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Composite Gel-Fibers and Solid-State-Processed Tapes Based on Disentangled Ultra-High Molecular Weight Polyethylene and Electrically Conductive Carbon Black: A Comparative Study

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Abstract

In this study, oriented nanocomposite gel-spun fibers and solid-state-processed tapes were manufactured and analyzed. The fibers and tapes were produced using a specific type of nascent disentangled ultra-high molecular weight polyethylene (UHMWPE) reactor powder. As the filler, commercially available electrically conductive carbon black (CB) was used. The ultra-high filler content values up to 75 wt.% were achieved for the UHMWPE/CB gel-spun fibers, while the degree of filling was limited (up to 30 wt.%) in the case of the solid-state processing approach. This was attributed to the type of the filler distribution achieved with both processing methods. The influence of the filler distribution on the composite characteristics in case of the homogeneous filler distribution in the gel-spun fibers and extremely segregated filler distribution in the solid-state tapes was studied. To this end, the resulting composite UHMWPE/CB gel-spun fibers and solid-state processed tapes were characterized using a combination of research techniques, including X-ray diffraction, scanning electron microscopy, mechanical testing, and conductivity measurements. A comparative study of the electrical conductivity of the gel-spun and solid-state-processed UHMWPE/CB composites was conducted for both the unoriented and oriented states of the composite materials. The obtained solid-state processed UHMWPE/CB tapes were characterized by a low filler percolation threshold value of 2.5 wt.%, while the percolation threshold for the composite gel-spun fibers exceeded 15 wt.%. Regardless of the filler distribution type, a notable reduction in electrical conductivity was observed following the orientation drawing of the composites. At the same time, while a notable reduction in the maximum achievable orientation deformation ratio and subsequent tensile strength decline was observed in the case of gel-spun fibers, no impact of the filling on orientation strengthening was detected in the case of solid-state processed tapes.

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INTRODUCTION

It is well established that electrical conductivity of polymer materials can be significantly improved through their modification with carbon-based micro- and nanoscale fillers [1,2]. Conductivity of the composite materials filled with carbon nanofillers can be varied controllably in a wide range of the values depending on the filler type, content, and distribution/morphology.

Ultra-high molecular weight polyethylene (UHMWPE) offers a unique combination of high-performance properties: low bulk density, chemical resistance in gas and liquid media, hydrophobicity, tribological robustness, stability at low temperatures, resistance to ionizing radiation. Therefore, UHMWPE is considered one of the most promising polymers for the design of electrically conductive composites [3–6].

Currently, three major processing routes exist, allowing to obtain UHMWPE-based composites containing carbon-based materials as fillers. The first method involves preliminary distribution of the filler particles on the surface of UHMWPE reactor powder (RP) particles, followed by compression molding of the resulting mixtures at the temperatures above the melting point of the UHMWPE. This approach makes it possible to create a segregated network made of the filler particles, significantly reducing the amount of filler required for polymer composite to become highly electrically conductive [7–9]. The intrinsic drawback of this processing method is that mechanical characteristics of the UHMWPE matrix decrease profoundly at the filler concentrations required to achieve relatively high conductivity values [9].

In order to overcome this limitation, the second processing route can be utilized. It involves direct solid-state processing of the filler-coated UHMWPE RP at the temperatures below the melting point of the polymer. This technique involves compactization of the UHMWPE RP with the filler and a subsequent monolithization of the compacted material by combining compression and uniform shear deformation. The resulting UHMWPE-based composite samples can then be oriented through uniaxial drawing to obtain high-strength tapes, successfully avoiding the brittle fracture [10]. Despite being industrially scalable and universal, this method has its own limitations. Solid-state processing generally requires UHMWPE RP to possess a special molecular structure involving stacked crystalline lamellas with a low number of intermolecular entanglements (the so-called “disentangled” UHMWPE) [11,12] and low bulk density. The second limitation results from the requirement for UHMWPE RP particles to be preliminary coated with the filler. This limits the highest achievable filler content value, which was earlier reported to be around 15 wt.% for anisometric carbon fillers (e.g. carbon nanotubes), 25 wt.% for graphite/graphene hybrid nanoplatelets, and around 35 wt.% for globular carbon blacks (CBs) [3,4,13,14]. While these contents values are high enough for the corresponding composites to be highly electrically conductive, increasing the filler content even further might potentially prove useful in order to obtain composites with enhanced thermal conductivity, thermal, stability, tribological properties, and interface adhesion strength [15,16]. For example, Liu et al. [17] successfully fabricated UHMWPE-based composites that exhibited high thermal conductivity and thermal stability. This was achieved through solid-state processing of mixtures of UHMWPE RP and boron nitride, with the filler content reaching up to 30 vol.%.

The third processing route to obtain UHMWPE-based composite materials modified with carbon fillers involves the gel-spinning of UHMWPE solutions. During the gel processing, the UHMWPE RPs are mixed with the carbon filler powders and dissolved in decalin, vaseline [18], vegetable [19], or turpentine [20]. UHMWPE/filler solutions undergo the gel transition and are subjected to the spinning process, which involves extruding a heated gel through a single or multiple spinnerets. The resulting plasticized fibers are subsequently washed, dried, and orientation drawn. Previously, gel-spinning was successfully applied to obtain UHMWPE gel-fibers containing multi-walled carbon nanotubes [21,22] and CB [23], although the reported filler content values were relatively low.

It should be noted that gel-spinning generally requires UHMWPE to have high specific density (0.8 – 0.9 g/cm^3), which limits the polymer concentration in a spinning solution/gel. Additionally, this also

makes comparative studies involving UHMWPE gel-fibers and solid-state processed tapes much harder to execute, since the latter requires UHMWPE RP specific density to be in range of 0.05-1.5 g/cm^3).

Therefore, the current work is dedicated to the study of a possibility to obtain composite UHMWPE-based gel-spun fibers, containing high amounts of electroconductive CB and the solid-state processed composite UHMWPE/CB tapes, utilizing the same UHMWPE RP and CB powder for the both processing techniques. This work also aims to provide an important information about the difference between the gel-spun UHMWPE-based composites, characterized by a uniform filler distribution, and solid-state processed composites, which possess extremely segregated filler distribution morphology.

