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Vadivel, H., Bek, M., Sebenik, U. et al (2021). Do the particle size, molecular weight, and processing of UHMWPE affect its thermomechanical and tribological performance?. *Journal of Materials Research and Technology*, 12: 1728-1737.  
<http://dx.doi.org/10.1016/j.jmrt.2021.03.087>

N.B. When citing this work, cite the original published paper.

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

**jmr&t**  
Journal of Materials Research and Technology  
journal homepage: [www.elsevier.com/locate/jmrt](http://www.elsevier.com/locate/jmrt)



## Original Article

# Do the particle size, molecular weight, and processing of UHMWPE affect its thermomechanical and tribological performance?☆



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## ARTICLE INFO

## Article history:

Received 28 October 2020

Accepted 22 March 2021

Available online 1 April 2021

## Keywords:

UHMWPE

Rheology

Viscoelasticity

Tribology

## ABSTRACT

UHMWPE has exhibited excellent performance when used as contact surfaces in tribological contacts. Traditionally, only UHMWPE grades, with narrow particle size and molecular weight distribution, have been deemed suitable for such applications. Now, various UHMWPE grades are available that are different from each other based on their particle size and molecular weight distribution. The question of whether the particle size of UHMWPE affects its performance and properties presents a research gap. The present study attempts to address this question. Additionally, the effect of processing of the UHMWPE is studied. It is observed that although minor differences were observed in the properties of the various grades of UHMWPE, they are inadequate to conclusively determine that the particle size and processing effect the properties and performance of the material.

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## 1. Introduction

Ultra High Molecular Weight Polyethylene (UHMWPE) is a thermoplastic material with good wear resistance, high impact strength, self-lubricating properties, excellent corrosion resistance and, is lightweight [1]. It exhibits a low

coefficient of friction due to its self-lubricating properties. Also, it has low compressive creep, excellent machinability without melting and low water absorption. Due to the combination of these properties, UHMWPE is used as a replacement for metals in various tribological applications [2–4].

Commercial UHMWPE grades can have different particle sizes and molecular weights. Until a few years back, UHMWPE

☆ This document is the result of the research project funded by Kempestiftelserna and financial support from the Slovenian Research Agency (research core funding No. P2-0264 and No. P2-0191).

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<https://doi.org/10.1016/j.jmrt.2021.03.087>

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grades of only a very narrow particle size distribution were available. These UHMWPE grades were produced targeting specific applications and were limited by production techniques [2,5]. However, with the development of manufacturing techniques at present, numerous UHMWPE grades of various particle sizes and molecular weights exist in the market. If a thermoplastic material like UHMWPE has to be used targeting a specific application, it is necessary that the influence of particle size and molecular weight on the thermomechanical properties and tribological performance is studied and known. The thermomechanical properties can have directly influence the performance of the material in tribological applications [6–8]. UHMWPE components can experience cyclic loading and diverse temperature and frequency conditions.

Both the particle size and molecular weight of a material can influence its properties, processing, and, consequently, performance. Having a lower molecular weight can mean a reduced melt viscosity leading to easier processing. It has been observed that natural rubber and cast Poly(Methyl Methacrylate), which have molecular weights of the order of  $10^6$  g/mol, cannot be melt processed until the chains have been broken down into smaller units [9]. The role of particle size and polymer molecular weight in the formation and properties of a calcium aluminate cement-poly(vinyl alcohol) composite was investigated. It was found that both polymer molecular weight and cement particle size affect the mechano-chemistry, the “window of processability”, and mechanical properties of the hardened matrix [10]. The particle size of UHMWPE was found to affect its motion and heating in a hot gas jet deposition process [11]. High molecular weight and high melt viscosity restrict ordering mechanisms such as crystallisation, affecting various physical properties and tribological performance. With increasing crystallinity, better tribological performance of UHMWPE has been observed. This improvement in performance was accompanied by an increase in hardness, scratch resistance, and elastic modulus [12]. The effect of particle size can be more pronounced in the case of composites involving UHMWPE and other reinforcement materials [13]. These types of UHMWPE based composites are popular and used widely due to their excellent tribological performance. On the comparison between two UHMWPE grades, it was found that the UHMWPE with a smaller particle size showed marginally better tribological performance [14].

In many instances and practical applications, reinforcement materials are added to UHMWPE to obtain composites with improved material properties and tribological performance [14–17]. The process of ball milling is commonly used to homogeneously disperse these reinforcement materials in UHMWPE [14]. However, ball milling can lead to the breakage of polymer molecules if the suitable parameters of time and speed are not used. Consequently, this can affect the material properties and tribological performance of the composite. Comparison of the effect of processing on different UHMWPE grades and their thermomechanical properties has not been studied yet.

With the availability of a variety of UHMWPE grades, the need arises to examine further the influence of particle size and molecular weight on the properties and performance of

the material. Will a difference in particle size and molecular weight translate into a significant difference in performance? How does processing affect the properties of UHMWPE? This is an uncharted area to the best of the authors' knowledge. There exists no information on whether a particular size of UHMWPE is suitable for a specific application, especially in the field of tribology. The objectives of the present study are thus multifold. The first is to use thermomechanical analysis to determine the effect of particle size and molecular weight on the viscoelasticity of various UHMWPE grades. The second objective is to investigate whether or not tribological performance is affected by the presence of or the lack of difference in thermomechanical properties. In the process, the effect of processing on the various UHMWPE with relation to their thermomechanical properties is investigated.

## 2. Experimental work

### 2.1. Materials and processing

For the purpose of this study, UHMWPE grades of different particle diameters (Table 1) were obtained in granular form from the manufacturers. UHMWPE of particle diameter  $140\ \mu\text{m}$  was obtained from *Celanese Corporation, USA*, while the rest were obtained from *Mitsui Chemicals GmbH, Germany*. As can be seen from Table 1, all the UHMWPE grades had similar density and physical properties [18,19]. Except for  $140\ \mu\text{m}$ , all the other grades had relatively similar molecular weight values. This choice was made intentionally with the purpose of investigating the effect of molecular weight on thermomechanical and tribological performance.

A mixture of ethanol and UHMWPE material was milled in a *PM100, Retsch GmbH, Germany* planetary ball mill. The slurry obtained after milling was dried in an oven to evaporate the ethanol. The powder obtained after drying was moulded into plates of different dimensions using the Direct Compression Moulding (DCM) method. The parameters of the processing were adopted from studies carried out already [14–16]. To determine the relationship between particle size, molecular weight, processing, properties, and performance, the processed or Milled samples were compared with As Received samples. Unprocessed UHMWPE obtained from the suppliers was directly moulded using Direct Compression Moulding (DCM) into samples which are called As Received samples here.

