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SPECIALTY SECTION

This article was submitted to Polymeric and Composite Materials, a section of the journal Frontiers in Materials

RECEIVED 22 December 2022

ACCEPTED 17 January 2023

PUBLISHED 26 January 2023

CITATION

Miao Y, Chen Q, Li Y, Zhuo D and Wang R (2023), Tribological properties of carbon nanotube/polymer composites: A mini-review.

Front. Mater. 10:1129676.

doi: 10.3389/fmats.2023.1129676

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Tribological properties of carbon nanotube/polymer composites: A mini-review

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With the development of modern industry, the requirements for mechanical equipment are increasingly stringent, and increasing attention has been paid to reducing wear or lubrication in the movement of mechanical structural parts. Polymers are widely used in the field of mechanical structural parts due to their high processing performance and comprehensive performance. However, the relatively weak mechanical and tribological properties of polymers limit their further application in mechanical equipment lubrication. Incorporation of fillers is a common method to improve the friction properties of polymers. Among various fillers, carbon nanotubes (CNTs) are considered the ideal fillers to significantly improve the tribological properties of polymers. Therefore, this paper reviews the tribological properties of carbon nanotube modified polymer materials. The tribological wear mechanism of polymers and the influence of friction-reducing fillers on the tribological properties of polymers and the related lubrication mechanism explanation are outlined, and the factors influencing the tribological properties of composites by carbon nanotubes and the related lubrication mechanism explanation are analyzed. The presented review will be beneficial for the production of high-performance polymer nanocomposites.

KEYWORDS

carbon nanotube, polymer, composite, tribological properties, mechanical properties

Introduction

In recent years, due to the development of society and the growing depletion of the traditional fossil energy, the requirements for energy saving and environmental protection of machinery and equipment have increase. Reducing wear loss and strengthen the lubricating between the mechanical moving parts are the important ways to achieve the energy saving and material loss, and therefore wear-resistant materials, as an essential component in the operation of equipment, have increasingly high requirements for their frictional properties (Lin et al., 2011; Kuang et al., 2022). The use of lubricating oil or the self-lubricating structural parts is a common method to reduce friction and anti-wear (Maruyama et al., 2017; John and Menezes, 2021). However, liquid lubricating materials are susceptible to environmental factors and lose their lubricating effects in the harsh scenarios such as high vacuum, high load and extreme high or low temperature environments (Kian et al., 2019). Therefore, the role of lubricated, wear-resistant solid materials in machinery and equipment is becoming increasingly important.

Polymers are compounds with relative molecular masses of several thousand to several million, with the excellent processing properties and comprehensive performance, widely used in people's clothing, food, housing, transportation, various sectors of the national economy and

cutting-edge technology (Moreno-Navarro et al., 2017; Grancarić et al., 2018; Afolabi et al., 2019; Wang et al., 2022b). Polymers have important applications in wear resistant parts such as bearings. For example, epoxy resins are used in machinery and equipment as bearing materials and friction members due to their high corrosion resistance, low coefficient of friction (COF) and high dimensional stability (Bashandeh et al., 2021), polytetrafluoroethylene (PTFE) is used as oil-free lubricated mechanical parts due to high chemical resistance and low COF (Jang et al., 2007), etc. However, pure polymers are often difficult to use directly as wear-resistant materials (Unal et al., 2010; Kaybal et al., 2021). For the one hand, the intrinsic low thermal conductivity and heat resistance of polymers may lead to the significant changes in their mechanical properties under high temperature conditions, thus reducing their wear resistance and service life. For the other hand, different polymers have different properties and also exhibit different frictional behaviors. For example, PTFE, ultra-high molecular weight polyethylene (UHMWPE) and polyurethane (PU) have excellent self-lubricating properties, but their mechanical properties and heat resistance are relatively poor. Polyimide (PI), poly (ether-ether-ketone) (PEEK) and epoxy resin (EP) have better mechanical and thermal properties, but their COF are relatively high (Maksimkin et al., 2017; Lim et al., 2018; Arif et al., 2020; Cui et al., 2022; Ding et al., 2022). Therefore, these problems limit the universality of polymer applications in the actual mechanical equipment.

Compounding fillers or blending other polymers is the most common and effective way to improve the tribological properties of polymers. PTFE, UHMWPE, Molybdenum disulfide (MoS_2), SiC, carbon fiber, etc. are used as lubricant materials or reinforcing fillers to improve the friction properties of polymers (Li et al., 2007; Chanda et al., 2019; Salem et al., 2019; Cao et al., 2020). Among them, CNTs are the ideal modifiers for the fabrication of polymer composites with high tribological properties due to their unique structures and excellent properties.

