



Reinforcement of bulk ultrahigh molecular weight polyethylene by fluorinated carbon nanotubes insertion followed by hot pressing and orientation stretching



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ABSTRACT

The paper is devoted to reinforcement of bulk ultrahigh molecular weight polyethylene. Multi-stage process including insertion of fluorinated carbon nanotubes in ultrahigh molecular weight polyethylene matrix followed by hot pressing and orientation pulling at room temperature was applied. It was shown that fluorinated CNT are more efficient in reinforcement than pristine CNT. Below 250 °C fluorinated CNT did not influence composite thermal stability. SEM study confirmed that fluorinated CNT can act as crystallization centers and fluorinated CNT exhibit improved adhesion to polymer matrix as compared with pristine CNT. Composites with inserted fluorinated CNT have a block structure with high concentration of nanofibrils. The applied procedure resulted in an increase of the composite tensile strength from 22 to 132 MPa or by a factor of 6 as compared with pristine bulk UHMWPE. Previously reported in available literature tensile strength values of reinforced bulk ultrahigh molecular weight polyethylene did not exceed 40 MPa.

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1. Introduction

At present time carbon nanomaterials especially single-walled (SWCNT) and multi-walled (MWCNT) carbon nanotubes are widely used as fillers to reinforce polymer composites [1]. But in many cases low polarity of the carbon nanomaterial surface and also polymer matrix adhesion interaction between fillers and polymer matrix is too low to provide marked reinforcement [2–4]. Moreover, carbon nanomaterials tend to agglomerate in a polymer matrix [5]. To increase surface energy and adhesion properties fillers should be modified. A wide variety of modification methods are applied to modify carbon nanomaterials: plasma/plasma chemical treatment, chemical grafting of various monomers, acid

treatment etc [1–5]. One of the most prospective methods is the direct fluorination, i.e. treatment with gaseous fluorine at elevated temperature [6–11]. For the case of thermoplastic polymers (polyethylene oxide, polyamide-6 and polypropylene) insertion of fluorinated SWCNT into polymer matrix resulted in a marked increase of the tensile strength and modulus [12–14]. It was shown that fluorinated CNT are very effective in reinforcement of epoxy composites [11].

In our research we have focused our attention on the bulk ultrahigh molecular weight polyethylene (UHMWPE). This polymer possesses excellent mechanical properties being highly oriented. Highly oriented fibers tensile strength and modulus can reach more than 4 GPa and 100 GPa values respectively [15]. Oriented UHMWPA thin ribbons tensile strength and modulus can reach 900–1600 MPa and 30–140 GPa respectively [16,17] and can be used in medicine, anti-ballistic and high-modulus composite applications, in fabrication of defense cloths and ropes, for composites reinforcement etc. [18,19].

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In the present research we have fabricated reinforced bulk oriented nanocomposite based on UHMWPE. We have demonstrated that reinforcement procedure including fluorinated CNT addition to UHMWPE matrix accompanied with UHMWPE orientation resulted in a very marked composite reinforcement. Those composites must have the oriented structure but to exist as bulk materials (neither fibers nor thin ribbons). Also bulk oriented reinforced composites can be converted into a final polymer product. Polymer matrix orientation favors filler orientation what is very important for the case of carbon nanotubes with high length to diameter ratio [20]. Nanotubes orientation can improve a set of polymer composites properties [21–23]. But insertion of dispersed fillers in an isotropic UHMWPE resulted in a moderate reinforcement only. Insertion of 3 weight % nano- and microsize Al_2O_3 spheres into UHMWPE resulted in the tensile strength and modulus increase up to 40 and 1530 MPa respectively [24]. Addition of 5 weight % of MWCNT resulted in UHMWPE tensile strength and modulus increase up to 33 and 1370 MPa respectively [25]. Addition of 0.5 weight % of thermoexpanded graphite and 2 weight % of CNT into UHMWPE matrix resulted in a tensile strength increase to 22 MPa [26]. On the contrary insertion of 0.1 ... 10 weight % of MWCNT into UHMWPE resulted in a tensile strength monotonic drop from 21 to 12 MPa [27]. The review of available literature data indicated that nano-fillers insertion into UHMWPE can increase the tensile strength not more than up to 40 MPa.

2. Experimental

2.1. Materials and testing procedure

Multi-walled carbon nanotubes “Taunit-M” with internal and external diameters equal to 4–8 nm and 8–15 nm respectively were purchased from “Nanotechcenter Ltd” (Tambov, Russia). Fluorine had less than 0.1 volume % of admixtures. UHMWPE (GUR 4120 type) with molecular weight $5 \cdot 10^6$ was purchased from Ticona GmbH. FTIR spectrometer FT-02 (Lumex Ltd, Russia) was used to measure IR spectra of KBr pellets with inserted CNT. 1000 scans at 4 cm^{-1} resolution were collected to measure a single spectrum over $4000\text{--}400 \text{ cm}^{-1}$ spectral range. Influence of fluorination on the CNT surface chemical composition was studied by XPS spectrometer PHI 5500 ESCA (Perkin Elmer). Texture of composite materials was studied by scanning electron microscope JEOL JSM-6610LV at accelerating potential 20 kV. To avoid charge accumulation polymer surface was coated with Pt layer several nm in thickness. TA Instruments Q600 was used to study thermal stability in air flow at heating rate $10 \text{ }^\circ\text{C}/\text{min}$. Tensile strength was measured by Zwick equipment at $10 \text{ mm}/\text{min}$ loading rate according to ASTM D638. The samples were dumbbell-shaped. At least 5 measurements were used to get tensile strength for a single composite composition.