MATERIALS AND METHODS

Materials

Commercially available electroconductive carbon black (CB) P267E (Omsk Carbon Black Plant, Omsk, Russia) was used as a carbon-based filler for preparation and processing of the polymer composites. Full specification of the CB powder is provided in [24]. This specific carbon-based material was selected based on its high electrical conductivity [24], availability of the industrial-scale production, and the ability to form stable colloid dispersions in various polymers and liquid media [25].

Disentangled UHMWPE reactor powder (RP) was used as the matrix polymer for the solid-state processed and gel-processed composites modified with CB. UHMPWE RP was synthesized using a functionalized fluorine-substituted bis-(phenoxyimine) catalytic complex of titanium chloride (co-catalyst - methylaluminoxane at methylaluminoxane/Ti ratio = 500/1). The structure of the catalytic complex is described in the work of Ivanchev et al. [26]. The characteristics of the UHMWPE are provided in Table 1.

Gel-Fiber Fabrication

The fabrication of the UHMWPE-based gel-fibers consisted of multiple stages: (1) Dissolution of the UHMWPE RP, mixed with the filler, in a solvent; (2) Gelation of this dissolved mixture; (3) Dry-spinning of the obtained gel.

Prior to the dissolution of the UHMWPE RP, the weighted amounts of CB powder were added into a glass vessel containing turpentine oil. The resulting mixture was subjected to ultrasound treatment for 5 min using an I100-840 ultrasonic disperser (LLC «Ultrasonic technique — INLAB», Saint-Petersburg, Russia), characterized by the frequency of 22.5 kHz and adjustable power output (up to 1 kW). After the ultrasound treatment, the UHMWPE RP was added to the turpentine/CB dispersion. The weight value for UHMWPE RP was selected in order to achieve 1.4 wt.% of UHMWPE in the mixture. Additionally, an industrial antioxidant SONOX-1010 was introduced to prevent thermal-oxidative decomposition of UHMWPE during the preparation of the spinning gel and subsequent fiber spinning.

The dissolution of the UHMWPE RP to obtain the spinning gel was performed using a thermostatic bath filled with silicone oil, equipped with an overhead stirrer with a glass helical stirring rod. The glass vessel containing UHMWPE/CB/SONOX-1010/turpentine mixture was placed into a heated to 145 °C thermostatic bath and stirred at 120 rpm for 2 hours. After stirring, the resulting mixture was conditioned at room temperature for 12 hours. During the conditioning, a turpentine supernatant was observed. This was due to the gelation and syneresis of the mixture. Example images of the resulting gels containing unmodified and modified with 25 wt.% CB UHMWPE are provided in Figure 1.

Table 1. Characteristics of the UHMWPE RP used as a polymer matrix in the current study.

Intrinsic viscosity of the solution, dL/g	Mean molecular weight, 10^6 g/mol	RP bulk density, g/cm^3	Degree of crystallinity, %
23.92	4.16	0.05	72

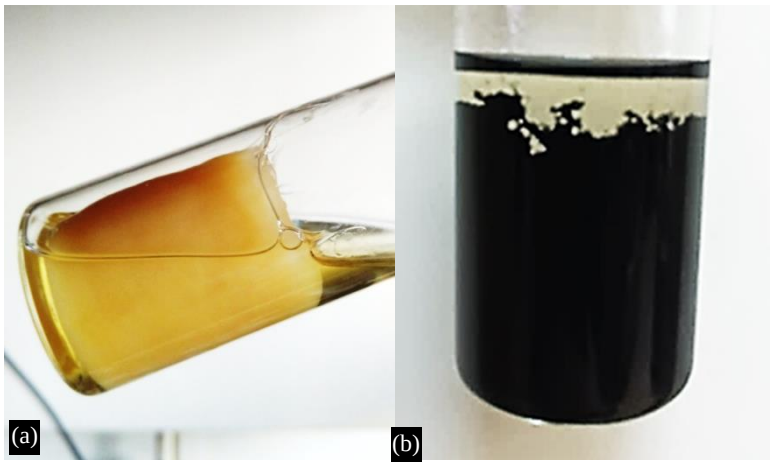
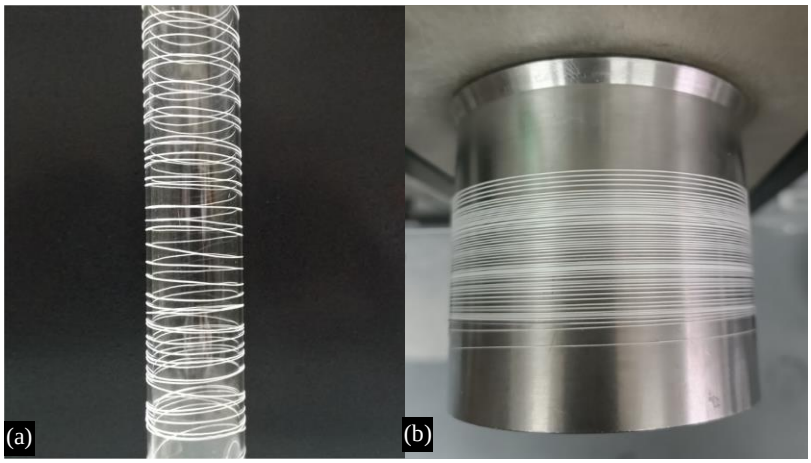


Figure 1. Images of UHMPWE gels containing (a) - 0 wt.% CB; (b) – 25 wt.% CB.

UHMWPE gel fibers were obtained through dry spinning using laboratory Spin Line multifunctional equipment (Daca Instruments, USA). The prepared gels were placed into a sealed dry spinning chamber and heated to 140 °C. After reaching the thermal equilibrium, the gels were extruded through a spinneret with a diameter of 1 mm at 2 mm/min speed of the piston. Upon exiting the spinneret, the extruded gel instantaneously solidifies in contact with the surrounding atmosphere. This solidified gel is conventionally considered to be a plasticized gel-fiber. The extruded gel-fibers were fed to a winder device with a receiver rotation rate of 0.13 m/min.

