

Carbon Nanofibre-Reinforced Ultrahigh Molecular Weight Polyethylene for Tribological Applications

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ABSTRACT: Carbon nanofibre (CNF)-reinforced ultrahigh molecular weight polyethylene (UHMWPE) nanocomposites containing up to 10 wt % of nanofibres were prepared by a novel solvent-assisted extrusion process using short chain oligomers to tailor the melt viscosity of the UHMWPE matrix. A detailed investigation of the resulting nanocomposite microstructure and of the static mechanical properties revealed that the carbon nanofibres lead to improved mechanical properties of the UHMWPE related to the wear performance of such systems. Unidirectional sliding tests against a 100Cr6 steel under dry conditions

verified the significant potential of dispersed carbon nanofibres to reduce the wear rate of this polymer. In light of the promising results, a further optimization of the processing conditions of such UHMWPE nanocomposites is expected to yield interesting future nanocomposite materials even for demanding applications such as artificial knee implants. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 4173–4181, 2007

Key words: reinforcement; biopolymers; additives; UHMWPE; nanocomposites

INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMWPE) is a polymer with a unique combination of wear resistance and low-friction surface properties and is also characterized by a good corrosion resistance and impact strength. As such, UHMWPE is exploited in a wide spectrum of applications such as bearings, pulleys, and as a lining of trucks or dock guards. Furthermore, UHMWPE plays a prominent role in artificial joint surgery as it is the only material that meets the requirements for tibia-inlays in modern knee implants.¹ In spite of the outstanding tribological performance level of UHMWPE, the main reason for revision of artificial joints today still is attributed to the debris created during wear *in vivo*. It is therefore not surprising that significant current research and development efforts worldwide are aimed at improving the wear resistance of UHMWPE even further.

Many attempts have been undertaken to achieve that aim, including self-reinforcement,² increasing the degree of crystallinity,³ or cross-linking of the polymer.^{4,5} Another approach is based on the incorporation of various fillers or fibers into the base polymer.^{6–10} One such composite that has already been used for implants is a short carbon fiber-rein-

forced UHMWPE, introduced as PolyII[®] in the 1970s.¹¹ This particular composite material showed an improved wear behavior in the laboratory; however, it was at the expense of the ductility and crack resistance of the polymer matrix. Furthermore, the modulus of elasticity was significantly increased due to the fibers, an effect that is believed to disfavor the wear performance.¹² As a consequence, this particular composite material ran the risk of early fracture and extensive delamination, issues that proved to be fatal *in vivo*. Similar problems are likely to occur with most macroscopic fillers, since such particles generate high stress concentrations at the interfaces.

A comparatively new but still promising opportunity is provided by reinforcing such a polymer with solid particles on the nanoscale. It has already been demonstrated that various nanomaterials can significantly improve the tribological behavior of different polymer matrices such as polystyrene, poly(ether ether ketone) or polycarbonate.^{13–15} In the case of UHMWPE, the incorporation of carbon nanotubes (CNT) especially has been shown to improve the wear performance.¹⁶ Similarly, carbon nanofibres (CNF) have received increasing attention as potential nanoscale reinforcements for such biopolymers due to their interesting intrinsic properties as well as their reported good cytocompatibility.¹⁷ The incorporation of such nanoparticles as compared to standard macroscopic fillers offers the advantage of maintaining the ductility of the base polymer.¹⁸ In the case of polyethylene-based nanocomposites, even increased

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elongations to failure—an effect that usually correlates with an enhanced crack resistance—have been reported.^{19–21} Last but not least, polymer nanocomposites usually exhibit smooth surfaces after processing, another important factor influencing the tribological performance of such polymer devices.

However, one of the key challenges regarding the manufacture of such nanocomposites for tribological applications is that only well distributed and dispersed nanoparticles lead to uniformly enhanced polymer properties. Agglomerates of filler particles with a size of several tens of microns in diameter can act as localized stress concentration sites. Regions within the polymer where the properties are enhanced due to a good dispersion of the reinforcement are often unable to fully compensate the disadvantages related to the presence of such aggregates. In the case of UHMWPE, the incorporation of any type of particle is greatly complicated by the extremely high viscosity of the matrix preventing the use of established melt-processing approaches. As a result, simple nanofiller incorporation and dispersion by shear mixing is not an option. Yet, for less viscous polymers, a good dispersion of carbon nanofibres for example by shear mixing can be easily achieved.^{13,19,22}

In general, methods for processing UHMWPE composites include solid-state mixing of the macroscopic particles or fibers with the UHMWPE-powder, followed by a subsequent sintering step.^{6,10,16} Independent of the small absolute size of carbon nanotubes and nanofibres, this approach is expected to lead to an arrangement of the nanoscale filler at the primary powder-grain boundaries only. Another established processing method for UHMWPE is based on solution-mixing and subsequent casting, an approach that works well for the manufacture of UHMWPE fibers or films.²⁰ Nevertheless, a transfer of this technique to the production of bulk components is difficult to realize due to the required high degree of dilution. Furthermore, dispersion of a nanoscale filler in a medium of such low viscosity can again be complicated as the dispersion process in such systems is often characterized by a rapid reaggregation process due to the significant particle-particle interactions. Another attractive possibility is an *in situ* polymerization as it has been attempted for Kaolin/UHMWPE and palygorskite/UHMWPE nanocomposites.^{23,24} This approach, however, requires very strict conditions during the polymerization and the problem of dispersing the nanoscale filler homogeneously in the monomers remains.

