Tribology of Self-Lubricating Polymer Nanocomposites

5

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Contents

Abstract

In the last few years, polymeric materials filled with different kinds of nanomaterials have attracted particular attention as useful alternatives in structural components subjected to severe friction and wear loading conditions. The intention of this chapter is to give a comprehensive picture of these nanofillers and to

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show their ability to improve friction and wear behavior of polymer composites. The aim is to organize the current state-of-the-art knowledge on these nanomaterials and point out on the key mechanisms governing their reinforcing effects. Despite the existing differences between literature results, there is a general agreement on the crucial role played by size, shape, concentration, and distribution of these fillers within the polymer matrix. The compatibility/interaction between filler and matrix is another important aspect in determining good filler dispersion and effective load transfer between the phases. As a consequence, the development of polymer nanocomposites showing high tribological features requires a deep selection of the nanofiller type and dimension along with its possible surface modification. Fortunately, modern technologies allow the design and the preparation of complex hybrid nanostructures able to put together the benefit of several structural factors. Although the state of the art demonstrates the potential of these materials, further researches are, however, necessary in order to definitely reach all possible improvements attainable for future high-demanding tribological applications.

5.1 Introduction

Nanotechnology promises breakthroughs in many areas such as materials and manufacturing, nanoelectronics, medicine and healthcare, energy, biotechnology, and food [1–3]. In the area of tribology, nanotechnology is expected to have a profound impact on design, friction reduction, wear resistance, and lubrication of moving/sliding surfaces [4–6]. The use of nanomaterials can offer a number of benefits for extending the systems lifetime, preventing their chemical and/or mechanical degradation and controlling temperature and moisture transmission [7, 8]. The key characteristic of nanomaterial is its enormous surface area-to-volume ratio, which in turn is the main responsible for the surprizing physical and chemical properties showed by these materials [9, 10]. When properly controlled, these features can be used to enhance efficiency and resistance of existing materials [11, 12]. Nanoparticles are already introduced in commercial liquid and semi-liquid lubricants for obtaining advanced capabilities and functionalities [13, 14]. Improved antiwear performances, thermal and chemical stability, as well as controlled fluidity and heat transfer, are some of the declared benefits [15, 16]. In several lubricant formulations, the aptitude of nanoparticles to carry a wide variety of additives, antioxidants, anticorrosion, and antifungal agents has been reported [17, 18].

Self-lubricant polymeric materials are normally used in applications where lightness, safety, versatility, and low cost are necessary [19]. Some examples of these applications include gears, bearing cages, artificial human joint bearing surfaces, food industry, aviation, or aerospace [20, 21]. Nanometric filler addition is a simple route to obtain a fine tuning of the mechanical and thermal properties of polymeric materials [7, 22]. In fact, a huge literature on the polymer/nanoparticles composites generally termed as “nanocomposites” reports excellent performance [23–25]. The reinforcing effects of these fillers depend on their dimensions, shape, dispersion, distributions, and compatibility with the matrix [26, 24]. When all these factors are carefully controlled, materials with impressive properties are obtained [27, 28]. Among the other factors, the filler dimensions have attracted particular interest in recent years [10, 29, 30]. The growing commercial availability of materials with controlled nanometric dimensions open the possibility to develop a plethora of new polymer-based composites [20]. Nanomaterials are generally classified according to the number of dimensions outside the range from 1 to 100 nm. Accordingly, the 0D-materials are particles with all the three dimensions below 100 nm, the 1D-materials have two dimensions below 100 nm, and the 2D-materials have only one dimension in the nanometer scale. Among the 0D-materials there are carbon nanomaterials, Al_2O_3, $CaCO_3$, CuO, SiO_2, SiC, Si_3N_4, ZnO, ZrO_2, and TiO_2. Classical examples of 1D-materials are the carbon nanotubes and carbon nanofibers. 2D-materials include the wide class of the layered materials such as natural cationic clays, graphene, and molybdenum disulfide.

Despite the actual availability, up to now, only a limited number of these nanomaterials have been tested in polymeric materials for tribological applications [7]. When properly combined, these nanomaterials strengthen the polymer matrix and increase its load-bearing capacity [10, 29, 31]. Such improvements can expand the use of polymer materials to the applications where the control of the chemistry and morphology occurring within a few nanometers are a critical factor determining friction, wear, and stick-slip [4, 8, 32]. A correct choice of the filler-matrix pair is a complex task [33]. The filler size, shape, concentration, and, of course, the materials itself influence the lubrication performance of a specific system [34, 35]. Experimental results on the tribology characterization of nanoparticle-filled polymers have shown interesting but sometimes contradictory results. In some cases, filler contributes to enhanced wear resistance, while in other cases they have contributed to the properties deterioration of the composite [36]. Sometimes the same filler shows opposite trends when was reduced in size or when was chemically changed its affinity with the polymer matrix. In literature, particular attention was devoted to the effect of the nanofiller on the transfer film formation [4, 8]. Often, the presence of nanoparticles renders the transfer film more thin and tenacious [37]. Dispersion is another important factor in order to yield a good property profile. The natural tendency to agglomerate of the nanoparticles is considered to be a common problem, especially at higher filler contents. Some of the gains in wear resistance was also attributed to an increase in the thermal conductivity of the nanocomposite. High thermal conductivity facilitates the dissipation of the heat generated during friction and thus lowers the working temperature of the system [38].

