



Article The Influences of Chemical Modifications on the Structural, Mechanical, Tribological and Adhesive Properties of Oriented UHMWPE Films

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Abstract: Preparing a friction pair "polymer-metal" using improved polymeric composites is contemplated a complicated task due to the inert surface of the polymer. Gluing polymer composites with improved mechanical and tribological properties on metals and saving their unique properties at the same time is considered the best way to prepare slide bearing products based on polymer/metal. In this work, ultraviolet initiation is used after a process of mixed acid pre-treatment. The surface of highly oriented films based on ultra-high molecular weight polyethylene (UHMWPE)/graphene nanoplatelets (GNP) is grafted with nanocellulose. The grafting treatment is analyzed using Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and contact angle measurements. Mechanical T-peel tests showed that the peel strength for the treated UHMWPE films increased by three times, up to 1.9 kg/cm, in comparison to the untreated films. The tensile strength of the treated UHMWPE films decreased by about 6% to 788 MPa. Tribological tests showed that the values of both friction coefficient and wear intensity of the treated UHMWPE films were increased insignificantly, which were 0.172 and 15.43 μm/m·m², respectively. The prepared adhesive tape based on UHMWPE films, which can withstand a weight of up to 6 kg per 1 cm^2 of the bonded surface, has a low coefficient of friction, high wear resistance, and high strength, and is considered a promising material for preparing slide bearing products.

Keywords: UHMWPE; adhesion; wear; friction coefficient; mechanical properties; slide bearing

1. Introduction

Currently, preserving the environment is considered the main key in scientific and technical research throughout the world. The use of mineral and synthetic oils in slide bearing applications raises concerns about the environmental impact of these lubricants in cases of pollution [1]. Slide bearing systems based on oil-free lubricants are considered the main direction for resolving our ecological problems. Bearing materials based on polymers are treated as the most promising materials, since polymers have several interesting properties, such as being lightweight and having a chemical inertness, low coefficient of friction, high wear resistance, and good impact toughness [2–4]. Polymeric slide bearing products can be found in a wide range of industrial applications, such as in the automotive, aerospace, hydropower, and robotics sectors, and in medical applications, such as total replacements [5–7].

Due to its excellent tribological and mechanical properties, self-lubricating characteristics, high chemical inertness, and biocompatible characteristics, ultra-high molecular



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). weight polyethylene (UHMWPE) is one of the most widely utilized polymers in many industrial and medical applications [3,4,8,9]. However, UHMWPE, with an isotropic structural state, has a low elasticity modulus and yield strength and has exhibited a considerable creep under constant and high loads. UHMWPE outperforms nylon and polyformaldehyde, which are frequently used in applications requiring a low coefficient of friction, in terms of their tribological properties [10-13]. Polytetrafluoroethylene and UHMWPE are comparable in terms of their friction coefficient; however, UHMWPE outperforms in terms of wear resistance [14]. Since using isotropic UHMWPE composites as antifriction bearing components for tribological purposes, improving the mechanical and tribological properties of UHMWPE composites using the process of orientation hardening, has attracted more attention from researchers [10,11,15]. A further intriguing enhancement technique is to incorporate certain second-phase particles with good tribological characteristics into a UHMWPE matrix to create UHMWPE nanocomposites [16]. In our previous work [17], highly oriented UHMWPE films filled with 2 wt.% graphene nanoplates/polyaniline (GNP/PANI) were prepared (Figure 1a), and they presented outstanding mechanical and tribological properties, such as a tensile strength of 836 MPa, Young's modulus of 35.8 GPa, COF of 0.122, and a linear wear intensity of 1.92 μ m/m·m², in comparison to isotropic UHMWPE (yield strength of \geq 17 MPa, Young's modulus of 720 MPa, COF of 0.269, and a linear wear intensity of 53.94 μ m/m·m²).

On the other hand, the main method used to bond UHMWPE with metals in the manufacture of a "polymer-metal" friction pair is thermal pressing, which leads to the loss of the unique mechanical and tribological properties of the highly oriented UHMWPE films due to applying high temperatures and pressures. Nevertheless, the best solution for bonding the oriented UHMWPE films to metals while preserving their unique properties is to glue them together. Bonding UHMWPE to each other or to metal materials is considered a very difficult task since the absence of polar groups in UHMWPE makes their surfaces very inert [18]. Therefore, to manufacture antifriction sliding surfaces based on oriented UHMWPE films, it is necessary to develop a method for the pre-treatment of the surfaces prior to the gluing phase. The main mechanism of surface modification is to increase its roughness using chemical etching techniques; this leads to an increase in wettability and an improvement in adhesion properties compared to unmodified UHMWPE [19,20].

Numerous significant qualities exist in cellulose, including abundance, light weight, renewability, nontoxicity, biocompatibility, biodegradability, and high stability [21,22]. It can be utilized in binders and water-soluble adhesives [23]. The cellulose carboxyl groups are crucial to the mechanisms involved in grafting techniques. For instance, a covalent grafting approach for the conjugation of benzophenone with cellulose has recently been developed for the UV-crosslinking of nanocellulose [24].