The aim of the present study was to evaluate a novel extrusion process for carbon nanofibre-reinforced UHMWPE-nanocomposites by tailoring the viscosity of the UHMWPE matrix by the addition of short chain oligomers. After the subsequent extrac-

tion of the oligomers and hot-pressing of specimens, detailed investigations of the thermal and mechanical properties of the nanocomposites were aimed at establishing the resulting structure-property-relationships. Dry sliding tests against a 100Cr6 steel indicated a significant potential of the carbon nanofibres to reduce the specific wear rate of UHMWPE, although the exact improvements in performance reflect the processing history and the resulting nanofibre dispersion.

MATERIALS AND METHODS

Materials

Vapor-grown carbon nanofibres (Pyrograf IIITM, PR-19-PS) were obtained from Pyrograf Products, USA. These particular nanofibres have an average outer diameter of between 100 and 200 nm and a typical length of 30–100 μm prior to processing, resulting in an aspect ratio of 150 to 1000. These carbon nanofibres consist mainly of graphitic planes arranged around a hollow core at an angle of about 15° with respect to the fiber axis. A detailed description of their particular structure is given elsewhere.¹³ The carbon nanofibres used in this study are pyrolytically stripped so that all polyaromatic hydrocarbons are removed from the surface. In the as-received state, the carbon nanofibres are highly entangled.

The UHMWPE used was GUR 1020TM, kindly supplied by Ticona. The polymer was delivered as a powder with grain sizes of between 50 and 200 μm with an average molecular weight of about 5×10^6 g/mol. As solvents for the processing procedure, paraffin oil (Merck: paraffin, highly liquid) and hexane (mixture of isomers) were used as-received.

Methods: Composite processing

At first, the necessary amounts of carbon nanofibres required for a given weight fraction in the final composite were hand-mixed with the liquid paraffin oil. After further addition of the UHMWPE-powder, the continuously stirred solution (using a magnetic stir bar) was slowly heated up to 125°C using a hot-plate. At that temperature, the UHMWPE grains swell fast and absorb the paraffin oil. Paraffin oil was used as it is nontoxic and is a saturated hydrocarbon of small molecules with the same composition as UHMWPE. Because of the swelling process, the short-chain oligomers increase the distance between the polymer molecules and lead to a higher chain mobility. Thus, the viscosity of the system is lowered significantly to a range that allows extrusion processing. The jelly material was cooled to room temperature and cut into small pieces prior to twin-

screw extrusion using a Brabender DSE 20/40 operating at a barrel temperature of about 190°C. Based on this approach, nanofibre contents of 5 and 10 wt % in the final UHMWPE were realized. After cooling, the oily strands were again cut into small pieces.

The oil was removed in a two-step extraction process in a soxhlet extractor using hexane. Prior to the second extraction step, the composites were cryomilled to enhance the diffusion processes and to achieve a powder with an average grain size of between 200 and 500 μm . Following the evaporation of the volatile hexane over a period of 24 h at ambient conditions and, additionally, under vacuum for 12 h, the powder was sintered using a hot-press (210°C, 10 MPa, 45 min) into rectangular plates with an area of $62 \times 83 \text{ mm}^2$ and a variable thickness of between 1 and 4 mm. A neat UHMWPE reference was directly hot-pressed under identical conditions from the as-received powder.

Testing procedures

To evaluate the processability of the swollen mixture of UHMWPE and paraffin oil, the shear rheological properties of both the untreated UHMWPE as well as of the UHMWPE/paraffin oil system were investigated by oscillatory parallel plate rheometry using a Rheometric Scientific RDA III at a temperature of 180°C, using hot-pressed specimens (diameter 25 mm, thickness 1 mm). Constant strain measurements were performed within the viscoelastic regime over a frequency range from 0.01 to 500 rad/s. A nitrogen atmosphere during testing was used to prevent oxidative degradation of the sample. To evaluate the materials characteristics, the complex viscosity, η^* , the storage modulus, G' , and the loss modulus, G'' , were obtained as a function of the angular frequency. To establish the influence of the processing history on the molecular weight of the UHMWPE matrix, the intrinsic viscosity of the two unfilled systems was determined by Ticona after processing.

