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Two-dimensional clay nanosheet-reinforced polytetrafluoroethylene composites and their mechanical/tribological studies

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Abstract

Polytetrafluoroethylene (PTFE) polymer is used extensively in industry as a solid lubricant because of its lack of reactivity with most industrial materials. However, PTFE has a low abrasive resistance, limiting its application. In this study, the mechanical and tribological characteristics of PTFE-based composites with the addition of clay nano-sheets (CNSs) were investigated. Clay nano-sheet-PTFE composites (CNSTCs) containing 1, 3, and 5 wt. % of CNSs were prepared by employing a compression moulding method. To investigate the tribological characteristics and wear mechanism of CNSTCs, a pin-on-ring test, scanning electron microscopy (SEM), and optical microscopy (OM) were employed. The results indicate that adding CNSs decreased the friction coefficient substantially. Additionally, the wear rates decreased from $1.09 \times 10^{-3} \text{ mm}^3/(\text{Nm})$ in the pure PTFE sample to $0.32 \times 10^{-5} \text{ mm}^3/(\text{Nm})$ for the 5 wt. % CNSs filled composite. This shows that

the wear rate of the PTFE-based composite is reduced by up to 340 times with the addition of 5 wt. % CNSs. SEM and OM observations revealed that CNSs could inhibit the growth of microcracks in CNSTCs and change the wear mechanism from adhesive to abrasive. Furthermore, adding CNSs resulted in a more uniform and thinner transition film formation, with reduced secondary wear and friction. The effects of the size, percentage, and type of embedded fillers were compared with previous studies. The analysis revealed that in addition to competitive cost and high availability, CNSs have superior characteristics and can be employed to enhance the tribological properties of PTFE nanocomposites.

Keywords: Clay Nano-Sheets, Tribology, Polytetrafluoroethylene, Nanocomposite, Wear Resistance

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1. Introduction

Improvement in the life cycle of contacting pairs has attracted global research interest and can be achieved through the enhancement of tribological properties. Insufficient control of wear and friction in sliding parts not only causes earlier failures in one or both parts, but is also the leading cause of energy dissipation in many systems. It is estimated that the direct and non-direct cost of tribological problems could be 2–7% of the Gross Domestic Product (GDP) of most developed countries [1–3].

Remarkable developments in polymer manufacturing processes have been made, yielding high strength-to-weight ratios, good processability, and favourable characteristics. Polymeric materials are now considered an attractive alternative to conventional metallic counterparts, and have already been used in wear and friction applications [4–7]. Pure polymers do not generally have desirable tribological characteristics; however, mixing them with other materials can improve their frictional properties. There are many reports of progress in using polymeric composites for engineering components such as gears, supports, ball bearings, tyres, rollers, plastic belts, clutch and brake pads, bone joints, and artificial teeth [8–11].

Polytetrafluoroethylene (PTFE, also known as “Teflon”) is a white and solid thermoplastic material with high viscosity and molecular weight. It is a stable thermoplastic substance and is considerably resistant at elevated temperatures owing to the strong carbon-fluorine bonds in its molecular structure. Owing to its excellent electrical insulation properties, chemical neutrality, and low friction coefficient at various working temperatures, PTFE has found numerous applications in fields ranging from electronic and electrical equipment to the aerospace and biomedical industries [12–14].

Despite these advantages, PTFE suffers from poor wear resistance, which limits its application in demanding engineering and tribological systems. Various metallic or ceramic fillers (e.g., fibres, sheets, or particles) have been added to PTFE-based composites [6, 15–19] to modify their mechanical behaviour and enhance their abrasion resistance.

Previous studies have revealed that using micron-sized fillers in Teflon composites can improve their wear resistance. However, such fillers incur limitations including high grain size, high weight to volume percent, increased friction coefficient, disruption of transition film formation, and corrosion of opposing surfaces [20, 21]. To solve these problems, nanosized additives are used to improve the mechanical and physical properties of PTFE composites [20, 22–24]. Gao et. al. investigated the tribological properties of a PTFE matrix filled with different amounts of polyether ether ketone (PEEK) (38 μm) and nano-ZrO₂ (20 nm) [18]. The study revealed that the friction coefficient and the volume wear rate of the PTFE composites were effectively reduced by adding nano-ZrO₂ and PEEK, separately or together. The best tribological properties were obtained when the composites were filled with 5–8 vol.% nano-ZrO₂. In another study [20], ZnO nanoparticles (50 nm) were mixed with a PTFE matrix, and the results showed up to 100 times greater abrasion resistance by adding 15 wt.% nano-sized zinc oxide. To enhance the wear performance of a PTFE matrix, 20 wt.% Al₂O₃ nanoparticles (~38 nm) were added, and a 600 times improvement was achieved [25, 26]. Cai et. al. [22] added 2 wt.% of single-walled carbon nanotubes (SWCNTs) to a PTFE matrix and showed that the ultimate engineering stress and true stress were improved by approximately 50% and 200%, respectively. Additionally, by adding 5 wt. % of SWCNT, wear resistance was enhanced by around 20 times, and the friction coefficient was raised by ~50% [27]. Lin et al. studied the friction coefficient and wear resistance of PTFE-based composites reinforced with SiC, Si₃N₄, SiO₂ (~0.5–5 μm), or h-BN (~3–5 μm) ceramic particles [15]. They found that