**Table 1 – Different UHMWPE grades; M – Milled, AR – As received.**

Designation and average particle size <sup>a</sup>	Average Molecular weight <sup>b</sup> ( $\times 10^4$ ) [g/mol]	Density <sup>c</sup> [kg/m <sup>3</sup> ]
10 $\mu\text{m}$ , M, AR	180	0.94
30 $\mu\text{m}$ , M, AR	200	0.94
120 $\mu\text{m}$ , M, AR	200	0.94
140 $\mu\text{m}$ , M, AR	350	0.93
160 $\mu\text{m}$ , M, AR	240	0.935

<sup>a</sup> MPC method.

<sup>b</sup> Solution viscosity method.

<sup>c</sup> ASTM D1505.

These two are denoted by *M* and *AR* in Table 1 and throughout this study. In both cases, UHMWPE forms obtained after the DCM process were used directly or machined into different shapes to be characterised.

## 2.2. Thermomechanical analysis

### 2.2.1. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out to determine the viscoelastic properties of the UHMWPE grades and to check how their properties change with frequency and temperature. Three sets of tests were performed: (i) amplitude and (ii) frequency sweep at a constant temperature in torsion and (iii) temperature ramp test in a tension configuration. Samples of dimensions  $50 \times 10 \times 3$  mm were used for frequency/amplitude sweep tests and samples of dimensions  $105 \times 2 \times 1$  mm were used for temperature sweep tests. Amplitude sweep tests were performed at  $37^\circ\text{C}$ , at a constant frequency of 1 Hz with increasing shear strain amplitude. Frequency sweep tests were also done at  $37^\circ\text{C}$  and at a constant shear strain of 0.03% (within the limits of linear viscoelasticity). The tests were performed within a frequency range of 0.1–100 Hz, with high frequencies simulating fast motion in a short time and low frequencies simulating slow motion on a longer timescale or in quasi-static conditions. The dynamic mechanical properties were also determined using a tension deformation test as a function of temperature. Tests were performed in a wide temperature range ( $-150^\circ\text{C}$  to  $180^\circ\text{C}$ ) in tension mode at a rate of  $2 \text{ Kmin}^{-1}$ . Experiments were carried out at 1, 2, 5, and 10 Hz frequencies (multi frequency mode), and the samples were tested in the range of linear viscoelastic response at a constant displacement of  $4 \mu\text{m}$ . Comparison between all the results is possible as long as all materials are tested within the linear viscoelastic region.

The DMA analysis was performed by applying a sinusoidal deformation through controlled oscillatory shear strain  $\gamma(t) = \gamma_0 \sin \omega t$ , where  $\gamma_0$  is the shear strain amplitude and  $\omega$  is the applied angular frequency, to a sample with known geometry and recording the phase-shifted shear stress response  $\tau(t) = \tau_0 \sin(\omega t + \delta)$ , which allows the determination of complex shear modulus  $G^*$ . The complex modulus is determined by decomposing the shear stress output into an in-phase and out of phase component and via  $G'$  and  $G''$ . All three moduli are related by Eq. 1

$$G^* = \sqrt{(G')^2 + (G'')^2} \quad (1)$$

While the above principle has been outlined in the case of a shear test, the same principle can be applied by imposing a tensile strain,  $\epsilon(t)$ , and based on the tensile stress,  $\sigma(t)$ , the (tensile) storage  $E'$  and loss  $E''$  moduli can be determined. The storage modulus  $G'$  ( $E'$ ) denotes the elastic response of the material, i.e. the stored energy within one loading cycle in the material due to stretching and extension of the internal bonds and structures, which constitutes the reversible part of the material deformation, providing no plastic deformation occurred. The loss modulus  $G''$  ( $E''$ ) characterises the viscous response of the material, i.e. the loss of energy due to internal friction during deformation, which is dissipated as heat and constitutes the irreversible part deformation [20,21]. These

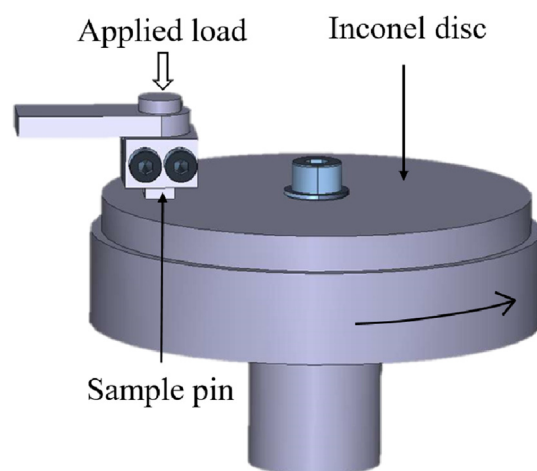


Fig. 1 – Pin on disc tribological test setup.

two moduli allow better characterisation of the material because we can now examine the ability of the material to return and dissipate energy. The storage and loss moduli are material properties and are independent of geometry. The ratio of the two modules is  $\tan \delta$ , is used as the measure of many properties [20] along with indicating how efficiently the material loses energy to molecular rearrangements and internal friction.

### 2.2.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements were performed on a Mettler Toledo DSC1 instrument with an intracooler using STAR software. Indium and zinc standards were used for the temperature calibration and for the determination of the instrument time constant. Samples of around 10 mg were weighed in standard  $40 \mu\text{L}$  alumina pans. A heating rate of  $10 \text{ K min}^{-1}$  was used and the purge nitrogen gas flow was maintained to be constant at  $30 \text{ mL min}^{-1}$  for all experiments. DSC was performed to obtain the degree of crystallinity and the thermal transition temperatures of the different UHMWPE grades. To calculate the degree of crystallinity, the enthalpy of fusion was determined using the melting peak and used in Eq. (2).

$$\text{Crystallinity} = \frac{\Delta H}{\Delta H_{100}} \times 100 \quad (2)$$

where,  $\Delta H$  is the enthalpy of the polymer and  $\Delta H_{100}$  is the enthalpy of fusion for a 100% crystalline UHMWPE ( $289 \text{ J/g}$ ) [22].

### 2.2.3. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of all the UHMWPE grades was performed using a PerkinElmer TGA 8000. The measurements were carried out under Nitrogen atmosphere, between  $30^\circ\text{C}$  and  $600^\circ\text{C}$ . A heating rate of  $10^\circ\text{C/min}$  was used to evaluate the thermal stability.

## 2.3. Tribological setup

Tribological measurements were carried out on a Pin-on-Disc tribometer (TE67, Phoenix Tribology, UK) with polymer pins and

Inconel 625 discs as the contact surfaces. The tribological tests were conducted in water lubrication for ease of comparison with other results [14–17,23]. Inconel with Ni (58 wt%), Cr (<23 wt%), Mo (<10 wt%), Nb (<4.15 wt%), Fe(5 wt%) as its major chemical constituents, was chosen for its good corrosion resistance. A schematic of the test configuration is shown in Fig. 1.

