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Bulk oriented nanocomposites of ultrahigh molecular weight polyethylene reinforced with fluorinated multiwalled carbon nanotubes with nanofibrillar structure

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ABSTRACT

Multi-stage process including grinding of fluorinated multi-walled carbon nanotubes (MWCNT) and ultrahigh molecular weight polyethylene (UHMWPE) mixture in a ball mill followed by hot pressing and orientation stretching resulted in UHMWPE tensile strength increase from 21 to 132 MPa or by a factor of 6.3 as compared with pristine bulk UHMWPE. Previously reported in literature tensile strength values of reinforced bulk UHMWPE did not exceed 40 MPa. Fluorinated MWCNT were more efficient in reinforcement than pristine ones. SEM study confirmed that fluorinated nanotubes can act as nucleation agents. Unique lamellar crystalline structure is formed onto the MWCNT surface which can be transformed into nanofibrillar structure under applied stress. Fluorinated MWCNT insertion resulted in an increase of nanofibrils amount due to a filler nucleation ability increase.

1. Introduction

Polymer materials are widely used in human life, medicine, industry, etc. But very often polymers have a lot of disadvantages such as insufficient strength, stiffness, creep and low usage temperature. To improve their properties supramolecular structure can be modified or reinforcing fillers can be used. Both traditional and especially developed methods are used to fabricate polymer based composites. Nowadays attention is paid to nanocomposites where nanosized fillers are applied.

The following factors should be taken into account to reach high mechanical properties when nanofillers are used:

(a) Uniform distribution of the nanofiller in the polymer matrix of a bulk sample will result in a composite physical and chemical properties uniformity over its volume (bulk) [1].
(b) Filler should not agglomerate inside the polymer bulk sample because it might act as stress concentrator [2].
(c) Fillers should be oriented. This factor is very important for fillers with large aspect ratio [3], e.g. carbon nanotubes [4–6].
(d) Interaction between fillers and polymer matrix should result in a composite supramolecular structure improvement. This process proceeds due to a crystalline phase formation on the nanofiller surface and results in a crystallinity degree increase [7,8]. The crystalline size and their growth orientation depend on the filler nature [9].
(e) Strong interfacial interaction between polymer matrix and filler surface can improve load transfer from matrix to reinforcing filler [1,10]. Adhesion can be due to a chemical bonding, mechanical interaction, electrostatic or Van-der-Waals forces.

Ultrahigh molecular weight polyethylene (UHMWPE) was used as a polymer matrix. UHMWPE exhibits very promising mechanical and tribological properties. The UHMWPE fibers tensile strength can exceed 4 GPa [11]. Coefficient of dry friction is around 0.08–0.12 [12–14]. Its wear resistance is the greatest among other thermoplastic polymers. UHMWPE is widely used to fabricate implants in medicine [15–19]. Unfortunately UHMWPE composites are difficult to fabricate because UHMWPE has no visco-liquid state

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and insertion of fillers into the melted UHMWPE is highly restricted. UHMWPE low polarity does not promote strong bonds with fillers. Also a very high molecular weight highly restricts polymer chains orientation.

Carbon nanotubes (CNT) are widely used to reinforce various polymer, metallic and ceramic composites [20–22]. Carbon nanotubes size is close to macromolecular dimensions, so formation of fiber–polymer matrix bonds can be facilitated. Nanotubes are very perspective for creation of oriented crystalline structure of semicrystalline polymers because of their high aspect ratio and oriented crystallization of a polymer on the fiber surface [4–6]. But usually CNT tends to agglomerate, so their surface should be functionalized prior to insertion into a polymer matrix. Two methods are usually used to improve CNT adhesion to a polymer matrix. The first method is a chemical modification via an attachment (preferably covalent bonding) of functional groups to the CNT surface. Fluorine, hydrogen, carboxylic and acidic groups can be attached to the CNT surface. Such modification can also improve the filler nucleation ability [1]. Formation of defects on the CNT surface and their ends can be considered as an another approach. Those sites have increased concentration of energy and become enhanced reactivity centers [23]. Disadvantage of that approach is a probable drop of CNT strength and hence drop of their reinforcing ability.

At present time we have found in available literature a limited amount of researches devoted to bulk UHMWPE reinforcement. Insertion of 3 wt% nano- and microsize Al_2O_3 spheres into UHMWPE resulted in the tensile strength and modulus increase up to 40 and 1530 MPa, respectively [16]. Addition of 5 wt% of MWCNTs resulted in UHMWPE tensile strength and modulus increase up to 33 and 1370 MPa, respectively [24]. Addition of 0.5 wt% of thermoexpanded graphite and 2 wt% of CNTs into a UHMWPE matrix resulted in a tensile strength increase up to 22 MPa [25]. On the contrary, insertion of 0.1…10 wt% of MWCNTs into UHMWPE resulted in a tensile strength monotonic drop from 21 to 12 MPa [26]. A review of available literature data indicated that nanofillers insertion into bulk UHMWPE can increase the tensile strength not more than to 40 MPa.