The two prepared nanocomposites were further analyzed by scanning electron microscopy (SEM) to evaluate the dispersion and distribution of the nanofibres in the extruded and subsequently hot-pressed ultrahigh molecular weight polyethylene as a function of the filler weight fraction. All specimens were fractured in a brittle manner using liquid nitrogen in such a way that the fracture surface is normal to the direction of the applied forming pressure.

Differential scanning calorimetry (DSC) was carried out using a Mettler Toledo DSC/SDTA 821e operating under nitrogen atmosphere. The as-pressed polymer was heated from 20 up to 180°C at a rate of 10°C/min, equilibrated for 3 min, and was subsequently cooled down to 20°C. After holding for

3 min, the samples were again heated to 180°C at a rate of 10°C/min. From the recorded thermograms, the degree of crystallinity was calculated according to:

$$X_C = \frac{\Delta H_C}{\Delta H_C^0} 100\% \quad (1)$$

where $\Delta H_C^0 = 291 \text{ J/g}$ is taken as the enthalpy of fusion of 100% crystalline UHMWPE.¹ For comparative purposes, the degree of matrix crystallinity of the nanocomposites was further normalized to the actual polymer weight fraction.

Thermogravimetric analysis (TGA) was conducted using a Mettler Toledo DMA/SDTA 821e to evaluate the decomposition behavior of the various systems in more detail and to reveal solvent residues. Twenty to thirty milligrams of the different materials were placed in an aluminum oxide crucible and were heated up under nitrogen atmosphere (heating rate of 10°C/min from 25 to 600°C). At least five samples of each composition were tested.

Tensile tests were performed using standardized test bars with a gauge length of 25 mm and a thickness of 1 mm cut from the hot-pressed sheets. The tests were performed at room temperature using a Zwick Z020. For the determination of the modulus, the crosshead speed was set at 1 mm/min and was then increased to 50 mm/min. For all prepared materials, at least eight specimens were tested.

For the universal hardness experiments, a Vickers pyramid was pressed into the surface of the samples at a constant speed up to a load of 100 N. The universal hardness is calculated from the penetration depth at the maximum load.

To evaluate the wear behavior of all composites, dry tribological tests were carried out using a pin-on-disk wear tester (Dr. Wazau GmbH). A rotating disk-shaped sample (effective radius 28 mm) was run against a steel (100Cr6) pin at a contact pressure of 3.5 MPa at room temperature. The pin specimen had a diameter of 6 mm with a 45° chamfer. The frequency was set to 180 rpm and 150,000 cycles were completed, corresponding to a linear sliding distance of 13.2 km. The wear of the specimens was determined by measuring the weight loss and, based on this data, the specific wear rate was calculated according to²⁵:

$$\dot{w}_s = \frac{\Delta m}{\rho L A_p p} \quad (2)$$

where Δm corresponds to the mass loss, ρ is the density, L is the sliding distance, A_p is the contact area, and p is the contact pressure.

Finally, the generated and collected wear particles were analyzed by scanning electron microscopy.

RESULTS AND DISCUSSION

Rheological characterization

In Figure 1(a), the frequency dependence (ω) of the complex viscosity η^* is shown for both the neat UHMWPE and the UHMWPE/paraffin oil mixture at 180°C. As can be seen, the paraffin oil acts as a plasticizing agent and, thus, significantly reduces the shear viscosity of the UHMWPE by about a factor of 10 at high shear rates and by a factor of 150 at low shear rates. The detailed analysis of the viscoelastic properties of the two systems shown in Figure 1(b) reveals further interesting features. Both the storage modulus and the loss modulus of UHMWPE are notably reduced by the addition of the paraffin oil. In contrast to the elastic behavior of the neat UHMWPE over the whole frequency range, a viscoelastic behavior is observed for the UHMWPE/paraffin oil system. As indicated by the crossover of G' and G'' , the viscous behavior dominates at low fre-