A good opportunity to improve the UHMWPE's adhesion properties exists thanks to chemical surface modification [19,25,26]. UHMWPE surface's characteristics have been enhanced using a variety of techniques [27]. The primary method of surface modification relies on chemical etching, which is used to oxidize and roughen the surface. Such treatments produce superior wettability and increase adhesive properties more in comparison to unmodified UHMWPE. The polar groups on the UHMWPE surface are substituted for the hydrogen atoms in the polymer chains in this etching mechanism, increasing the surface's wettability and providing potential locations for chemical interactions with other substances (Figure 1b) [28]. Ultraviolet (UV) irradiation, as a low-energy grafting technique for polymeric surfaces, is considered to be a promising method [29,30]. This is related to its low cost, effectiveness in functionalizing the substrate surface, quick reaction rate, and relatively small influence on the bulk polymers. In this article, and based on our previous work [31], the oriented UHMWPE films are exposed to UV radiation after being placed in the initiator solution (benzophenone). To obtain the desired amount of dormant semi-pinacol groups (Figure 1b), the initiator removes hydrogen from the UHMWPE chains [30,32]. The UHMWPE films, which were grafted with benzophenone, are then subjected to UV irradiation once more to cleave this bond again. The suggested reason for



grafting cellulose chains onto the surface of the UHMWPE films is the reactivation of the dormant semi-pinacol groups (Figure 1c) [33].

Figure 1. (**a**) Preparation of oriented UHMWPE/GNP/PANI films; (**b**) surface treatment of UHMWPE/GNP/PANI films by benzophenone; (**c**) surface treatment of UHMWPE/GNP/PANI films by cellulose grafting.

2. Materials and Methods

2.1. Materials

UHMWPE GUR 4120 with a molecular weight of 5×10^6 g/mol from "Ticona GmbH" (Frankfurt, Germany) and polyethylene wax PLWN-3W with a molecular weight of 4000 g/mol from "INHIMTEK LLC" (Novokuibyshevsk, Russia) were used. Graphene nanoplates (GNPs) were obtained by oxidative intercalation of expanded graphite with subsequent ultrasonic treatment and were purchased from Nanotechcenter Ltd. (Tambov, Russia). GNP was functionalized by the deposition of polyaniline (PANI) on the GNP surface because of the oxidative polymerization of aniline. All procedures and conditions

were broadly explained and described in the references [17,34]. p-xylene was used as a plasticizer for the UHMWPE composites at a ratio of 2.5 mL of a solvent per 1 g of the polymer blend. Benzophenone 99% was purchased from Alfa Aesar—Shanghai, China. Micro-cellulose was purchased from "Ruskhim Ltd." (Moscow, Russia). Ethanol, acetone, urea, and sodium hydroxide were used as solvents.

For adhesion mechanical tests (T-peel tests), two types of adhesive glue were used. The first one was a black double-sided adhesive tape on a foam basis 19 mm \times 2 m (Aviora). Its composition is acrylic—solvent, IXPE (irradiated cross-linked polyethylene foam). The second one was white cotton and synthetic rubber fabric double-sided tape 50 mm \times 10 m (Aviora). Its composition is synthetic rubber, acrylic 80%, and cotton 20%.

2.2. Processes for Producing Cellulose Nanoparticles (CNs)

Microcrystalline cellulose (MCC) was converted into nanocellulose (NC) using the technique developed by M. Adsul et al. [35]. Next, a 100-mL solution comprising 5 g of MCC, 7 g of NaOH, and 12 g of urea was prepared, stirred for 30 min at room temperature, and then kept in a freezer at -20 °C for 16 hrs. Afterwards, using distilled water, nanocellulose was regenerated, separated by centrifugation at 3000 rpm, and washed with distilled water 8–10 times to remove residual urea and NaOH.

2.3. Fabrication of UHMWPE Films

According to the method outlined in the reference [17], mixing UHMWPE, PE-wax, and GNP/PANI powders was carried out using a high-energy planetary ball mill (APF-3). Using gel-spinning technology, UHMWPE films were prepared using 2.5 mL of p-xylene for each gram of polymer powders. Then, UHMWPE/p-xylene gel was extruded at 150 °C using a ram extruder (UE-MSL) with a die size of 10×2 mm and an extrusion rate of 500 mm/min. Consequently, the extruded UHMWPE gels were allowed to dry for 48 h at room temperature. Using the drawing process, which was described in detail in reference [17], highly oriented UHMWPE/1 wt.% PE-wax/2 wt.% GNP/PANI films were prepared. These films had the following properties (Table 1).

Table 1. Mechanical and physical properties of highly oriented UHMWPE/1 wt.% PE-was/2 wt.% GNP/PANI films (± the standard deviation) [17].

Material	Draw Ratio	Young's Modulus, GPa	Tensile Strength, MPa	Elongation, %	Work of Fracture, MJ/m ³	T _m , °C	Crystallinity, %	COF	Linear Wear Intensity, I _{IW} µm/m∙m ²
Oriented UHMWPE films	47	35.8 ± 3.3	836 ± 88	6.6 ± 0.9	40.3 ± 11.6	143.6	87 ± 2	0.122 ± 0.002	1.92 ± 0.08

2.4. Treatment and Modification of UHMWPE Films' Surface

After being treated with a mixture of H_2SO_4 and HNO_3 (v/v: 3/1) mixed at 75 °C for one hour, the UHMWPE films were grafted with cellulose using a 10% nanocellulose and 90% ethanol (w/v) solution. The coupling agent was a 5% (w/v) solution of benzophenone in acetone. A device for UV cross-linking with a photon density of 900 mJ/cm² was used. The exposure's duration of the UV-induced reaction was 20 min. The reference [31] provided comprehensive explanation and description of all processes, techniques, and conditions.