After the dry spinning, both unmodified and CB-modified UHMWPE-based gel-fibers were subjected to washing and conditioning procedures to remove the residual turpentine. The washing procedure included 8-hour treatment in n-hexane followed by an 8-hour treatment in isopropanol. After washing, the fibers were dried at 75 °C under the vacuum. During this stage, the fibers were fixed onto a glass tube in order to prevent thermally-induced shrinking.

Orientation drawing of the dried UHMWPE fibers was performed using a dedicated module of a laboratory SpinLine instrument (Daca Instruments, USA), which consisted of two synchronized rollers rotating at different rates to achieve the desired drawing ratio. The feeding rate was 0.1 m/min. The drawing ratio varied in a 3.4 to 15 range depending on the composition of the fibers. During the drawing, the fibers were in contact with a shoe which was heated to 135 – 140 ºC. The images of the fibers containing unmodified UHMWPE before and after the orientation drawing, as well as the spinning process of a UHMWPE fiber filled with 25 wt.% CB are provided in Figure 2.



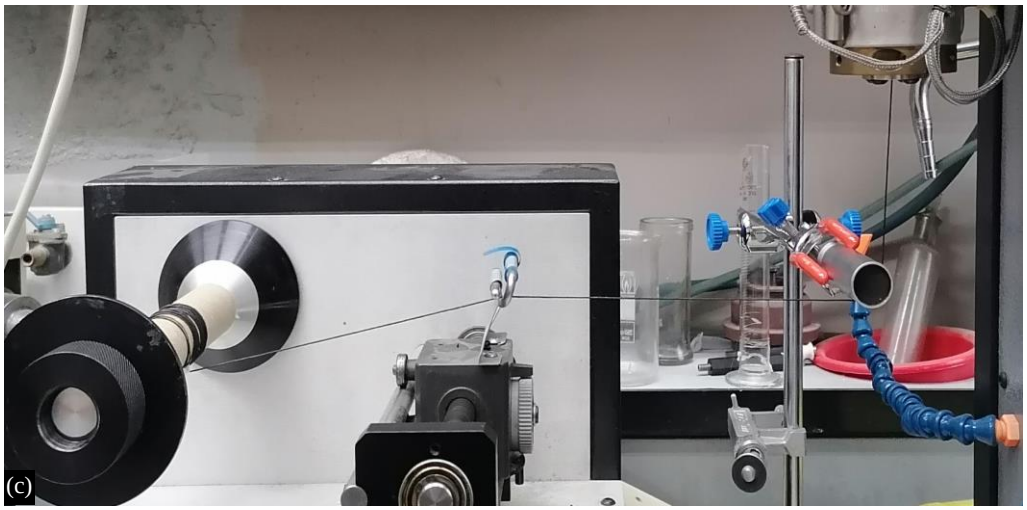


Figure 2. Images of the UHMWPE fibers (a) - before and (b) - after orientation drawing; (c) - spinning process of UHMWPE fiber containing 25 wt.% CB.

The composition of the obtained UHMWPE/CB gels is provided in Table 2.

Table 2. Composition of UHMWPE-based spinning gels obtained in the current study.

Polymer	Filler	Filler content (relative to polymer), wt. %	Polymer concentration in solution, wt. %
UHMWPE RP	P267E CB	5	1.4
		10	
		25	
		50	
		75	

The sample preparation procedure to obtain solid-state UHMWPE/CB composites comprised preliminary ultrasonication of the CB powder in n-hexane, followed by the addition of the UHMWPE RP into the CB dispersion. The resulting mixtures were subjected to additional ultrasound treatment. The ultrasound treatment of the filler dispersions and the mixtures of the UHMWPE RP and the CB was conducted using an I100-840 ultrasonic disperser (LLC «Ultrasonic technique — INLAB», Saint-Petersburg, Russia), characterized by the frequency of 22.5 kHz and adjustable power output (up to 1 kW). After the ultrasonication, the mixtures were dried out at room temperature until the complete n-hexane removal.

Solid-State-Processed Tape Fabrication

Solid-phase processing of the dried UHMWPE RP/CB mixtures was carried out by feeding the mixtures through the gap between two steel rollers with a diameter of 155 mm, heated to a temperature of 120°C with a molding speed of 400 mm/min. The extrusion ratio for the resulting monolithic tapes with a thickness of ~150 μm was ~5.5.

The obtained monolithic UHMWPE tapes were cut in the longitudinal direction into 10 mm wide strips for subsequent orientation drawing. Orientation drawing of the tapes was performed using a laboratory SpinLine instrument (Daca Instruments, USA) in contact with a table heated to 139°C at the relative deformation rate of 30 min^{-1}. Resulting orientation drawing ratio was ~24, which corresponded to the total drawing ratio ~132, taking into account the deformation during the extrusion. The resulting solid-state fibers had linear density of 35–40 tex with the width of 2 mm.

The compositions of the obtained in the work UHMWPE/CB tapes are provided in Table 3.

Table 3. Composition of UHMWPE-based tapes obtained by solid state processing.

Polymer	Filler	Filler content (relative to polymer), wt. %
UHMWPE RP	P267E CB	1
		2
		4
		7
		10
		12.5
		15
		20
		25

Methods of Investigation

The universal testing machine Ez Test Ez-LX (Shimadzu, Kyoto, Japan) equipped with a load cell of 500 N was used for the mechanical testing of the UHMWPE-based solid-state and gel-fiber samples. The traverse speed was set to 2 mm/min until the pretension of 0.5 N was reached. Thereafter, the strain rate was set to 1 mm/min with the initial distance between the clamps set at 50 mm. For each specimen three repeatable curves were obtained.

X-Ray diffraction (XRD) diffractograms (2θ = 10–60°) were obtained for CB powder and UHMWPE-based dried xerogel films using a D8 Advance (Bruker, Billerica, MA, USA) powder diffractometer ($\lambda(CuK_\alpha)$ = 1.5418 Å) equipped with a focusing germanium crystal monochromator, a Ni-filter, and a LYNXEYE 1D scintillating detector. XRD diffractograms were recorded in the transmission mode. During the measurements, CB powder sample was placed between two films of amorphous poly(ethylene terephthalate). In order to perform the XRD measurements, samples of UHMWPE-based gels (see Table 2) were subjected to the same washing and conditioning procedures as the spun gel-fibers. As the result, dried xerogel films with thickness of 1 mm were acquired.