In Fig. 5.1 the wear rates found in the literature for several polymer composites are reported [23]. In order to make a direct comparison between the different systems, results are normalized to that of the respective neat matrix. Obviously, better filler improvement is denoted by lower wear rate values at minimum filler additions [23]. It is quite evident from the plot that microcomposites require at least 10 wt% of loading for obtaining a reduction of 1 order of magnitude in the wear rate. Nanocomposites systems show a more complex behavior. In one case, filler

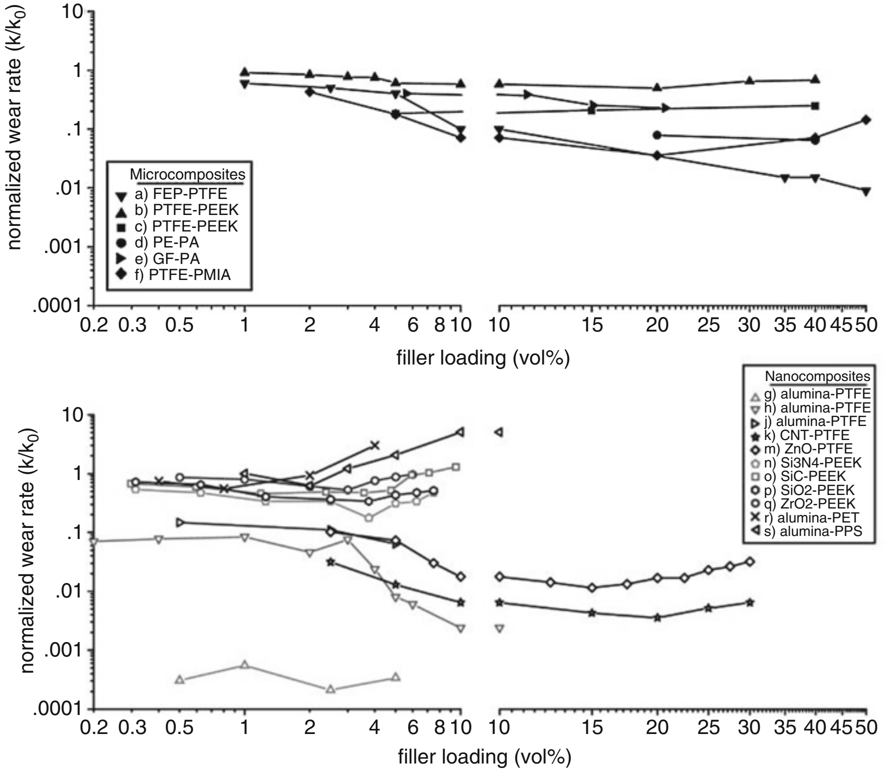


Fig. 5.1 Normalized wear rate plotted versus filler loading reported in the following references: (**a**) [39, 40]; (**b**) [41]; (**c**) [42]; (**d**) [43]; (**e**) [44]; (**f**) [45]; (**g**) [46]; (**h**) [47]; (**j**) [48]; (**k**) [49]; (**m**) [50]; (**n**) [51]; (**o**) [41]; (**p**) [52]; (**q**) [51]; (**r**) [53]; (**s**) [34]. (Reproduced from [23])

concentrations lower than 1 wt% is sufficient for obtaining reductions greater than 1000 times. Evidently, nanofillers have the potential to impart new and outstanding properties to the materials for tribological applications. However, there are several aspects of these systems that must be analyzed before to obtain a complete control of their improving mechanisms [8].

This chapter presents an overview of the principal nanometric fillers actually under investigations. They were grouped into filler dimensions and are analyzed with emphasis to their tribological behavior.

5.2 0-D Fillers

The well-known metallic, ceramic, or polymeric "nanoparticles" represent the broad class of zero dimensional fillers [54]. They can be hard or soft, composed of single or multichemical elements, and exhibit various shapes and forms [55]. Up to now, several types of such nanoparticles have been incorporated into polymer matrices to improve their wear performances. In general was found that they became effective in change the matrix wear properties at very low concentrations. It generally means that the resulting composite can be improved while retaining other properties such as density or color. Probably, the most interesting and used of these nanoparticles are those inorganic and hard. The interest in this type of nanoparticles is related to their ability to improve the mechanical modulus and the impact resistance of the polymer matrix [1].

Soft polymeric nanoparticles are also used as filler for reducing the friction [18]. Even if, in this case, the composite material becomes somewhat less tough in comparison to the pristine polymer and thus more prone to wear, a proper optimization can avoid these problems.

Current technologies allow to synthesize nanoparticles with any type of shape or dimension, either immobilized or coated onto different surface types [7, 54]. A complete and updated list of all available nanoparticles is really hard to compile [8, 18]. In the following are reported, some of the most important along with exemplary experimental results found in the literature.