The tests were conducted at room temperature for a duration of 50h with a contact pressure of 5 MPa and a speed of 0.13 m/s. The counter surface discs were ground to a surface roughness  $R_a = 0.25 \mu\text{m}$  before being used in the tests. The parameters for contact pressure and surface roughness of counter surface were chosen to accelerate the tests while avoiding creep of the polymers and to minimise hydrodynamic effects while at the same time obtaining data over a long duration. Friction values were taken only from the steady-state region of the tests, while wear was calculated for the tests' whole duration. A Linear Variable Differential Transformer (LVDT) sensor was used to observe the vertical displacement of the pin holder and determine the wear depth continuously in the tests. The wear rates were calculated using Eq. (3).

$$\text{Wearrate} = \frac{\text{Volumeloss}}{(\text{Load})(\text{Slidingdistance})} \left[ \frac{\text{mm}^3}{\text{Nm}} \right] \quad (3)$$

No surface roughness difference is observed between the tribological test samples of Milled and As Received UHMWPE since the same molding process is used to form the test samples. Moreover, the wear behaviour is not related to the processing (ball milling and compression molding) of the UHMWPE. In studies already carried out, the processing parameters, including ball milling, were optimised with regards to UHMWPE [14,17,24].

#### 2.4. Scanning electron Microscopy(SEM)

The morphology of the particles and the topography of the wear tracks were investigated using an FEI Magellan 400 XHR, USA high-resolution scanning electron microscope. Energy-dispersive X-ray spectroscopy was also carried out on the

wear tracks to gain a better understanding of the wear and tribological mechanisms involved.

#### 2.5. Contact angle measurements

The wettability of the UHMWPE grades was measured using the sessile drop method with a Biolin Scientifica Theta tensiometer, Sweden. 4  $\mu\text{L}$  of distilled water was deposited on flat surfaces of UHMWPE obtained after direct compression moulding and contact angle measurements were taken 1s after deposition. Water contact angles can affect tribological performance and therefore is crucial to know the wettability character of the various UHMWPE grades.

### 3. Results and discussions

#### 3.1. Thermomechanical properties

##### 3.1.1. Dynamic mechanical analysis

For amplitude and frequency sweep tests, 4 Milled samples were analysed while only 1 As Received sample was analysed. Preliminary tests confirmed the authors' suspicion that DMA of As Received samples would provide the same results every measurement, i.e. pre-processing of granular UHMWPE does not affect material properties. Fig. 2a and b shows the results of amplitude sweep for Milled and As Received specimens, respectively. As can be observed by the closeness of results in both the plots, the various UHMWPE grades behave similarly. The difference in  $G'$  and  $G''$  values between 10  $\mu\text{m}$  and 160  $\mu\text{m}$  are on average 31% and 11%, respectively.

Some of the UHMWPE grades show a relatively larger variation in values near 1% shear strain which can be attributed to limitations of the test equipment used and the fact that these materials display linear viscoelastic behaviour only until 1% shear strain. Therefore, the variation in values is not material behaviour and can be ignored.

Fig. 3a and b shows the results for frequency sweep of Milled and As Received specimens. As in amplitude sweep results, there is some difference in values between the different

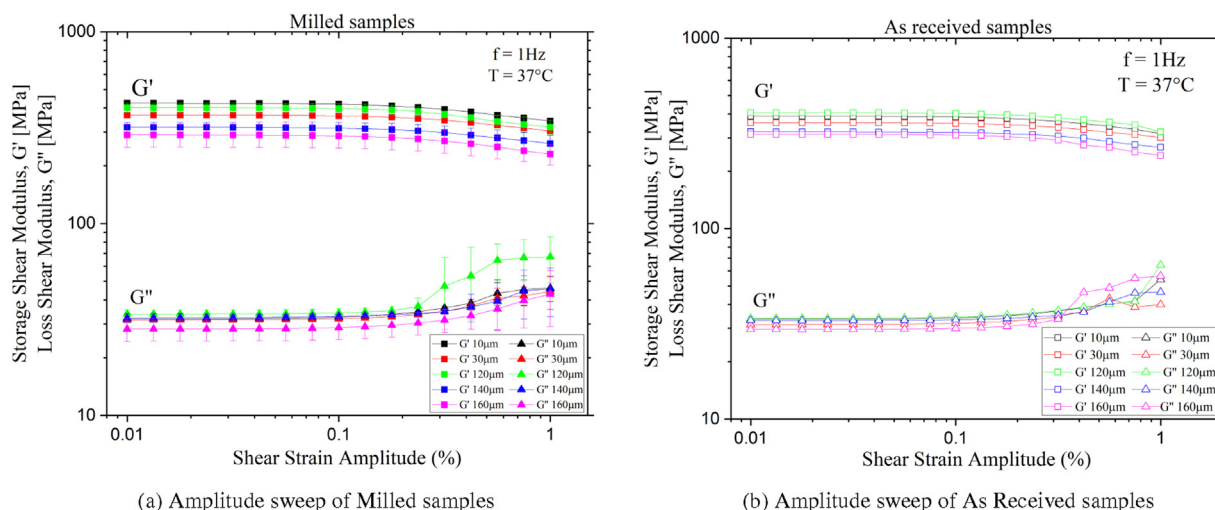
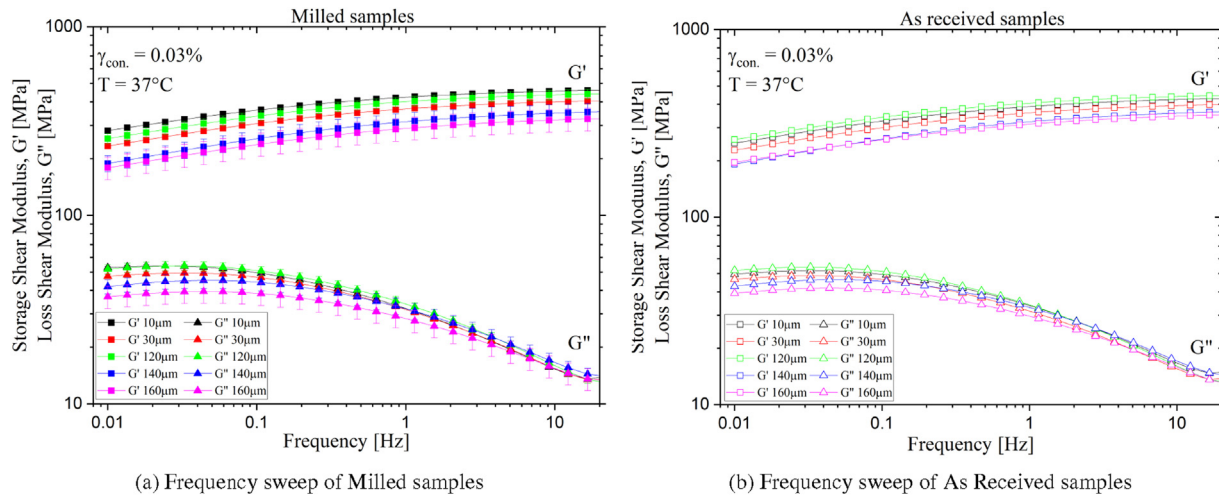


Fig. 2 – Amplitude sweep of Milled and As Received UHMWPE grades.