Wide-angle XRD 2D-patterns for oriented UHMWPE gel-fibers were obtained at a laboratory X-Ray station (Rigaku, Tokyo, Japan) equipped with a MicroMax-007 HF rotating anode source, a cooled Saturn 944HG CCD-detector and a confocal VariMax-HF optical system.

Microphotograph of the surfaces of the spun and drawn UHMWPE gel-fibers filled with CB were obtained using a JCM-6000PLUS (Jeol, Tokyo, Japan) scanning electron microscope at the high-tension voltage of 10 kV. Prior to the measurements, the fiber samples were fixed on a carbon tape and coated with gold to prevent excessive accumulation of the electrical charge.

Electrical resistance measurements of the UHMWPE-based solid-state-processed tapes and gel-fibers were performed via the four-probe method using a 34401A multimeter from Agilent (Santa Clara, USA).

RESULTS AND DISCUSSION

The obtained UHMWPE-based gels were studied using the XRD technique. The XRD-patterns for the obtained films are provided in Figure 3.

The results in Figure 3 suggest that the CB presence does not prevent UHMWPE polymer matrix from partially crystallizing even at the content values as high as 50 wt.% or even 75 wt.%. This is an important observation, since the presence of a polycrystalline phase is required in order to perform orientation drawing of gel-fibers.

During the orientation drawing of the UHMWPE and UHMWPE/CB fibers, a correlation was observed between the CB content and the highest achievable drawing ratio. The values of the ratios are given in Table 4.

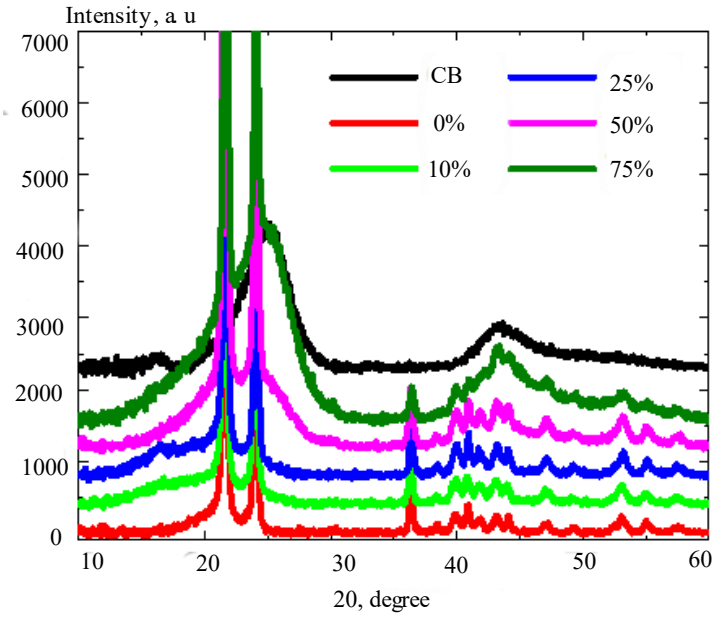


Figure 3. XRD patterns for the unfilled UHMWPE and UHMWPE/CB xerogels. For each curve the content value of CB in a gel is provided. The black curve corresponds to the XRD pattern of the CB powder.

Table 4. Highest achievable orientation drawing ratio for UHMWPE-based gel-fibers as a function of CB content.

CB content, wt.%	**0**	**5**	**10**	**25**	**50**	**75**
Max. orientation drawing ratio	15.0	9.4	7.5	6.7	6.1	3.4

As suggested by the data in Table 4, an increase in CB content results in a decrease of the highest drawing ratio of the fibers. Consequently, the molecular orientation of the polyethylene chains is higher for the oriented unmodified UHMWPE fibers compared to, e.g., UHMWPE fibers containing 50 wt.% CB, as suggested by the azimuthal distribution of X-Ray scattering intensity in 2D XRD patterns, presented in Figure 4.

The results of uniaxial loading tests demonstrated the influence of the difference in the maximum orientation drawing ratios on the mechanical properties of the fibers. In Figure 5 the representative stress-strain curves are provided for the unmodified and composite UHMWPE-based gel-fibers oriented to the maximum drawing ratio (Table 4).

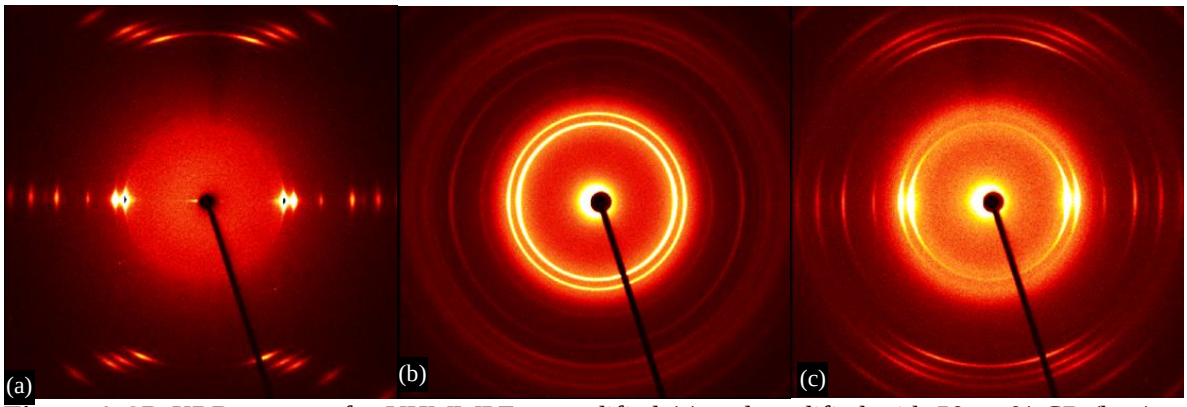


Figure 4. 2D XRD patterns for UHMWPE unmodified (a) and modified with 50 wt.% CB (b, c) gel-fibers before (b) and after (a, c) the orientation drawing to the maximally achievable ratio (Table 3).