5.2.1 Alluminia Oxide

Probably the alumina nanoparticles are the class of nanofiller more investigated and utilized in tribological applications [47, 56]. Lower concentrations of nanometric Al_2O_3 in polyamide produce a significant reduction in wear rates [57]. Similar results were found in polyimide nanocomposites, where reduction in friction coefficient and wear volume is observed at very low filler concentrations. In both cases, the filler addition changes the rate in transfer film formation and modifies its morphology. The wear resistance has been found to increase also in other thermoplastic materials such as poly(ethylene terephthalate) (PET) and PTFE [53]. In both cases, filler content up to 5 vol% was found to enable the deposition of thin uniform transfer films on the counterface. Higher concentrations in Al_2O_3 generally results in filler agglomeration with a resulting degradation of the transfer film. The wear rate of polyphenylene sulphide (PPS) filled with Al_2O_3 nanoparticles was studied by Schwartz and Bahadur [34]. Also in this case, the formation of the transfer film and thus the steady state wear rate resulted strongly influenced by the concentration of the filler addition. However, the coefficient of friction results almost unaffected. The reduction in wear rate was related to the increase in bond strength between the transfer film and the counterface [34].

The roughness of the counterface has a strong effect on the wear resistance of the Al_2O_3/PPS nanocomposites [58]. For the counterface with the lower roughness, the addition of Al_2O_3 nanoparticles did not have an effect on the wear rate. A morphological investigation revealed that by decreasing the roughness of the counterface the transfer film becomes nonuniform with much of the metal surface exposed. As the percentage of uncovered metal is the main responsible for the wear rate, the filler resulted less active in the case of the smoothest counterface [58].

The effect of the filler size on PTFE wear resistance was studied by Mcelwain in his master thesis [59]. α phase alumina particles with different sizes were used as filler for the PTFE matrix. In Fig. 5.2 is reported the evolution of the wear volume

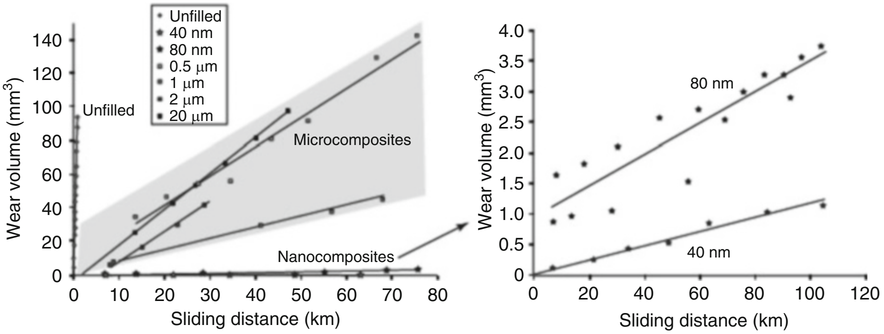


Fig. 5.2 Effect of the particle size on the wear volume of PTFE filled with 5 wt% of α phase alumina filler. (Reproduced from [59])

with the sliding increase obtained with a three-pin-on-disk tribometer (speed of 10 mm/s and contact pressure of 3.1 MPa). It is clear from the Fig. 5.2 that the wear resistance progressively increases with the reduction in the filler dimension.

The effects of Al_2O_3 nanoparticles on tribological properties of polyoxymethylene (POM) nanocomposites have been investigated under dry and oil lubricated sliding conditions [56]. Polymeric coatings containing Al_2O_3 nanoparticles showed enhanced abrasive and scratch resistance compared to that of the neat polymer [60]. The improvement was attributed to the hardening effect of Al_2O_3 nanoparticles on the polymer matrix.

For phenolic composites, an optimal Al_2O_3 filler content was found to be less than 3 wt% [61]. The detrimental effects of the agglomeration of Al_2O_3 nanoparticles in the transfer film of epoxy composites have been reported [35]. The same authors [62] report that the combination of nano- Al_2O_3 (13 nm) and micro-$CaSiO_3$ (4-15 µm) induced some kind of synergistic effect and improved both the wear resistance and the stiffness of epoxy.

In summary, the existence of an optimum filler concentration has been explained by the formation of abrasive agglomerates within the protective transfer films [63]. In all cases analyzed, the transfer film was reported to become discontinuous and poorly bonded to the counterface with increasing the filler concentration. It has been showed that the chemical grafting of the Al_2O_3 nanoparticles prevents agglomeration of the particles at the sliding interface and increase the abrasive wear resistance of the composite [35, 64].

5.2.2 Copper Nanoparticles

Copper-based particles in both micro- and nano sizes have been extensively investigated as polymer filler in tribological applications. CuO in micrometer size was added to high-density polyethylene [65, 66], polyamide [67], PEEK [68], polyphenylene sulfide (PPS) [69], and thermosetting polyester [70]. In all cases, a good enhancement in the wear resistance was obtained. Similar results were obtained by adding micrometric CuS to PTFE [71], polyamide [72], PEEK [73], and PPS [74, 75] systems. Several investigations have pointed out that the same benefits of microsize Cu-based fillers can be obtained by using the same filler in nanometric dimensions. In this case, however, the best results are obtained at extremely smaller volume fractions [76]. The addition of 1–4 vol% of CuO nanoparticles to a PPS matrix leads to a strong reduction of the wear rate in the transient stage. The improvement is maintained also in the steady state where the wear volume per unit sliding distance reduces from 0.291 mm^3/km of the unfilled PPS to 0.047mm^3/km of the sample added with 2 vol% of CuO [76]. The reduction in wear rate was attributed to the development of a more uniform and better-bonded transfer film over the counterface [76].