**Fig. 3 – Frequency sweep of Milled and As Received UHMWPE grades.**

UHMWPE grades. These difference are relatively small. For instance, at a frequency of 1Hz, the difference in  $G'$  and  $G''$  values between 10  $\mu\text{m}$  and 160  $\mu\text{m}$  is on average approximately 31% and 11% respectively.

It can be concluded from the DMA analysis that no significant difference in results between *Milled* and *As Received* samples are observed. The difference between these two groups of samples is that *Milled* samples are processed using ultrasonication and ball milling while *As Received* samples are not. Processing does not seem to influence or affect the dynamic mechanical behaviour of different grades of UHMWPE significantly. Since the UHMWPE grades differ in terms of particle size and molecular weight, the argument can be extended that these two parameters do not affect the processing and the dynamic mechanical behaviour of the UHMWPE grades. The small differences seen in dynamic mechanical behaviour can be a plausible reason for further investigation but are out of the scope of this study.

Fig. 4a and b shows the complex shear modulus of *Milled* and *As Received* UHMWPE grades in both amplitude sweep and frequency sweep modes, respectively. UHMWPE with the highest and lowest molecular weight, 140  $\mu\text{m}$  and 10  $\mu\text{m}$ , display the highest and lowest complex modulus as expected. Higher molecular weight can translate to a tougher material. However, the difference in values is not significant enough to affect properties and performance, as we have seen earlier and will see in further sections.

### 3.1.2. DMA tension deformation tests

Although tension deformation tests were conducted at various frequencies, Fig. 5a and b shows the results of storage, loss, and complex modulus for 1 Hz. No frequency dependence was observed for all the UHMWPE grades. No significant difference can be noticed between the various UHMWPE grades both in *Milled* and *As Received* states, as can be seen by the closeness of the curves. For example, the average loss tangent values for all the UHMWPE grades at 37°C, both *Milled* and *As Received*, is 0.12. The UHMWPE with the smallest (10  $\mu\text{m}$ ) and the largest (160  $\mu\text{m}$ ) particle size differ as little as 7%, and the UHMWPE with the lowest (10  $\mu\text{m}$ ) and highest

(140  $\mu\text{m}$ ) molecular weight differ as little as 23% in terms of loss tangent values.

It can be seen in Fig. 5b that all the UHMWPE grades display similar behaviour. The effect of processing is also negligible, while the effect of particle size and molecular weight can be detected. However, these differences are relatively small, and, as shown in continuation, they do not significantly affect the tribological properties. The glass transition ( $T_g$ ) and the melting point ( $T_m$ ) can be observed to be around  $-90^\circ\text{C}$  and  $136^\circ\text{C}$ , respectively. These two thermal transition points can also be seen in the  $E'$ ,  $E''$  plot in Fig. 5a. The small variations observed in some samples cannot be attributed to any thermomechanical phenomena and are insignificant.

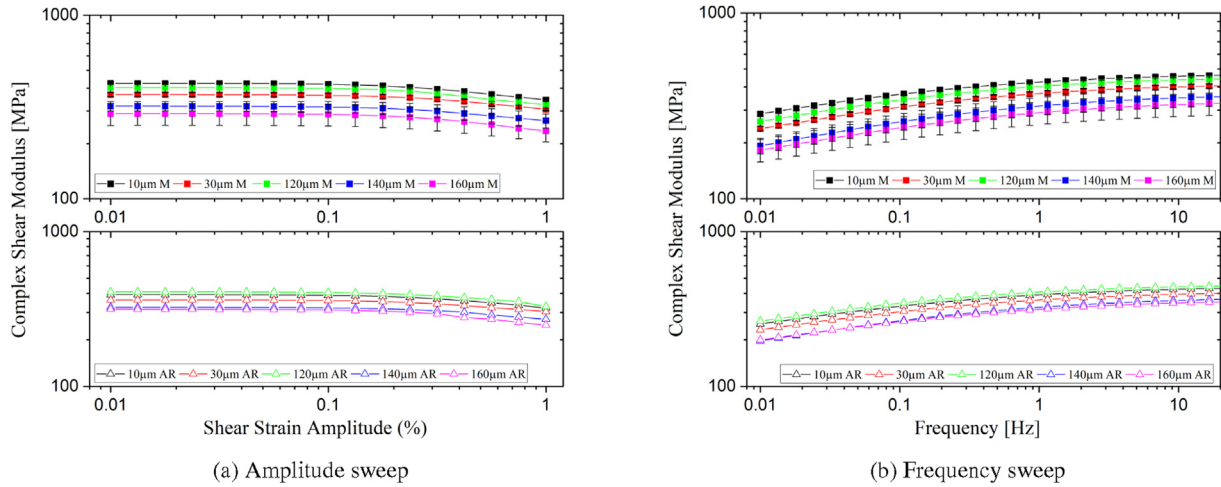
### 3.1.3. Cole–Cole plot analysis

So far, no significant differences have been observed in the thermorheological response of the various UHMWPE grades. Cole–Cole plots are very sensitive and provide more insight into the thermorheological/viscoelastic character of a material. Fig. 6 presents the Cole–Cole plots at a frequency of 1 Hz for both the *As Received* and *Milled* UHMWPE samples. Temperature decreases from left to right in plots.

As UHMWPE is semi-crystalline, its complex thermorheological response is reflected in the formation of multiple peaks in the Cole–Cole plots. The multiple peaks are due to the slower relaxation mechanisms of polymer chains at lower temperatures through which molecular motions become difficult. The two peaks can indicate two relaxation modes [25].

Three second-order phase transitions are generally identified in polyethylene, which are notated in descending order from the melting temperature as  $\alpha$ ,  $\beta$  and  $\gamma$  [26]. The  $\alpha$  and  $\beta$  peaks can be seen in Fig. 6. The  $\alpha$  relaxation is associated with an interlamellar shear process (motion of short molecular sequences in the crystalline region), while the  $\beta$  relaxation can be attributed to the motion of very loose folds in the amorphous region [27]. The  $\gamma$  relaxation is identified with the glass transition.