the crystallinity of the PTFE matrix was promoted by applying these ceramic fillers. Furthermore, this study proved that the brittleness of the ceramic particles could play a vital role in the anti-wear performance of PTFE composites.

Since the early 1990s and the successful addition of clay to nylon 6 by Toyota [28], various industrial sectors such as construction, transportation, medical, and packaging have benefitted from the mechanical characteristics of clay-reinforced polymeric nanocomposites and their improved functional properties (e.g. ablation performance, fire retardancy, and gas permeability). The literature shows that introducing nanoparticles into a PTFE matrix can enhance the tribological properties of PTFE-based composites. However, adding these nanoparticles increases the final cost of the product, and improvements in both the mechanical and functional performance of the various polymeric systems are dependent on the degree of clay dispersion in the polymeric matrix [29, 30]. The benefit of CNSs is that they have competitive cost and superior characteristics that improve the mechanical behaviour of the host polymers [30–32]. CNSs also benefit from having a 2D structure [33–37], in comparison to other nanoparticles (e.g. Al_2O_3 or ZnO).

In this study, functionalized clay nano-sheets with organic modifiers were used to allow the required miscibility within the polymer and better incorporation/exfoliation. The effects of adding CNSs on the wear resistance, friction coefficient, and wear mechanism of PTFE-based nanocomposites in a dry environment were investigated. It should be noted that embedding CNSs within a polymer matrix produces a dense composite with high consistency, while also affecting the polymer crystallisation behaviour. Furthermore, intermediate phases may be developed because of the CNSs in the polymer matrix, possibly affecting the mechanical characteristics of the manufactured nanocomposites [30, 38]. It has been reported that polymeric nanocomposite coatings containing 5% CNSs have a homogenous structure with no cracks [39].

A literature review showed that there has been limited research on the enhancement of the mechanical characteristics and evaluation of the physical behaviour of CNSs/polymer nanocomposites. Additionally, there are no reports of mechanical and tribological studies of two-dimensional CNS-reinforced ring-shaped bulk PTFE composites. In this work, CNS/PTFE samples were prepared by a compression moulding method and subsequent sintering processes. The dispersion of CNSs in the polymeric matrix, wear resistance, friction coefficient, and its mechanisms were studied by conducting XRD, EDX, and pin-on-ring measurements as well as optical and scanning electron microscopies.

2. Experimental Procedure

2.1. Materials and Processing

Commercially available polytetrafluoroethylene powder (Dyneon™ PTFE, Dyneon LLC, USA) with an average grain size of 550 µm and modified nano-clay sheets (Cloisite 30B, Southern Clay Co. USA) with an average grain size of 200 nm were used as the starting materials. Cloisite 30B is a type of Cloisite Na⁺ that, according to the manufacturer specifications, has been organically modified via an ion-exchange reaction with a quaternary ammonium salt. Methyl tallow bis-2-hydroxyethyl ammonium cations are the organic modifier of Cloisite 30B, at a loading of 90 meq/100 g clay, and the tallow is ~65% C₁₈, ~30% C₁₆ and ~5% C₁₄ (Fig. 1). The goal of the current work was to develop composites with an appropriate CNS distribution in the PTFE matrix to enhance the density of the as-sintered samples. Fig. 1 shows a schematic of the experimental process.

To evaluate the influence of CNSs on the anti-abrasive characteristics of the PTFE-based composites, CNSs were added to the PTFE matrix at various contents (1, 3, and 5 wt. %).

