Properties of Ultra High Molecular Weight Polyethylene Fibers After Ion Beam Treatment

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ABSTRACT: Ultrahigh molecular weight fibers were treated by low energy ion beam in a pulse regime. Results of infrared and WAXD analyses showed the change of both chemical structure and morphology of the fiber surface. Adhesion of the treated fiber surface to conventional binders appeared to be two times higher than that of untreated fiber. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1628–1633, 2011

Key words: polyethylene; fibers; irradiation; modification; infrared spectroscopy; functionalization; WAXS; morphology; composites; adhesion

INTRODUCTION

Gel-spun ultra high molecular weight polyethylene (UHMWPE) fiber is one of the most extensively studied materials due to its extremely high specific mechanical characteristics, such as tensile strength and modulus of elasticity[1] several times exceeding similar characteristics of steel and rigid chain polymer fibers. Moreover, low density, high water resistance, UV-irradiation resistance, and slow aging make the fiber in certain cases a more preferable filler for composite manufacturing than rigid chain polymer fibers.

UWMPE fiber found a wide application in various fields, for example, manufacturing of sporting equipment, cords, and ropes for shipbuilding, etc. However, there are very few successful attempts of producing of UWMPE fiber-based composites because of its low adhesion to conventional binders and rather low heat resistance, limiting its application as reinforcing filler in composites. Some surface modification techniques are known to be the way of increasing of wettability and surface energy and hence running ability of this material.[2]

Recently modification of polymer materials by ion beam surface treatment (IBST) has drawn increasing attention of the researchers. IBST induces structural changes in the surface layer of the polymer film, the depth of the modified layer, and its chemical composition being dependent on the treatment conditions and type of the ion.[3,4] For example, in Ref. [3] the number of crosslinks is supposed to be dependent on linear energy transformation (LET), ion energy and irradiation dose. It was shown that many operating characteristics, viz., surface conductivity, optical properties, adhesion, wear resistance, and biocompatibility,[5–8] of the polymer surface were modified as a result of IBST.

Some researchers tried to improve the surface properties of UHMWPE fibers by such procedures as chemical grafting,[9] acid etching,[10] corona discharge treatment,[11] plasma deposition,[12] and also high-energy laser and UV -irradiation treatment.[13] The aim of all these works was to increase adhesion of the fibers to different binders—methylmethacrylates, vinylester resins, etc.—and at the same time to retain their physical-mechanical characteristics. Modification is often connected with some difficulties—undesirable use of chemicals, disturbance of the fiber structure,[14] or ineffectiveness because of high crystallinity of initial polymer.[15]

As a rule, low beam current densities (0.05–5 A/cm^2)[16] are used for modification of the polymer materials to avoid heating of the sample. Pulse periodical regime allows high current density of the beam to be applied without a risk of thermal decomposition or total amorphization of the polymer material. This is especially important for polyethylene, as its melting temperature is rather low in comparison with rigid chain polymers, besides the use of the beam with high current density leads to the same modification degree in a minimal period of time.

There are numerous studies devoted to modification of the surface of UHMWPE prepared by

powder compaction which is applied as polymer implant in medicine, so the change in its tribological[17] and adhesion[18] properties and load bearing capacity[19] has been investigated. Also significant improvement in the surface hardness was observed for ion-implanted UHMWPE in the whole range of indentation depth.[20]

A number of attempts to create a composite based on modified UHMWPE fibers have been already made, for example, filament-wound composite consisting of "cold" plasma-treated PE fibers and epoxy matrix[4] and high strength fabric from UHMWPE Spectra 1000 fibers treated by gas-plasma prior to the composite lay up, the latter being tested for radiation shielding properties.[21] However, there is no technology which can be considered an optimal one from the point of view of adhesion improvement without the change of the ordered fiber structure.

So, the aim of the work was to study the chemical structure and morphology of UHMWPE fiber modified by ion beam treatment and estimate its potential application for composite manufacturing.

