Hugely improved electromagnetic interference shielding and mechanical properties for UHMWPE composites via constructing an oriented conductive carbon nanostructures (CNS) networks

Huibin Cheng
Fujian University of Technology

Guoliang Lin
Fujian University of Technology

Xiaoyi Zhang
Fujian University of Technology

Chen Wu
Fujian University of Technology

Shenglan Ma
Fujian University of Technology

Xuhong Liu
Fujian University of Technology

Baoquan Huang
Fujian Normal University

Qinghua Chen
Fujian Normal University

Qingrong Qian
Fujian Normal University

Changlin Cao (caochlin3@fjnu.edu.cn)
Fujian Normal University

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Abstract

To address the practical application challenges of conductive polymer composites (CPCs) in portable electronics equipment, such as their low thermal conductivity (TC) and poor electromagnetic interference (EMI) shielding effectiveness (EMI SE), it is crucial to improve their TC, electrical conductivity ($\sigma$), and EMI SE of CPCs. In this work, we present a conducting composite made of ultrahigh molecular weight polyethylene (UHMWPE) and carbon nanostructures (CNS) with a unique segregated structure. This structure is achieved through a simple high-speed mechanical mixing and compression molding process. Microscopy characteristics demonstrated that both the matrix and segregated conductive network were in-situ oriented along the compress direction of UHMWPE granules under the static hot-pressing field. CNS are compacted together at the interface between UHMWPE granules to form an oriented and interconnected conductive pathways at low CNS loading levels. The resultant UHMWPE/CNS composites with 10 wt% CNS content exhibits excellent EMI shielding performance, with EMI SE of 60.7 dB (at X-band), high conductivity of 2.42 S/cm, and acceptable thermal conductivity of 0.7217 (W/m K). High EMI shielding performance and absorption dominant mechanism are benecial from the unique segregated structure, and individual CNS coated UHMWPE granule are similar to an electromagnetic cage. Additionally, the ultimate tensile strength of the composite remains high at 37.6 MPa even at 10.0 wt% CNS loading, and it shows effective thermal stability. These properties are attributed to the strong interfacial bonding between CNS and UHMWPE. These materials have potential applications in efficient thermal management and EMI shielding for high-performance intelligent electrical devices.

1. Introduction

The explosive development of mobile phones and computers brings many conveniences to people and improves the quality of life. However, these electronic devices constantly create electromagnetic waves radiate, and will cause more serious electromagnetic radiation pollution issues. Moreover, excessive operating temperatures may affect the performance and service life of electronic devices[1, 2]. Therefore, efficiently blocking electromagnetic waves and eliminating heat accumulation has become an inevitable issue[3]. The segregated conductive polymer composites (s-CPCs), due to the merits of lightweight mechanical flexibility, and facile fabrication, have provided an excellent new opportunity for electromagnetic interference shielding (EMI) and thermal management performance[4, 5]. However, a high content of conductive fillers loadings is often needed to achieve the required electrical conductivity, this methodology can make the materials difficult to process and become expensive [6, 7]. To address the issue of the unforeseen comprehensive properties of s-CPCs materials at high filler content, various methods have been explored to tune the conductive network and reduce the filler content while maintaining electrical conductivity. These methods include functional filler hybridization [8], selective dispersion of filler in immiscible polymer blends, oriented alignment of fillers [9], and construction of a segregated structure[10]. Among these above-mentioned strategies, the construction of an oriented segregated structure is particularly effective in achieving a low percolation threshold.
Li. et al. [11] prepared UHMWPE composites with high CNTs content by solution mixing and hot pressing. When CNTs content was 60 wt%, the composites had a high electrical conductivity of 5649 S/m. The high content CNTs/UHMWPE composites did not mention serious deterioration of mechanical properties, and the tensile strength was only 14.5 ± 0.7 MPa. Yu et al. [12] reported an ultra-high molecular weight polyethylene/carbon nanotube (UHMWPE/CNT) composites via a hot stretched in the solid phase process exhibit a unique oriented segregated structure that leads to superior mechanical strength and selective EMI shielding performance. This high performance is correlated to this obtained special segregated structure, which is effective at blocking electromagnetic waves through multiple scattering, interfacial polarization, and electron hopping at the interfaces. This is mainly attributed to the conductive particles in these composites are located at the interfaces between polymer domains rather than being dispersed randomly throughout the composite, which creates interconnecting conductive networks that enhance the electrical conductivity loss. Additionally, polarization loss caused by the interface between different components is also effective at attenuating and blocking electromagnetic waves. However, UHMWPE composites with the special conductive networks how to play a role in shielding interference mechanism of electromagnetic wave still need further study.