129 Additionally, a pure PTFE specimen was fabricated without any CNS added. To prepare the
130 CNS/PTFE composites at the predefined compositions, firstly, CNSs were ultra-sonicated for ~20
131 min in an acetone medium to de-agglomerate them. Subsequently, PTFE powder was added and
132 the dispersion process continued for an additional 30 min. Second, acetone was removed from the
133 mixture by heating the slurry on a hotplate magnetic stirrer at 80 °C for 30 min. Third, the samples
134 were compressed using a hydraulic press machine at 50 MPa for 15 min. Finally, a sintering
135 procedure was performed using a tubular furnace because of the high-temperature reactivity of
136 fluorine-ethylene in the PTFE matrix. An inert gas (argon) flowed through the furnace during the
137 sintering process. The samples were sintered for 3 h at a controlled heating/cooling rate and a
138 dwelling time at the maximum temperature of 350 °C. Pure PTFE samples (without CNSs) were
139 also prepared following the same procedure, for comparison purposes. Samples were heated from
140 room temperature to 300 °C at a rate of 55 °C/h and held at 300 °C for 90 min. Subsequently, the
141 samples were heated from 300 to 350 °C at a rate of 23 °C/h and held at the sintering temperature
142 (350 °C) for 3 h. Samples were then cooled from 350 to 320 °C at a rate of -9°C/h, followed by
143 cooling from 320 to 300 °C at -10 °C/h. The process was completed by cooling from 300 °C to
144 room temperature at a rate of -55 °C/h. Ring-shaped samples with an inner diameter of 24.7 mm
145 and an outer diameter of 30.7 mm were finally obtained.

146 **Fig. 1**

148 **2.2. Characterisation**

149 X-ray diffraction patterns (XRD, D5000, Siemens Co., Germany) at 40 kV, 60 mA, 1500 W, with
150 Cu-K α (λ =0.154 nm) at 2θ angles from 0 to 40° were assessed. The goal of the current study was

to prepare composites with an appropriate CNS distribution in the PTFE matrix and produce dense composites with high consistency. Therefore, to verify the uniform distribution of CNSs in the polymeric matrix, energy-dispersive X-ray spectroscopy (EDX, attached to a scanning electron microscope (FE-SEM, MIRA3, Tescan Co., Brno, Czech Republic)) and XRD data were used for qualitative elemental analysis.

To evaluate the mechanical properties of the manufactured samples, a tensile test (Zwick Roell Z010, USA) was conducted in accordance with the ASTM 638 standard, with a load rate of 50 mm/min at ambient temperature. To calculate abrasion resistance, a pin-on-ring wear test was conducted on the specimens at 25 °C at a relative humidity of 25–35%. The pin surface was made of SAE 304 stainless steel with a surface roughness of 0.1 µm Ra. After each test, any adhered material was removed from the surface of the pin using sandpaper. The surfaces of the samples were thoroughly cleaned before the measurement to avoid any bias in the evaluation of wear behaviour. For all tests, the contact pressure on the pin was 1.13 MPa, the pin speed was 60 mm/s, and the wear length for the pure PTFE and samples containing 1, 3, and 5 wt.% was 1000 m. After each test, samples were weighed to ascertain the mass of the removed material. The topography of the samples after the wear and tensile tests was also studied. The fragments obtained from each test during the wear evaluation were also gathered for further study.

Surface observation and assessment of the samples, prior to and after evaluations, were carried out using a scanning electron microscope (SEM, VEGA TESCANA, Czech Republic). A gold sputtering apparatus (Emitech K550, Kent, UK) was used to coat the samples with a thin gold layer before the SEM assessment. Additionally, the formation of a transition film on the opposing surfaces was investigated using an optical microscope (Nikon Eclipse ME 600, Japan). All reported data in this study are the average of three measurements.

3. Results and Discussion

3.1 X-Ray diffraction measurements

It has been frequently reported that controlling the distribution and uniformity of the secondary phases in filler-reinforced PTFE composites is difficult because of the absence of *in-situ* polymerisation and fusion processes. To resolve this in the current work, a two-step mixing method was used to break down/exfoliate any possible agglomerations of CNSs and fully disperse them in the PTFE matrix. To ensure that the CNSs were not agglomerated and the sheets were exfoliated appropriately as well as to investigate the distribution of CNSs in the PTFE matrix, EDX and XRD analyses were used (Fig. 2). Five samples, including pure CNSs without treatment, pure PTFE, and the composite specimens containing 1, 3, and 5 wt.% CNSs, were studied.