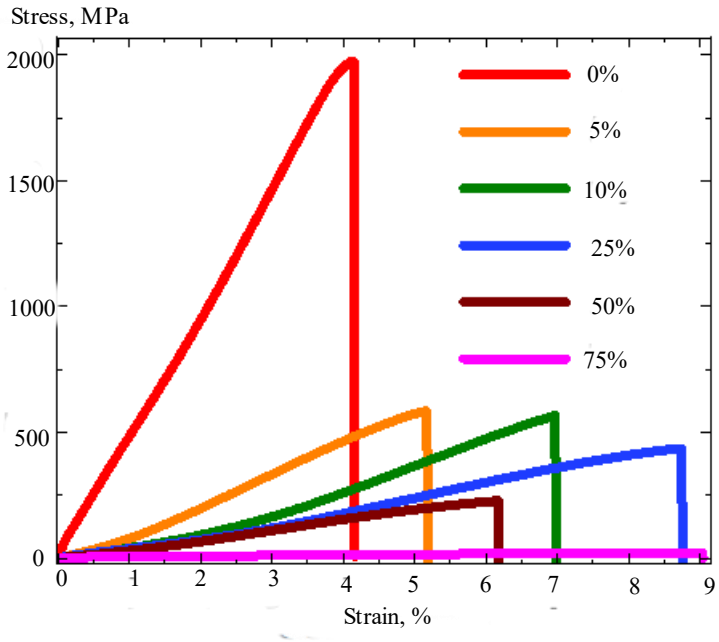


Figure 5. Stress-strain curves for the unmodified and composite UHMWPE gel-fibers. For each curve the weight content of CB is provided.

The tensile strength, Young's modulus, and strain at break values obtained from the stress-strain curves (Figure 5) are summarized in Table 5.

Table 5. Mechanical properties of the UHMWPE-based gel-fibers obtained by uniaxial loading tests.

CB content, wt.%	Young's modulus, GPa	Tensile strength, MPa	Elongation, %
0	4.7 ± 0.5	1970 ± 50	4.1 ± 0.1
5	1.5 ± 0.1	671 ± 5	5.2 ± 0.6
10	0.87 ± 0.05	568 ± 6	7 ± 0.2
25	0.47 ± 0.04	449 ± 5	8.7 ± 0.5
50	0.44 ± 0.04	230 ± 30	6 ± 1
75	0.24 ± 0.02	21.3 ± 2.5	9 ± 2

The analysis of the stress-strain curves in Figure 5 and the data in Table 5 allows for a conclusion that while the decrease in the mechanical properties is evident for the fibers containing 5, 10, 25 and 50 wt.% CB, it becomes critical at 75 wt.% CB content. According to the data in Table 4, the maximum orientation drawing ratios for the fibers containing 50 and 75 wt.% CB differ by the factor of 2, and yet the mechanical properties of the latter exhibit a 10-fold comparative decrease.

This observation can be explained by the excessive presence of structural defects in UHMWPE fibers modified with 75 wt.% CB. This assumption is supported by the results of the SEM images analysis for the composite UHMWPE/CB fiber surfaces. Corresponding images are provided in Figure 6.

According to the SEM images, the surfaces of the UHMWPE-based fibers modified with 75 wt.% CB are defective, compared to the surfaces of the fibers with lower CB content. Excessive surface defects can hinder the orientation of the fiber during drawing, promoting instead a local cohesive failure and subsequent longitudinal fracture of the fiber when drawing force is applied. In this case, the observed drawing ratios would not entirely reflect the molecular orientation of the fiber, but rather include a fracture deformation component. Contrary to this, the drawing of the UHMWPE fiber modified with 50 wt.% CB resulted in an increase of molecular orientation, as suggested by the 2D XRD patterns provided in Figure 4.