In the AR state, all UHMWPE materials exhibit the same thermorheological behaviour. However, a trend among the



**Fig. 4 – Complex modulus of Milled and As Received UHMWPE grades in amplitude and frequency sweeps.**

various Milled UHMWPE can be observed. There is the influence of the milling on the  $\beta$  relaxation. With increasing average particle size, the  $\beta$  relaxation process is suppressed. The processing of the UHMWPE is suspected to affect the relaxation process of the crystalline and amorphous regions in the UHMWPE. This influence of processing can also be noted in the slight difference in crystallinity the various UHMWPE have (see Table 2).

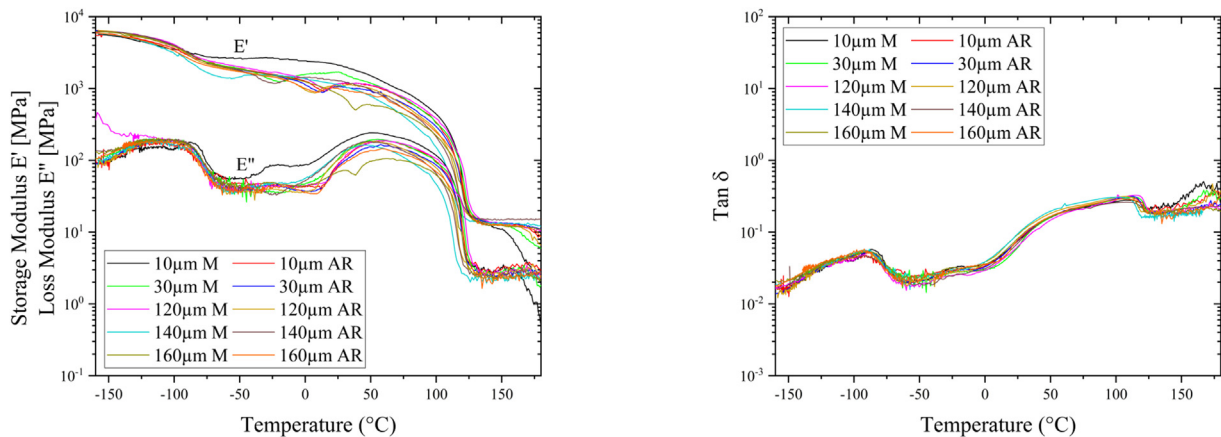
Since the objective of this work is to examine if there are differences between the various UHMWPE grades, we will not delve deeper into the thermal transitions the UHMWPE grades undergo. The majority of the thermorheological tests indicate no differences between the various UHMWPE grades. Cole–Cole analysis however, shows that the processing has affected the response of the UHMWPE materials, albeit to different intensities. The tribological testing of As Received UHMWPE grades is deemed unnecessary as no effect of the processing is noticeable on the thermomechanical behaviour of the UHMWPE grades. Since most commercially available UHMWPE material is processed in some manner before being used in an application, tribological tests for only Milled UHMWPE grades are conducted.

3.1.4. *Differential scanning calorimetry*

In the larger picture, the degree of crystallinity, melting point, and glass transition temperatures of the UHMWPE grades was observed to not vary significantly. Therefore, it could be concluded the particle size and molecular weight of the various UHMWPE grades did not affect the processing and consequently the crystallinity of the material. If one considers, in the case of Milled UHMWPE, the crystallinity to reduce slightly with larger average particle size, the beta relaxation is also suppressed. This suppression is not as evident in the case of As Received UHMWPE.

3.1.5. *Thermogravimetric analysis*

Fig. 7a shows the TGA curves of various Milled UHMWPE grades, while Fig. 7b show the average of all the data in Fig. 7a. It can be seen in Fig. 7b that the TGA curve of the UHMWPE grades consists of a single step degradation behaviour in the range from 441 to 509°C. The decomposition is due to the breakdown of polymer chains. The temperature of the maximum decomposition rate is around 491°C. The decomposition is due to the breakdown of the polymer chain. For comparison, the data for AR UHMWPE grades is shown in Table 3. There is minimal effect of the processing on the



**Fig. 5 – Tension deformation mode DMA of various UHMWPE grades.**

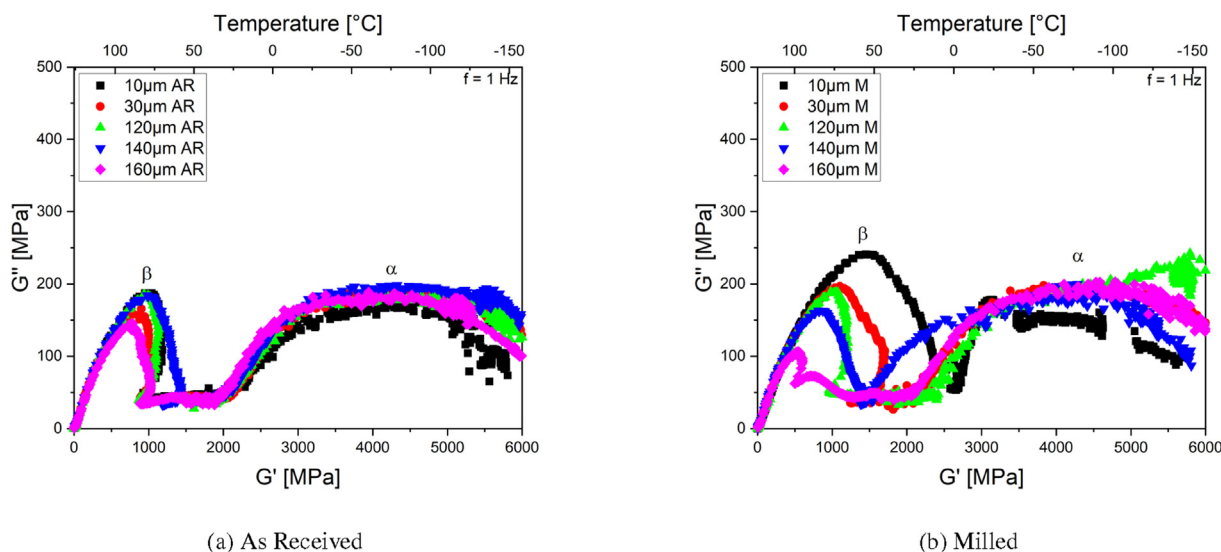


Fig. 6 – Cole–Cole plots of various As Received and Milled UHMWPE.

thermal degradation of the UHMWPE grades. A similar slight decrease is also observed in PEEK for similar processing [28].