****Fig. 2****

As shown in the XRD results (Fig. 2a), the pure CNSs showed a characteristic peak at $2\theta = 4.8^\circ$. This was used to measure the sheet distance in the CNSs for use in the Bragg equation ($n\lambda = 2d_{(hkl)}\sin\theta$), and $d_{(hkl)}$ was calculated to be 18.5 Å. Additionally, a strong peak at $2\theta = 18^\circ$ corresponds to the characteristic peak of PTFE. The XRD patterns of the sintered composites revealed no peaks for CNSs; the characteristic peak of PTFE was dominant in all samples. The absence of the characteristic peak of CNSs in the XRD patterns of the nanocomposites indicates destruction of the layered structure and exfoliation of the clay in the PTFE matrix. However, a low level of roughness was observed on the surface of the sample containing 5 wt % clay (Fig. 2c) as well as the existence of some lumps in Fig. 4. This implies that a highly exfoliated state was achieved, while a small proportion of the clays was intercalated owing to the clay concentration.

This has also been observed for the dispersion of CNSs in high-density polyethylene [40] and some other polymeric composites [41–44].

Considering the EDX spectrum and the chemical formula of PTFE (C_2F_4)_n, the detection of carbon (C) and fluorine (F) elements can be ascribed to the presence of PTFE. Furthermore, because CNSs are mainly made of silica layers, the peak for the silicon (Si) element indicates the presence of CNSs in the sample (Fig. 2b). Taking this fact into account, a normalising process based on these three elements (i.e. C, F, and Si) was used to calculate their weight percentage, but this does not represent the exact weight percentage of the analysed elements in the prepared sample. Consequently, these elements can be qualitatively detected in the sample, and the uniform distribution of CNSs in the sample can be seen in Fig. 2c. The results were further confirmed by SEM observations.

Individual layers of CNSs were not found in the SEM images (Figs. 2c, 4, and 8). The absence of these layers in a broad range of the investigated samples suggests that the CNSs were dispersed/exfoliated adequately. The dispersing method used in this study was therefore able to break down and exfoliate the agglomerations of CNSs and led to effective distribution of CNSs in the PTFE matrix. Regarding the manufacture of PTFE-based nanocomposites, the second phase distribution has a significant role in the tribological characteristics of the prepared material. As a result of the appropriate dispersion of CNSs in the PTFE matrix, the mechanical characteristics of the prepared composites in this work are in good agreement with previously published studies on the properties of PTFE nanocomposites [21, 25, 34, 40].

3.2 Tensile properties

To investigate the effect of CNSs on the tensile behaviour of the PTFE-based composites, various

samples, including pure PTFE and CNS/PTFE nanocomposites, were studied (Fig. 3). Fig. 3a shows the stress-strain curves of the prepared samples. Figs. 3b–d illustrate the effect of adding CNSs on the elastic modulus, ultimate tensile strength (UTS), and strain at UTS, respectively.

****Fig. 3****

It can be inferred from Fig. 3a that the strength of the samples decreases in the plastic region as the CNC content increases. In the curve for the pure PTFE, the strength continuously increases because of the strain-hardening phenomenon until the UTS is reached. However, after the UTS, the pure sample shows a necking tendency before fracture. No evidence of the necking phenomenon in the CNS-reinforced PTFE samples is observed. The presence of CNSs reduces the elongation of the samples, and the fracture mode tends to be more brittle. As is evident in Figs. 3b–d, adding CNSs decreases the fracture strength of the samples. The most probable reason for this is a weak interaction between the CNSs and the PTFE matrix, which also reduces the tensile strength of the samples.

It is also observed that adding CNSs considerably increases the elastic modulus. Furthermore, a direct relationship between the CNS content and the elastic modulus of the samples was found. This can be explained by the following reasons. First, CNSs have a greater modulus (4.657 GPa) [45] than the PTFE matrix (3.9 GPa), so the addition of CNSs can improve the elastic modulus. Secondly, CNSs can restrain the movement of polymer molecular chains. This is because the fully exfoliated CNSs can be appropriately incorporated within the polymer matrix and enhance their interactions with the polymer, minimising chain mobility and creating reinforcement effects [29, 46, 47]. Finally, CNSs can resist plastic strain and subsequently cause an increase in the slope of the stress-strain curve in the elastic region, as observed here and reported in the literature [40, 45].

3.3 Fractographic assessments

SEM images of the fractured surfaces of the samples after the tensile test are presented in Fig. 4. In Fig. 4a, it is evident that the fractured surface of the pure PTFE shows slip lines (i.e. a micro-ductile fracture mode) with the formation of small pits or micro-craters. The observed fibrous structure in Fig. 4 could be related to the ductility and cohesive fracture of the prepared samples (shown in Fig. 3), because of the high elongation characteristics of pure PTFE.