UHMWPE has the potential to be used in a variety of fields due to its unique properties[13, 14]. However, there are many challenges and processing limitations that prevent its widespread use[15–17]. One way to overcome these challenges is to use UHMWPE or other polymer as the matrix for segregated conductive polymer composites, such as polyvinylidine fluoride (PVDF) [18, 19], thermoplastic polyurethane (TPU) [20, 21], polypropylene (PP) [22], and high-density polyethylene (HDPE) [23]. By using conductive fillers with high surface area and aspect ratio, researchers can create dense conductive networks in the polymer matrix, which can improve the material's overall properties[24]. This approach is significant for both academic research and industrial production. Researchers have been working hard to overcome the challenges of dispersing and improving the interfacial adhesion of carbon nanotube (CNT)[25], graphite(G)[26] and graphene nanoplatelets (GNPs)[27–29]. However, the methods currently-used for surface modification are complex and tedious, making it difficult to scale up their fabrication and use in academia and industry. Improving the interface interactions between additives and between the polymer matrix and additives is crucial for creating high-performance composites, but current methods are not effective enough. Therefore, it is important to find a simple and effective approach for fabricating high-performance composites.

Carbon nanostructures (CNS) are a novel type of cross-linked, branched carbon nanotube material that can be used as conductive additives in thermoplastics and thermosets at very low loadings[30]. These materials have excellent dispersion quality and superior EMI shielding effectiveness, making them a promising prospect for use in industrial applications[31, 32]. However, few studies have investigated the incorporation of unique carbon nanostructures conductive fillers into the UHMWPE matrix, and the impact on the material's mechanical, electrical, and thermal properties. in this study, UHMWPE was used as a polymer matrix and electrically conductive UHMWPE composites with varying CNS loadings were fabricated through a simple mechanical mixing and compression molding method. We comprehensively investigated the effects of varying the CNS content on the phase morphology, electrical conductivity, EMI
shielding performance, mechanical properties, and melt-crystallization properties of the UHMWPE/CNS composites.

2. Experiment

2.1 Materials

Carbon nanostructures (CNS) with the crosslinked branched carbon nanotubes, containing > 97% carbon, were purchased from Cabot Co., Ltd, USA. UHMWPE under the trade of SLL-2, with the average molecular weight of 3.00×10^6 g/mol was supplied by Shanghai Lianle Chemical Industry Science and Technology Co., Ltd. (Shanghai, China). All raw materials were used as received without further modification.

2.2. Preparation of UHMWPE/CNS segregated composites

CNS particles and UHMWPE powders have been dried in a vacuum oven at 80°C for 6 h. Then, UHMWPE powders together with large-specific-surface-area CNS particles (the weight ratios of 99.5/0.5, 99/1, 97/3, 95/5, 93/7, and 90/10, respectively) were high-speed mechanically mixed in the crusher (800Y, Yongkang Platinum Ou Hardware Products Co. Ltd, China), under the condition of the rotation speed of 34000 r/min for 50 s, obtaining the different concentration CNS-coated UHMWPE mixtures. Afterward, the resultant compounds were compression molded at the temperature of 200°C, the pressure of 17 MPa, time of 20 minutes on a flat vulcanizing machine, followed by cold compression molded to room temperature at a pressure of 17 MPa. The final prepared specimens were designated as UHMWPE/CNS \( x \) composites, in which \( x \) means that the weight fraction of CNS particles. The preparation of UHMWPE/CNS \( x \) samples was illustrated in Fig. 1.