EXPERIMENTAL

Ion-beam modification was carried out using the ion source designed by the Institute of Electrophysics (the Ural Branch of Russian Academy of Sciences). The installation generates wide beams (within the range 100–200 cm^2) of low-energy ions of nitrogen, argon, and hydrocarbons; current density is 5 mA/cm^2, pulse frequency is 1 and 3 Hz, and pulse duration is 1 and 0.3 ms. The UHMWPE fiber (SK-60 DSM Dyneema) in the form of woven material with untwisted threads (each about 100 single fibers 30 μm thick) was treated from both sides in the chamber of the ion source by different doses of nitrogen ions with the energy of 20 and 30 KeV. Some samples of UHMWPE fibers were annealed at the temperature in the range 60–100°C in the interval 30–180 min.

The samples of the model three-layered laminated composites, containing polyurethane elastomer (A) or cured epoxy resin (B) as a polymer matrix and the initial and treated by different doses textile woven of UHMWPE fibers as a reinforcing filler were prepared according the following technique:

The 2-mm thick plates of polyurethane elastomer were prepared. The formulation of the polyurethane composition: diisocyanate prepolymer of oligotetramethylenglycol, oligotetramethylenglycol, 3,3′-dichloro-4,4′-diaminodiphenylmethane in the molar ratio 1.0 : 0.3 : 0.7. A drop of tin dibutyldilaurate was added as a catalyst of low temperature curing. Both initial and treated by different doses textile was applied for manufacturing of model composites. A sample of textile was put onto the plate and impreg-

nated by the adhesive of the same formulation. In the case of testing of adhesion to epoxide polymer, a composition containing epoxy resin (bisphenol A diglycidilic ester) as a polymer matrix and polyethylenepolyamine as a curing agent in the mass ratio 10 : 1 was used. A definite quantity of an adhesive, sufficient for forming of a 0.5 mm thick layer of the cured polymer, was poured onto the impregnated fabric. The sample obtained was gripped in a steel mold and cured at room temperature for 60 h. As-cured plates were cut by a guillotine cutter by several rectangular samples of 10 × 50 mm.

The surface structure of treated UHMWPE fibers before and after their application as a filler in a model composite was examined by electron microscopy using field-emission scanning electron microscope Hitachi S-800 with resolution of 2 nm. X-ray analysis of initial and treated fiber was carried out at Dron–3M difractometer in a standard cylinder dish on copper emitter with a nickel filter.

The strength of adhesion bond, or interlaminar strength of polyurethane-based composites, was determined using Instron 3565 tearing machine with the force applied at the angle of 180°C so that delaminated layers were at the same plane according to a conventional testing technique, the so-called peel test.[22] The test was carried out at room temperature and at the rate of the active gripper feed 100 mm/min. Adhesive bond strength was determined by division of averaged strain values by the width of the sample, dimensionality of σ_{adh} being kgf/cm.

Infrared attenuated total reflection (IR ATR) spectra were recorded using an IFS-66 (Bruker) spectrometer with Fourier transformation with ATR accessory, containing a KRS-5 crystal (refractive index is 2.37, the reflection angle is 45°, and the number of reflections is 25).

DISCUSSION

SEM results

First of all, it should be noted that the difference of the surface of initial and treated UHMWPE fiber is clearly seen on the microphotos (Fig. 1). There are few visible surface defects in the case of initial fiber which are something like longitudinal and diametrical cracks [Fig. 1(a)]. However, numerous diametrical folds are clearly distinguishable on the surface in the case of the fiber treated by high irradiation doses [Fig. 1(b)], so it can be concluded that applied irradiation dose caused local overheating, i.e., melting followed by recrystallization, which led to the shrinking of initially ultradrawn polyethylene chains. The undestructive effect of the pulsed ion beam treatment was shown at the example of low density polyethylene film[3] using XPS, UV, and IR
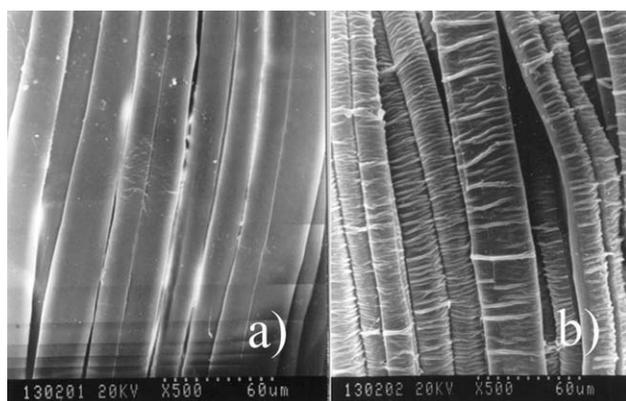
Figure 1 Micrographs of (a) initial and (b) treated by the dose 10^{15} ion/cm^2 UWMW PE fiber.