This paper reviews the tribological properties of carbon nanotube modified polymer materials. Firstly, the tribological wear mechanism of polymers, the friction-reducing fillers on the tribological properties of polymers and the related lubrication mechanism explanation are outlined. Then, the factors influencing the tribological properties of carbon nanotube/polymer composites and the related lubrication mechanism explanation are analyzed. Finally, the challenges and prospects of carbon nanotube/polymer composites with high tribological properties are summarized.

Friction and wear behavior and improvement mechanism of the polymers

The wide range of variations in the mechanical properties of polymers and their strong dependence on temperature, deformation rate and the sensitivity of their failure process to environmental conditions make the polymer wear process much more complex compared to metals. Most scholars now classify this complex process into four types: adhesive wear, corrosive wear, abrasive wear and fatigue wear, and the various types of wear can undergo transformation (Lancaster, 1978).

In the relative motion of the friction vice, the surface of the friction couples, although the surface appears flat, the micro-surface is still

uneven, which only shows the local contact. At this point, even if a smaller load is applied, the local stress on the actual contact surface is sufficient to cause plastic deformation, so that the oxide film on this part of the surface, etc. is squeezed, and the atoms of the two contact surfaces will be bonded due to bonding interaction. In the subsequent continuation of sliding, the adhesion point is sheared off and transferred to the counterpart surface, which comes off to form abrasive chips, resulting in the loss of material on the surface of the part (Archard, 1953; Belyi et al., 1977; Bijwe et al., 2001; Fukuda and Morita, 2017; Paul and Bhowmik, 2022). Abrasive wear is also caused when hard particles are present within the contact surface. The polymer undergoes a cutting process like planing under the action of abrasive particles, and this process can directly cause material removal and form a chip, which is micro cutting. In contrast, plowing is the extrusion of the polymer by abrasion to the sides, which does not directly cause material removal, but after several deformations can produce shedding and secondary chip formation. The rougher the counterpart surface, the greater the wear rate (WR) of the polymer (Dmitriyeva and Grayevskaya, 1983; Njoku et al., 2021). There may also be fatigue wear on the rough pair surface, when the friction pair slides against each other, the rough peaks of the soft surface are easily deformed, while the soft rough peaks break first under cyclic loading, resulting in a smoother surface. In this way, the contact state is no longer rough peak to rough peak, but the hard surface of the rough peak on the relatively smooth soft surface sliding. When the hard surface rough peak slides on the soft surface, the points on the soft surface are subjected to a cyclic load, which produces shear plastic deformation in the surface layer and accumulates, causing dislocation buildup at a certain depth under the surface, which leads to the formation of cracks or pores. When the crack is formed at a certain depth, according to the stress field analysis, the positive stress on the parallel surface prevents the crack from expanding in the depth direction, so the crack extends in the direction of the parallel surface at a certain depth. When the crack extends to a critical length, the material between the crack and the surface will flake off in the form of flakes of abrasive chips (Atkins et al., 1984; Bogdanovich, 2013; Hussain and Khan, 2022; Zhou et al., 2023). While the corrosive wear of polymers mainly takes place in the form of chemical degradation and oxidation, the high temperature generated at the sliding interface can cause severe degradation or softening of some polymers. In addition to temperature, many factors influence the chemical degradation of polymers, such as the catalytic effect of some oxygen species, the activation energy of polymer degradation and interfacial contact stress (Chen et al., 2014).

Based on the friction and wear behavior of polymers, incorporation of functional fillers to affect the friction process, leading to the improvement of tribological properties of polymer is an effective and viable way. In filler modified polymer composites, the fillers can be classified into reinforcing fillers and lubricating fillers according to their functions.

The lubricant fillers include the familiar PTFE, graphite, MoS_2 , etc (Lu and Friedrich, 1995; Qiao et al., 2007; Khare et al., 2015; Zalaznik et al., 2016; Chen et al., 2020; Li et al., 2022b). Gu et al. found that the wear surface of polymethyl methacrylate (PMMA) was uneven with many torn flakes and surface bumps, and the COF curve fluctuated in a wide range, while the wear surface of PTFE/PMMA composites filled with PTFE was relatively smooth with only slight scratches and a smoother COF curve, indicating that the friction process of PMMA-based composites is more stable by filling with PTFE. This is because