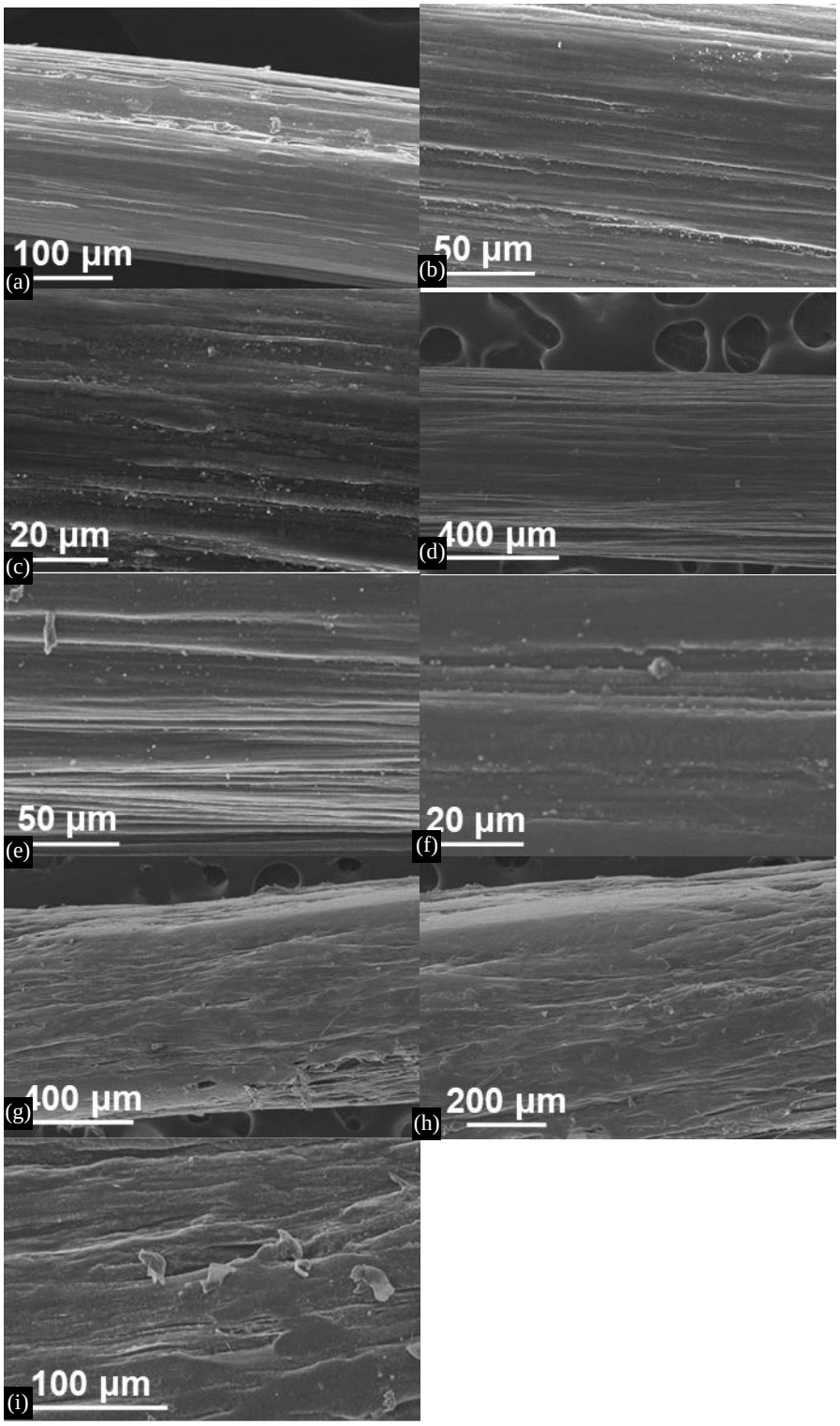


Figure 6. SEM images of the composite UHMWPE/CB fibers surface. (a – c) – 10 wt.% CB; (d – f) – 25 wt.% CB; (g – i) – 75 wt.% CB.

High CB content could potentially increase the electrical conductivity in UHMWPE fibers. In order to provide experimental evidence to this assumption, electrical conductivity was measured for UHMWPE and UHMWPE/CB fibers before orientation drawing and after drawing them to the highest achievable ratio (see Table 4). As predicted, the unmodified UHMWPE fibers were non-conductive.

The UHMWPE fibers modified with 5 and 10 wt.% CB were also insulating, and a measurable conductivity manifested only at CB content values exceeding the threshold of 25 wt. %. Corresponding results are provided in Figure 7.

As observed in Figure 7, the electrical conductivity of UHMWPE/CB fibers increased upon their orientation drawing. Surprisingly, this effect was more pronounced for UHMWPE fibers modified with 75 wt.% CB, as compared to the fibers containing 50 and 25 wt.% CB. Indeed, the drawing of the fibers containing 75 wt.% CB to a 3.4 ratio resulted in the conductivity decrease by the factor of ~11, while the orientation drawing of the UHMWPE-based fibers modified with 25 and 50 wt.% CB decreased their conductivity by the factors of ~4.5 and ~4.3 (drawing rations being ~6.7 and ~6.1, see Table 4), respectively. This effect can be attributed to the defect-induced cohesive longitudinal tearing of the UHMWPE/CB fibers containing 75 wt.% CB during their drawing.

The difference in the relative electrical conductivity decreases for the orientation-drawn UHMWPE/CB fibers containing 25 and 50 wt.% was unexpected, since it was viable to assume that the contacts between CB particles in the conductive network can be disrupted more efficiently at the lower CB content values. Apparently, the CB percolation cluster undergoes a structural reorganization during the deformation of the polymer matrix. This reorganization seems to be more pronounced at 50 wt.% CB content, as the CB particles become increasingly confined in the amorphous phase of UHMWPE.

Electrical conductivity of the composite gel-fibers was compared to the conductivity of UHMWPE/CB tapes obtained by solid-state processing. Corresponding plots of electrical conductivity against the CB weight content for unoriented tapes and fibers are presented in Figure 8.

The results of electrical conductivity measurements suggest that the filler percolation threshold for UHMWPE/CB composites is achieved at the CB content of 15 – 20 wt.% for gel-fibers and approximately 2.5 wt.% for solid-state processed tapes. This result can be explained by the morphological difference in the filler distribution inside of gel-fibers and solid-state processed tapes.

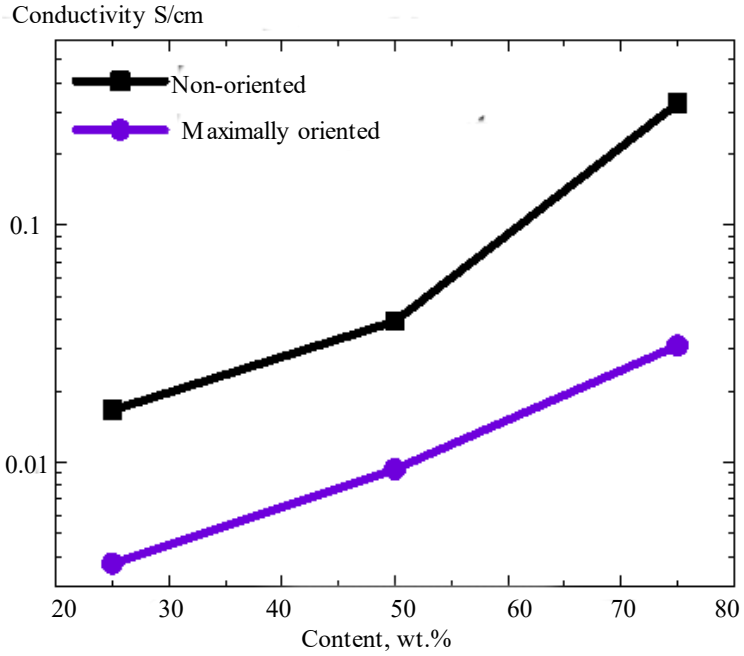


Figure 7. Electrical conductivity of UHMWPE/CB composite fibers before and after orientation drawing to the maximally achievable deformation ratio (Table 4) versus CB weight content. Nonmodified UHMWPE fibers and UHMPWE/CB fibers containing 5 and 10 wt.% CB were non-conductive and therefore not included in the plot.