2.3 Characterization

The morphology of UHMWPE/CNS \( x \) composites was investigated using a cold field emission scanning electron microscope (FE-SEM, Regulus 8100, Hitachi, Japan) at an accelerating voltage of 10 kV. The microscopic structure of CNS was analyzed by transmission electron microscope (TEM, Tecnai G2 F30, FEI, USA). To examine intuitively the conductive networks of the UHMWPE/CNS composites, Optical microscopy (OM) was used. Raman mapping was performed by a micro-laser confocal Raman spectrometer (Thermo Scientific DXR2xi, America) for pure UHMWPE, UHMWPE/CNS composites. The test condition of Raman mapping measurement was that the laser power is 1.5 mW, and the total exposure is 30 times with 0.025s exposure time for each spectrum. The microstructure of CNS particles and UHMWPE matrix on the cross-sectional surface of UHMWPE/CNS composites was obtained on atomic force microscopy (AFM) measuring system (JPK NanoWizard 4, Bruker, Germany). A silicon probe (resonant frequency 320 kHz, spring constant 42 N m\(^{-1}\)) and Quantitative Imaging (QI) mode were used for study.
The electrical conductivity was measured by a high-resistance meter (ZC-90G, Shanghai Taiou Electronics Co. Ltd., Shanghai, China) higher than $10^{-5}$ S/m, four-point probes resistivity measurement (RTS-9, Guangzhou Four Probe Technology Co. Ltd., Guangzhou, China) below $10^{-5}$ S/m. The thermal conductivity was tested by a hot–wire thermal conductivity instrument (Xiatech TC3000E, Xian, China) according to ASTM D5930. The electromagnetic interference (EMI) shielding performance was measured by a vector network analyzer (Agilent 5230, Agilent, USA) in the X-band (8.2–12.4 GHz) frequency at room temperature. The corresponding reflection (R), absorption (A), and transmission (T) coefficient parameter calculation and the detailed characterization information was obtained via using the following equations[33, 34]:

\[ T = |S21|^2 = |S12|^2 \quad (1) \]

\[ R = |S11|^2 = |S22|^2 \quad (2) \]

\[ A + R + T = 1 \quad (3) \]

\[ SE_R = -10 \log(1-R) \quad (4) \]

\[ SE_A = -10 \log(T/1 - R) \quad (5) \]

\[ EMI\ SE = SE_R + SE_A + SE_M \quad (SE_M can \ be \ negligible \ when \ SE \geq 15 \ dB) \quad (6) \]

The sheets were cut into dumbbell-shaped specimens for the evaluation of the mechanical properties using a universal testing machine (CMT4104, Shenzhen Sans Material Inspection Co. Ltd., Shenzhen, China).

The measurements were repeated five times to get the average values. Thermo gravimetric analysis (TGA) is used to evaluate the thermal stability of UHMWPE/CNS composites and the interaction between UHMWPE matrix and CNS by analyzing the relationship between sample mass and temperature or time at programmed temperature. Crystalline and melting properties of the composites were performed on a Differential scanning calorimeter (DSC) (Q20, TA Instruments, USA), The degree of crystallinity ($X_c$) was calculated using the following equation [35]:

\[ X_c = \frac{\Delta H_m}{\Delta H_m^0 \cdot \omega} \times 100\% \]

Where $\Delta H_m$ is the fusion enthalpy calculated from the area of the endothermic melting peak, $\Delta H_m^0$ (289.3 J/g) is the theoretical heat of fusion for a 100% crystalline UHMWPE, and $\omega$ represents the UHMWPE weight fraction in the composites.
3. Results And Discussion

We firstly investigated the morphology, specific surface area, and graphitic structure of CNS particles using FE-SEM, TEM, BET measurements, and Raman spectroscopy. The specific surface area was calculated by the BET method, as shown in Fig. S1 and Tab. S1. In Fig. S1a-c, BET and Raman test results indicated that the CNS materials are highly graphitized, have strong adsorption and desorption capabilities, and have a high specific surface area. These structural characteristics can promote better physical bonding between the polymer matrix and the CNS. SEM and TEM structural characterization analysis revealed that CNS is a macroscopically crosslinked, branched carbon nanotube with a dense and continuous 3D or 2D network structure, which has good dispersion. To better understand the distribution of CNS in UHMWPE, the microstructure of the obtained UHMWPE/CNS composite was studied using Optical microscopy (OM), FE-SEM, Raman spectroscopy, and atomic force microscopy (AFM). Figure 2 presents the optical images and corresponding SEM micrographs of the UHMWPE/CNS composites with the same CNS content. SEM and OM image reveals the segregation of the CNS network in the UHMWPE/CNS composite.