ATR spectroscopy as well as TRIM (Transport and Range Ions in Matter) simulation.[23] Thus, though the surface layer ca. 1 μm was heated and folded as a result of IBT, we can expect that the core of the fiber was not affected by the ion beam.

A qualitative estimation of adhesion was carried out by a visual study of the microphotos of the substrate surface, in our case, the fiber surface, after breaking of the composite. It is a matter of common knowledge that visual observation of the interface after adhesion joint is damaged can give a certain notion about the place and type of its failure. The surface of untreated fiber is smooth and seems to have no defects and the damage can be considered adhesive, though cases of true adhesive fracture are rare. In the case of a model composite with irradiated UHMWPE fabric surface defects in the form of torn-out fibrils were observed, i.e., the fiber surface was fibrillated. Here the partial fracture of the substrate takes place, what can be explained by mixed adhesive–cohesive character of the adhesive fracture.

Microscopic examination of the destruction fragments of the model composites based on epoxy matrix and both initial and ion-beam modified fiber as reinforcing filler gave another interesting result. The surface of the samples out of destruction area is shown on Figure 2. A distinct difference of destruction surfaces of UHMWPE fibers in the woven material is observed at a higher (1000 fold) magnification [Fig. 2(b)]. There are no defects on the surface of initial fiber and its imprint; both are rather smooth, which is characteristic for adhesive fracture. In the case of a model composite with irradiated UHMWPE, woven material surface defects in the form of torn out fibers were observed, i.e., the surface is fibrillated. Thus, electron microscopy data indicated the destruction character of the interface "fiber-matrix" in the case of ion-beam treated PE fibers to be cohesive.