2.5. Testing Procedures

The structure of the treated UHMWPE films was investigated using a JEOL JSM-6610LV (JEOL Ltd., Tokyo, Japan) scanning electron microscope operating at a 20 kV accelerating potential. The polymer surface was coated with a Pt layer that was 10–20 nm thick (magnetron deposition equipment JFC-1600 (JEOL Ltd., Tokyo, Japan) was utilized) in order to prevent a charge accumulation.

Using a Nicolet 380 IR-Fourier spectrometer (Thermo Scientific, Waltham, MA, USA), FT-IR spectroscopy was carried out in attenuated total reflection (ATR) mode: the spectral range was $4000-450 \text{ cm}^{-1}$ with a resolution of about 0.9 cm⁻¹, and the accuracy of the wave number was 0.01 cm⁻¹. OMNIC Lite Software (version 1.7) was used to analyze the results. For each sample, at least 5 measurements were carried out.

Sessile drops were used in the measurement of the contact angle to gauge changes in the samples' hydrophilicity, and the EasyDrop wetting angle measurement apparatus was utilized. According to the scope of the camera lens, the sample was set down on a table and a lifting mechanism was installed. The surface of the sample was wetted with a 5 μ L drop of distilled water using a standard dosing system (ASTM D724-99) [36]. The formation of the drop on the surface was captured by the camera. The baseline and contact angle calculations were performed using DSA3 software (version 1.7.3). For each sample, at least 5 measurements were carried out.

Using Zwick/Roell Z020 universal testing machine (Zwick Roell Group, Ulm, Germany), the tensile tests for the oriented UHMWPE/PE-wax/GNP/PANI films were carried out in accordance with ASTM D882-10 [37] at a loading rate of 10 mm/min. At least five samples were measured for each UHMWPE composite.

To evaluate the peel resistance of the adhesive bonds between flexible adherends, T-peel testing configuration according to ASTM 1876-01 [38] was used. Also, at least 10 measurements were applied for each type of glue. For the T-peel testing of film–glue samples, the UHMWPE sample dimensions were $100 \times 3.5 \times 0.2 \text{ mm}^3$. The glue dimensions were $100 \times 3.5 \times 0.25 \text{ mm}^3$ for the white cotton and synthetic rubber fabric double-sided tape, and were $100 \times 3.5 \times 0.7 \text{ mm}^3$ for the black double-sided adhesive tape. For the T-peel testing of film–film samples, the UHMWPE sample dimensions were $100 \times 3.5 \times 0.2 \text{ mm}^3$. The glue layer dimensions between the UHMWPE films were $50 \times 3.5 \times 0.25 \text{ mm}^3$ for the white cotton and synthetic rubber fabric double-sided tape, and were $50 \times 3.5 \times 0.2 \text{ mm}^3$ for the black double-sided tape, and were $50 \times 3.5 \times 0.2 \text{ mm}^3$ for the black double-sided tape, and were $50 \times 3.5 \times 0.2 \text{ mm}^3$ for the black double-sided tape, and were $50 \times 3.5 \times 0.7 \text{ mm}^3$ for the black double-sided tape, and were $50 \times 3.5 \times 0.7 \text{ mm}^3$ for the black double-sided tape, and were $50 \times 3.5 \times 0.7 \text{ mm}^3$ for the black double-sided adhesive tape. The glued UHMWPE samples were stored at room temperature for 1 day before mechanical testing. T-peel testing configuration for glued samples was carried out by using Zwick/Roell Z020 universal testing machine at a loading rate of 10 mm/min.

The tribological tests were performed using Tribometer—CETR—UMT—3 (Bruker Corporation, Karlsruhe, Germany) in the dry friction mode in accordance with ASTM G 99-95a [39]. Using a friction pair (pin on disk), a normal loading force of 30 N and a linear speed of 1 m/s were applied. After traversing a path (L) of 21.6 km, the tribological characteristics were determined. A 440C stainless steel counter-body with a diameter of 62 mm was used. The counter-body was polished before each test using diamond lapping paste with grits of 40–60 microns. Film samples with dimensions of 20 mm in length and 2.5–4 mm in width were fixed to a metallic cylinder with a diameter of 20 mm (Figure 2). Linear wear intensity (I_{IW}) was calculated using Equation (1) as follows:

$$I_{lw} = \frac{\Delta Z}{L \cdot S_f} \tag{1}$$

where ΔZ —change in sample height after the test, *L*—friction path, and *S*_f—initial sample surface area.



Figure 2. Scheme of the tribological tests (**a**); pin form in tribological tests: (**b**) pin form without sample, (**c**) pin form with UHMWPE film sample.

3. Results

Table 2 presents the FT-IR spectrum peaks for all chemical groups, and Figure 3 shows the FT-IT measurements for the virgin UHMWPE films, oriented UHMWPE/PE-wax/GNP/PANI films, and treated oriented UHMWPE/PE-wax/GNP/PANI by cellulose grafting. As can be seen in Table 2 and Figure 3, the presence of GNP/PANI in the oriented UHMWPE films is related to the peaks at 803, 1115, 1261, and 1295 cm⁻¹. Peaks at 808 and 1629 cm⁻¹ are related to the presence of benzophenone, whereas the peaks at 1031, 1099, and 1261 cm⁻¹ are related to the grafted cellulose. As can be noted in Figure 3, the -OH groups of the cellulose, which have an intensity range between 3100 and 3600 cm⁻¹, disappeared in the treated UHMWPE/PE-wax/GNP/PANI films. This can be related to the reactions that took place between the -OH groups of the cellulose and both of the ketones groups of the benzophenone and C–H groups of the UHMWPE, which had led to the formation of the C-O-C (ethers) (peaks in the range of 1150–1200 cm⁻¹) [40].