5.2.3 Zinc Oxide

The addition of nanometric ZnO to polyurethane (PU) coatings has proven to decrease the friction coefficient and the wear rate of these materials [77]. Results showed that the presence of ZnO nanoparticles can help the adhesion of the transfer films to the counterface. In contrast, the addition of ZnO nanoparticles to a PPS matrix strongly decreases its wear resistance during sliding against a tool steel counterface [78]. In this case, a discontinuous and poorly bonded transfer film was produced during sliding. Li et al. [50] have shown that the addition of nanometric ZnO to a PTFE matrix lead to an increase in wear resistance. Probably, the contradictory results found with ZnO nanoparticles are due to their abrasive properties. Different filler sizes, as well as changes in the test conditions, are responsible for the different tribological behavior showed by these nanocomposites.

5.2.4 Titanium Dioxide

The addition of 1–5 wt% of TiO_2 nanoparticles in the range 30–50 nm to a PPS matrix was effective in reducing the composite wear rate [78]. Similarly to that found for other nanoparticles, lower filler additions ensure the formation of a uniform transfer film on the counterface. With the increase in TiO_2 concentrations, the transfer film became thick and lumpy, and it also did not cover the counterface completely. As a result, wear rate increased considerably up to exceed that of the unfilled PPS. The effects of the particle dimensions on the wear resistance of epoxy resin have been investigated [79]. TiO_2 particle in nanometric dimensions was found more effective in wear reduction than that in the micrometer dimensions [79]. Increasing the bond between the filler and the matrix has also been shown to have positive effects on the wear resistance. Chang et al. [80] showed that the addition of 5 vol% TiO_2 nanoparticles to poly(etherimide) (PEI) containing short carbon fibers and graphite flakes increased the wear resistance of the composite.

Also in the case of polyamide 66 (PA66) containing short carbon fibers and graphite flakes, the addition of TiO_2 nanoparticles produces a strong increase in the wear resistance [81, 82]. Similar synergisms were found with epoxy matrix filled with short carbon fibers, graphite flakes, and TiO_2 nanoparticles [79, 83].

5.2.5 Silica Nanoparticles

The use of SiO_2 nanoparticles as fillers in polymer matrices has shown mixed results on wear. The tribological characterization of PEEK filled with SiO_2 nanoparticles has shown a positive effect of this filler on the wear rate and friction coefficient of the composite [52]. Opposite effects were found for a poly(phthalazine ether sulfone ketone) (PPESK) matrix [84]. In that case, both micro- and nano SiO_2 particles induce a significant abrasive wear loss. For an epoxy matrix, SiO_2 nanoparticles were shown to increase the wear resistance with the increase of bond strength between the particles and the matrix [85]. Polycarbonate (PC) filled with nanometric SiO_2 showed high hardness and stiffness with respect to the polymer matrix [86]. Smaller scratch depth and lower frictional coefficient were found by tests carried out on the PC/SiO_2 nanocomposites. The wear mechanism of polyamide-1010 (PA-1010) filled with nanometric SiO_2 showed lower friction and better wear resistance with respect to the pure PA-1010 [87].

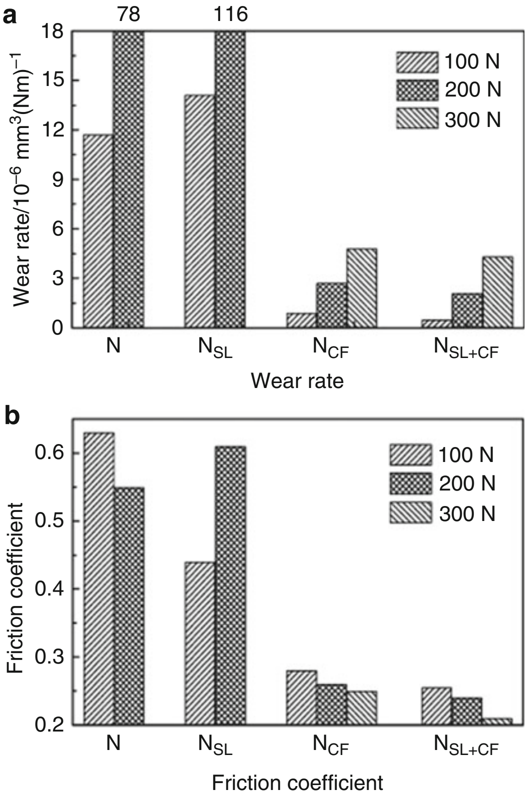
Also for the nanometric SiO_2, filler dimensions, as well as particles agglomeration, are the key factors for the nanocomposites improvement.

5.2.6 Carbon Nanomaterials

Carbon nanomaterials (CN) such as carbon black, fullerenes, and its derivate have been investigated as fillers for tribological applications. They have high surface area, are chemically and thermally stable, have relatively low cost, and generally are environmentally friendly. Melt compounding is generally sufficient to achieve a good distribution of carbon nanomaterials in the bulk of thermoplastics polymers [88–91]. However, the dispersion of these nanomaterials can be optimized by applying combined processes, such as chemical and mechanical pretreatments of the polymer and nanofiller [7, 92–94]. The addition of CN to a PTFE matrix results in a both compressive strength and hardness increase [95, 96]. The wear rate was found to decrease up to 150 times for PTFE containing 2 wt% of carbon nanomaterials [96]. Small quantities (<1 wt%) of C_{60} fullerene added to a natural rubber caused great variations in the friction coefficient [97]. Different types of fluorocopolymers added with 10–15 wt% of carbon nanomaterials increased resistance to abrasive surfaces.