X-ray difractometry results

Degree of crystallinity was estimated using X-ray analysis data. Degree of crystallinity of initial and ion-beam treated fibers calculated by Hermans-Weidinger method[24] appeared to be almost the same, though qualitative changes are evident—number, shape, and position of the peaks have changed (Fig. 3). There are three reflections corresponding to monoclinic lattice in addition to two reflections (110 and 200) of orthorhombic lattice on the X-ray pattern of the initial UHMWPE fiber within the interval of 19–26°. A shift of the intensive maximums to a low angle area can be explained as a consequence of an increase of crystal lattice size. X-ray diffraction patterns of the fibers annealed at 100°C were compared with those of ion beam treated from the viewpoint of the influence on the morphology of the fibers, i.e., concluding that the ion beam treatment leads to surface melting and recrystallization of the fibers or not. It is seen, that in the case of the fibers annealed at 100°C a similar phenomenon is observed, though it is more pronounced since the bulk of the polymer is affected. There are only high-angle reflections in the diffractogram of the annealed polyethylene fibers corresponding to the orthorhombic phase, as the monoclinic phase transforms into the orthorhombic one as a result of annealing at 90–100°C.[25] The monoclinic phase is known to be metastable[25] and transforms into a stable orthorhombic, the fact being confirmed for the case of the fibers annealed at the temperature about 100°C during 2–3 h. The decrease of the monoclinic phase content till its complete disappearance was observed at increasing of the treatment dose up to 10^{15} ion/cm^2. The calculated degree of crystallinity decreases monotonously from 89 ± 2% in the case of the initial fiber to 75 ± 3% in the case of the irradiated one.
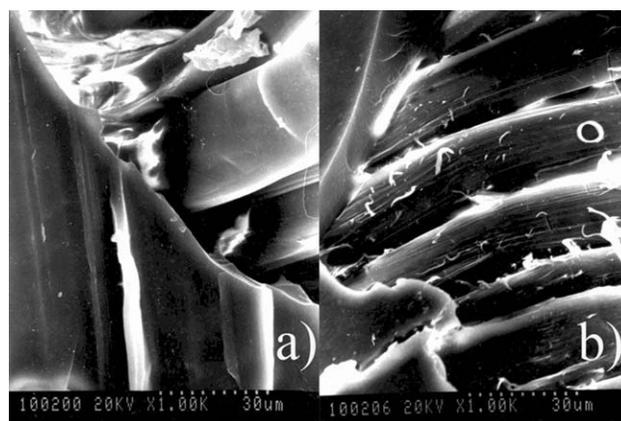
Figure 2 Micrographs of destruction surface of the model composite with (a) initial and (b) treated by the dose 10^{15} ion/cm^2. UHMWPE fiber(as a constituent part of woven material).
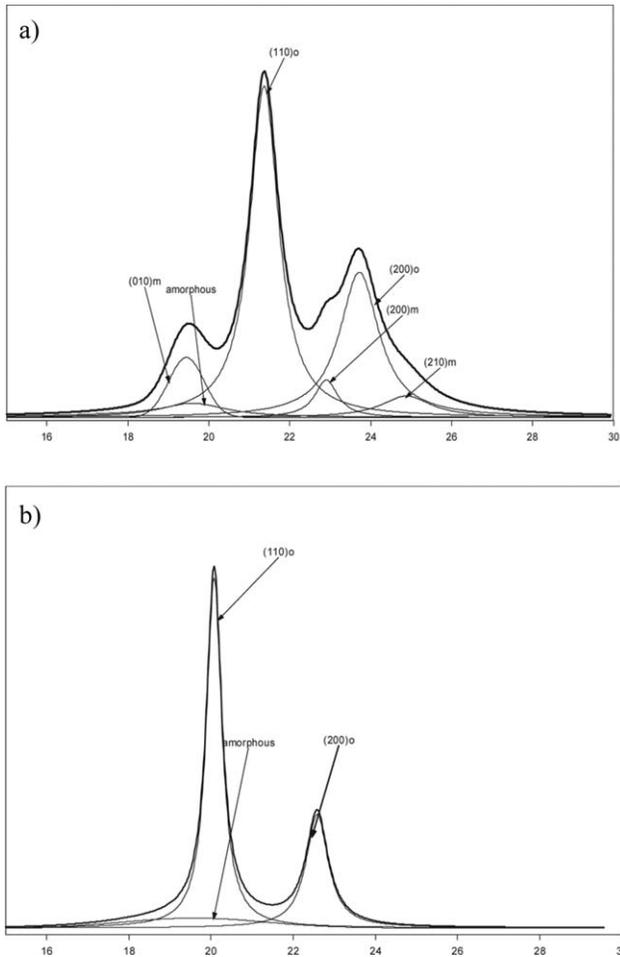
Figure 3 X-ray diffraction patterns of UHMWPE fiber: (a) initial; (b) treated by the dose 3.6 10^{15} ion/cm^{-1}.

Mechanical testing results

Then mechanical characteristics of the laminated composites consisting of a layer of UHMWPE woven material as a reinforcing filler and two elastic layers of polyesterurethane compound were determined. The interlaminar strength as a function of the treatment dose is presented in Figure 4. The interlaminar strength value was found to increase with the increase of the dose. Actually low irradiation doses lead to almost twofold increase of the interlaminar strength, i.e., adhesion strength. It should be noted, that compared to the films the effect of irradiation is not so pronounced. Obviously, the character of the composite destruction in the case of the untreated woven material is partially cohesive due to the so-called effect of the mechanical interlocking, as the uncured binding agent fills interfiber and interyarn space and tearing of these "bridges" is necessary for delamination of the composite.