****Fig. 4****

The slip lines in Figs. 4b–d do not occur in the vicinity of the CNSs and weak interfaces between the CNSs and the PTFE matrix. This could be related to the nonpolar characteristics and low energy level of PTFE. Because of these conditions, CNSs are simply separated from the surrounding PTFE matrix. Conversely, the interfaces of CNSs and PTFE could act as stress concentration regions for microcrack initiation. Such micro-cracks would connect as the load increases, ultimately leading to sample failure. In summary, CNSs interrupt the cohesion of PTFE molecules; hence, they cannot endure applied force as well as the pure PTFE. As shown in Fig. 4d, the number of slip lines is considerably reduced, verifying that a relatively brittle fracture is dominant in the sample containing 5 wt. % CNSs.

As mentioned previously, controlling the uniformity and distribution of CNSs in the PTFE matrix is difficult because of the absence of fusion processes and *in-situ* polymerisation. Hence, other procedures should be employed to disperse an additive in the PTFE matrix. Because of a lack of uniformity when dispersing fillers in a PTFE matrix, they are sometimes agglomerated around the PTFE powder. In all PTFE-based composites, the distribution and uniformity of the embedded fillers are linked to the grain size of the employed PTFE powder.

To overcome this problem, (i.e. the inherent difficulty of uniformly distributing fillers and the difficulty of mixing CNSs into the PTFE matrix), modified CNSs were used and mixed through several steps (Fig. 1) to disperse CNSs into the PTFE. However, lumps that were detected (represented by circles) in Fig. 4 and the probability of these lumps occurring in other samples could be related to the accumulation of CNSs on the surface of the PTFE powder. The grain size of the PTFE used in the current work is approximately 550 μm , and the embedded CNSs have a size of approximately 200 nm. As the grain size of PTFE powder is 2.75×10^3 times larger than that of the CNSs, the PTFE powder could be surrounded by CNSs during the mixing and preparation of the nanocomposites. Consequently, the agglomeration of CNSs around the PTFE grains could decrease the binding force between the grains of the matrix and lead to a reduction in the homogeneity of the prepared nanocomposites. This is in addition to having adverse effects on their mechanical characteristics, as shown in Fig. 3. In the worst case, CNSs agglomerate around the PTFE powder and the developed composites behave as microcomposites; however, the data from the present study show good conformity with previously published works regarding PTFE-based nanocomposites [11, 15, 18, 19, 21, 25–27, 34, 40, 48, 49] (Table 1). Sawyer et al. [26] showed that matrix PTFE particles were much larger than embedded Al_2O_3 nanoparticles after compression moulding. They indicated that the resulting structure was probably cellular, with PTFE islands surrounded by a continuous casing of Al_2O_3 rich composite material. The enhancement in the wear resistance resulting from this casing material interrupts the wear process of the PTFE.

3.4 Tribological characteristics

To assess the tribological characteristics of the prepared nanocomposites and pure PTFE samples, abrasion evaluations were conducted. Data for the friction coefficient versus wear distance in the

CNS/PTFE composites at various contents of CNSs are provided in Fig. 5. The average value of the friction coefficient was calculated according to Eq. 1.

$$\bar{\mu} = \frac{1}{t} \int_0^t \mu dt \quad (1)$$

where t represents the total time of the test. The average friction coefficients for specimens containing 0, 1, 3, and 5 wt. % CNSs were calculated to be 0.127, 0.057, 0.066, and 0.071 respectively.

****Fig. 5****

The pin-on-ring friction measurement system used in this study includes one brittle material (stainless-steel pin) and one soft material (PTFE). Although both friction mechanisms are always active (i.e. adhesion and ploughing), the dominant friction mechanism is ploughing [50]. In the ploughing mechanism, the shear strength of the soft material dictates the friction rate of the system. When CNSs are added to PTFE, the number of defects and weak interfaces between CNSs and the PTFE matrix increases, decreasing the shear strength of the material. This fact is also evident in Fig. 3, which shows a reduction in the mechanical strength of the PTFE-based composites after incorporating the CNSs. This means that adding CNSs reduces the mechanical strength of the PTFE, resulting in a reduced friction coefficient, as shown in Fig. 5.