the PTFE carbon chain backbone can only accommodate the bulk F atoms in a helical conformation, and the whole macromolecular chain presents a stiff rod-like structure. Due to the strong electrostatic repulsive force of F atoms around the carbon chain and the bulk effect of fluorine atoms, the smooth linear chains without branching side chains are connected by weak van der Waals forces, and the PTFE macromolecule chains are very easy to unwind and slip, and form transfer film and reduce the COF, but the filling of PTFE will make the hardness of the composite material decrease and cause the increase of WR (Gu et al., 2018). Because of the weak van der Waals force between the layers and interlaminar sliding occurs easily, graphite was considered as a typical lubricant filler. Zhang et al. found that the COF of graphite/PTFE composites decreased gradually with the increase of graphite content. During the sliding process, the graphite flakes become thinner and fall off, exposing the surface of the friction substrate, while the peeled graphite micro flakes form a hard transfer film on the surface of the friction substrate, which can effectively reduce the COF (Zhang et al., 2008). The other lubricant fillers such as MoS₂ (Yang et al., 2020), Hexagonal boron nitride (h-BN) (Rao et al., 2021), Zirconium phosphate (ZrP) (Cai et al., 2023), etc. were also reported to improve the tribological properties of polymers by forming the complete transfer film on the surface of the friction substrate, thus reducing the COF of the composite. However, the addition of lubricant fillers adversely affects the WR. The increase of WR can be attributed to the decrease in the hardness of the resultant composite caused by the addition of the lubricant fillers. The wear resistance of the composites depends to some extent on the hardness of the composites, so the decrease in hardness will cause a decrease in the wear resistance of the composites.

Unlike abrasion-reducing fillers, the addition of reinforcing fillers aims to improve the mechanical properties of the composite material such as hardness, strength, impact resistance, creep resistance, etc. (Lustiger et al., 1990; Friedrich et al., 1993; Friedrich et al., 1995). The elastic modulus and tensile strength of the reinforced filler are generally higher than those of the polymer, which in turn leads to filler composite reinforcement (Papon et al., 2012). When the complex is subjected to external stress, the stress is transferred to the filler particles through the resin-filler phase interface, making the filler particles the main stressed phase. The stress transfer mechanism is applicable to both zero-dimensional, one-dimensional and two-dimensional nano-reinforced fillers (Papageorgiou et al., 2020). The improved mechanical properties of polymeric materials increase the load-bearing capacity of polymeric materials, meaning that the material is less prone to plastic deformation and spalling during friction. At the same time, it can maintain the structural integrity of the composite material under high loads (Su et al., 2016). In addition, the excellent mechanical properties significantly inhibit the creation and spread of cracks on the wear surface, thus improving wear resistance (Huang et al., 2013). He et al. found that Perfluoroalkoxy filled with Al₂O₃ particles exhibited ultra-high load-bearing capacity and low COF under sliding conditions (He et al., 2017). Li et al. demonstrated that glass fiber incorporation can substantially improve the mechanical properties of the composites such as tensile strength, tensile modulus, flexural strength, and flexural modulus, and at the same time, the composites exhibit excellent wear resistance (Li et al., 2013). This is due to the strong interfacial bonding between glass fibers and polyether ether ketone, which leads to the interruption of the fiber removal process and causes

the accumulation of abrasive particles near the glass fibers, thus avoiding the abrasion of the matrix resin. Nemati et al. studied the effect of graphene on the wear resistance of PTFE was investigated, and the results showed that the addition of graphene effectively improved the wear resistance of the PTFE coating. When graphene was added up to 15 vol%, the friction factor and WR were significantly reduced to 0.1 and $0.65 \times 10^{-9} \text{mm}^3/(\text{N}\cdot\text{m})$, respectively (Nemati et al., 2016).

Tribological properties of CNT/polymer composites

Although remarkable achievements have been made in the researches of the friction properties of polymer composites, there are still some technical problems. The addition of the solid lubricating fillers can significantly reduce the friction coefficient of polymer composites, but the friction loss effect is not obvious due to the adverse effects on the hardness, modulus and other properties of polymer composites. With regards to the reinforced fillers, they can significantly improve the mechanical properties of polymer composites, but the large amounts of loadings are often needed to achieve the required friction properties, which may affect other properties of the polymer. Therefore, it is still important to research the new wear-resistant fillers.

CNTs

CNTs are an ideal one-dimensional nanomaterial currently prepared artificially as hollow cylinders enclosed by concentric graphitic surfaces, which exhibit many unique physical properties due to the uniqueness of their own compositional structure (Jun and Gai, 2015; Zang et al., 2015). CNTs have strong wear resistance and self-lubricating properties, with a wear resistance 100 times higher than that of bearing steel and a COF of 0.06–0.1. CNTs also have excellent Thermal stability and electrical conductivity (He et al., 2018; Cui et al., 2021). CNTs have received a great deal of attention from researchers since their introduction in 1991.