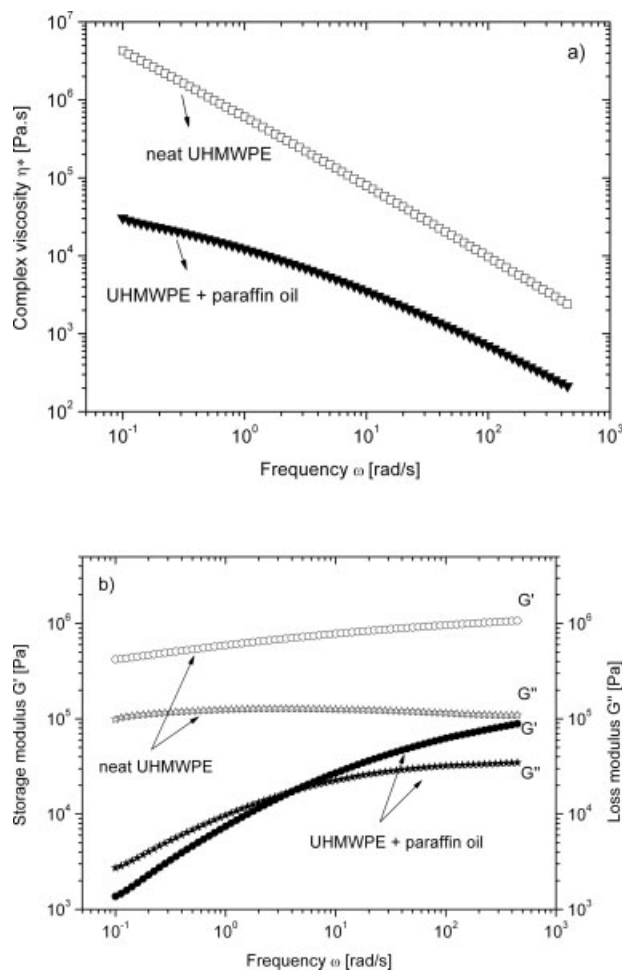


Figure 1 Frequency dependence (ω) of the (a) complex viscosity η^* and of the (b) storage and loss modulus for neat UHMWPE and UHMWPE/paraffin oil mixtures at 180°C.

quencies and can further be related to the onset of the Newtonian flow regime. In summary, the addition of the paraffin oil effectively enhances the poor melt-processability of the UHMWPE to a level that can be handled by standard twin-screw extruders.

Extrusion processing

The dispersion process of the as-received carbon nanofibres in the paraffin oil at room temperature led, within minutes, to a homogeneous dark color of the dispersion. After the addition of the UHMWPE powder, the polymer was observed to transform into a gel by taking up the nanofibre-oil dispersion at a temperature of about 123°C. The excess oil became clear again, indicating that all carbon nanofibres were taken up by the polymer. Following the extraction process using hexane, homogeneously colored nanocomposite batches containing 5 and 10 wt % of carbon nanofibres, respectively, were obtained.

The final sample batches were granulated prior to the extrusion process. Unfortunately, the materials showed a strong tendency to clump together and a constant and homogeneous gravimetric feeding to the twin-screw extruder turned out to be complicated. The large particle size and associated initial feeding problems subsequently required the use of rather unfavorable extrusion conditions. The extruder had to be operated at low speeds, conditions that minimized the shear forces and led to rather long residence times. Nevertheless, the extrudates appeared to be of a homogeneous color with very smooth surfaces. Similarly, the subsequent hot-pressing process of the granulated extrudates led to homogeneously colored specimens with a very smooth surface finish. The surface roughness of all specimens was identical as it is determined by the roughness of the mold.

The comparative determination of the intrinsic viscosity of the two as-processed unfilled UHMWPE samples revealed a decreased molecular weight of the matrix as a result of the particular nature of the extrusion process. The intrinsic viscosity of the extruded material relates to an average molecular weight of 1.5×10^6 g/mol as compared with the 5×10^6 g/mol of the base material that was maintained during hot-pressing. This matrix degradation is a direct consequence of the as yet not optimized extrusion conditions; an improved feeding and optimized screw design is expected to lead to significantly reduced residence times in the extruder and, therefore, to a minimized decrease of the matrix molecular weight.

The TGA-experiments showed a stable weight of the samples up to about 400°C. As shown in Figure 2, no evidence for the release of any volatile solvent residue could be detected within experimental accu-

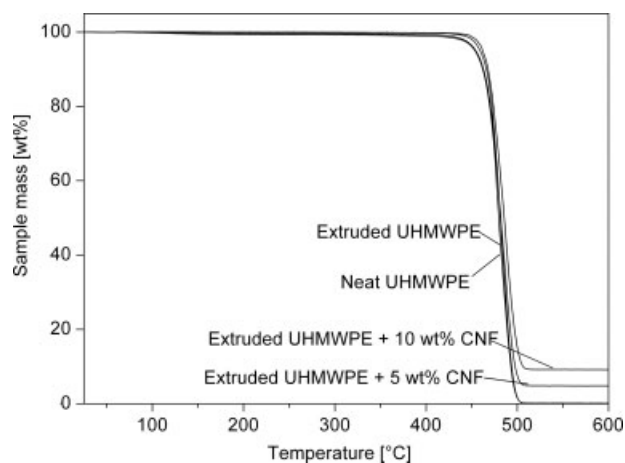


Figure 2 Comparative plot of the sample mass loss of neat UHMWPE and the different nanocomposites as a function of the temperature.

racy. This observation implies a solvent residue of <math><0.0035\text{ wt \%}</math>, independent of nanofibre content. At higher temperatures, thermal degradation of the neat UHMWPE starts, with the onset associated with composition appearing at around 26–28 such carbon nanostructures contain acceptor-like localized states, due to lattice defects (e.g., vacancies, dangling bonds, OH and CO attachments). The presence of such sites mainly is responsible for radical termination during polymer degradation, a similar effect appears likely for the present nanofibre-filled UHMWPE.²⁹ At temperatures above

Composite microstructure

Scanning electron microscopy investigations of fracture surfaces of the hot-pressed nanocomposites revealed that the carbon nanofibres were only partially dispersed in the UHMWPE during the extrusion process. For the lower nanofibre content of 5 wt %, only a few small nanofibre aggregates remained, as evidenced by the micrograph shown in Figure 3(a). With increasing nanofibre content, the number and size of the CNF agglomerates increased, as highlighted by the micrograph in Figure 3(b). It is inter-

esting to note that these nanofibre clusters were nevertheless homogeneously distributed and appeared fully infiltrated by the polymer matrix and, therefore, do not represent classical voids.