Figure 5.3 shows the wear rate and the friction coefficient of nylon 1010 and its composites filled with MoS_2 (SL) microparticles and chopped carbon fiber

Fig. 5.3 Wear rate and Friction coefficient of Nylon 1010 and its composites filled with MoS_2 (SL) microparticles and chopped carbon fiber under various loads in dry sliding friction. (Reproduced from [98])



(CF) under various loads in dry sliding friction [98]. Unfilled nylon sample showed excessive wear probably due to the melting process taking place during the frictional process. Similar results were found by adding 10 wt% of MoS_2 microparticles. On the opposite, by adding 10 wt% of chopped carbon fiber, the wear rate was approximately reduced by a factor of 10. More interesting, the reduction in wear was greater when chopped carbon fiber and MoS_2 microparticles were combined. The authors found that the combination of the two fillers helps the formation of thin, uniform, and continuous transfer film [98].

The wear behavior of epoxy matrices in the presence of glass fibers and graphite was investigated by Suresha et al. [99]. The authors reported a pronounced reduction in wear rate as well as in frictional coefficient. A similar behavior was found for composites of PEI, carbon fibers, and graphite [80]. The incorporation of graphite particles (GPs) significantly reduces friction of polymer composites [100, 101]. It was proposed that the nanoparticles removed from the matrix debris act as third body elements in the contact region. Thus, they can reduce the shear stress in the contact region and accordingly enhance the matrix damage [102].

5.2.7 Other Nanoparticles

Schwartz and Bahadur [75] identified two opposite behaviors in polymeric composites filled with inorganic fillers. They found that AgS and CuS fillers contribute to increasing the wear resistance of a PPS matrix, whereas the same addition of ZnF_2 and SnS particles strongly reduced wear resistance. The authors suggested that this opposite behavior is due to the different mechanical properties of the filler [75]. In particular, the AgS and CuS particles are more prone to be deformed during flow with respect to the hard and abrasive ZnF_2 and SnS particles. Similar conclusions were reached using copper particles added to polyoxymethylene (POM) [103]. Also in this case, results have been explained by a predominantly plastic deformation mechanism of Cu particles [103]. However, the abrasive properties are strongly depended by the particle size used [15, 34, 53, 104, 105]. Wang et al. [51] investigated the influence of several ZrO_2 nanoparticles, varying from 10 to 100 nm, in reducing the wear of a PEEK matrix. Effective reduction of the wear rate was monitored only when the particles were less than 15 nm in size. Xing and Li [106] evaluated the wear properties of an epoxy matrix filled with spherical particle varying from 120 to 510 nm. They also found that the smaller the particles used as fillers, the better was the wear resistance of the composites.

Si_3N_4 and SiC nanoparticles grafted with polyacrylamide (PAAM) were used as filler for epoxy matrix [105]. Experimental results show that the compatibilization of the filler contributes to increased wear resistance of the epoxy composite. Inorganic nanoparticles such as $CaCO_3$ were added to several self-lubricating composites containing glass fibers with the aim to improve the adhesion between the reinforcing fibers and the matrix [107]. The resulting materials were able to operate under more severe sliding conditions than the composites with nanoparticles alone.

5.3 1-D Fillers

Filler with one dimension outside the nanometric range includes nanotubes, nanorods, nanofibers, and nanowires. They can be metallic, ceramic, or polymeric and can be amorphous or crystalline. The addition of these fillers to a polymer matrix has shown interesting results in terms of load-bearing capacity and toughness. These fillers can promote the formation of a tenacious and thin transfer film on the counterface and reduce the wear of the composites.

5.3.1 Carbon Nanotubes

Carbon nanotubes (CNT) are excellent filler for reinforcing polymers. They are exceptionally stiff and strong with a Young's modulus in the order of TPa and a tensile strength 100 times stronger than that of steel [29, 108]. Also, the nanometer size ensures extremely large interface and potentially excellent bonding [109, 110]. CNT-based nanocomposites are expected to have excellent tribological properties [111, 112]. For that reason, several investigations have focused on the friction properties of thermoplastic and thermosetting composites filled with carbon nanotubes [113–115]. Results show that the experimental factors that are the main responsible for the tribological behavior of the CNT-nanocomposites are [116–118]:

(a) The preparation and purification method of the nanotubes
(b) The dispersion method
(c) The filler concentration in the nanocomposites
(d) Compatibilization with the polymer matrix

The effect of the addition of CNT on the wear life and load-bearing capacity of common polymers in tribological applications, such as polyethylene (HDPE and UHMWPE), has been analyzed by several authors [119–122]. The wear resistance of the composites is generally improved by the addition of low CNT concentrations [123]. It was explained by the reinforcement effect of CNT. However, CNTs are not easily dispersed in the polymer matrix and, especially at high concentrations (>5%), they tend to form large agglomerates. For this reason, poor mechanical and tribological properties are sometimes observed [119]. Low friction coefficient was obtained for nanocomposite reinforced with amino-functionalized CNT [124]. The conclusion was that a uniform distribution of CNTs in the matrix is a prerequisite for lowering friction.