Table 2. The FT-IR spectrum peaks for all components.

UHMWPE [41,42]		GNF	GNP/PANI [43,44]		Benzophenone [45]		Cellulose [46,47]	
Wave Number, cm ⁻¹	Functional Group	Wave Number, cm ⁻¹	Functional Group	Wave Number, cm ⁻¹	Functional Group	Wave Number, cm ⁻¹	Functional Group	
717	rocking vibration peak due to the high degree	803	aromatic C–H out-of-plane bending vibration (GNP)		808 C-CO-C sym. str.	1031 C-O stretcl group of 3 anhydrogala	C. O stratching	
730	of polymerization and long molecular chain of	800–1115	C–H stretching (PANI)	808			group of 3,6- anhydrogalactose	
_	UTIMIVITE	1261	N–Q–N–Q stretch of the quinoid ring			1099		
1460	in-plane bending							
1471	vibration peak of C–H							
2848	sym. stretching vibration peak of C–H	1295	C-N stretching (GNP)	1627	C=O stretch	1261	C–OH bending at	
2912	asym. stretching vibration peak of C–H						20	



Figure 3. FT-IR spectra of the virgin UHMWPE film, oriented UHMWPE/GNP/PANI film, and treated oriented UHMWPE/GNP/PANI film by cellulose grafting.

The presence of the cellulose on the treated UHMWPE/PE-wax/GNP/PANI films was also demonstrated in the SEM images (Figures 4 and 5). As it can be seen in Figure 4, the acid pre-treatment led to the formation of micro-pores and grooves on the surface of the UHMWPE films, and to the increase in the surface roughness. These changes in surface morphology can improve the effective contact area between the surface and the adhesive materials that are in contact with it. Figure 5 illustrates the distribution of the adhered cellulose on the treated surface of the UHMWPE/PE-wax/GNP/PANI films. The distribution densities indicate the cellulose's high adherence to the treated UHMWPE films. Figure 6 demonstrates the changes in the surface morphology of the treated UHMWPE films and how grafting cellulose improves the adhesion properties of the treated UHMWPE films in comparison to the untreated ones.



Figure 4. SEM images of the surface of the UHMWPE films before (a) and after (b) acid treatment.



Figure 5. SEM images of the surface of the UHMWPE films after benzophenone and cellulose grafting with different magnifications (a) 20 μ m; (b) 5 μ m.



Figure 6. Proposed diagram that illustrates the gluing process for (**a**) untreated and (**b**) treated UHMWPE/PE-wax/GNP/PANI films with metallic or plastic materials.

The processes of the acid pre-treatment and cellulose grafting have led to an enhancement in the UHMWPE's hydrophilicity (Table 3 and Figure 7). However, the GNP/PANI filler contains some functional groups, such as ethers, carboxyls, or hydroxyls. As can be seen in Table 2 and Figure 3, the untreated UHMWPE/PE-wax/GNP/PANI film had a lower water contact angle in comparison to the untreated virgin UHMWPE film The water contact angle value of the treated UHMWPE/PE-wax/GNP/PANI film was decreased to 91° in comparison to the untreated virgin UHMWPE film's value, which was 120°. Since the water contact angle of 90° is considered the boarder value between the hydrophilic and hydrophobic materials, the value of the water contact angle of the treated UHMWPE/PE-wax/GNP/PANI film is also considered a boarder value [48–50]. This increase in the hydrophilicity indicates an increase in the free energy of the UHMWPE material's surface [51], which led to an improvement of its adhesion properties.

Table 3. Contact angle results for the untreated virgin UHMWPE as well as untreated and treated UHMWPE/PE-wax/GNP/PANI films grafted by cellulose (\pm the standard deviation).



Figure 7. Contact angle measurement: (**a**) untreated virgin UHMWPE film, (**b**) untreated UHMWPE/PE-wax/GNP/PANI film, and (**c**) treated UHMWPE/PE-wax/GNP/PANI film.

Table 4 shows the tensile mechanical properties of the treated UHMWPE/PE-wax/ GNP/PANI film after acid pre-treatment and cellulose grafting. As can be seen in Table 4, its tensile strength was decreased a little by about 6% as a result of the acid pre-treatment process. Moreover, the values of Young's modulus, elongation, and work of fracture were almost the same after the treatment by cellulose grafting. This small decrease in the mechanical tensile properties in the UHMWPE/PE-wax/GNP/PANI film is related to the semi-crystalline structure of the UHMWPE. In other words, in the acid pre-treatment process, the mixed acids attack the polymer macromolecules in the amorphous regions (weak zones), leading to an etching process in the UHMWPE structure that led to a small decrease in the mechanical properties of the oriented films [52].

Table 4. Mechanical tensile properties of the UHMWPE/PE-wax/GNP/PANI films before and after acid treatment (\pm the standard deviation).