Taking into account the previously mentioned difficulties of homogeneously feeding the masterbatch into the extruder, these initial results regarding the dispersion and distribution of carbon nanofibres in the UHMWPE during the extrusion step highlight the significant potential of this approach to obtain homogeneous nanocomposites. An improved gravimetric feeding of smaller masterbatch particles is expected to lead to a significantly improved dispersion of the nanoscale filler because of the greatly enhanced shear forces achievable in the extruder, as it has already been observed for other CNF-reinforced polymers processed under similar conditions.²²

The detailed DSC evaluation of all processed UHMWPE specimens did not reveal any significant changes in the matrix microstructure, neither as a function of the processing history nor as a function of the nanofibre content. As summarized in Table I, the onset temperature to melting at about

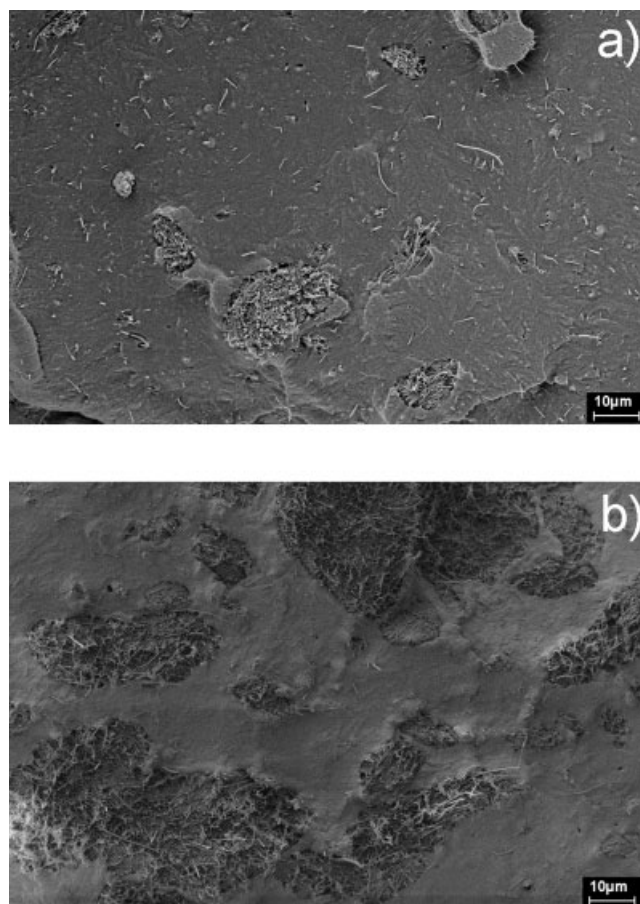


Figure 3 Representative scanning electron micrographs of fracture surfaces of extruded UHMWPE-nanocomposites containing (a) 5 wt % and (b) 10 wt % of carbon nanofibres.

TABLE I
Thermal Parameters of All Investigated Materials as Obtained by DSC Analysis

	Reference	Extruded UHMWPE	Extruded UHMWPE + 5 wt % CNF	Extruded UHMWPE + 10 wt % CNF
1 Heating				
Crystallinity (%)	46.6	49.5	46.9	43.1
T_{onset} (°C)	125.3	124.7	127.7	127.2
T_{peak} (°C)	135.2	136.4	135.8	136.4
2 Heating				
Crystallinity (%)	48.0	51.0	47.4	44.0
T_{onset} (°C)	125.1	124.7	123.9	124.4
T_{peak} (°C)	135.7	137.2	137.7	136.8
Cooling				
Crystallinity (%)	47.8	51.6	48.3	45.2
T_{onset} (°C)	121.8	121.4	121.5	121.8
T_{peak} (°C)	116.6	114.6	115.3	115.9

the melting peak temperature at about 137°C were not affected, within experimental error. In addition, the slow cooling experiments in the DSC also did not indicate any change in the crystallization behavior of the nanocomposites as compared to the two neat samples. Again, neither the onset temperature to crystallization at about 121°C nor the crystallization peak temperature at about 115°C was affected within experimental error. The nanofibres clearly did not act as nucleation sites in this particular matrix, in contrast to their influence on the crystallization behavior of polypropylene, reported in Ref. 30 or to that of nanotubes in UHMWPE reported in Ref. 31

The slightly larger degree of crystallinity of the extruded UHMWPE as compared to the neat reference system is not surprising, taking into account the decreased average molecular weight of the extruded material which leads to a higher chain mobility. Similarly, the nanocomposites revealed a slight decrease in the degree of crystallinity with increasing nanofibre content, a result of the decreasing molecular mobility with increasing filler content in these cases.