A decrease in the wear rates of PTFE sliding over steel can be achieved by adding CNTs [49, 125]. The friction coefficient was observed to increase for the same CNT concentration [49]. The effect of the CNT on the friction coefficient on different polyamides (PA) was analyzed under dry and lubricated wear conditions [126–128]. In these cases, CNTs were able to reduce both the friction coefficients and the wear rates. The decrease in friction coefficients is ascribed to the improved strength properties of the polymer along with the lubricating action of CNT [49]. CNTs were also able to increase the wear resistance of epoxy resin [117, 129] and high resistant composites such as PEEK reinforced with carbon fibre [130]. In this case, the favorable effect of CNT was explained by the enhanced resistance of the matrix to the shear stresses [131].

5.3.2 Carbon Nanofibers

Carbon nanofibers (CNFs) are morphologically differentiated from carbon nanotubes by the orientation of the graphene planes [132]. They can be imagined as stacked graphitic discs, truncated cones, or planar layers along the filament length. These nanostructures have an outer diameter in the range 50–100 nm. However, commercial CNF fibers are slightly larger (100–200 nm) in diameters. This particular micrometric structure confers to the carbon nanofibers a semi-conducting behavior [133]. These fillers also have chemically active end planes on both the inner and outer surfaces [134]. CNFs are particularly suitable as reinforcing fillers in polymeric composites [135] and as an additive in carbon fiber reinforced plastics

[136, 137]. The addition of CNFs to a PEEK matrix strongly reduces unlubricated wear over alloy steel [138]. They result effective also when were added to a ternary composite such as PEEK reinforced with ordinary carbon fibers or PTFE. It was suggested that CNFs reduce to small graphitic debris particles during shear stress. These nanoparticles can anchor to the counterface and reduce its roughness [139, 140]. In addition, CNFs are able to reinforce the transfer film [107].

5.4 2-D Fillers

Two-dimensional nanomaterials such as clay, graphene, metal chalcogenides, and transition metal oxides are a broad range of materials that cover a variety of different properties. They have a layered structure with weak van der Waals interactions between them. Typically, the single layers of these materials are few nanometers thick with extraordinary electronic, magnetic, and thermal properties. The use of 2D nanomaterials for controlling friction and wear has received increased attention over the past few years [141, 142].

5.4.1 Clays

The most common clay materials are that identified as 2:1 phyllosilicates (montmorillonite, saponite). They are diffuse in nature as micron-size multilayered tactoids [143]. The individual layers having thicknesses of about 1 nm and surface lengths on the order of 100–1000 nm [144]. The layered structure of silicate makes it possess good solid lubrication [145]. Exfoliation and dispersion of natural clay in the polymer matrix are the necessary prerequisite for the nanocomposite formation [146, 147]. Several modification procedures were developed for expands the spacing between the individual clay layers and improves their compatibility with polymers [148, 149]. The effectiveness of these methods is found strongly dependent on the processing conditions as well as the polymer characteristics [26, 94, 150]. The clay sheets act like impermeable obstacles for gases or vapor diffusing through the matrix [30]. Good dispersion and surface interaction between filler and polymer are necessary for the mechanical and barrier improvements [24, 31, 144]. Dispersion is also responsible for the increase in wear resistance of several polymer nanocomposites [151, 152]. Yuan et al. [153] studied the scratch resistance of a polypropylene (PP) reinforced with an organo-modified montmorillonites. Figure 5.4 shows the surface deformation morphology of neat PP and PP modified with 4 wt% of nanoclay under identical scratch test conditions. Both samples showed periodic multiple ripple-type deformation tracks. However, nanoclay reinforcement decreases the susceptibility of the system to micro- and nanoscale deformation. It was attributed to the increased in modulus and yield strength of the composite [153].

Polyamide 6 (PA6) modified with neat or organically modified clay show different behaviors. Increased wear resistance was observed only for nanocomposites containing organically modified clays [151]. The authors suggest that the increase

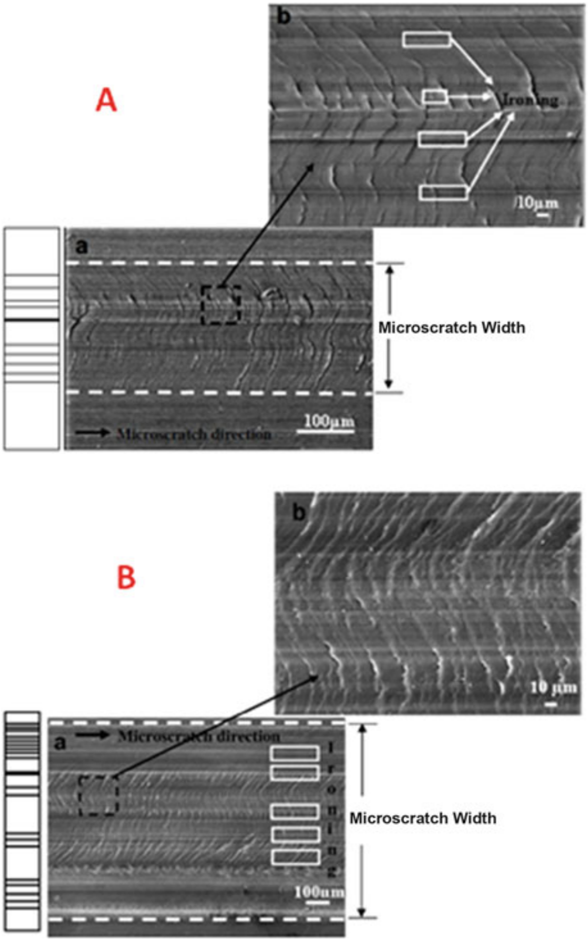


Fig. 5.4 Surface deformation morphology of microscratches: (**a**) Pure PP and (**b**) PP-4 wt% clay nanocomposite. (Reproduced from [153])