As we have already stated, surface modification of UHMWPE fibers makes sense only when it causes no change in their mechanical characteristics. One can notice that the strength and modulus of elastic-
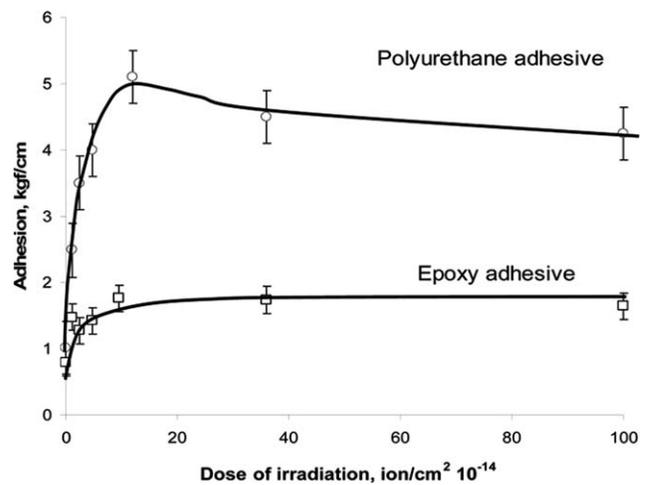
Figure 4 Interlaminar strength of a model three-layer composite as a function of the treatment dose.

ity of UHMWPE fibers decrease only in the case of high irradiation doses, more than 10^{15} ion/cm^2 (Fig. 5). Taking into account the fact that adhesion of the fibers to the binders reaches its maximal value at low irradiation doses, one can determine optimal treatment parameters for modification of the UHMWPE fibers destined for application in composite manufacturing—less then $2 \cdot 10^{15}$ ion/cm^2.

ATR FTIR results

It is a matter of common observation that the increase of adhesion strength occurs due to the appearance of chemically active oxygen-containing groups and introduction of unsaturated C=C groups into the polymer chains of the surface layer of an inert polymer.[14] So, degree of modification can be also estimated quantitatively via concentration of these groups, according IR-spectroscopy data.
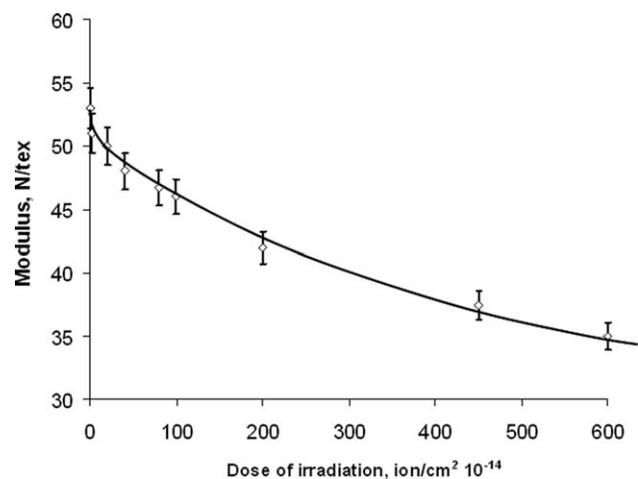
Figure 5 Modulus of UHMWPE fiber as a function of the treatment dose.