In summary, the detailed thermogravimetric evaluation of all as-pressed samples indicated that the paraffin oil was completely removed during the extraction procedure. Furthermore, the results of the thermal analysis verify that neither the processing approach nor the incorporation of the carbon nanofibres led to significant variations in the polymer matrix microstructure.

Mechanical performance of the nanocomposites

Representative engineering tensile stress-strain curves of the two UHMWPE samples and the two nanocomposites are highlighted in Figure 4(a). As can be seen, the extrusion process of the neat UHMWPE material led to a slight degradation of the

mechanical properties. The tensile stiffness, the yield stress as well as the stress increase in the strain-hardening regime of the extruded material are lower than those of the neat reference. Although these effects most likely again reflect the degradation of the molecular weight as a result of the extrusion process, the elongation to failure of these specimens appears only moderately decreased. Furthermore, the addition of 5 wt % of carbon nanofibres improves the tensile properties again, the modulus as well as the yield stress of this nanocomposite clearly exceeds the values of both neat matrices. Increasing the nanofibre content to 10 wt % does not lead to a further increase in yield stress, most likely as a result of the presence of the larger CNF clusters in these samples. Nevertheless, even the presence of these nanofibre clusters does not degrade the ductility of the nanocomposite.

The observed trends in tensile modulus are further summarized in Figure 4(b). As can be seen, the addition of 5 wt % of nanofibres leads to a nanocomposite modulus exceeding the absolute value of the neat UHMWPE reference, although a nanofibre content of 10 wt % leads to little additional benefits. The nonlinear increase in nanocomposite tensile modulus with increasing nanofibre content reflects the decreasing quality of the nanofibre dispersion. Improved processing conditions eliminating the remaining nanofibre aggregates should nevertheless lead to a further increase in nanocomposite modulus at higher nanofibre contents; comparable nanocomposite systems have shown a linear increase in modulus up to nanofibre loadings of 15 wt %.²²

Similar trends to the modulus increase were also observed for the universal hardness of all materials, as summarized in Figure 5. Again, there is a slightly decreased hardness of the extruded UHMWPE as compared with the neat reference. Nevertheless, the addition of the carbon nanofibres leads to an approximately linear increase in hardness exceeding the

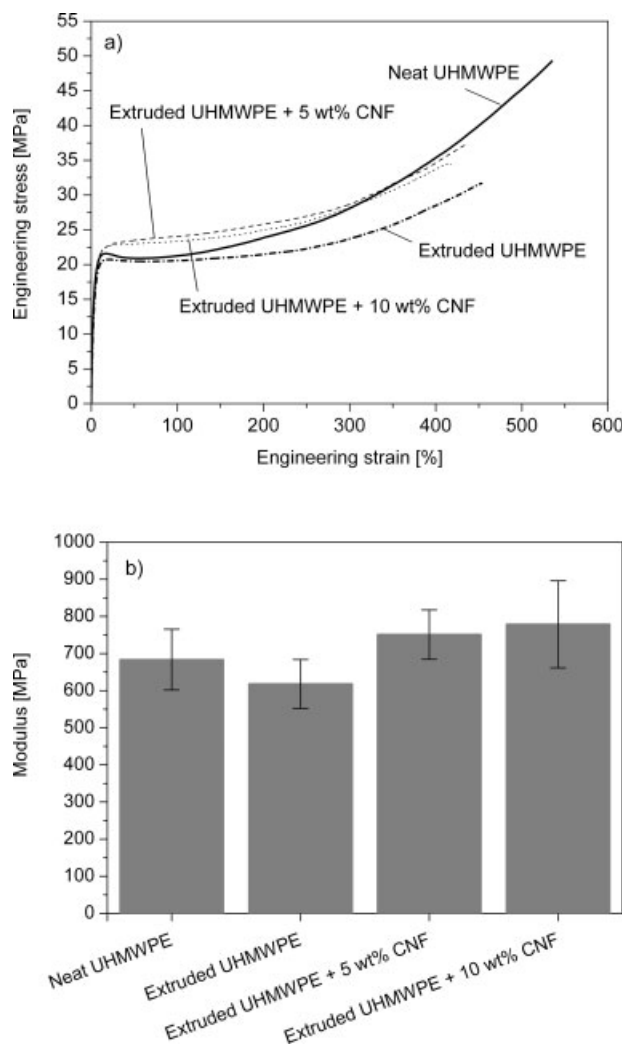


Figure 4 (a) Representative engineering tensile stress-strain curves of neat UHMWPE and UHMWPE nanocomposites and (b) summary of the tensile modulus as a function of processing history and carbon nanofibre content.

values observed for the neat reference material. Interestingly, the presence of the nanofibre aggregates in the 10 wt % samples does not degrade this linear increase in hardness with the nanofibre content. This observation relates to the small size of the aggregates and to the small average distance between the clusters as compared to the size of the indenter penetrating into the material.