Due to the unique structure and excellent properties, CNTs were introduced to modify polymer for improving the properties of polymer such as mechanical properties, electrical properties, and thermal stability, which have been confirmed by the previous reports (Kotop et al., 2021; Parnian and D'Amore, 2021). Kang et al. prepared CNT/PP composites by melt injection molding method. It was found that the thermal degradation temperature of PP increased by 50°C after filling with CNT, and the thermal conductivity and tensile strength increased with the increase of CNT content (Kang et al., 2010). Liang et al. showed that the flexural modulus of PP increased with increasing CNTs content when filled with CNTs, indicating that CNTs can effectively improve the flexural stiffness of the polymer (Liang et al., 2018). Also, the fracture impact strength of CNT/PP with 4% wt. was increased by 40% compared to pure PP. In addition to this, the addition of CNTs to rubber materials can also reduce the adhesion strength of ice to rubber materials, allowing rubber-based components to work in extreme weather (Valentini et al., 2018). Therefore, the addition of CNTs is an effective method for developing high-performance polymer nanocomposites.

TABLE 1 Tribological properties of polymer nanocomposites based on CNT.

Polymer	Types of CNT	Test conditions	Wear rate	Friction coefficient	References
POM	Pure MWCNT	POD; Steel; Dry; AL: 15, 25, 35 N; SV: 1 m/s; ST: 30 min; Ra: 0.25 μ m	-9%	-20%	Goriparthi et al. (2019)
	Acid-treated MWCNT		-19%	-19%	
	Silanized MWCNT		-45%	-27%	
	Carbonylated MWCNT		-28%	-21%	
	Aminated MWCNT		-31%	-22%	
	CNT D: 10nm; L: 2.5 μ m	POD; Steel; Dry; AL: 12 N; SV: 1 m/s; ST: 120 min	-70%	N/A	Yousef et al. (2016)
	POD; Steel; Water; AL: 12 N; SV: 1 m/s; ST: 120 min	-60%			
	POD; Steel; Oil; AL: 12 N; SV: 1 m/s; ST: 120 min	-33%			
PTFE	CNT	Dry; AL: 101 kPa	N/A	-25%	Song et al. (2019)
		BOD; Dry; AL: 5 mN, 20 mN; SV: 4 mm/s; SD: 2mm, 1000 cycles	-31%	-60%	Lim et al. (2018)
PEEK	MWCNT OD: 10–15 nm; L: 0.1–10 μ m	BOD R); AISI E52100 stainless-steel ball; Dry; AL: 10 N; SV: 5 Hz; SD: 10,000 cycles	+142%	-67%	Arif et al. (2020)
	CNT D: 10–30 nm; L: 5–30 μ m	POD; SiC; Dry; AL: 1.5N; SV: 300rpm; ST: 5min	-7.32%	-6.71%	Cui et al. (2022)
UHMWPE	Fluorinated MWCNT	POD; Steel; Dry; AL: 32 N; SV: 2.6 m/s; SD: 2355 m	-27%	-95%	Maksimkin et al. (2017)
	MWCNT OD: 30–50 nm; ID: 5–15 nm; L: 10–20 μ m	POD; Titanium alloy; Dry; AL: 60N; SV: 15 mm/s; ST: 24 h	-54%	-21%	Naresh Kumar et al. (2016)
	CNT OD: 10–12 nm; L: 8–12 μ m	BOD; Steel; Dry; AL: 5 N; SV: 0.06 m/s; SD: 460 m	-20%	-36%	Manoj Kumar et al. (2019)
	CNT D: 25–26 nm	BOD(R); 440C stainless steel; Dry; AL: 30 N; SV: 0.06 m/s; SD: 68.2 m, 5000 cycles	-63%	+35%	Ali et al. (2017)
		BOD(R); 440C stainless steel; Water; AL: 50 N; SV: 0.06 m/s; SD: 6 k m, 150,000 cycles	-47%	+30%	
	CNT D: 50–100 nm; L: 10–20 μ m	POD; Titanium alloy; Dry; AL: 1 kg; SV: 120 prm; SD: 250 m	-25%	-10%	Deenoi and Dechjarern, (2019)
	CNT D: 40–60 nm; L: 1–2 μ m	BOD; 440C stainless steel; Dry; AL: 7,9, F12, 15 N; SV: 0.1 m/s; SD: 5000 cycles	-44%	-38%	Ahmed Baduruthamal et al. (2019)
EP	CNT	POD; Steel disc; 50% relative humidity; AL: 30, 40 N, 50N; SV: 200, 300, 400 rpm	-53%	N/A	Venkatesan et al. (2018)
	CNT L: 10–15 μ m; D: 15–20 nm	POD; Steel disc; Dry, Oil-lubricated, and argon; AL: 40 N-120N; SV: 500 rpm; SD: 2.827 km	-18%	-20%	Agrawal et al. (2021)
	MWCNT	POD; 316 L steel disc; Dry; AL: 5 N; SV: 2 Hz; SD: 5 mm	-83%	-31%	Chen et al. (2017)
	Untreated MWCNT	ROD; AL: 10 N; SV: 2.5 m/s; SD: 20000 m	-41%	N/A	Sapiai et al. (2021)
	Silane-treated MWCNT		+23%		
	Acid-treated MWCNT		+9%		
	MWCNT L: 1–10 μ m; Number of walls: 3–15	BOD; Bearing steel SAE 52,100 balls; Dry; AL: 2 and 4 N; SV: 0.28 m/s (1000 rpm)	-36%	-78%	Upadhyay and Kumar, (2018)
	poly (urea-formaldehyde) shells assembled with polydopamine-functionalized oxidized CNT	POD; Dry; AL: 1 MPa; SV: 0.5 m/s; ST: 30min	-99%	-64%	Li et al. (2018)