It can be observed from the zoomed-in insets in Fig. 7a that increasing particle size results in delayed temperature of degradation. 10  $\mu\text{m}$  UHMWPE has the earliest degradation temperature, while 160  $\mu\text{m}$  has the most delayed degradation. This can be attributed to the heat needed to melt the particles and the particle size, which may have different surface morphology, roughness, and structure. The thermal stability of Polypropylene particles has been shown to initially decrease and then increase as particle size further decreases to the nanometer scale [29]. There are no studies that analyse the effect of UHMWPE size on its thermal degradation behaviour to the best of the authors' knowledge. However, studies on other materials have shown that thermal stability decreases with particle size [30–32]. The trend observed in thermal degradation is also seen in the residual weight at 600°C. The thermomechanical study of the UHMWPE so far in this study indicates that AR and M UHMWPE display similar behaviour, and the difference between them is insignificant if non-existent. Reinforcements and fillers are regularly

included with UHMWPE to make composites that are used in real-world applications. Manufacturing a composite involves various methods of processing, including ball milling. Therefore, Milled UHMWPE is chosen to be tested for its tribological performance.

### 3.2. Tribological performance

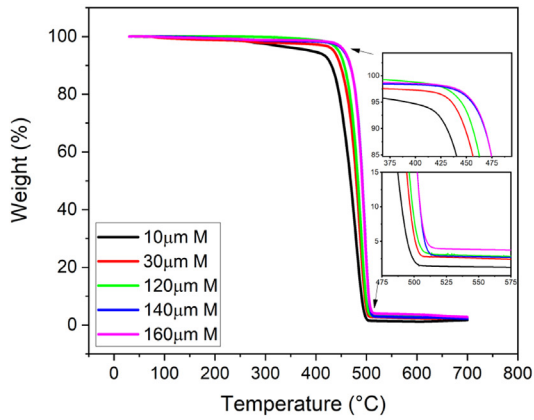
As water wettability can affect the tribological performance of the UHMWPE grades, contact angle measurements were carried out. Fig. 8 show the water contact angle values for both Milled and As Received UHMWPE. No significant difference is observed between the various UHMWPE grades.

Fig. 9a and b shows the friction coefficient and specific wear rate of the various UHMWPE grades. The friction coefficient shown here is the average for the last 10 h of a 50 h test. Although it may seem at first glance from Fig. 9a that the UHMWPE with the larger particle size has a higher friction coefficient, the standard deviation and the closeness in values stops one from conclusively saying that the friction coefficient is dependent on the particle size. The friction coefficient values in increasing order are for 30<10<140<120<160  $\mu\text{m}$  UHMWPE. The specific wear rate of the various UHMWPE approximately follows the same order. No distinct effect of particle size or molecular weight on the tribological performance is noticed. Material crystallinity plays an important role in the wear behavior of a material, and it is known that during testing, the crystallinity can change and thus affects the wear rate [33]. As the difference in wear rate of tested UHMWPE samples is small, we can conclude that if the local crystallinity changes occurred, they did not significantly affect the wear rate.

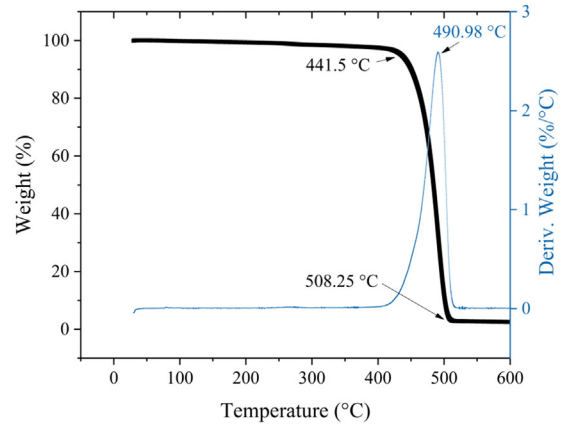
Fig. 10 shows the SEM micrographs of the pin surface and counter surface post pin on disk tests. The arrow marks indicate the orientation of the roughness profile. It can be seen

Table 2 – DSC analysis of UHMWPE grades.

UHMWPE grade		Melting point °C	Crystallinity %
10 $\mu\text{m}$	M	136.58	54.99
	AR	136.16	54.78
30 $\mu\text{m}$	M	135.73	54.99
	AR	136.16	54.78
120 $\mu\text{m}$	M	135.73	54.99
	AR	137.95	51.42
140 $\mu\text{m}$	M	136.49	53.63
	AR	135.04	52.28
160 $\mu\text{m}$	M	136.84	53.17
	AR	137.01	52.39

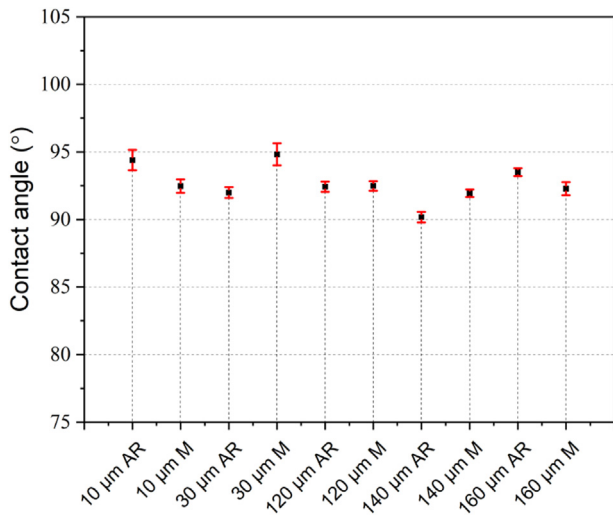


(a) TGA curves of various *Milled* UHMWPE grades.