In summary, the results of the preliminary mechanical tests reveal attractive improvements in those properties related to the wear behavior of the UHMWPE due to the addition of the carbon nanofibres. The extruded nanocomposite stiffness, yield stress as well as the hardness exceed the values of the neat UHMWPE reference, although the extrusion process as such has slightly degraded these properties of the pure matrix. Furthermore, the nanocomposites maintain a high ductility, independent of the presence of remaining filler particle aggregates. This

behavior is in contrast to that observed for UHMWPE reinforced with conventional short carbon fibers. Here, a significantly increased stiffness coupled with a dramatically lower ductility has been proposed to be a crucial factor leading to early failure of such materials used in knee implants.¹¹ The modulus increase observed here for the nanocomposites is comparatively low, and more importantly, the matrix ductility can be maintained.

Tribological properties of the nanocomposites

The specific wear rate as obtained from the pin-on-disk tribometer tested against the 100Cr6 steel is summarized for all tested materials in Figure 6(a). The results of this particular dry wear test again confirm the general trends discussed before. The extrusion conditions and the subsequent decrease of the matrix molecular weight have somewhat degraded the wear performance of the neat UHMWPE. In poly ethylene in general, the wear behavior is crucially dependent on the molecular weight of the polymer.¹ It is therefore not surprising that the specific wear rate of the extruded UHMWPE is increased by almost an order of magnitude as compared to the neat reference. Nevertheless, the 5 wt % nanocomposite shows a highly improved specific wear rate as compared to the extruded UHMWPE reference. The addition of the nanofibres effectively decreases the specific wear rate again by an order of magnitude. Interestingly, the presence of the larger nanofibre clusters appears to degrade the wear performance, as evidenced by the again increasing wear rate for the composite containing 10 wt % of nanofibres.

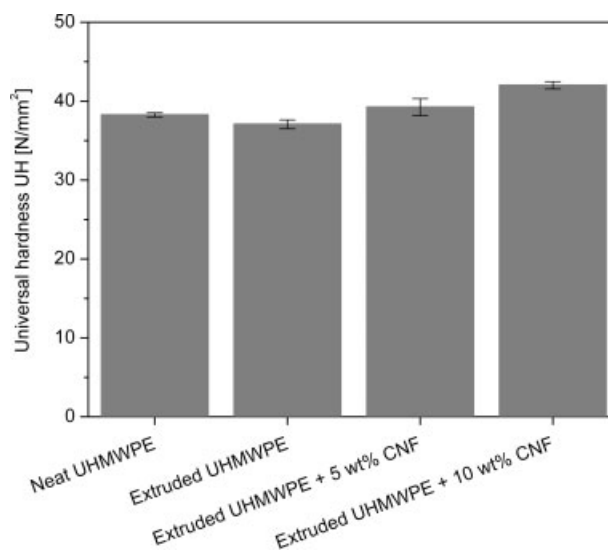


Figure 5 Comparative plot of universal surface hardness of neat UHMWPE and UHMWPE nanocomposites as a function of processing history and carbon nanofibre content.

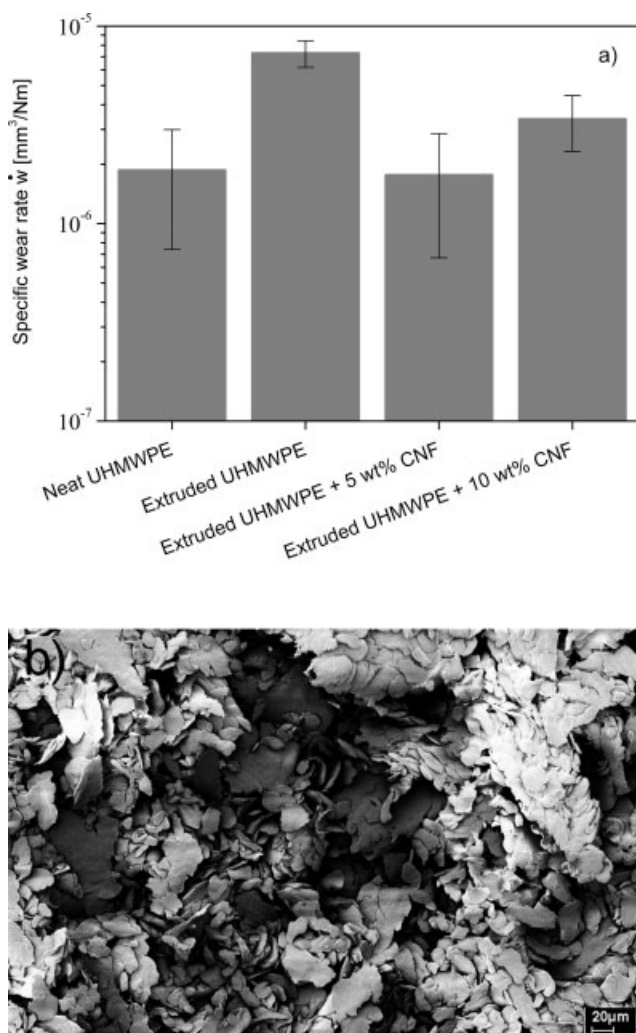


Figure 6 (a) Specific wear rate of neat UHMWPE and of UHMWPE nanocomposites as a function of processing history and carbon nanofibre content; (b) representative scanning electron micrograph of wear debris of the 10 wt % nanocomposite sample generated during the pin-on-disk test.