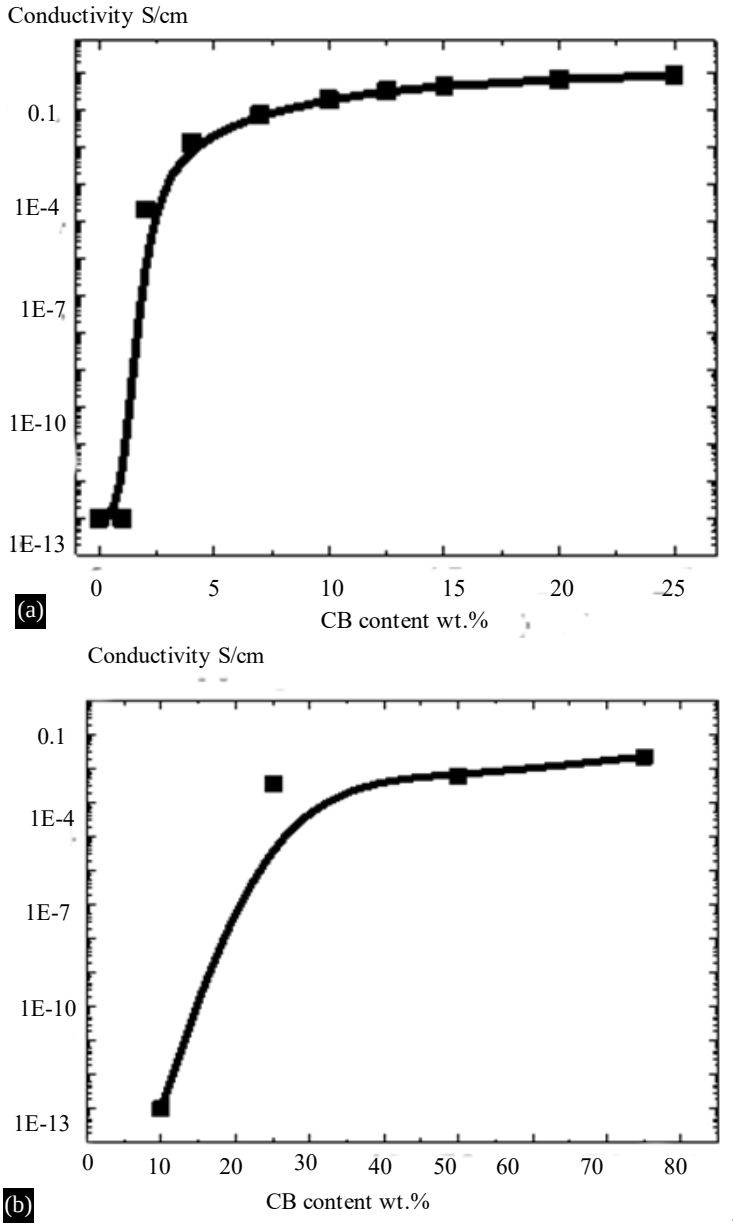


Figure 8. Electrical conductivity of UHMWPE/CB composites plotted against the CB weight content. (a) – unoriented tapes obtained by solid-state processing; (b) – unoriented gel-fibers.

While the UHMWPE/CB fibers obtained by the gel processing route featured a close to a homogeneous volume distribution of the CB particles (to the extent of possible filler aggregation during the gelation), the solid-state-processed tapes exhibited an extremely segregated filler morphology which resulted directly from the processing conditions. According to the solid-state processing procedure, CB particles coated the surface of UHMWPE RP particles during the ultrasound treatment. As the resulting UHMWPE RP/CB material underwent monolithization below the UHMWPE melting point, the CB particles became confined at the boundaries of the compressed UHMWPE RP particles. Subsequently, segregated CB-enriched regions were formed in a resulting UMHWPE/CB tapes [4,27].

The extremely segregated filler structure in the UHMWPE/CB solid-state-processed composites turned out to be affected by orientation drawing, resembling the discussed previously phenomena observed for the UHMWPE/CB gel-fibers. The dependence of relative conductivity on deformation ratio achieved during the uniaxial orientation of the UHMWPE solid-state-processed tapes modified with 10 wt.% of CB is provided in Figure 9a.