In Fig. 2(a₁-c₁), UHMWPE/CNS₁ composite appears to have some poorly connected conductive channels, indicating that the effective conductive network has not yet been fully developed. As the CNS content increases from 1 wt% to 5 wt%, the CNS layers (the dark region) are selectively located at the interfaces between UHMWPE domains (the bright region) and are well-connected, forming a dense and complete conductive network with a segregated structure (Fig. 2b₁ and Fig. 2b₂). Furthermore, when the CNS content is increased to 5 wt%, it is clear that in situ formation of a synergistic orientation composed of both the segregated conductive filler network and the polymer matrix, along with enhanced interfacial bonding, further promotes the development of additional conductive pathways. Additionally, with further increases in CNS content, the uniform dispersion of CNS, intensive interfacial adhesion, and improved CNS network in UHMWPE are beneficial for the mechanical performance of the UHMWPE/CNS composites and are expected to have significant impacts on EMI shielding and mechanical performance (Fig. 2c₁ and Fig. 2c₂).

AFM is an effective way to study the detailed microstructure of polymer/carbon filler composites. This is because carbon materials have higher stiffness and Young's modulus compared to the soft polymer matrix. Thus, we further investigate the interfacial mechanism of CNS particles and UHMWPE. Fig. S2 shows the surface topography and 3D topography. Apparently, the dark region represents CNS particles and the bright parts are the UHMWPE matrix, and with the addition of CNS increase, there is an ordered alignment of the CNS particles along a certain direction, forming a well-improved oriented network in the UHMWPE matrix as shown in Fig. S2a₁-b₁. This indicates that the CNS particles are attached to the UHMWPE molecular chain during the hot-pressing process, forming strong interfacial bridging effects through physical absorption of the high aspect-ratio structural CNS. Raman spectroscopy is a quick and powerful tool for characterizing the selective distribution of carbon materials[36]. Therefore, in the case of the UHMWPE/CNS composite materials, the presence of an interconnected conductive layer of CNS with a 3D network structure can be clearly observed via using Raman mapping, providing evidence for the
interface bridging effect between the UHMWPE particles under heat and pressure. Confocal microscopy and polarized Raman spectroscopy can be used to further analyze the microstructure and orientation of the composite materials. In the Raman mapping Fig. 3, the red area is the UHMWPE phase and the blue area is the CNS phase. There are obviously many transition layers (green transition layers) between the three-dimensional network structure of the CNS conductive layer and UHMWPE, as shown in Fig. 3a-c. The transition layers between the CNS conductive layer and UHMWPE can be seen in the Raman mapping, indicating the presence of interpenetrating diffusion at the interface between the UHMWPE molecular chains, which is consistent with the interface bridging effect characterized by AFM. Additionally, the comparison and analysis of Raman spectra at the interface of pure UHMWPE, UHMWPE/CNS\textsubscript{5}, and UHMWPE/CNS\textsubscript{10} composite materials show that there is a low crystallinity at the interface transition layer. The characteristic peak of UHMWPE at 1131 cm\textsuperscript{-1} and 1064 cm\textsuperscript{-1} shows a blue shift in the Raman shift of the composites. Furthermore, compared to the characteristic peak at 1416 cm\textsuperscript{-1} of pure UHMWPE, the peak intensity at the characteristic peak of the composite material is significantly reduced, indicating that the presence of CNS restricts the movement of the UHMWPE molecular chain and reduces its crystallinity, as shown in Figure S3.

Polarized Raman spectroscopy was used to determine the YX0° and YY90° spectra of the surface and cross-section of the composite material to demonstrate the effect of heat and pressure on the orientation of the CNS network induced by the UHMWPE matrix. Figure 4 shows the polarized Raman spectra of the surface and cross-section of UHMWPE, UHMWPE/CNS\textsubscript{5}, and UHMWPE/CNS\textsubscript{10} composites. The change in the Raman spectra of the UHMWPE crystalline region (-CH\textsubscript{2}- group) and CNS was analyzed. The effect of thermal pressure on the interface-induced orientation of UHMWPE and its composites was calculated by using the orientation degree(f) formula\cite{37–39}:

\[ f = \frac{R-1}{R+1} = \frac{A_{0^\circ}}{A_{90^\circ}}. \]