In the composite samples with 1 and 3 wt. % CNSs, the friction coefficients were approximately half of that of the pure PTFE. However, increasing the CNS content up to 5% showed a negligible increase in the friction coefficient. According to the curve for 5 wt. % CNSs, the friction coefficient remained almost constant until 1000 m abrasion. One reason for this phenomenon could be related to the erosion of some CNSs and their presence between the two sliding surfaces (i.e. the pin and

the sample). Additionally, this phenomenon could be explained by a change in the surface roughness. A fracture could liberate some CNSs, which would increase the surface roughness of the parent surfaces and lead to an increase in adhesive friction [50]. This is evident in Fig. 5 for 5 wt. % CNSs. However, as discussed, the contribution of the adhesive friction mechanism was not significant for the system containing the stainless-steel pin and PTFE composites. Therefore, its effect on the friction coefficient was negligible.

In Fig. 6, the temperature variation as a function of wear distance in the CNS/PTFE composites is presented.

****Fig. 6****

As shown in Fig. 6, by increasing the distance travelled, the temperature between the sliding surfaces increases owing to heat produced by the friction. The measurements show that the temperature increases up to 80 °C in the sample containing 5 wt. % CNSs. For abrasion distances up to ~1000 m, the slope of the temperature-distance curve in the CNS/PTFE composites is lower than that of the pure PTFE. The main reason for this behaviour may be linked to the reduction in friction imparted by the CNSs (Fig. 5). For the samples containing CNSs, the friction coefficients were initially raised due to the presence of the filler at the surface and then reduced, potentially due to the formation of a transition film.

Eq. 2 was used to calculate the special wear rates (W_s) of the samples during the abrasion test.

$$W_s = \frac{\Delta m}{FL\rho} \quad (2)$$

where W_s is the special wear rate (mm^3/Nm), Δm is the mass loss within the wear test (g), L represents the wear distance (m), F is the vertical force applied to the specimen (N), and ρ is the

density of the sample (g/mm^3).

The special wear rates for the specimens containing 0, 1, 3, and 5 wt. % CNSs were $1.09 \times 10^{-3} \pm 1.07 \times 10^{-5}$, $0.19 \times 10^{-3} \pm 1.02 \times 10^{-5}$, $3.59 \times 10^{-5} \pm 1.15 \times 10^{-6}$, and $0.32 \times 10^{-5} \pm 2.32 \times 10^{-7}$, respectively.

It can be concluded that adding CNSs significantly reduces the wear rate. In a comparison with the wear rate of pure PTFE, it was revealed that adding CNSs to PTFE causes a wear resistance improvement of approximately six times for the sample containing 1 wt. % CNSs. For the samples with 3 and 5 wt. % CNSs, the improvements in abrasion properties are ~ 30 and ~ 340 times, respectively.

The tribological performances of all PTFE composites could be influenced by the following three issues:

- (I) the mechanical and geometrical conditions of the slip interfaces between the sample and pin,
- (II) the mechanical characteristics of the matrix,
- (III) the characteristics of the transition film, as discussed further in the following section.

Table 1 presents a comparison of the wear resistance of the nanocomposite in the current study (5 wt. % CNSs-PTFE) with other studies. The effect of the filler content, size, and type of the embedded nanoparticles is assessed.

Table 1: Comparison of abrasion test results of PTFE-based nanocomposites

Type of additives	Size of additives (nm)	Additive content (%)	Wear rate (mm^3/Nm)	Test medium	Ref.
Clay nano-sheets	200	5	0.32×10^{-5}	dry	Current work
Al ₂ O ₃	40	6	3.00×10^{-5}	dry	[26]
Al ₂ O ₃	40	5	29.4×10^{-5}	dry	[49]
ZnO	80	6	1.30×10^{-5}	dry	[25]
SiO ₂ nanospheres	60	5	2.50×10^{-5}	dry	[11]
ZrO ₂	20	8	0.37×10^{-5}	dry	[18]
single-walled carbon nanotubes	2	5	3.10×10^{-5}	dry	[27]

Expanded graphite	-	5	0.23×10^{-5}	dry	[48]
Ag ₂ S	25-40	15	5.60×10^{-5}	dry	[19]
SiC	500	15	14.0×10^{-5}	deionized water (DW)	[15]
Si ₃ N ₄	500	15	46.0×10^{-5}	DW	[11]
SiO ₂	500	15	31.0×10^{-5}	DW	[11]

As can be seen in Table 1, the effect of adding CNSs in the current study is comparable to that of other studies in the literature, considering the content and its particle size. In addition, the size and amount of the fillers, filler type, and their geometric shape can also affect the tribological characteristics of the prepared nanocomposites. Consequently, CNSs as a 2D material with high availability and competitive costs can effectively enhance the tribological performance of PTFE-based nanocomposites.