2.2. CNT fluorination and composites fabrication

CNT fluorination has been carried out in a closed reaction vessel at fluorine pressure 0.7–0.8 bar and $150 \text{ }^\circ\text{C}$ temperature during 2 h. CNT were inserted in UHMWPE by solid-state mixing in a ball mill [28,29]. CNT were mixed with UHMWPE in a high-energy planetary ball mill APF-3 in 900 ml steel vials during 45 min. Balls diameter was 7–9.5 mm and rotation speed was equal to 450 rpm. Weight of UHMWPE was close to 60 g. Amount of CNT in a composite was varied over 0.1 to 1 weight %. In principle fluorinated CNT could be defluorinated during mixture. The evolved fluorine can be detected by smell because fluorine can be detected when its concentration in air is higher than 1 ppm. Amount of fluorinated CNT in a ball mill vial (900 ml in volume) was 0.06–0.6 g so fluorine could be

detected in case of $\sim 10^{-5}$ g fluorinated CNT defluorination (below we have shown that fluorinated CNT chemical composition was as follows: C:O:F = 78:1.3:20.7). But we did not detect any smell inside the ball mill vial so the amount of defluorinated CNT was definitely smaller than $\sim 10^{-2}\text{--}10^{-3}\%$ with respect to the CNT amount.

Formation of oriented bulk nanocomposites consisted of several stages. At first mixture of UHMWPE and CNT powders were pressed at $180 \text{ }^\circ\text{C}$ and 25 MPa pressure and stored 30 min at $180 \text{ }^\circ\text{C}$. At the second stage pressed composites were stretched at room temperature to provide oriented structure. At the final stage the oriented samples were pressed at $130 \text{ }^\circ\text{C}$ under 50 MPa pressure and stored during 30 min at $130 \text{ }^\circ\text{C}$ to fabricate samples for testing.

3. Results and discussion

3.1. FTIR spectroscopy

FTIR spectra of virgin and fluorinated CNT are shown in the Fig. 1. Spectra were corrected with respect to KBr absorption. Fluorination of CNT resulted in a formation of a wide diffuse band over $1300\text{--}900 \text{ cm}^{-1}$ with maximum at $\sim 1200 \text{ cm}^{-1}$ which is due to an absorption of covalent C-F_x bonds and in an increase of the $1720\text{--}1700 \text{ cm}^{-1}$ band which can be attributed to C=O groups formation due to an oxygen admixture in used fluorine [7,8,24].

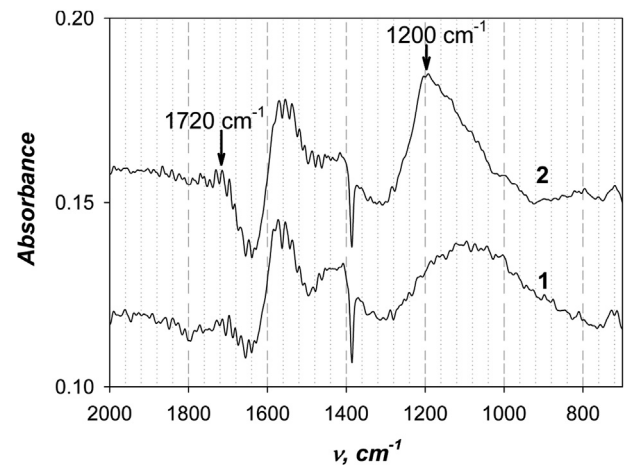


Fig. 1. Spectra of virgin (1) and fluorinated (2) CNT.

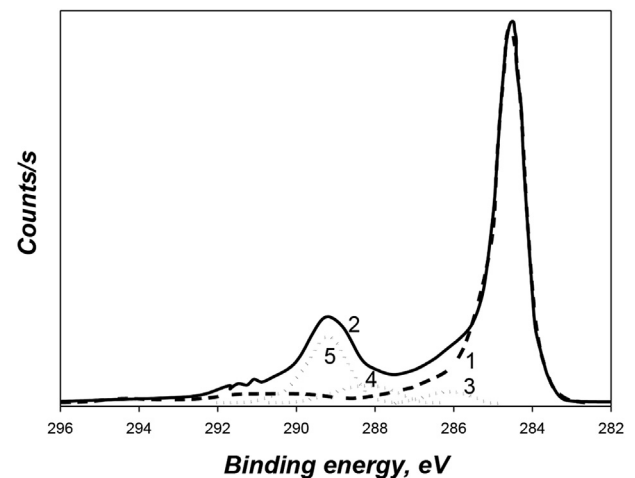


Fig. 2. XPS spectra of pristine (1, dashed line) and fluorinated at $150 \text{ }^\circ\text{C}$ (2, solid line) CNT. 3, 4 and 5 – fitted bands for fluorinated CNT.

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