In this above-formula, A\textsubscript{0°} is the Raman peak area of the -CH\textsubscript{2}- group of the UHMWPE crystalline region at 1131 cm\textsuperscript{-1} or 1064 cm\textsuperscript{-1} in the YX0° Raman spectrum, and A\textsubscript{90°} is the Raman peak area of the UHMWPE at 1131 cm\textsuperscript{-1} or 1064 cm\textsuperscript{-1} in the YX90° Raman spectrum. The higher the f value, the higher the orientation degree\cite{40}. In Fig. 4, there is a significant change in the intensity of the polarized Raman characteristic peaks in the range of 1000–1800 cm\textsuperscript{-1} on the outer surface and cross-section of the composites. The f analysis of pure UHMWPE and its composites reveals that the orientation effect of the outer surface of pure UHMWPE is significantly higher than that of the cross section. When CNS is introduced into UHMWPE, the f values of the outer surface and cross section of the resulting UHMWPE/CNS composites increases with the increasing CNS content. This suggests that CNS undergoes interfacial induced crystallization under hot pressing between UHMWPE particles, which leads to a certain orientation effect in the UHMWPE matrix\cite{40}.
To identify the potential superiority of the oriented segregated UHMWPE/CNS composites, Fig. 5a-b display that the electrical conductivity ($\sigma$) and thermal conductivity (TC) of UHMWPE/CNS composites are studied as a function of CNS concentration. In Fig. 5a, a clear transition from electrical insulator to conductor is observed at around 0.5 wt% CNS. Above the transition region, the electrical conductivity of the UHMWPE/CNS composites improves significantly with the increase of CNS. This behavior can be explained by classical percolation theory, which states that the electrical conductivity of a composite material is determined by the volume fraction of conductive fillers, the percolation concentration, and the critical exponent that reflects the dimensionality. According to the classical percolation theory\[41, 42]\: $\sigma = \sigma_0 (\varphi - \varphi_c) t$, where $\varphi$ is the volume fraction of the fillers, $\varphi_c$ is the volume percolation concentration, $\sigma$ and $\sigma_0$ represents the electrical conductivity of the composites and the conductive fillers, respectively. And $t$ represents the critical exponent reflecting the dimensionality of the system. Moreover, for a single percolation system, the $t$ depends only on the dimensionality of the composites and follows a power-law dependence of approximately 2 (1.6-2) in a three-dimensional, and 1-1.3 in a two-dimensional system\[43\]. Therefore, the percolation threshold value of UHMWPE/CNS composites is estimated to be only 0.48 wt%, and the critical exponent $t = 2.43$ from theoretical percolation fitting indicates that the CNS conductive pathway has a three-dimensional structure in these composites, which is beneficial for high EMI shielding performance \[44\]. Besides, owing to the formation of a segregated CNS network, the UHMWPE/CNS composites achieve exceptional electrical conductivity, and thermal conductivity as high as 0.7217 (W/m K) at low content loading 10 wt% CNS, which is about two times than pure UHMWPE (Fig. 5b). Figure 5c presents the EMI shielding performance of segregated UHMWPE/CNS composites with different CNS concentrations. The UHMWPE/CNS$_3$ shows a stable EMI SE of 28 dB in the X-band (8.2–12.4 GHz), making it suitable for many commercial applications in the computer and electronics industries. In Fig. 5d-e, we observed that all UHMWPE/composite materials with CNS content exceeding a certain threshold value exhibit highly efficient EMI SE performance. Even at a CNS content of just 1 wt%, which surpasses the percolation threshold of 0.48 wt%, the UHMWPE/CNS composite showed a total EMI SE (SE Total) of around 7.07dB at X band. This low EMI SE value is related to the incomplete conductive network, which is consistent with the SEM results. As the CNS content increases, EMI SE values of composites increase sharply due to the increased electrical conductivity and the synergistic effect of the interfacial polarization of conductive CNS layer between UHMWPE particle multi-interfaces. Figure 5f shows the total SE (SE$_T$), absorption (SE$_A$), and the reflection (SE$_R$) as a function of CNS concentration at 10.3 GHz. The significant increase in SE$_T$ is primarily due to the improvement in SE$_A$, rather than SE$_R$, demonstrating an absorption-dominated shielding mechanism for the UHMWPE/CNS composite. The high EMI shielding performance and absorption-dominated mechanism are beneficial from the oriented segregated structure. CNS are compacted together at the interface between UHMWPE granules to form an interconnected conductive network, and individual CNS-decorated UHMWPE granules can be regarded as electromagnetic cages, as supported by SEM and Raman mapping results. To further clarify the EMI shielding mechanism in the segregated UHMWPE/CNS composites, Fig. S4 displays the reflection(R), absorption (A), and transmission (T) coefficient values of different composites at 12.4 GHz. As the content of CNS increases, T always keeps at quite a low level. For R, while there is a significant increase
with CNS content, this is due to the impedance mismatch at interfaces caused by the increasing conductivity. A value shows an increasing and then decreasing trend, which is caused by the huge increase in R. This implies that the EMI shielding mechanism of composites is an absorption-dominated shielding mechanism[45]. Furthermore, the addition of 10% CNS to UHMWPE creates a composite material with superior electromagnetic interference (EMI) shielding performance. The thicker CNS layer and multiple interfaces effectively interact with incident radiation, resulting in an average EMI shielding effectiveness of 60.7 dB, which is comparable to metal-based composite shielding materials. This range of 60–90 dB not only meets the requirements of precision instruments and military equipment, but also makes the UHMWPE/CNS composite an ultra-efficient material for EMI shielding applications[46].