It was shown before[3] that the chemical composition of the surface of commercial polyethylene film changes drastically after ion-beam treatment carried out using the ion source. IR ATR spectra of the initial and irradiated samples of UHMWPE woven material are presented in Figure 6. One can notice that the intensity of the signal is not high; however, handling of the spectral data by means of "Opus 6.5" software product, or so-called contour division procedure, allowed a correct comparative analysis of the treated and untreated fibers to be carried out. There are at least two reasons of a lower intensity of the bands in the range 1680–1750 cm^{-1}, corresponding to oxygen-containing groups, such as 1726.5, ketonic; 1740.5, aldehydic; 1708 cm^{-1}, carboxylic group and others. The first is only a partial contact of the fabric with the crystal of ATR accessory because of an uneven surface of the material. The second can be connected with an ultradrawn structure of the polymer which is difficult for disrupting. For qualitative estimation of the degree of crystallinity the so-called "crystalline" doublet in the area 720–730 cm^{-1} was used.[26] The adsorption band 720 cm^{-1}, typical for polyethylene melt and related to the pendular oscillations of $-CH_2-$ groups in a molecular segment where $2 \leq C \leq 7$ splits into two peaks at 720 and 730 cm^{-1} when formation of the crystalline phase takes place. The appearance of the
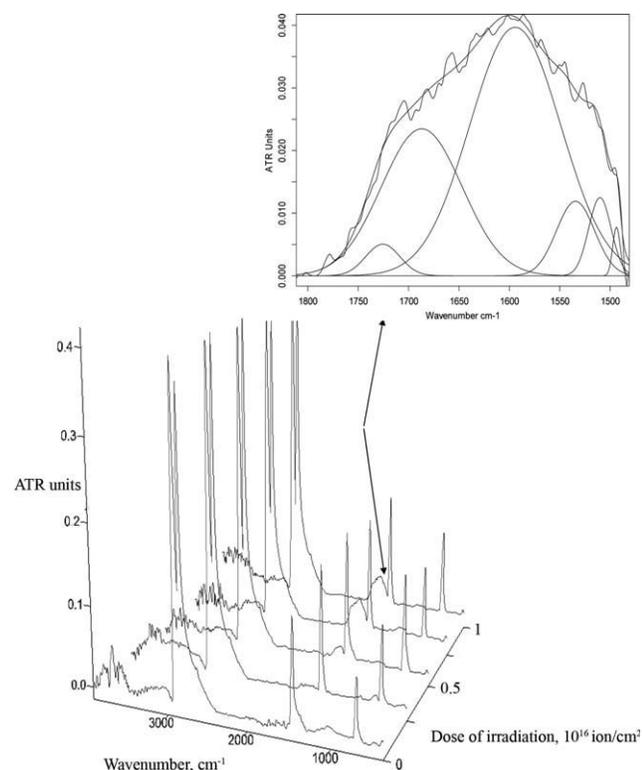
Figure 7 Relationship of the relative intensities of 730 and 720 cm^{-1} bands in IR ATR spectrum of initial and treated UHMWPE fiber as a function of the treatment dose.

second band is connected with a separation of the pendular oscillations of $-CH_2-$ groups into the two types, polarized along a and b axes of a unit cell. Thus, the higher the ratio of these bands, the lower degree of crystallinity is. The relative intensities of 720 and 730 cm^{-1} bands after contour division procedure as a function of a treatment dose is presented on Figure 7. An analysis of the spectral data showed the change of the degree of crystallinity to be nonmonotonic. The relationships obtained showed the decrease of crystallinity degree in the surface layer of the treated fiber to be insignificant.

CONCLUSIONS

It was found that pulse periodical ion beam treatment causes significant changes in chemical structure and topology of the UMWPE fiber surface layer as well as in its morphology.

Oxygen-containing functional groups have been detected in IR ATR spectra of the fibers.

X-ray diffractometry showed a small decrease of crystallinity with the treatment dose, orthorhombic phase being partially replaced by hexagonal one.

According to SEM data $\sim$ 1-µm thick transverse folds appeared on the UHMWPE fiber surface as a result of ion-beam treatment.

Examination of the composites showed twofold increase of adhesion of the irradiated fabric to polyurethane binder.

The dose $\sim 2 \cdot 10^{15}$ was found to be optimal one as it provides combination of high adhesion and negligible decrease of modulus. Thus, so-modified UHMWPE fabric can be an alternative for existing reinforcing constituents of laminates.

Figure 6 IR ATR spectrum of (a) initial and (b) treated by different doses UWMW PE fiber.

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