(b) Derivative weight

**Fig. 7 – TGA data of various UHMWPE grades.**

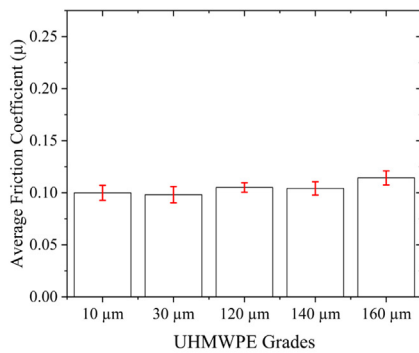


**Fig. 8 – Water contact angle values for various UHMWPE.**

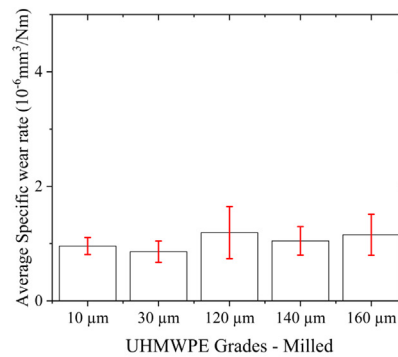
**Table 3 – Thermal properties obtained from TGA analysis of Milled (M) Vs. As Received (AR).**

Type	Temp. of initial decomposition (°C)	Temp. of Maximum decomposition rate (°C)
M	441.5	490.98
AR	444.75	495

from Fig. 10a that UHMWPE can experience both adhesive and abrasive wear in such conditions [34–36]. Abrasive and adhesive wear are the most common mechanisms to be experienced by UHMWPE, which induce the observed surface damage and degeneration of UHMWPE [37]. Abrasive wear of UHMWPE is predominantly a function of the roughness of the counter surface, while adhesion is mainly dependent on parameters like velocity, load, contact area, and the atomic forces between the two contacting surfaces [34,38]. The counter surface has a strong influence on the wear and friction behaviour of UHMWPE due to its abrasive properties and adhesive interaction [34]. Thermoplastics like UHMWPE have

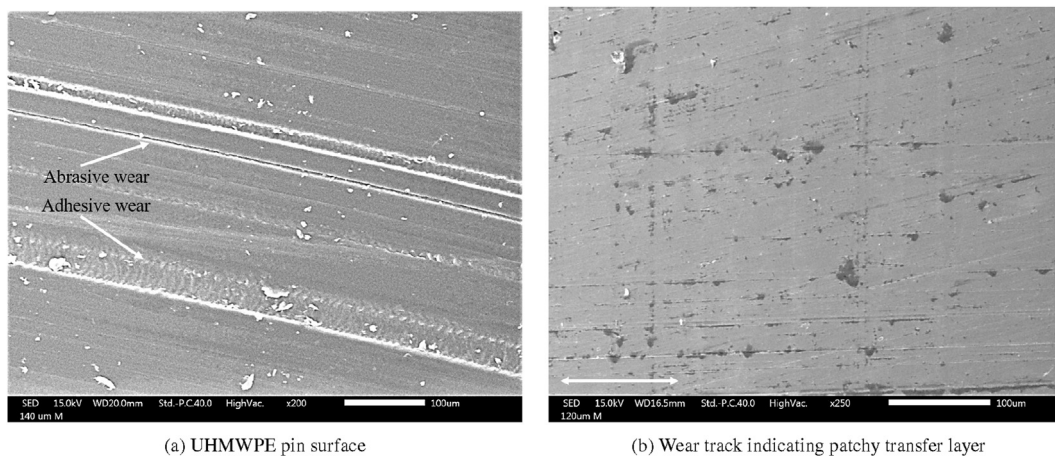


(a) Friction coefficient of various UHMWPE grades - Averaged for last 10 hours of the test



(b) Specific wear rate of various UHMWPE grades - Averaged for last 10 hours of the test

**Fig. 9 – Pin on disk results of the various UHMWPE grades.**



(a) UHMWPE pin surface

(b) Wear track indicating patchy transfer layer

**Fig. 10 – SEM micrographs of the polymer pin surface post tribological test, Wear track indicating patchy transfer layer.**

self-lubricating properties. Material is transferred from the thermoplastic to the counter surface to form a ‘transfer layer’. The formation of a transfer layer on the counterpart in UHMWPE bearing systems is often described as being a clear indication of strong adhesive forces. This layer prevents asperity to asperity contact, thereby reducing friction and promoting wear reduction. However, the presence of water as a lubricant inhibits the formation of such a transfer layer. The bonding between the transferred material and the Inconel is not strong enough to withstand the flow/motion of water. This is evident in Fig. 10b where it can be seen that the transfer layer is very patchy. A continuous layer that can help reducing friction is not formed. EDS analysis comparison of the wear track (Fig. 10b) and the pre-test Inconel surface confirmed the presence of the patchy transfer layer on the former. EDS of the patchy layer showed a higher percentage of carbon while the EDS of the counter surface outside the patchy layers did not.

#### 4. Conclusion

The objectives of the present study were multifold. The first was to determine the effect of particle size and molecular weight on the viscoelasticity of various UHMWPE grades. It was observed through dynamic mechanical analysis in amplitude sweep, frequency sweep, and temperature test that the particle size and molecular weight did not significantly affect the storage, loss, and complex moduli, especially in the context of their tribological properties. Similarly, no difference in behaviours was observed between Milled and As Received samples meaning that the processing did not affect the thermomechanical properties of the various UHMWPE grades. DSC and TGA measurements support this conclusion. Tribological tests indicated that there was no or insignificant difference in the performance of the various UHMWPE grades, and their behaviour could not be described by any trend. However, a more in-depth analysis involving Cole–Cole plots indicates to suppression of the  $\beta$  relaxation processes of Milled UHMWPE. We can say that there is no significant effect of processing on the various UHMWPE grades on their tribological performance. Their thermomechanical properties are

similar except with regards to their Cole–Cole analysis and this can be investigated further to gain more understanding of the particle size on the relaxation behaviour of processed UHMWPE. This can affect their application in real-world applications where cost is a significant factor.

#### Author contributions

**Hari Shankar Vadivel:** Conceptualisation of study, Preparing UHMWPE composites, Tribological and TGA tests, various analyses. **Marko Bek:** Rheology and DMA tests in amplitude and frequency sweep modes. **Urška Šebenik:** DMA tests in tension deformation mode, DSC tests. **Lidija Slemenik Perše:** Conceptualisation of study, DMA tests. **Roland Kádár:** Analytical inputs. **Nazanin Emami:** Conceptualisation of study. **Mitjan Kalin:** Conceptualisation of study.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### REFERENCES

- [1] Gauthier M. *Engineered materials handbook*. ASM International; 2000.
- [2] Kurtz SM. *UHMWPE biomaterials handbook*. 3rd ed. Academic press; 2009.
- [3] Orndorff RL. New UHMWPE/rubber bearing alloy. *J Tribol* 1999;122(1):367–73.
- [4] Qin H, Zhou X, Zhao X, Xing J, Yan Z. A new rubber/UHMWPE alloy for water-lubricated stern bearings. *Wear* 2015;328–329(Supplement C):257–61.
- [5] van Dingenen JIJ. High performance dyneema fibres in composites. *Mater Des* 1989;10(2):101–4.
- [6] Lewis Gladius. Polyethylene wear in total hip and knee arthroplasties. *J Biomed Mater Res* 1997;38(1):55–75.
- [7] Gladius L, Rogers C, Trieu HH. Dynamic thermomechanical properties and crystallinity of ultrahigh molecular weight