is achieved only if a good dispersion of the clay platelets in the polymer matrix is combined with a high level of compatibility between the clay and the polymer matrix. Similar results were found for PA nanocomposites systems filler with different types of organically modified clays [154, 155]. The addition of these nanomaterials also affects tribo-chemical processes taking place in friction contact zone. The dispersion of clay particles in a PI matrix was found to inhibit the degradation of macromolecules. As a result, wear resistance of the PI nanocomposite is enhanced. However, at higher clay concentrations the formation of large clay aggregates was observed on the counterface [92]. This was associated with high wear degradation rate. Nanoclay fillers were reported to increase the wear resistance of many thermoplastic polymers such as polycarbonate, polyester, polyamide, and polyvinylidenefluoride (PVDF) [156]. Tribological tests indicate that the addition of organo-modified montmorillonite enhanced wear resistance, antifriction property, and better fabric integrity of self-lubricating liners [157].

5.4.2 Graphene

Graphene sheets formally are two-dimensional layers of sp2-bonded carbon. The one-atom thick structure is expected to have a range of unusual properties [158]. High-quality graphene can be synthesized by chemical-vapor deposition [159]. It has been used in transparent conductors, flexible electronics, field-effect transistors, fuel cells, batteries, solar cells, biomaterials, biosensors, and water purifiers [160–162].

Graphene has been proposed as an alternative to conventional filler in the fields of transportation and electronics. Unfortunately, its cost and the difficulty to obtain as free single layers have limited its applications. Two derivates of graphene materials, namely, graphene oxide (GO) and reduced GO (rGO), have been proposed as substitutes [163, 164]. They are formally derived from low-cost graphite by chemical oxidation or electrochemical exfoliation and can be easily dispersed into polymeric materials [165–167]. The unique physical, mechanical, and chemical properties of graphene-like make it an attractive candidate for many tribological applications [168, 169].

Graphene oxide has been added to UHMWPE and characterized with a microhardness tester and high speed reciprocating tribometer [170]. Results show that the wear resistance and hardness of the composites are improved significantly, while the coefficient of friction increases rapidly. GO/polyimide (PI) nanocomposites were prepared by in situ polymerization techniques. The GO/PI exhibited better mechanical and thermal properties. Also the wear resistance of PI was found to increase [171]. Pan et al. [172] analyzed the tribological performance of graphene modified PI coatings. They found a sensible increase in the wear resistance of the coating. Better performances were found by increasing the interaction between the graphene filler and polyimide matrix [173]. PI/GO nanocomposites have demonstrated good tribological properties also under seawater-lubricated conditions [171]. Song et al. [174] prepared Cu nanoparticles decorated on polydopamine (PDA) functionalized graphene oxide (GO) nanosheets. Tests with sliding steel surfaces showed that the soybean oil with 0.1 wt% Cu/PDA/GO nanocomposites had the lowest friction coefficient under all of the sliding conditions. Kalin M et al. [175] investigated the effect of solid lubricant nanoparticles on poly-ether-ether-ketone (PEEK) composites. In the PEEK matrix, different types of nanoparticles were added, like graphene, WS_2 needle-like, WS_2 fullerene-like, and CNT. The results obtained under dry sliding conditions show that the morphology of the nanoparticles has an important effect on the friction coefficient and the wear behavior [175].

5.4.3 Molybdenum Disulfide

Molybdenum disulfide (MoS_2) is a naturally mined inorganic material that occurs as the mineral Molybdenite. Molybdenum disulfide has many unique properties, which makes it one of the most popular solid lubricants on the market [176, 177]. Similar to graphite, these materials possess layered structures that can be exfoliated into small thicknesses containing mono- or multilayers [178, 179]. Among the 2D materials, molybdenum compounds are probably the most interesting for tribological applications. In particular, the interest for the molybdenum disulfide (MoS_2) in nanometric dimensions has increased exponentially due to their impressive chemical and physical properties [180, 181]. Nanometric MoS_2 have shown better lubrication performance than bulk MoS_2 [98]. Thus, considerable attention has been given to the preparation of MoS_2-based nanocomposites. Even if the MoS_2 can be easily dispersed and exfoliated in polymers [182–188], its tendency to re-organize in large agglomerate is still a big problem. Several synthetic routes were suggested to obtain 2D crystals of MoS_2 on a stable nanometric scale [189, 190]. Intercalation-exfoliation methods in common liquid solvents [191] and micromechanical exfoliation of natural molybdenite crystals were also proposed [192]. A simple and versatile method for the production of 2D nanosheet crystals of MoS_2 was proposed [5, 193, 194]. The nanosheets covered by a protective oleylamine coating were successfully tested as additives for high-performance liquid and solid lubricants [5]. Moreover, hybrid organic-inorganic oleylamine@MoS_2-CNT nanocomposites were obtained and successfully tested as nanoadditive for grease lubricant [195].