(Continued on following page)

TABLE 1 (Continued) Tribological properties of polymer nanocomposites based on CNT.

Polymer	Types of CNT	Test conditions	Wear rate	Friction coefficient	References
	MWCNTs–alumina	POD; EN8 steel disc; Dry; AL:50N; 100N; 150N; SV:200prpm; SD:1250m; ST:30min	–31%	–52%	Saravanan et al. (2019)
	MWCNT-COOH functionalized L: 10–30µm; OD: 20–30 nm; ID:5–10 nm	POD; 100 cr6 steel pin; Dry; AL:20,60,100N; SV:0.1 m/s; SD:1000 m	–87%	–20%	Adarmanabadi et al. (2021)
PP	CNT	POD; Steel disc; Dry; AL: 50 N; SV: 56.5 m/min; ST: 30 min	–12%	–48%	Mertens and Senthilvelan, (2018)
		POD; EN-32 steel; Dry; AL: 10–50 N; SV: 1–5 m/s	–50%	–44%	Ashok Gandhi et al. (2013)
	As-received CNT L: 1.5µm; D: 9.5 nm	BOD(R); steel; Dry; AL: 2 N; SV:0.0128 m/s; SD:200 m	34%	–8%	Ali et al. (2014)
	Purified CNT L: 1.5µm; D: 9.5 nm		–36%	–21%	
TPU	Plasma-treated CNT	Sandpaper; Dry; AL: 0.08N; SV: 7300 rpm	N/A	–55%	Ogawa et al. (2022)
	MWCNT OD:20–30 nm; L:10–30 µm	ROD; Dry; AL: 300N; SV: 0.341 m/s	–52%	–34%	Song et al. (2011)
Polyamide 6	MWCNT L: 20–30µm; OD: 20–30 nm; ID: 10–20 nm	POD; Dry; AL:20–100N; SV:200rpm; SD: 80 mm; ST:3min	–31%	–72%	Chopra et al. (2018)
	CNT	BOR; Dry; GCr15 steel; AL:100–250N	–38%	N/A	Zhang and Deng, (2011)
		BOR; Dry; Quenched medium carbon steel; AL:100–200N; SV: 0.42 m/s; SD: 0.1–0.5 km; ST:0–90min	–30%	–31%	Chang et al. (2013)
	CNT D:50–80 nm, L:5–20 µm	POD; Dry; AL:20–50N; SV: 1 m/s	–33%	–29%	Meng et al. (2009)
POD; Water; AL:20–50N; SV: 1 m/s		–13%	–93%		
PI	CNT loaded with MoS ₂	BOD(R); Stainless-steel ball; Dry; AL:6N; SV:10Hz; SD:10 mm; ST:10min	–31%	–84%	Xin et al. (2018)

Remark, Tribological performances were reported as compared to neat polymer or otherwise stated; D, diameter; OD, outer diameter; ID, inner diameter; L, length; POD, pin-on-disc; BOD, ball-on-disc; BOR, block-on-ring; ROD, ring-on-disc; R, reciprocating mode; AL, applied load; SV, sliding velocity; SD, sliding distance; ST, sliding time.