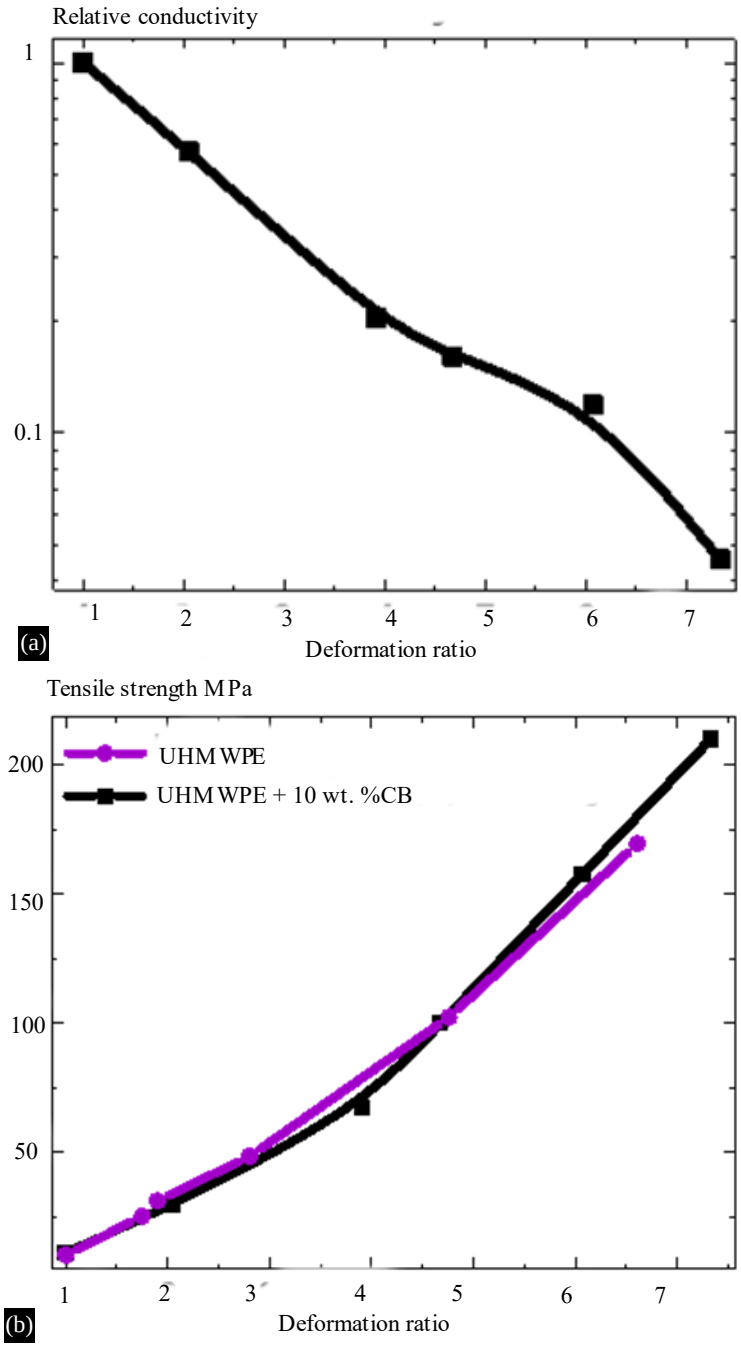


Figure 9. Dependence of electrical conductivity (a) and tensile strength (b) of UHMWPE solid-state tapes modified with 10 wt.% CB on deformation ratio, achieved during uniaxial orientation drawing.

As observed from Figure 9a, the orientation drawing of UHMWPE/CB composite tape resulted in a significant decrease of the relative conductivity, despite the CB content value (10 wt.%) significantly exceeding the percolation threshold of 2.5 wt.% (Figure 8a). Upon reaching the deformation ratio of 7.3, the electrical conductivity decreased by the factor of ~22. Remarkably, this effect could not be attributed to the macroscopic defects similarly to UHMWPE-based gel-fibers modified with 75 wt.% CB. Indeed, the results presented in Figure 9b suggest that there was no observed difference in the dependence of UHMWPE tensile strength on deformation ratio for pure UHMWPE solid-state tape and a composite tape containing 10 wt.% CB. Meanwhile, the presence of macroscopic defects should have affected the mechanical properties of the solid-state UHMWPE/CB tapes, as was observed for gel-fibers containing 75 wt.% CB.

It is known that the process of orientation of macromolecular chains of polymeric materials results in an increase in the mechanical properties of the polymer in the direction of orientation [28]. According to the data of XRD analysis (Figure 3 and Figure 4) and mechanical tests (Figure 5), the orientational strengthening of UHMWPE governs the mechanical properties of the composite material independently of the amount of modifying filler and is determined purely by the degree of polymer orientation. The filler, in turn, determines the maximum achievable degree of orientation of the polymer material (Table 4). At the same time, the influence of the alignment of the filler particles along the orientation direction on the mechanical properties for a given degree is not obvious. Simultaneously, conductivity loss occurs during orientation drawing, indicating loss of contacts between clusters of filler particles. This suggests that the contribution of percolation cluster continuity breakage to the change in conductivity is significantly larger than the possible contribution of nanoparticle alignment along the orientation direction.

CONCLUSIONS

In the presented study, a possibility to obtain composite UHMWPE-based oriented fibers containing high amounts of carbon nanofillers was demonstrated. Utilizing the gel-processing approach it was made possible to achieve the content values up to 75 wt.% for electroconductive CB in UHMWPE matrix. Although at the content of 75 wt.% of CB the fibers became defective and their mechanical characteristics decreased significantly, the corresponding gels could still be processed by conventional gel-spinning through a 1 mm spinneret, yielding continuous and flexible monofilament composite fibers. At 25 wt.% and 50 wt.% CB content values the UHMWPE/CB composite fibers retained the possibility of orientation drawing up to 6.4 and 6.1 ratios, respectively. At these content values the UHMWPE/CB fibers were found to be electrically conductive, with conductivity of $6 \cdot 10^{-4}$ S/cm prior to the orientation drawing.

Alternatively, composite UHMWPE/CB tapes obtained through solid-state processing expressed the same conductivity at 3 wt.% CB. At 25 wt.% of CB, which was the highest achieved filler content for the solid-state processed UHMWPE/CB composites, the conductivity of non-oriented tapes was 0.86 S/cm. The percolation threshold for the solid-state-processed UHMWPE/CB tapes was estimated to be an order of magnitude lower than the threshold for gel-spun fibers.

Considering that both gel-spun fibers and solid-stated processed tapes were obtained from the same UHMWPE RP and using the same CB filler, the difference in electrical conductivity and percolation thresholds can be attributed to different structural organization of the filler inside the polymer matrix. Indeed, during the preparation of the spinning gel, CB particles were mixed homogeneously with the UHMWPE macromolecules in solution. Some degree of CB aggregation inevitably was expected during the gelation, as well as during partial UHMWPE crystallization at dry spinning stage and due to solvent removal at the conditioning stage. However, this thermodynamically-driven aggregation occurred statistically randomly, so the CB particles were considered to be distributed homogeneously (if not uniformly) inside the amorphous phase of UHMWPE. Contrary to this, the solid-state processing procedure was specifically tailored to retain the segregation of CB filler on the UHMWPE RP grain boundaries. Since the CB-coated UHMWPE RP particles underwent a pressure-induced compaction below the UHMWPE melting point and the degree of UHMWPE crystallinity was high, the segregated structure of the filler retained. This meant that the filler was extremely localized inside the polymer matrix, which resulted in a significant decrease of the percolation threshold. However, the relative drawback of the solid-state approach is that exceeding 25 wt.% CB contents was proven to be impossible.

Irrespective of the filler distribution type (homogeneous in the case of gel fibers or extremely segregated in the case of solid-state tapes), a notable reduction in electrical conductivity was observed following orientation drawing. This was an unanticipated and substantial outcome, as it suggests that both the homogeneous and segregated percolation clusters are readily disrupted by deformation, even

with the polymer matrix being chemically inert and thus unable to form strong chemical bonding with the filler. At the same time, the degree of the physical interaction between the polymer matrix and the filler highly depends on the degree of filler segregation in a polymer composite. This was substantiated by a notable reduction in the maximum achievable orientation deformation ratio and subsequent tensile strength decline in the case of gel-spun fibers, as well as the absence of any influence of the filling on orientation strengthening in the case of solid-state processed tapes.

Overall, the application of two different processing techniques to the same constituent materials (UHMWPE RP and CB filler) provided an opportunity to directly compare the properties of the UHMWPE-based composites featuring two distinctive types of filler distribution in the polymer matrix.

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