Although the results of this particular test indicate the presence of an apparent optimum nanofibre loading fraction of as little as 5 wt %, similar studies¹³ have indicated that a further improvement of the tribological performance can be expected for higher nanofibre contents—given that a well-dispersed state can be achieved by the extrusion process.

It is interesting to compare the wear reducing mechanism of the carbon nanofibres in the UHMWPE with those proposed for conventional, larger fibers.²⁵ On the one hand, the addition of both dispersed and aggregated carbon nanofibres leads to moderate improvements in the mechanical properties of the polymer without inducing significant variations in the matrix microstructure and without degrading the ductility; effects that are often observed for standard

microscopic fibers. Therefore, in contrast to short carbon fiber-reinforced UHMWPE, dispersed nanofibres appear to show a positive effect on the crack initiation and propagation behavior and are likely to avoid the problems observed in the case of PolyII™. Yet, the observed increase in matrix modulus, yield stress and hardness due to the nanofibres clearly improves the tribological performance of the UHMWPE; individual nanofibres contribute some load-bearing capacity and reduce the matrix stresses, in analogy to macroscopic fibers.²⁵

Furthermore, the detailed SEM evaluation of the wear surfaces and debris verified that nanofibres pulled out of the matrix must break up, as no nanofibre segments were observed in the debris. This degradation of the nanofibres is an indication for the biocompatibility of the wear debris. Even in the case of the 10 wt % nanocomposite [Fig. 6(b)], no intact nanofibres or nanofibre segments could be detected. In addition, pulled out nanofibres or broken nanofibres should essentially act as a lubricant under the selected dry sliding conditions. Given the small size and the intrinsic graphitic structure of the nanofibres, nanofibre pull-out is also not expected to lead to any macroscopic surface roughness on either bearing surface. Last but not least, the nanofibres may act to reinforce the transfer film seen on all metal pins used for the tests, effects which have been observed for other nanoscale fillers in thermoplastics.^{32,33}

CONCLUSIONS

Vapor-grown carbon nanofibres represent a promising additive for improving the tribological performance of ultrahigh molecular weight polyethylene. In homogeneously dispersed systems, these nanofibres can significantly reduce the wear rate of UHMWPE under dry testing conditions against 100Cr6 steel. The novel solvent-assisted twin-screw extrusion process applied in this study has shown interesting potential to manufacture such bulk UHMWPE nanocomposites suitable for tribological applications. The investigations reported here support the following conclusions:

1. Nanoscale reinforcements such as carbon nanofibres can be incorporated and dispersed in the UHMWPE by simple twin-screw extrusion given that the viscosity of the polymer matrix is adjusted by short chain oligomers which can subsequently be removed by an extraction process. Further optimization of the extrusion processing protocol is expected to lead to an even further enhanced nanofibre dispersion. In addition, improved shear conditions and reduced

residence times in the extruder should allow a maintaining of the matrix molecular weight.

2. The addition of carbon nanofibres to such extruded UHMWPE composites leads to improved mechanical properties such as modulus and yield stress while maintaining the ductility of the matrix. In addition to a smooth surface finish of the specimens provided by the nanoscale of the reinforcement, the nanocomposite hardness is increased. In summary, mechanical properties critically related to the wear performance of the UHMWPE are enhanced by the incorporation of the nanoscale reinforcement while the matrix microstructure is not affected by the presence of the nanofibres under these novel processing conditions.
3. The presence of dispersed carbon nanofibres leads to a significantly reduced wear rate of the polymer whereas large nanofibre agglomerates offset this enhancement to some extent. Under dry sliding conditions, pulled out or broken nanofibres themselves might act as a lubricant, at the same time eliminating the presence of nanofibre segments with a high aspect ratio in the debris.

As in conventional melt-processable thermoplastic systems, the addition of carbon nanofibres to UHMWPE via a solvent-assisted extrusion process suggests a significant potential to enhance the tribological properties of this particular polymer suitable for biomedical applications. Nevertheless, further improvements in UHMWPE nanocomposite processing techniques based on such solvent-assisted extrusion are required to fully establish their potential. In addition, suitable surface treatments^{19,21} of the carbon nanofibres should be considered to further enhance the interfacial bonding to the polymer matrix and to aid processing.

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