The introduction of MoS_2@oleylamine into a Polystyrene matrix was found to reduce its mechanical properties [196, 197]. A noticeable reduction of both the glass transition temperature and the elastic modulus was observed. The friction coefficient, as well as the wear resistance of PS nanocomposites, was found to decrease [196, 197].

Several polymeric matrices were proposed as a matrix for MoS_2 nanocomposites. They include polyoxymethylene (POM) [198, 199] and high-density polyethylene (HDPE) [200].

MoS_2 as micro- and nano-platelet and sphere were added to POM and HDPE matrices [200, 201]. Results show that the two structures exhibited a similar performance in friction reduction under dry friction. However, in the case of HDPE matrix, the nano-platelet MoS_2 showed lower friction coefficients than both microplatelets and nano-spheres. Chemical intercalation of MoS_2 can help its dispersion during the mechanical mixing [202]. However, the chemical intercalation can destroy the crystal structure of MoS_2 and negatively affect its lubrication performance [199].

Xin et al. [203] prepared a self-lubricating and antiwear polyimide composites by adding different percentages of graphene oxide/nano-MoS_2 hybrid. Figure 5.5a shows the friction coefficient of the various composites analyzed in the paper. The hybrid addition was found to reduce the friction coefficient. However, a fluctuation phenomenon appears in the curves when the filler concentration became higher than 0.5 wt%. The authors suggested [203] that at high concentrations the self-lubricating effect receded, due to the stacking of the nano-hybrid sheets. The effect of various additives on the friction coefficient is shown in Fig. 5.5b. A combination of the protective effect of graphene sheets, rolling friction effect of the detached nano-MoS_2 particles, and a transfer film composed of MoS_2 were proposed as a synergic mechanism for the enhancement of the tribological properties.

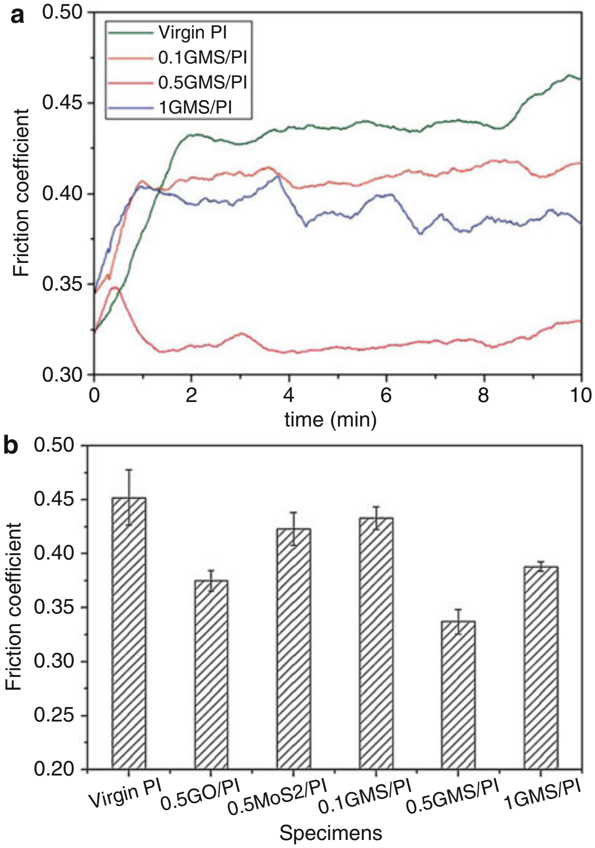


Fig. 5.5 (**a**) Friction coefficients of neat polyimide (PI), 0.1 wt% of graphene oxide/nano-MoS_2 in PI matrix (0.1GMS/PI), 0.5 wt% of graphene oxide/nano-MoS_2 in PI matrix (0.5GMS/PI), and 1 wt% of graphene oxide/nano-MoS_2 in PI matrix (1GMS/PI) specimens as a function of sliding time. (**b**) Friction coefficients of virgin PI, 0.5 wt% of graphene oxide in PI matrix (0.5GO/PI), 0.5 wt% of MoS_2 in PI matrix (0.5MoS_2/PI), 0.1 wt% of graphene oxide/nano-MoS_2 in PI matrix (0.1GMS/PI), 0.5 wt % of graphene oxide/nano-MoS_2 in PI matrix (0.5GMS/PI), and 1 wt% of graphene oxide/nano-MoS_2 in PI matrix (1GMS/PI) specimens. (Reproduced from [203])

5.5 Trends and Perspectives

The trend in the area of polymers composites for tribological applications is quickly moving towards multifunctional materials and coatings. Materials that can sustain high pressure and velocity with low wear rate are needed for the incoming high-tech applications. Nanomaterials offer new and intriguing possibility to design and develop innovative materials with these advanced properties. They will positively affect the quality, safety, and security of the polymer composites. The main advantage of these materials over traditional fillers is in its ability to improve mechanical, electrical and chemical properties at very low concentrations. As a matter, several examples of nanotechnology-based composites materials are already present on the market. The actual limitation to the definitive diffusion of these materials is the lack of information about their tribology performance. In fact, the tribological research on these systems is still at a relatively early stage. Additional experimental results and innovative research works are thus necessary. New chemical and physical approach are necessary for improving the compatibility of the nanofillers with the matrix. Attention must be devoted to the development of new methods for achieving controlled in situ structuring of particles in three-dimensional structure. Researchers are called to further improve the performances of these materials and expand their use in newer tribological applications.

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