Material	Young's Modulus, GPa	Tensile Strength, MPa	Elongation, %	Work of Fracture, MJ/m ³
Untreated oriented film Treated oriented film	$\begin{array}{c} 35.8 \pm 3.3 \\ 34.7 \pm 2.8 \end{array}$	$\begin{array}{c} 836\pm88\\ 788\pm64\end{array}$	$\begin{array}{c} 6.6 \pm 0.9 \\ 6.7 \pm 0.8 \end{array}$	$\begin{array}{c} 40.3 \pm 11.6 \\ 39.4 \pm 9.7 \end{array}$

Table 5 and Figure 8 show the tribological properties of the untreated and treated UHMWPE/PE-wax/GNP/PANI films in comparison to the isotropic UHMWPE films. As can be seen, the cellulose grafting processes led to an increase in the COF of the treated UHMWPE films up to 0.172 in comparison to the untreated UHMWPE films with a COF of 0.122. Moreover, the linear wear intensity increased from 1.92 μ m/m·m² for the untreated UHMWPE films and up to 15.43 μ m/m·m² for the treated UHMWPE films. Here, it can be noted that the applied tribological conditions are considered very harsh (a load of 30 N "about 4 MPa", and dry friction), and the decrease in the tribological properties is related to the presence of the cellulose on the UHWMPE surface of the treated films causing a change in surface morphology. Under the tribological tests and due to high surface roughness, the presence of the cellulose led to an increase in the deformation component of the friction coefficient (increasing the penetration of the counter-body into the surface of the material), and the friction between the counter-body and treated UHMWPE films caused cellulose erosion in the beginning of this process [53,54]. Afterwards, the COF stabilized at a value of 0.172.

Table 5. Tribological properties of the UHMWPE/PE-wax/GNP/PANI films before and after cellulose grafting processes (±the standard deviation).

Material	GNP/PANI Content, wt.%	COF	Linear Wear Intensity, I _{lw} , µm/m∙m ²
Isotropic virgin UHMWPE	0	0.269 ± 0.015	53.94 ± 0.27
Untreated UHMWPE/PE- wax/GNP/PANI film	2.0	0.122 ± 0.002	1.92 ± 0.08
Treated UHMWPE/PE- wax/GNP/PANI film	2.0	0.172 ± 0.004	15.43 ± 0.32



Figure 8. Coefficient of friction (**a**) and linear wear intensity (**b**) of the UHMWPE/PE-wax/GNP/PANI films before and after cellulose grafting processes.

Tables 6 and 7 show the results of the T-peel tests for the treated UHMWPE/PE-wax/GNP/PANI films. In order to investigate the adhesion strength for the treated UHMWPE films, two T-peel tests were carried out using two different types of adhesive tapes. The first T-peel test was carried out for the adhesion strength between the treated UHMWPE films and adhesive tapes, whereas the second one was carried out between two treated films bonded by two adhesive tapes (Tables 6 and 7). As can be seen in Table 6, by using the acrylic foam-based tape, the peel strength between the UHMWPE films and adhesive tape was increased from 0.9 kg/cm up to 1.8 kg/cm (100%) for the

untreated films. Oppositely, when using the synthetic rubber fabric double-sided tape, the peel strength between the UHMWPE films and adhesive tape increased from 0.6 kg/cm up to 1.9 kg/cm (217%) for the untreated films. Table 7 shows the adhesion strength between two treated UHMWPE films using two adhesive tapes. As can be seen, the peel strength was increased from 0.8 kg/cm up to 2.8 kg/cm (250%) for the untreated films, whereas the peel strength between the UHMWPE films and adhesive tape increased from 0.4 kg/cm, for the untreated films, up to 1.5 kg/cm (275%) using synthetic rubber fabric double-sided tape.

Type of Glue	Type of Film	Peel Strength, kg/cm
Black double-sided adhesive tape	Without treatment Treated UHMWPE films	$0.9 \pm 0.2 \\ 1.8 \pm 0.16$
White cotton and synthetic rubber fabric double-sided tape	Without treatment Treated UHMWPE films	$0.6 \pm 0.1 \\ 1.9 \pm 0.4$

Table 6. The mechanical properties of the film–glue specimens (\pm standard deviation).

Table 7. The mechanical properties of the film–film specimens (\pm standard deviation).

Type of Glue	Type of Film	Peel Strength, kg/cm
Black double-sided adhesive tape	Without treatment Treated UHMWPE films	$0.8 \pm 0.2 \\ 2.8 \pm 0.4$
White cotton and synthetic rubber fabric double-sided tape	Without treatment Treated UHMWPE films	$0.4 \pm 0.1 \\ 1.5 \pm 0.5$

It should be noted that T-peel tests were also carried out to investigate the adhesion strength between the treated UHMEPE films and metals (stainless steel 316L), and the occurrence of the bonding separation between the UHMWPE films and the adhesive tapes was observed, which meant that the adhesion strength between the metals and adhesive tapes was higher than the one that between the treated UHMWPE films and the adhesive tapes.

The main aim of this work was to develop a product in the form of a high-strength adhesive tape based on UHMWPE films, which has a low coefficient of friction, high wear resistance, and high strength (Figure 9). These adhesive tapes are considered promising materials for creating plain bearings, various guides, etc.



Figure 9. A photo demonstrated high-strength adhesive tape based on UHMWPE films.

