terahertz Radiation Center. Measurements were made in the Bragg-Bertrand geometry, using a weakly divergent X-ray beam and a crystal analyzer, which made it possible to exclude peak broadening and displacement caused by sample geometry. The X-ray wavelength used was 1.54 Å, with a scan step of 0.02°.

3. Results and discussion

The UHMWPE/MWCNT 130 °C composite has low conductivity equal to $3 \cdot 10^{-9}$ Sm/m, increased dielectric constant ($\epsilon = 4.5$) compared to pure UHMWPE ($\epsilon = 2.3$), and small dielectric loss ($tg = 10^{-2}$), which is independent of the frequency, therefore the frequency dependence is not shown. Low conductivity indicates that the material does not have a through conductive network of contacts. The increased DP and low dielectric loss in this composite can be explained by the polarization of uniformly distributed small clusters and individual MWCNTs that are not in contact with each other under the influence of external electric field. The conductivity of UHMWPE/MWCNT 90 °C is higher by seven orders of magnitude, and it has high $tg\delta$. This points to the presence of large aggregates of MWCNT in the matrix.

Table 1 presents the characteristics of the samples, and Fig. 1 shows the curves plotted in the coordinates of the nominal stress (σ) versus relative tensile elongation (A) obtained by stretching the samples of UHMWPE, UHMWPE/MWCNT 130 °C and UHMWPE/US 130 °C. The curves of the UHMWPE/MWCNT 90 °C sample and initial UHMWPE are similar.

One can see in Fig. 1 that the stress-strain diagram of initial UHMWPE is typical for this kind of polyethylene, with the areas of elastic deformation and deformation strengthening, characterized by an increase in stress with an increase in elongation. The original UHMWPE has the tensile strength of 30 MPa, elastic modulus of 257 MPa, and maximum elongation at break of 288%. The distinctive property of UHMWPE/MWCNT 90 °C composite obtained by mixing in the AGO-2M high-energy planetary mill (Table 1) is reduced abrasion, which is typical for the case when MWCNT particles are introduced into UHMWPE [19]. UHMWPE/MWCNT 130 °C and UHMWPE/US 130 °C composites are characterized by high plasticity (maximum elongation of 700 and 710%) and increased modulus of elasticity of 308 and 300 MPa, respectively.

In this case, UHMWPE/US 130 °C, subjected to ultrasonic treatment without MWCNTs, retains the tensile strength of initial polymer, 29 MPa. In contrast, the UHMWPE/MWCNT 130 °C composite

Table 1
Characteristics of the samples.

No	Sample	Modulus of elasticity, MPa	σ , MPa	Conductivity, Sm/m	A, %	Δ , %	$tg\delta$	ϵ
1	UHMWPE	257	30	–	288	–	10^{-4}	2.3
2	UHMWPE/MWCNT 130 °C	308	24	$3 \cdot 10^{-9}$	702	37	0.01	4.5
3	UHMWPE/US 130 °C	300	29	–	710	37	10^{-4}	2.3
4	UHMWPE/MWCNT 90 °C	264	30	$5 \cdot 10^{-2}$	270	5	>1	–

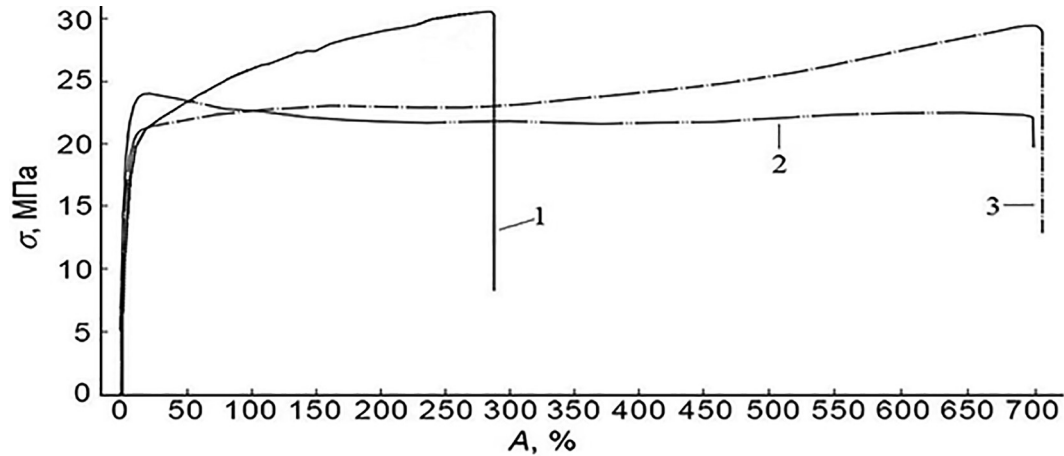


Fig. 1. Dependences of nominal stress on the relative tensile elongation for UHMWPE (1); UHMWPE/US 130 °C (3); UHMWPE/MWCNT 130 °C (2).