An elemental distribution assessment was conducted on the sample containing 5 wt. % CNSs (Fig. 7).

****Fig. 7****

From the EDX data, the percentage distributions of the elements Si, C, and F were measured to be 5.3%, 31.8%, and 54.7%, respectively. It is shown that the percentage content of Si increased following the wear test (Fig. 2b). Consequently, it can be concluded that the CNSs were eroded less in comparison with the PTFE matrix during the wear test.

3.5 SEM investigations after tribological tests

To investigate the effects of CNSs on the tribological characteristics of the PTFE nanocomposites and to study the wear mechanisms, the topography of the prepared samples after abrasion tests was studied by SEM (Fig. 8). Additionally, the transition film formation on the opposing surfaces was studied using an optical microscope (Fig. 9).

****Fig. 8****

The wear mechanism of the samples could be different based on the abrasive environment. Among various wear mechanisms, abrasive and adhesive mechanisms are dominant. These two mechanisms are more relevant for the condition of this study due to the abrasion effects of two objects and poor interaction of PTFE with other materials.

Fig. 8a shows the surface of the pure PTFE specimen, where the direction of sliding was from left to right (the erosion pattern of the steel pin is clear). As the wear surface is smooth and uniform, the wear mechanism of the pure PTFE is predominantly an adhesive one. Fig. 8b shows the surface of the 1 wt. % CNS-reinforced PTFE sample where, in comparison to the pure PTFE, some disruption and cracks (represented by arrows) can be seen. Additionally, CNSs tend to be cut from the surface as the CNS content increases (indicated by circles), clearly signalling a shift of the wear mechanism from adhesive to abrasive.

In the pure PTFE samples, only two materials (PTFE as the test sample and the 304 stainless-steel pin) are present in the sliding system. However, in the composite PTFE, CNS particles are trapped between the rubbing surfaces. Due to the hardness of the CNS swarf, scratches are caused on the PTFE material (the trace of this phenomenon is indicated by the arrows in Fig. 8 c and d). This causes the wear mechanism to change from adhesive to abrasive. Uneven surfaces are observed, with numerous cracks and disruptions (ridges and grooves) in the samples with 3% and 5 wt. % CNSs (Figs. 8c and d). It can be concluded that by increasing the content of CNSs, the wear mechanism changes from an adhesive type (cutting of thin sheets) to an abrasive one. In the samples with 5 wt.% CNSs the dominant wear mechanism has three-component abrasive wear. The production of swarf in the nanocomposite is due to the abrasive characteristics of the cut CNSs. Furthermore, it can be seen that the swarf produced between the pure PTFE and the sliding

pin surface is composed of very thin sheets with relatively coarse dimensions when compared to the swarf from the 5 wt.% CNSs-PTFE nanocomposite (Figs. 9a and b).

It has been shown that when polymers are modified by adding various fillers, transfer film formation can affect their tribological behaviour. Some fillers affect the development of the transfer film and enhance its adhesion to the counterface. Such fillers reduce the wear rate of the polymer, often dramatically [51]. The results of the friction and wear behaviour for embedded CNSs are discussed in view of the transfer film characteristics in the current study. CNSs, as hard minerals with a desirable wear resistance compared to the PTFE matrix, could increase the wear resistance of the final nanocomposites.

Transition film formation is directly affected by the formation of swarf. In the case of pure PTFE, because of the geometrical shape and size of these fragments, they cannot locate themselves adjacent to other fragments to create a uniform layer (transition film). The formed fragments are cut and piled up around the contact interfaces, preventing full formation of a transition film and causing the abrasive pin to be in constant contact with the sample surface. This is observed on the abrasive surface shown in Fig 9c.