4. Conclusions

UHMWPE is recognized worldwide as the polymer of the future, as a result of the possibility of creating various composite materials with unique mechanical, tribological, and functional properties. In this work, using ultraviolet initiation after a pre-treatment process with mixed acids, the surface of the oriented UHMWPE films was grafted by cellulose. Using Fourier transform infrared spectroscopy (FT-IR), the presence of GNP/PANI, cellulose, and benzophenone on the treated UHMWPE films was demonstrated. Using scanning electron microscopy (SEM), the presence of cellulose on the treated UHMWPE films was also demonstrated. The contact angle measurements showed that its value decreased from 120° to 91° after the treatment procedure. Mechanical T-peel tests showed that the peel strength for the treated UHMWPE films increased from 0.6 up to 1.8 kg/cm in comparison to the untreated films. However, it was found that the treatment procedure led to a slight decrease in the tensile strength of the treated UHMWPE films by about 6% to 788 MPa. Tribological tests showed that the values of both the friction coefficient and wear intensity were insignificantly increased up to 0.172 and 15.43 μ m/m·m², respectively, for the treated UHMWPE films. The use of high-strength-oriented UHMWPE films instead of isotropic thermally pressed UHMWPE films could significantly increase the performance and service life of various anti-friction sliding surfaces for industrial and medical slide bearing applications, such as bearings, rollers, various guides, and as a lining. The proposed method for modifying the surface of UHMWPE films allows us to increase the adhesion properties of these films by more than 200%, while the mechanical and tribological properties can only be insignificantly reduced. It should be noted that because of carrying out chemical modifications on both UHMWPE surfaces, a reduction in the coefficient of friction and wear was recognized. Therefore, to preserve tribological properties, it is better to apply chemical modifications on one polymer surface that will be adhered to the metals being used.

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References

- 1. Golchin, A.; Simmons, G.F.; Glavatskih, S.; Prakash, B. Tribological Behaviour of Polymeric Materials in Water Lubricated Contacts. *Proc. Inst. Mech. Eng. Part J J. Eng. Tribol.* 2013, 227, 811–825. [CrossRef]
- Friedrich, K.; Schlarb, A. Tribology of Polymeric Nanocomposites, Friction and Wear of Bulk Materials and Coatings, 1st ed.; Tribology and Interface Engineering Series; Elsevier Ltd.: Amsterdam, The Netherlands, 2008; pp. 10–50. ISBN 9780080559087.
- Dougherty, P.S.M.; Pudjoprawoto, R.; Higgs III, C.F. An investigation of the wear mechanism leading to self-replenishing transfer films. Wear 2011, 272, 122–132. [CrossRef]
- 4. Rhee, S.H.; Ludema, K.C. Mechanisms of formation of polymeric transfer films. Wear 1978, 46, 231–240. [CrossRef]
- Walczak, M.; Jacek Caban, J. Tribological characteristics of polymer materials used for slide bearings. *Open Eng.* 2021, 11, 624–629. [CrossRef]
- 6. Pruitt, L.; Golchin, A. Polymeric Materials for Bearing Applications, Tribological Studies in Lubricated Conditions. Ph.D. Thesis, Luleå University of Technology, Graphic Production 2015, Lulea, Sweden, 2015.
- 7. Furmanski, J. Polymeric biomaterials for load-bearing medical devices. JOM 2009, 61, 14–20. [CrossRef]