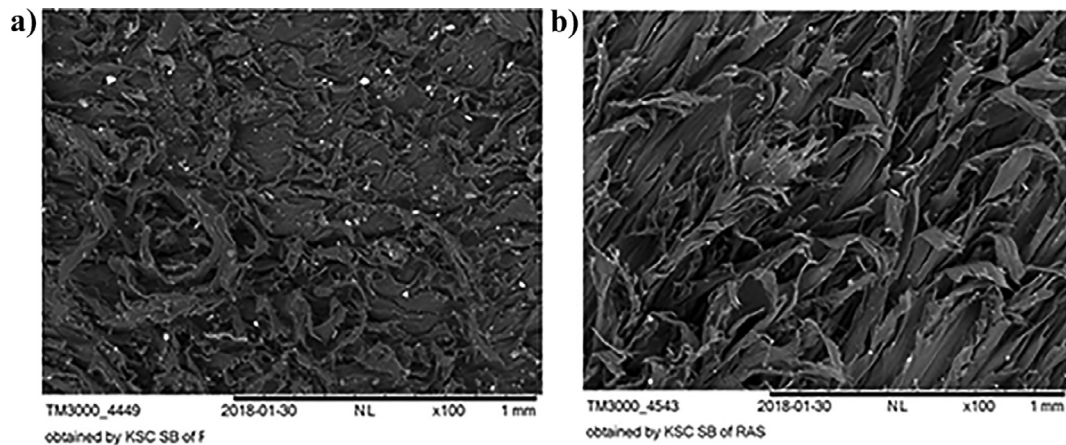


Fig. 2. The friction surface of a) sample of initial UHMWPE, b) UHMWPE/US 130 °C.

has a pronounced yield strength at the stress of 24 MPa, after which the deformation stress decreases to 22 MPa, and then the specimen deforms at a constant stress to break.

The surfaces of UHMWPE/MWCNT 130 °C and UHMWPE/US 130 °C samples after the wear resistance test are characterized by pronounced fibrous structure in contrast to the friction surfaces of initial UHMWPE (Fig. 2).

The abrasion resistance of UHMWPE/MWCNT 130 °C and UHMWPE/US 130 °C is higher by 37% compared to the initial UHMWPE (Table 1).

According to DSC data, the melting temperature of the initial UHMWPE sample and UHMWPE/MWCNT 90 °C sample is equal to 139 °C, and the degree of crystallinity is 46%. As for the composite UHMWPE/MWCNT 130 °C and the UHMWPE/US 130 °C sample, the melting temperature is equal to 142 °C, and the degree of crystallinity is 56%.

According to the results of XRD studies, the degree of crystallinity for initial UHMWPE is 70%, and for the materials UHMWPE/MWCNT 130 °C and UHMWPE/US 130 °C it is 80%. Significant difference in the degree of crystallinity determined by means of DSC and XRD require a separate study. It is important that both methods confirm a 10% increase in the degree of crystallinity after ultrasound treatment of UHMWPE at 130 °C in a solvent. According to XRD data, the regions of coherent scattering increased from 350 Å for the initial UHMWPE to 430 Å for the materials UHMWPE/MWCNT 130 °C and UHMWPE/US 130 °C.

The authors of [20] came to similar conclusions, according to which the composites based on polyethylene with the addition of MWNT obtained by *in situ* polymerization were studied by means of XRD. Thus, the factor determining the physical and mechanical characteristics of the UHMWPE/MWCNT 130 °C composite is not the presence of nanotubes in it, but the ultrasonic effect used in the process of its preparation. Most likely, the ultrasonic effect on the UHMWPE solution at the temperature of 130 °C leads to the violation of van der Waals bonds between the individual polymer chains, which are distributed in the solvent in the form of individual chains or loosely bound bunches. When the solution is cooled, free polymer chains form energetically favorable crystalline phases with lower potential energy, which was recorded by means of DSC and XRD. At the same time, the size of structural formations increases, which results in an increase in the elastic modulus of materials. It can be suggested that the amorphous phase of the polymer is less confused than the original UHMWPE, which explains the increased ductility of the materials obtained at 130 °C. An increase in wear resistance can also be attributed to a decrease in interweaving of polymer chains in the material, which reduces the ability of the abrasive particles of sandpaper used in abrasion testing to tear the fragments out of the sample. As a result, the material surface after abrasion acquires a fibrous textured structure (Fig. 2b), in contrast to the surface of pure UHMWPE (Fig. 2a). The introduction of MWCNT into UHMWPE at the temperature of 130 °C reduces the tensile strength of the

composite (Fig. 1). Apparently, there is no reliable connection between UHMWPE and MWCNT, which are the defects distributed in the polymer matrix.

4. Conclusions

Ultrasonic treatment of UHMWPE in xylene with the intensity of 100 W/cm² at 130 °C leads to the change in the supramolecular structure of the polymer. As a result, UHMWPE structure with increased crystallinity, increased abrasion resistance, and 2-fold elongation at break is formed. Ultrasonic treatment of UHMWPE with 1% MWCNT in xylene melt leads to the uniform distribution of MWCNT in UHMWPE matrix. The resulting composite has the increased dielectric constant with low dielectric loss. At the same time, MWCNT particles are defects in UHMWPE matrix reducing the polymer strength.

CRedit authorship contribution statement

I.A. Markevich: Investigation. **G.Ye. Selyutin:** Conceptualization, Supervision. **V.A. Poluboyarov:** Writing - review & editing. **N.A. Drokin:** Investigation. **A.G. Selyutin:** Investigation. **M.A. Matzko:** Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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