For the moment, the role of CNTs in wear reduction and wear resistance is also very impressive, mainly as the reinforcement of complexes and additives to lubricating fluids, and the like (Wang et al., 2020; Li et al., 2022a; Wang et al., 2022a). Chen et al. prepared CNTs-reinforced EP composites using oligoaniline assisted dispersion method and investigated their tribological properties (Chen et al., 2017). It was found that the CNTs of the composites had good dispersion, based on which the crystallinity and tribological wear properties of the composites were improved, and the composites had lower WR and COF. Gao et al. showed that significantly lower COF for CNT bio-lubricants compared to dry conditions, showing optimal and durable antifriction characteristics (Gao et al., 2021). It was beneficial to suppressing the removal of multifiber block debris, tensile fracture, and tensile-shear fracture, with the advantages of tribological properties and material removal behavior. CNT improves the wear resistance of polymers more than some other fillers. Remanan et al. added CNT and B₄C to Poly Aryl Ether Ketone. Comparing B₄C, the WR of the composites was reduced by 34% with the addition of CNT (Remanan et al., 2017). Ren et al. added CNT and Mo₂S to EP. at the same 4% content, the WR of the CNT/EP composite was 50% less than that of the Mo₂S/EP composite (Ren et al., 2019). Surya et al. used fibers to reinforce natural rubber materials. CNT and graphite nanofibers reinforced compounds improved the wear resistance simultaneously by 43% and 33% respectively, while SiC and aramid nanofibers improved it by 10% and 8% respectively (Surya et al., 2022).

Recent researches on the tribological performance of CNT/polymer nanocomposites were summarized in Table 1.

The reason why CNT improves the frictional properties of polymers is not just a single effect like other conventional fillers, but the result of a synergistic effect of several factors (Figure 1). First of all, due to the special characteristics of the CNT structure, a carbon film is formed regardless of whether the CNT is attached to the polymer matrix or when it falls into the gap of the friction substrate due to wear. This hard and self-lubricating carbon film effectively avoids direct scraping of the friction substrate and reduces the COF and WR (Zhang et al., 2020; Dwivedi et al., 2022). In the next place, when the CNT/polymer composite is subjected to stress, it is transferred to the CNT through the bonding interface, making the CNT the main stressor. Due to the ultra-high aspect ratio and strength of CNT, the strength of the composite is also enhanced, which is less prone to plastic deformation and improves the wear resistance of the polymer (Zare and Rhee, 2020; Duan et al., 2021). Meanwhile, when the composite material produces microcracks due to friction, CNT can effectively inhibit the growth of microcracks, reduce grinding chips, and improve the wear resistance of the material (Bahramnia et al., 2021). The CNT incorporation also improves the thermal conductivity and thermal stability of the composite material, preventing it from softening under the high temperature conditions of frictional heating and failure, which affects wear resistance and service life (Shimizu et al., 2020; Yan et al., 2020).