****Fig. 9****

Transition film formation and its characteristics are among the crucial parameters in decreasing the wear rate of various engineering components, particularly under dry abrasion conditions. Images of the fragments formed after surface erosion and the formed transition layers for the nanocomposite containing 5 wt. % CNSs are shown in Figs. 8 and 9. It is clear that the erosion surface is somewhat interconnected and uniform (Fig. 8d). Additionally, Fig. 8d shows that the obtained fragments are cut by a slip mechanism (unlike the anchoring mechanism, which occurs

in the pure PTFE samples). Consequently, it can be stated that the abrasion behaviour of the manufactured pure PTFE and composites is not similar. The first reason for the change in the abrasion mechanism of pure PTFE and its nanocomposites can be due to transition film formation. Unlike pure PTFE, a uniform transition layer can be formed in the samples containing 5 wt. % CNSs (Fig. 9d). This uniform and continuous transition film covers the surface of the abrasive pin. Hence, in these samples, the surface of the composite is not constantly in contact with the abrasive pin. However, to investigate transfer films in more detail, X-ray photoelectron spectroscopy (XPS) is suggested, as a further study.

Evaluation of the formed fragments in the reinforced samples after the wear test shows that they remained in position, potentially progressing to form a single layer. Considering the morphology of the investigated nanocomposites, it can be stated that by increasing the filler content, the surface of the samples was more interconnected and uniform after the wear test. Based on these observations, in the CNS/PTFE composites, the wear mechanism is of the adhesive type; however, the abrasive mechanism occurs because of clinging between a formed transition film and the sample surface.

4. Conclusions

Experimental investigations were performed to evaluate the effects of adding clay nano-sheets on the mechanical properties of PTFE. PTFE composites with 1, 3, and 5 wt. % CNSs as well as pure PTFE samples were prepared. The characteristic peaks of CNSs were not detected by XRD analysis of the composite samples, and individual layers of CNSs were not found in the SEM images, demonstrating that the methodology used to create the composites fully dispersed the CNSs into the PTFE.

Tensile results showed that adding CNSs to PTFE decreased the UTS and strain at UTS because of weak bonding between the PTFE and CNSs. Topographical studies of the tested specimens using SEM indicated that the interfaces of CNSs and PTFE could act as stress concentration regions for microcrack initiation, decreasing the tensile strength. Increasing the CNC content in the PTFE also reduced its ductility. However, the presence of CNSs improved the elastic modulus. This could be attributed to the capability of CNSs to restrict the slip of the molecular chains of PTFE in the composite.

Wear tests revealed that adding CNSs up to a specific value (5 wt. %) reduced the friction coefficient. The main reason for this phenomenon was a reduction in the real contact area between the sliding surfaces. SEM and optical microscopy investigations showed that the dominant wear mechanism in the pure PTFE was adhesive, which changed to abrasion with the addition of CNSs. This change could be attributed to the formation of a uniform transition film. This enhanced the wear resistance of the CNS/PTFE nanocomposites. Among the test samples used in this study, 5 wt. % CNS-reinforced PTFE composite showed the best wear resistance, with an improvement of 340 times that of pure PTFE.

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583 **Figure captions**

584 Fig. 1: Schematic of the experimental process.

585 Fig. 2: (a) XRD curves of clay nano-sheets (CNSs), pure Teflon (PTFE), 1, 3, and 5 wt. %
586 CNSs/PTFE composites, (b) EDX analysis from the surface of PTFE/5 wt. % clay nano-sheets
587 composite, (c) FE-SEM image from the surface of PTFE/5 wt. % clay nano-sheets composite.

588 Fig. 3: (a) Stress-strain curves of pure PTFE, 1, 3, and 5 wt. % clay nano-sheets (CNSs)/PTFE, (b)
589 elastic modulus vs. CNS content, (c) ultimate tensile strength vs. CNS content, and (d) strain at
590 UTS vs. CNS content.

591 Fig. 4: SEM images of fracture surfaces of (a) pure PTFE, (b) 1 wt. % clay nanosheets
592 (CNSs)/PTFE, (c) 3 wt. % CNSs/PTFE, and (d) 5 wt. % CNSs/PTFE composites.

593 Fig. 5: Friction coefficient vs. the abrasion distance for pure PTFE, and PTFE composites
594 containing 1, 3, and 5 wt. % clay nano-sheets.

595 Fig. 6: Temperature variations vs. the abrasion distance for pure PTFE, and PTFE composites
596 containing 1, 3, and 5 wt. % clay nano-sheets.

597 Fig. 7: EDX analysis from the eroded surface of PTFE/5 wt. % clay nano-sheets composite.

598 Fig. 8: SEM images of abrasive surfaces for (a) pure PTFE, and PTFE composites containing (b)
599 1, (c) 3, and (d) 5 wt. % clay nano-sheets after the abrasion tests.

600 Fig. 9: Swarf produced after wear tests (a and b) and formation of transition films (c and d) in the
601 pure PTFE and 5 wt. % clay nano-shets/PTFE composite, respectively.