- polyethylene tibial inserts. *J Biomed Mater Res* 1998;43(3):249–60.
- [8] Kurtz SM, Villarraga ML, Herr MP, Bergström JS, Rimnac CM, Edidin AA. Thermomechanical behavior of virgin and highly crosslinked ultra-high molecular weight polyethylene used in total joint replacements. *Biomaterials* 2002;23(17):3681–97.
- [9] Gilbert M. Chapter 4 - relation of structure to thermal and mechanical properties. In: *Brydson's plastics materials*. 8th ed. Butterworth-Heinemann; 2017. p. 59–73.
- [10] Tan LS, Mchugh AJ. The role of particle size and polymer molecular weight in the formation and properties of an organo-ceramic composite. *J Mater Sci* 1996;31(14):3701–6.
- [11] Bao Y, Zhang T, Gawne DT. Influence of composition and process parameters on the thermal spray deposition of UHMWPE coatings. *J Mater Sci* 2005;40(1):77–85.
- [12] Kanaga Karupiah KS, Bruck AL, Sundararajan S, Wang J, Lin Z, Xu Z, et al. Friction and wear behavior of ultra-high molecular weight polyethylene as a function of polymer crystallinity. *Acta Biomater* 2008;4(5):1401–10.
- [13] McNally T, Pötschke P. Introduction to polymer-carbon nanotube composites. In: *Polymer-carbon nanotube composites*, woodhead publishing series in composites science and engineering. Woodhead Publishing; 2011. xxi–xxvii.
- [14] Vadivel HS, Golchin A, Emami N. Tribological behaviour of carbon filled hybrid UHMWPE composites in water. *Tribol Int* 2018;124:169–77.
- [15] Enqvist E, Ramanenka D, Marques PAAP, Gracio J, Emami N. The effect of ball milling time and rotational speed on ultra high molecular weight polyethylene reinforced with multiwalled carbon nanotubes. *Polym Compos* 2016;37(4):1128–36.
- [16] Enqvist E, Emami N. Nanodiamond reinforced ultra high molecular weight polyethylene for orthopaedic applications: dry versus wet ball milling manufacturing method. *Tribol Mater Surface Interfac* 2014;8(1).
- [17] Golchin A, Wikner A, Emami N. An investigation into tribological behaviour of multi-walled carbon nanotube/graphene oxide reinforced UHMWPE in water lubricated contacts. *Tribol Int* 2016;95:156–61.
- [18] Celanese - The chemistry inside innovation™.
- [19] Mitsui Chemicals Europe PLC.
- [20] Menard KP. *Dynamic mechanical analysis: a practical introduction*. CRC Press; 2008.
- [21] Starkova O, Aniskevich A. Limits of linear viscoelastic behavior of polymers. *Mech Time-Dependent Mater* 2007;11(2):111–26.
- [22] F2625-10. Standard test method for measurement of enthalpy of fusion, percent crystallinity, and melting point of ultra-high-molecular weight polyethylene by means of differential scanning calorimetry. Technical report. ASTM International; 2016.
- [23] Golchin A, Simmons GF, Glavatskih S, Prakash B. Tribological behaviour of polymeric materials in water-lubricated contacts. *Proc IME J J Eng Tribol* 2013;227(8):811–25.
- [24] Suner S, Joffe R, Tipper JL, Emami N. Ultra high molecular weight polyethylene/graphene oxide nanocomposites: thermal, mechanical and wettability characterisation. *Compos B Eng* 2015;78:185–91.
- [25] Gaska K, Manika GC, Gkourmpis T, Tranchida D, Gitsas A, Kádár R. Mechanical behavior of melt-mixed 3d hierarchical graphene/polypropylene nanocomposites. *Polymers* 2020;12(6):1309.
- [26] Ratner S, Pegoretti A, Migliaresi C, Weinberg A, Marom G. Relaxation processes and fatigue behavior of crosslinked uhmwpe fiber compacts. *Compos Sci Technol* 2005;65(1):87–94.
- [27] Drakopoulos SX, Psarras GS, Forte G, Martin-Fabiani I, Ronca S. Entanglement dynamics in ultra-high molecular weight polyethylene as revealed by dielectric spectroscopy. *Polymer* 2018;150:35–43.
- [28] Liang M, Lu C, Huang Y, Zhang C. Morphological and structural development of poly(ether ether ketone) during mechanical pulverization. *J Appl Polym Sci* 2007;106(6):3895–902.
- [29] Paik P, Kar KK. Kinetics of thermal degradation and estimation of lifetime for polypropylene particles: effects of particle size. *Polym Degrad Stabil* 2008;93(1):24–35.
- [30] Sovizi MR, Hajimirsadeghi SS, Naderizadeh B. Effect of particle size on thermal decomposition of nitrocellulose. *J Hazard Mater* 2009;168(2):1134–9.
- [31] Saleh M, Nugroho YS. Thermogravimetric study of the effect of particle size on the spontaneous combustion of Indonesian low rank coal. *Appl Mech Mater* 2013;330:101–5.
- [32] Çoban O, Bora MÖ, Sinmazçelik T. Effect of mixed size particles reinforcing on the thermal and dynamic mechanical properties of Al<sub>2</sub>O<sub>3</sub>/PPS composites. *Polym Compos* 2015;37(11):3219–27.
- [33] Gofman IV, Yudin VE, Orell O, Vuorinen J, Grigoriev A Ya, Svetlichnyi VM. Influence of the degree of crystallinity on the mechanical and tribological properties of high-performance thermoplastics over a wide range of temperatures: from room temperature up to 250 °C. *J Macromol Sci, Part B* 2013;52(12):1848–60.
- [34] Galetz MC, Seiferth SH, Theile B, Glatzel U. Potential for adhesive wear in friction couples of UHMWPE running against oxidized zirconium, titanium nitride coatings, and cobalt-chromium alloys. *J Biomed Mater Res B Appl Biomater* 2010;93B(2):468–75.
- [35] Nusbaum HJ, Rose RM, Paul IL, Crugnola AM, Radin EL. Wear mechanisms for ultrahigh molecular weight polyethylene in the total hip prosthesis. *J Appl Polym Sci* 1979;23(3):777–89.
- [36] Gul RM, McGarry FJ, Bragdon CR, Muratoglu OK, Harris WH. Effect of consolidation on adhesive and abrasive wear of ultra high molecular weight polyethylene. *Biomaterials* 2003;24(19):3193–9.
- [37] Dowson D, Atkinson JR, Brown K. The wear of high molecular weight polyethylene with particular reference to its use in artificial human joints. *Adv Polym Frict Wear* 1974:533–51.
- [38] Nielsen LR. Polymer rheology. *Br Polym J* 1978;10(2). 161–161.