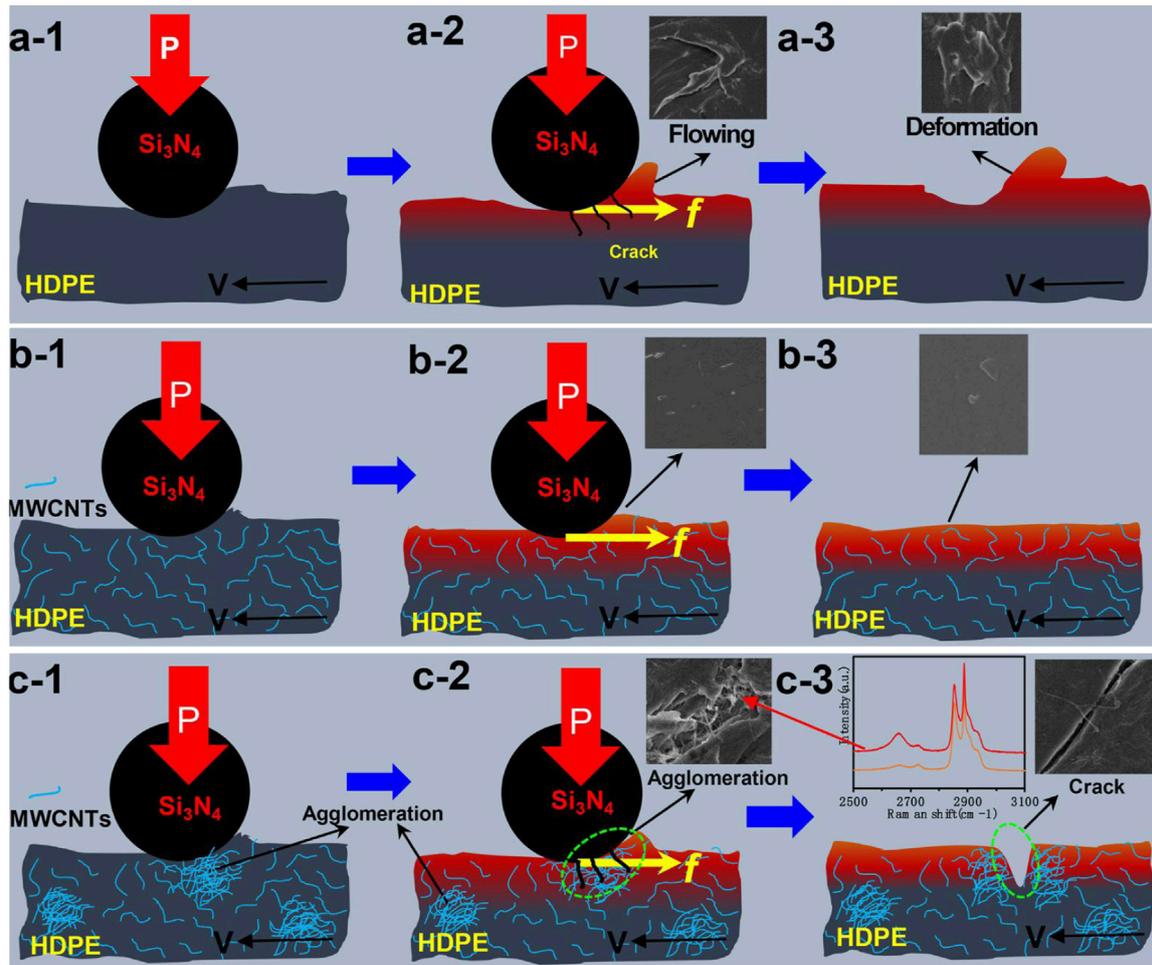


FIGURE 1

Friction reduction models of HDPE (a-1, a-2, a-3), HDPE with moderate 5p [6-xujyho] MWCNTs (b-1, b-2, b-3), and excess MWCNTs (c-1, c-2, c-3) (Wu et al., 2021).

The improvements of the tribological properties of polymer composites by incorporation of CNTs had been confirmed by the previous researches, but in fact, some important factors in CNTs/polymer composites needed to be clarified.

Type of CNTs

CNTs are classified as multi-walled carbon nanotube (MWCNT) and single walled carbon nanotube (SWCNT). Meanwhile, the same type of CNTs have different lengths and diameters. Adrian Cotet et al. compared the effect of SWCNT and MWCNT on the tribological properties of vinyl ester nanocomposites (Cotet et al., 2019). MWCNT decreased the COF of nanocomposites, but the addition of SWCNT increased the COF at high sliding velocities. It was shown that the presence of MWCNT in the fragments contributed to the lubrication effect due to the strong interaction of MWCNT with the polymer matrix, while SWCNT in the fragments played the role of a third body in the sliding motion. Liu et al. introduced two different diameters of MWCNTs to

bismaleimide resin, and the significant difference on WR and COF between the resultant MWCNT/bismaleimide composites was observed. Li et al. added CNT to grease to prepare lithium-based grease and investigated the effect of tube diameter and tube length on its frictional properties (Li et al., 2019). The results show that the tube diameter of CNTs has little effect on the friction reduction performance of CNTs, and the COF becomes slightly larger when the tube diameter is larger, and the COF curves all fluctuate not much. However, the length of CNTs has some influence on the friction performance of grease, and the WR is lower when the tube is longer. Due to the strong interaction between CNTs, they are very agglomerated when added to the matrix of polymers, leading to the degradation of composite properties. Therefore, achieving uniform dispersion of CNTs in the matrix resin is the key to prepare high-performance composites. Simultaneously, there are large differences in the properties of the polymer matrix and CNTs, and the regions connecting the transition interact chemically or physically to form interfaces with different properties, and the interface state of CNTs and the matrix has a correlation with the friction properties.

Modification of CNTs

As described above, the interaction between CNTs and polymer matrix is an important factor in the tribological properties of CNTs/polymer composites. Therefore, it can be seen that the modification of CNT has a great influence on the friction properties of the composites. Nowadays, the commonly used modification methods of CNT are covalent bond modification and non-covalent bond modification (Bhattacharyya et al., 2004; Lou et al., 2004; Bahun et al., 2006; Xu et al., 2007; Yan et al., 2011; Zhang et al., 2012; Amirkhani et al., 2020; Atif et al., 2020; Kim et al., 2021). Bhanu et al. explored the changes in the frictional properties of MWCNTs by different functionalizations of MWCNTs, which were prepared into composites with polyformaldehyde (POM), respectively, and found that the WR and COF of 0.5% wt. silylated MWCNTs/POM composites were reduced the most, compared with pure POM, followed by aminated, carbonylated, acid-treated and finally pure MWCNT, which can be attributed to the better dispersion of silylated MWCNTs and stronger interfacial bonding between silylated MWCNTs and POM matrix. However, the excessive modification can greatly destroy the graphite structure of CNTs, leading to the significantly decrease of the intrinsic mechanical properties of CNTs. Therefore, the modified method and the degree of modification needed to be optimized (Goriparthi et al., 2019).