The high EMI SE values are mainly due to the unique segregated structure. The shielding mechanism of UHMWPE/CNS composites is shown in Fig. 6. At the micro-zone interface of UHMWPE particles, CNS is compacted into an interconnected oriented conductive network. Additionally, UHMWPE like a "cell-like structure" segregated unit can be regarded as an electromagnetic cage (Fig. 6). When electromagnetic waves enter the interior of the composite material, the incident electromagnetic waves will be trapped in the cell-like cage for many times of reflection/scattering and reabsorption, and finally dissipated through the outer CNS network structure in the form of heat. Therefore, the "electromagnetic cage" effect allows most of the electromagnetic energy in the form of absorption and reflection to be dissipated in the CNS dual-function network by converting into heat energy[45].

Poor mechanical performance is a bottleneck restricting the applications of the segregated CPCs. To further confirm the superiority of the mechanical properties, the mechanical properties tests are conducted to evaluate the mechanical properties of pure UHMWPE and UHMWPE/CNS composite samples. Figure 7 shows the mechanical properties of pure UHMWPE and UHMWPE/CNS composite. Tensile stress-strain curves of UHMWPE/CNS composites with various CNS contents is displayed in Fig. 7a, and the related parameters, including ultimate tensile strength, yield strength, and elongation at break are shown in Fig. 7b-d. With the addition of CNS content increases to 0.5 wt% and 1.0 wt%, the ultimate tensile strength of segregated UHMWPE/CNS$_{0.5}$ and UHMWPE/CNS$_{1}$ composite is 45.7 MPa, and 46.2 MPa respectively. Compared to pure UHMWPE (42.8 MPa), UHMWPE/CNS composite exhibits a higher tensile strength. More importantly, with increasing CNS concentration, the changing trend of the tensile strength is almost not affected, and the ultimate tensile strength of the composite remains at a high level of 37.6 MPa even at 10.0 wt% CNT loading content (Fig. 7a-b). This excellent mechanical properties is completely distinguished from the reported literature about the prepared segregated structural UHMWPE/CNT[47], UHMWPE/GNP [48], and hybrid UHMWPE/G-CNT composites via a same process. Research findings is attributed to the incorporation of CNS with unique microstructure into UHMWPE forming the oriented segregated structures during compression molded process, which is consistent with the above-mentioned OM and SEM results. Owing to the synergistic effect of the formation of the oriented segregated structure and the intensive interfacial interaction between CNS and UHMWPE, resulting in UHMWPE/CNS composite possibly forms the improved crystallization structure. Besides, the yield strength of the UHMWPE/CNS composite shows a gradually increasing trend compared
to pure UHMWPE, which suggests the stiffness of the composite was significantly enhanced with the incorporation of CNS fillers. The elongation at break of the composite sample first increased and then decreased, with the CNS content increases from 0.5 wt% to 10 wt%, and the value dropped to 150% when filler content was as high as 10 wt%. This result indicates high loadings aggregated conductive fillers as stress center are not beneficial to improve the toughness in the composite. Hence, to avoiding to forming a more stress center in filled composite, introducing a moderate amount of the inorganic fillers with heterogeneous nucleating effect into the polymer can endow enhanced stiffness due to the inherently physical characteristics of inorganic fillers compared to pure polymer matrix, thereby improving the shortcoming of poor mechanical properties and thermal properties of the polymer. As we mentioned above, when the addition of CNS content into UHMWPE is 3 wt%, it is found that the tensile stress-strain curves of UHMWPE/CNS composite present a distinct change. This is likely to the incorporation of CNS into UHMWPE forms the enhanced crystallization structure, this is, CNS with high aspect ratio physical absorbed in the UHMWPE molecular chains via high-speed mixing and compression molding, then the obtained composites clod compression molded to the room temperature, while the CNS absorbed UHMWPE molecular chains align along a certain direction as well. The special oriented crystallization structure is formed due to the strong Van der Waals forces of CNS. To verify the probability of the formation of a new crystallization structure and matrix-filler interaction, we carried out DSC and TGA measurement, further analyze the cooling, melting behavior of pure UHMWPE and its composites, and CNS-UHMWPE interaction of composites, as is shown in Fig. S5. The detailed DSC and TGA values are listed in Tab. S2 and Tab. S3. There is a sustained rise, from 45.4% and 50.5%, of the crystallinity as the CNS content increases. In addition, the width at half-height of the melting peak usually reflects the interfacial compatibility of the components in blends. In Tab. S2, with increasing CNS concentration, the width at half-height of the melting peak of all the composites gradually reduces, the interfacial compatibility was improved. And with CNS content increases, this melting peak of composites gradually became sharper, particularly for the UHMWPE/CNS$_3$ composite, a significant and special transition of tensile stress-strain present in our works is found. Moreover, the strong thermal stability and improved interfacial interaction of the composite are obtained, as listed in Tab. S3. These results all confirm the formation of oriented structures of both CNS and UHMWPE matrix in the composites.