- 8. Sturzel, M.; Mihan, S.; Mulhaupt, R. From Multisite Polymerization Catalysis to Sustainable Materials and All-Polyolefin Composites. *Chem. Rev.* **2016**, *116*, 1398–1433. [CrossRef]
- 9. Schwartz, C.J.; Bahadur, S. Studies on the tribological behavior and transfer film-counterface bond strength for polyphenylene sulfide filled with nanoscale alumina particles. *Wear* 2000, 237, 261–273. [CrossRef]
- Galetz, M.C.; Blaβ, T.; Ruckdäschel, H.; Sandler, J.K.W.; Altstädt, V.; Glatzel, U. Carbon nanofibre-reinforced ultrahigh molecular weight polyethylene for tribological applications. J. Appl. Polym. Sci. 2007, 104, 4173–4181. [CrossRef]
- 11. Sreekanth, P.S.R.; Kanagaraj, S. Influence of multi walled carbon nanotubes reinforcement and gamma irradiation on the wear behaviour of UHMWPE. *Wear* 2015, 334, 82–90. [CrossRef]
- 12. Typical Properties of NYLON. Curbell Plastics Acquired Nationwide Plastics in 2019. Available online: https://www.curbellplastics.com/Research-Solutions/Materials/Nylon (accessed on 23 November 2023).
- 13. Typical Properties of ACETAL. Curbell Plastics Acquired Nationwide Plastics in 2019. Available online: https://www.curbellplastics.com/Research-Solutions/Materials/Acetal (accessed on 23 November 2023).
- 14. Budinski, K.G. Resistance to particle abrasion of selected plastics. Wear 1997, 203–204, 302–309. [CrossRef]
- Eddoumy, F.; Addiego, F.; Dhieb, H.; Célis, J.-P.; Muller, R.; Toniazzo, V.; Ruch, D. Sliding wear behaviour of oriented ultrahigh molecular weight polyethylene. *Polym. Int.* 2012, 62, 867–877. [CrossRef]
- 16. Li, J.; Guo, Z.; Hua, M.; Qin, X.; Wen, S. Tribological characteristics of UHMWPE composite and relationship with its compressive behavior. *Sci. China Ser. G Phys. Mech. Astron.* 2004, 47, 79–87. [CrossRef]
- Dayyoub, T.; Maksimkin, A.; Olifirov, L.K.; Chukov, D.; Kolesnikov, E.; Kaloshkin, S.D.; Telyshev, D.V. Structural, Mechanical, and Tribological Properties of Oriented Ultra-High Molecular Weight Polyethylene/Graphene Nanoplates/Polyaniline Films. *Polymers* 2023, 15, 758. [CrossRef]
- Van Vrekhem, S.; Vloebergh, K.; Asadian, M.; Vercruysse, C.; Declercq, H.; De Wilde, L.; De Geyter, N.; Morent, R.; Van Tongel, A. Improving the surface properties of an UHMWPE shoulder implant with an atmospheric pressure plasma jet. *Sci. Rep.* 2018, *8*, 4720. [CrossRef]
- Oosterom, R.; Ahmed, T.J.; Poulis, J.A.; Bersee, H.E.N. Adhesion performance of UHMWPE after different surface modification techniques. *Med. Eng. Phys.* 2006, 28, 323–330. [CrossRef]
- Gul, R.M.; McGarry, F.J.; Bragdon, C.R.; Muratoglu, O.K.; Harris, W.H. Effect of consolidation on adhesive and abrasive wear of ultra-high molecular weight polyethylene. *Biomaterials* 2003, 24, 3193–3199. [CrossRef]
- 21. Jorfi, M.; Foster, E.J. Recent advances in nanocellulose for biomedical applications. J. Appl. Polym. Sci. 2015, 132, 41719. [CrossRef]
- 22. Azouz, K.B.; Ramires, E.C.; den Fonteyne, W.K.; Kissi, N.E.; Dufresne, A. Simple Method for the Melt Extrusion of a Cellulose Nanocrystal Reinforced Hydrophobic Polymer. *ACS Macro Lett.* **2012**, *1*, 236–240. [CrossRef]
- Vieira Ferreira, L.F.; Costa, A.I.; Ferreira Machado, I.; Branco, T.J.F.; Boufi, S.; Rei-Vilar, M.; Botelho do Rego, A.M. Surface Photochemistry: Benzophenone as a Probe for the Study of Modified Cellulose Fibres. *Res. Lett. Phys. Chem.* 2008, 2007, 18278. [CrossRef]
- 24. Biyani, M.V.; Jorfi, M.; Wedera, C.; Johan Foster, E. Light-stimulated mechanically switchable, photopatternable cellulose nanocomposites. *Polym. Chem.* 2014, *5*, 5716–5724. [CrossRef]
- 25. Kwon, O.H.; Nho, Y.C.; Lee, M.Y. Radiation-induced grafting of methylmethacrylate onto ultrahigh molecular weight polyethylene and its adhesive characteristics. *J. Mater. Sci. Mater. Med.* **2000**, *11*, 593–600. [CrossRef]
- 26. Zhao, J.R.; Feng, Y.; Chen, X.F. Graft modification of highly chlorinated polyethylene (HCPE) with methyl methacrylate by the mechanochemistry reaction. I. Synthesis and characterization. *J. Appl. Polym. Sci.* **2003**, *89*, 811–816. [CrossRef]
- Fu, Z.S.; Xu, J.T.; Zhang, Y.Z.; Fan, Z.Q. Chain structure and mechanical properties of polyethylene/polypropylene/poly(ethyleneco-propylene) in-reactor alloys synthesized with a spherical Ziegler-Natta catalyst by gas-phase polymerization. *J. Appl. Polym. Sci.* 2005, *97*, 640–647. [CrossRef]
- 28. Silverstein, M.S.; Breuer, O. Adhesive properties and failure of etched UHMW-PE fibres. *J. Mater. Sci.* **1993**, *28*, 4718–4724. Available online: https://link.springer.com/content/pdf/10.1007/BF00414263.pdf (accessed on 14 January 2024). [CrossRef]
- 29. Li, Z.; Zhang, W.; Wang, X.; Mai, Y.; Zhang, Y. Surface modification of ultra high molecular weight polyethylene fibers via the sequential photoinduced graft polymerization. *Appl. Surf. Sci.* **2011**, 257, 7600–7608. [CrossRef]
- Deng, J.; Wang, L.; Liu, L.; Yang, W. Developments and new applications of UV-induced surface graft polymerizations. *Prog. Polym. Sci.* 2009, 34, 156–193. [CrossRef]
- Dayyoub, T.; Maksimkin, A.V.; Senatov, F.S.; Kaloshkin, S.D.; Zimina, A.; Kolesnikov, E.A. Treating UHMWPE surface for enhancing the adhesion properties by cellulose grafting. *Int. J. Adhes. Adhes.* 2020, 98, 102535. [CrossRef]
- 32. Yu, H.; Xu, Z.; Yang, Q.; Hu, M.; Wang, S. Improvement of the antifouling characteristics for polypropylene microporous membranes by the sequential photoinduced graft polymerization of acrylic acid. *J. Membr. Sci.* **2006**, *281*, 658–665. [CrossRef]
- 33. Orelma, H.; Campbell, J.M.; Vuoriluoto, M.; Filpponen, I.; Johansson, L.; Biesalski, M.; Rojas, O.J. Preparation of photoreactive nanocellulosic materials via benzophenone grafting. *RSC Adv.* **2016**, *6*, 85100. [CrossRef]
- Dayyoub, T.; Maksimkin, A.V.; Kaloshkin, S.; Kolesnikov, E.; Chukov, D.; Dyachkova, T.P.; Gutnik, I. The Structure and Mechanical Properties of the UHMWPE Films Modified by the Mixture of Graphene Nanoplates with Polyaniline. *Polymers* 2019, *11*, 23. [CrossRef]
- 35. Adsul, M.; Soni, S.; Bhargava, S.; Bansal, V. Facile approach for the dispersion of regenerated cellulose in aqueous system in the form of nanoparticles. *Biomacromolecules* **2012**, *13*, 2890–2895. [CrossRef]