Loading of CNTs

In addition to the type and modification of CNT, the CNT content in the composites also affects the frictional properties of the polymers. Chopra et al. prepared MWCNT/butylene polyterephthalate (PBT) composites with low filler content and investigated their frictional properties using melt compounding method (Chopra et al., 2017). The results showed that the COF of the composites decreased with the increase of carbon nanotube content and the effect of load was not significant. As the carbon nanotube content increased, the wear of the composites was the first to decrease and then to increase. As a matter of fact, the loading of CNTs often relates the dispersion of CNTs in polymer matrix. Severe agglomerates usually observed in the high loading of CNTs/polymer composites fabricated by traditional dispersion technologies, which cause the inefficient improvement of CNTs in the tribological properties of polymer composites. However, Han et al. made a buckypaper (BP) of MWCNT, into EP to improve the frictional properties of BP/EP composites, while solving the dispersion problem of MWCNT with high loading (about 40% wt.). Under the given experimental conditions, BP/EP composites have a lower COF and wear than pure EP. In the case of ozone-modified BP/EP, it has better frictional properties up to four times that of pure EP (Han et al., 2015). Therefore, the method such as pre-building buckypaper may provide a viable way to fabricate the high loading of CNTs/polymer composites with the homogeneous dispersion, which may have unexpected tribological properties.

Comparing with the other fillers, such as PTFE, graphite, UHMWPE, carbon fiber etc., CNTs exhibit some unique features, i) CNTs not only show the self-lubricating effect (low COF), but also strengthen the polymer, indicating the CNTs/polymer composites have low COF and mass loss, and these excellent overall

performances make CNTs/polymer composites are more adaptable for mechanical parts (Golchin et al., 2016; Sakka et al., 2017; Chen et al., 2018). ii) CNTs also are other fillers for fabricating functional polymer composites, for example, the network of CNTs can act as the electrical conductive paths and mass transfer barrier for improving the electrical conductivity, electromagnetic shielding, fire retardance and water-resistance of polymer composites (Kashiwagi et al., 2005; Spitalsky et al., 2010; Xia et al., 2022).

Discussion

According to literature, the incorporation of CNTs can significantly improve the tribological properties of polymer, and the improvement mechanism was researched systematically. However, some problems of the application of CNTs in polymer are still needed to be further clarified. 1) The improvement mechanism of CNTs in the tribological properties of polymer is still not entirely clear, especially in the more complex scenario in terms of wear mechanism and wear-debris formation. The tribological behavior of CNTs/polymer composites is influenced by many factors, and it is difficult to evaluate these factors. Therefore, how to quantify analysis the influences of the factor may help to comprehend the improvement mechanism. 2) The dispersion, appropriate modification and high loading of CNTs are often difficult to achieve. Because of the strong interaction between the nanotubes, CNTs are difficult to achieve the prospective dispersion and the high loadings, leading to the low efficiency of improvements of CNTs in polymer.

Overall, the field of high wear resistant CNTs/polymer composites is still in its infancy. The future development trend of high wear resistant CNTs/polymer composites should focus on refining the theory, optimizing the preparation process (the dispersion and modification of CNTs methods) and achieving the higher loading. Furthermore, the high wear resistant CNTs/polymer composites are rarely in practical applications at present, which means and they have great practical value and broad development prospects.

Conclusion

In order to meet the current manufacturing, the requirements for wear resistance of polymers are increasing, and the design of composite materials with low COF and low WR is of practical importance for energy saving and safety. Filler modification has been the mainstream method to improve the wear resistance of polymers. Since the introduction of CNT, it has been widely used in the research of improving the wear resistance of polymers because of its unique physical properties and advantages. Nowadays, people have gradually overcome the difficulties in the application of CNT and understand its wear resistance mechanism. In the future, starting from the physical and chemical structure of the polymer itself, it will be an important research direction for polymer-based composites to establish the linkage and mechanism between the maintenance of mechanical strength and tribological applications during the service of CNT/polymer, and to provide scientific data and theoretical guidance for the long-term application of polymer lubricant materials.

Author contributions

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

Funding

This research was financially supported by the Open Project Program of Fujian Key Laboratory of Novel Functional Textile Fibers and Materials, Minjiang University, China (No. FKL7FM 2010), National Natural Science Foundation of China (52103356), Fujian Provincial Department of Science and Technology (2020H0045, 2020J01770) and the Bureau of Science and Technology of Quanzhou (2021C009R, 2020C060).

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