Tensile fractured surfaces of UHMWPE/CNS$_3$, UHMWPE/CNS$_5$, and UHMWPE/CNS$_{10}$ composites were examined to further elucidate fracture and enhancement mechanisms. In Fig. S6, the fracture surfaces of all UHMWPE/CNS composites are quite rough, and numerous matrix fibrils are formed on the fracture surface of UHMWPE/CNS composites, indicating a typical ductile fracture (Fig. S6a$_2$-c$_2$). At high magnification, the intensive linkages between CNS and UHMWPE matrix are visible, resulting in some strong points that can resist crack formation and propagation under external stress and impede mechanical failure (Fig. S6b$_2$). Furthermore, the interface between CNS and UHMWPE is difficult to distinguish, and abundant CNS is pulled out, suggesting the effective load transfer from the UHMWPE matrix to the CNS (Fig. S6c$_2$). The simultaneous improvement in the strength and fracture toughness of UHMWPE/CNS composites is thus ascribed to the formation of compact segregated structure. A small amount of CNS can penetrate the UHMWPE matrix due to the strongly mechanical interlocking state,
which is achieved to improve interfacial bonding and is thought to be very useful for stress transfer between adjacent UHMWPE granules[49]. This work improves strength and fracture toughness while maintaining EMI shielding performance, making the UHMWPE/CNS composite more competitive as EMI shielding materials that can withstand high stress in some specific fields[45].

According to recently reported electrical conductivity and EMI SE of the segregated conductive UHMWPE composites, many approaches to designing conductive UHMWPE segregated composites usually result in only one performance improvement, either EMI shielding performance or mechanical performance. Tab. S4 provides a comprehensive comparison of most CPCs for detailed EMI shielding and mechanical performance. Figure 8 reveals the superiority of our work compared to the recent literature. When combined with the detailed research results of Tab. S4, it is evident that we prepared the UHMWPE/CNS composite that exhibits a superior EMI SE and excellent mechanical properties compared to the current reported research work. Liu et al.[47] reported that an advanced microwave (MW)-assisted sintering molding methodology was used to prepare conductive polymer composites with high mechanical properties and EMI shielding performance. The obtained segregated UHMWPE/CNT composite with 5 wt% CNT content presented outstanding electrical conductivity, EMI shielding performance, and tensile strength of 49.3 S/m, 50 dB, and 25.7 MPa, respectively. Li et al. [50] developed an EMI shielding material based on UHMWPE loaded with economical graphite-carbon black (G-CB) hybrid fillers. A 15 wt% G-CB hybrid filler caused the G-CB /UHMWPE composite with a satisfactory electrical conductivity of 33.9 S/m and superior shielding effectiveness of 40.2 dB. Furthermore, with the addition of 15% wt% G-CB (1/3, W/W) hybrid fillers, the composite's tensile strength reached 25.3 MPa. Among these reported segregated UHMWPE composites, which have relatively lower mechanical performance compared to pure UHMWPE. This is attributed to the poor interfacial interaction between filler and polymer matrix. Consequently, aside from a novel advanced molding technique and a one-of-a-kind oriented segregated UHMWPE composite. The high-performance conductive filler choice is vital for constructing a highly efficient filler network, which is more conducive to building the segregated network at a low percolation threshold for the actual production application of CPCs.