- ASTM Standard D724-99; Standard Test Method for Surface Wettability of Paper (Angle-of-Contact Method). ASTM International: West Conshohocken, PA, USA, 2003.
- ASTM Standard D882-10; Standard Test Method for Tensile Properties of Thin Plastic Sheeting. ASTM International: West Conshohocken, PA, USA, 2012.
- 38. *ASTM Standard 1876-01;* Standard Test Method for Dynamic Young's Modulus, Shear Modulus, and Poisson's Ratio by Impulse Excitation of Vibration. ASTM International: West Conshohocken, PA, USA, 2022.
- 39. ASTM Standard G 99-95a; Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus. ASTM International: West Conshohocken, PA, USA, 2017.
- 40. Rocha, M.; Mansur, A.; Mansur, H. Characterization and Accelerated Ageing of UHMWPE Used in Orthopedic Prosthesis by Peroxide. *Materials* 2009, 2, 562. [CrossRef]
- 41. Pang, W.; Ni, Z.; Chen, G.; Huang, G.; Huang, H.; Zhao, Y. Mechanical and thermal properties of graphene oxide/ultrahigh molecular weight polyethylene nanocomposites. *RSC Adv.* **2015**, *5*, 63063–63072. [CrossRef]
- 42. Stojilovic, N.N.; Dordevic, S.V.; Stojadinovic, S. Effects of clinical X-ray irradiation on UHMWPE films. *Nucl. Instrum. Methods Phys. Res. B* 2017, 410, 139–143. [CrossRef]
- Mahdavi, H.; Kahriz, P.K.; Gholipour-Ranjbar, H.; Shahalizade, T. Synthesis and performance study of amino functionalized graphene aerogel grafted with polyaniline nanofibers as an efficient supercapacitor material. *J. Mater. Sci. Mater. Electron.* 2016, 28, 4295–4305. Available online: https://link.springer.com/article/10.1007/s10854-016-6053-5 (accessed on 14 January 2024). [CrossRef]
- 44. Yanza, E.R.S.; Tan, G.M.C.; Querebillo, C.J.U.; Somintac, A.S.; Salvador, A.A.; Enriquez, E.P. Polyaniline In Situ Grafted to Graphene Sheets. *KIMIKA* **2014**, *25*, 23–35. [CrossRef]
- Juchnovski, I.; Kolev, T.; Stamboliyska, B. Infrared Spectra of Benzophenone-Ketyls. Effects of Meta- and Para-Substituents on the vC[dbnd]O Frequencies. Correlation Of vC[dbnd]O Of Substituted Benzophenone-ketyls With The Hueckel PC[dbnd]O Bond Order. Spectrosc. Lett. Int. J. Rapid Commun. 1993, 26, 67–78. [CrossRef]
- 46. Agarwal, U.P.; Atalla, R.H.; Isogai, A. *Nanocelluloses: Their Preparation, Properties, and Application*; ACS Symposium Series; ACS Publications: Washington, DC, USA, 2017; Volume 1251, ISBN 9780841232174. [CrossRef]
- 47. Fan, M.; Dai, D.; Biao Huang, B. Fourier Transform Infrared Spectroscopy for Natural Fibres. In *Fourier Transform—Materials Analysis, Salih Mohammed Salih*; IntechOpen: London, UK, 2012. [CrossRef]
- Förch, R.; Schönherr, H.; Tobias, A.; Jenkins, A. Surface Design: Applications in Bioscience and Nanotechnology; Wiley-VCH: New York, NY, USA, 2009; p. 471. ISBN 978-3-527-40789-7.
- 49. Zisman, F.; Fowkes, W.A. Contact Angle, Wettability, and Adhesion. Am. Chem. Soc. 1964, 43, 1–51.
- 50. Garbassi, F.; Morra, M.; Occhiello, E. *Polymer Surfaces: From Physical to Technology*; John Wiley and Sons: Chichester, NH, USA, 1997; ISBN 978-0-471-97100-9.
- Kurtz, S. Ultra High Molecular Weight Polyethylene in Total Joint Replacement and Medical Devices; Academic Press: San Diego, CA, USA, 2009; p. 568. ISBN 9780080884448.
- 52. Pascale, J.V.; Rentzepis, P.M. Response of polyethylene to acid etching. J. Appl. Polym. Sci. 1965, 9, 2641–2649. [CrossRef]
- 53. Dharmastiti, R.; Barton, D.C.; Fisher, J.; Edidin, A.; Kurtz, S. The wear of oriented UHMWPE under isotropically rough and scratched counterface test conditions. *Biomed. Mater. Eng.* **2001**, *11*, 241–256.
- 54. Hang, N.; Bellare, A.; Cohen, R.E.; Spector, M. Wear behavior of bulk oriented and fiber reinforced UHMWPE. *Wear* 2000, 241, 109–117. [CrossRef]

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