In this paper, we propose a novel method for producing bulk composites based on the use of the orientation of polymer matrix and fluorination of the reinforcing filler. This process leads to the formation of bulk nanocomposites with nanofibrils and increase in tensile strength in 6 times.

2. Experimental

UHMWPE (GUR 4120 type) with a molecular weight of 5×10^6 was purchased from Ticona Gmbh. Multi-walled carbon nanotubes “Taunit-M” were purchased from “Nanotechcenter Ltd” (Tambov, Russia). Their internal and external diameters were equal to 4–8 nm and 8–15 nm, respectively and length exceeded 2 μm. TEM image of virgin MWCNT is shown in the Fig. 1. MWCNT were treated by direct fluorination to increase surface polarity and decrease agglomeration. MWCNT fluorination has been carried out in a closed reaction vessel at fluorine pressure 0.7–0.8 bar at 150 °C during 2 h [27,28]. Fluorine had less than 0.1 vol% of admixtures. The direct fluorination was chosen as a functionalization method due to the following reasons. Fluorine will be covalently attached to carbon atoms and the MWCNT surface will become more polar as compared with pristine MWCNT. The paper authors have idea how to attach fluorine atoms to the MWCNT surface without its structure destruction. The direct fluorination is widely used in practice to make MWCNT surface more polar [29]. Fluorinated MWCNT can be well dispersed in liquid solvents and in a polymer matrix as we have shown in our paper [27]. In the same paper we have presented a literature review on efficiency of various nanomaterials used to reinforce epoxy composites together with our experimental data.

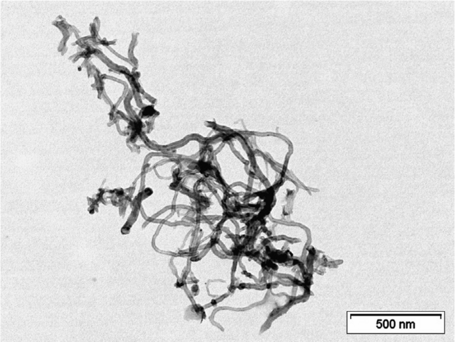

Fig. 1. TEM image of virgin MWCNT.

MWCNT 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 [30]. The concentration of MWCNT (virgin and fluorinated) in UHMWPE was equal to 0.1, 0.5 and 1 wt%.

Formation of oriented bulk nanocomposites consisted of several stages. At first, mixture of UHMWPE and CNT powders was pressed at 180 °C and 25 MPa pressure and stored during 30 min at 180 °C. Then composites were slowly cooled at constant pressure of 25 MPa. Monolithic isotropic nanocomposites were fabricated at this stage. Fabricated at this stage composite will be denoted as “isotropic nanocomposite”. At the second stage pressed composites were stretched at room temperature to provide oriented structure. The length of the composites was increased by 200% ($\lambda = 3$). Composite will be mentioned as “precursor of oriented nanocomposite”. At the final third stage the oriented samples were pressed in temperature range from $T_{\mathrm{m}}^{\mathrm{onset}} = 125$ °C (beginning of melting) to $T_{\mathrm{m}} = 132$ °C (maximum of melting peak), see Fig. 2, under 50 MPa pressure and stored during 30 min to fabricate samples for testing. The pressing pressure was increased up to 50 MPa in order to reduce the mobility of UHMWPE macromolecules and to prevent the loss of their oriented state. Those composites will be entitled “oriented nanocomposite”. The third stage was necessary for the formation of nanofibrillar structure in the oriented nanocomposites. Deviation from the specified temperature range during compression shown in Fig. 2, did not lead to a

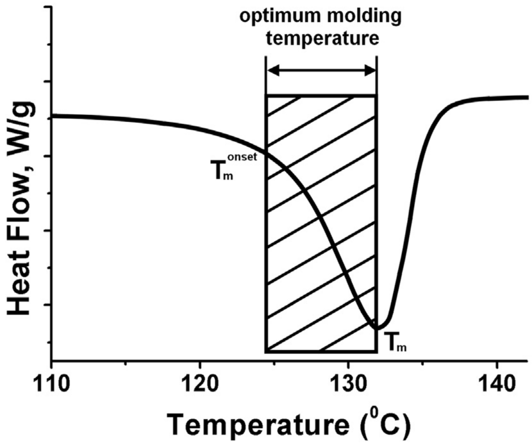

Fig. 2. DSC of precursor of oriented nanocomposite fabricated at the second stage. Dashed line indicates the optimum temperature range to transform the precursor of oriented nanocomposite fabricated at the second stage to the oriented nanocomposite.