4. Conclusion

UHMWPE/CNS composites with the oriented segregated conductive network were successfully prepared using simple and effective high-speed mechanical mixing and compression molding methods. The morphological observation indicates the presence of an oriented interconnected CNS conductive network in the UHMWPE matrix. The classical threshold mechanism reveals that the composites have a relatively low percolation threshold (0.49 wt%). When CNS loading concentration exceed its electrically conductive threshold, the effectiveness of both electrical conductivity and EMI SE is significantly enhanced. Especially, the resultant UHMWPE/CNS composite with 10 wt% CNS loading exhibits an outstanding EMI SE value of 60.7dB and a thermal conductivity of the composite is as high as 0.7217 (W/m K). UHMWPE/CNS composites have excellent mechanical properties as well. Furthermore, the tensile strength and elongation at break of UHMWPE/CNS are 46.51 MPa and 350%, respectively, due to the
formation of the oriented structure of both filler and polymer matrix, outperforming the tensile strength of pure UHMWPE. The yield strength of the UHMWPE/CNS$_3$ composite is twice that of pure UHMWPE and much higher than the yield strength of its composites (UHMWPE/CNS$_5$, UHMWPE/CNS$_7$, and UHMWPE/CNS$_{10}$). The addition of CNS effectively increases the crystallinity of UHMWPE, and the continuous and oriented CNS network structure in situ in Polymeric composite enhances the heat energy transfer, which is the main reason for the enhanced thermal conductivity of UHMWPE/CNS composites. As a result, this high-performance multifunctional composite material that conducts both thermally and electrically is a promising candidate for EMI applications.

**Declarations**

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**Authorship contribution statement**

**Huibin Cheng:** Conceptualization, Methodology, Data curation, Investigation, Writing - original draft.  
**Guoliang Lin:** Supervision, Writing - review & editing. **Xiaoyi Zhang:** Methodology, Supervision, Writing - review & editing. **Shenglan Ma:** Conceptualization, Supervision. **Xuhong Liu:** Conceptualization, Supervision. **Baoquan Huang:** Methodology, Formal analysis, Writing - review & editing. **Qingrong Qian:** Methodology, Funding acquisition, Writing - review & editing. **Qinghua Chen:** Methodology, Funding acquisition, Writing - review & editing. **Chen Wu:** Methodology, Funding acquisition, Writing - review & editing.

**References**


Figures

![Preparation of segregated UHMWPE/CNS composites](image)

**Figure 1**

Preparation of segregated UHMWPE/CNS composite
Figure 2

OM images of the Cross-sectional microstructures of composites with the different CNS contents: 1 wt% (a1), 5 wt%(b1), and 10 wt% (c1); corresponding SEM morphology of the cryo-fractured surface of UHMWPE/CNS composites with the same CNS content: (a2-a3) 1 wt%, (b2-b3) 5 wt% and (c2-c3) 10 wt%.
Figure 3

Cross-section of Raman mapping images 150×150 μm \((a_2-c_2)\) of the UHMWPE/CNS composites with different CNS content and Raman mapping images of the Cross-section at interfacial region observation: \((a_1, a_2)\) 1 wt%, \((b_1, b_2)\) 5 wt%, and \((c_1, c_2)\) 10 wt%. 
Figure 4

Polarization Raman spectrum for the outer surface and cross section of UHMWPE, UHMWPE/CNS$_5$ and UHMWPE/CNS$_{10}$ composites
Figure 5

Electrical conductivity, thermal conductivity and EMI SE of UHMWPE/CNS composites: (a) electrical conductivity; (b) thermal conductivity; (c) $SE_T$, (d) $SE_A$, (e) $SE_R$, (f) comparison of $SE_T$, $SE_R$ and $SE_A$ at the frequency of 10.3 GHz for UHMWPE/CNS composites with different CNS content.
Figure 6

Schematic representation of the EMI shielding mechanism for UHMWPE/CNS composites.
Figure 7

Tensile stress-strain curves (a), tensile strength (b), yield strength (c), and elongation at break (d) of pure UHMWPE and UHMWPE/CNS composites.
Figure 8

Comparison of the superiority of this work compared to the recently literature reported the segregated conductive polymer composites: (a) EMI SE vs filler content, (b) Tensile strength vs filler content

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