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Abrasion Resistance of Polymer Nanocomposites – A Review

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1. Introduction

In order to be suitable for tribological applications, polymeric materials, which can usually exhibit mechanical strength, lightness, ease of processing, versatility and low cost, together with acceptable thermal and environmental resistances, have to show good abrasion and wear resistance. This target is not easy to achieve, since the viscoelasticity of polymeric materials makes the analysis of the tribological features and the processes involved in such phenomena quite complicated.

Indeed, it is well-known that an improvement of the mechanical properties can be effectively achieved by including "small" inorganic particles in the polymer matrices (Dasari et al., 2009).

For applications taking place in hard working conditions, such as slide bearings, the development of composite materials, which possess a high stiffness, toughness and wear resistance, becomes crucial. On the one hand, the extent of the reinforcing effect depends on the properties of composite components, and on the other hand it is strongly affected by the microstructure represented by the filler size, shape, homogeneity of distribution/dispersion of the particles within the polymer, and filler/matrix interface extension. This latter plays a critical role, since the composite material derives from a combination of properties, which cannot be achieved by either the components alone.

Thus it is generally expected that the characteristics of a polymer, added of a certain volume fraction of particles having a certain specific surface area, are more strongly influenced when very small particles (*nanofillers*), promoting an increased interface within the bulk polymer, are used (Bahadur, 2000; Chen et al., 2003; Karger-Kocsis & Zhang, 2005; Li et al., 2001; Sawyer et al., 2003). However, this happens only when a high dispersion efficiency of the nanoparticles within the polymer matrix is assessed: indeed, nanoparticles usually tend to agglomerate because of their high specific surface area, due the adhesive interactions derived from the surface energy of the material. In particular, the smaller the size of the nanoparticles, the more difficult the breaking down of such agglomerates appears, so that their homogeneous distribution within the polymer matrix is compromised.

As a consequence, the development of nanocomposites showing high tribological features requires a deep investigation on their micro-to-nanostructure, aiming to find synergistic mechanisms and reinforcement effects exerted by the nanofillers (Burris et al., 2007).

In addition, the way in which nanofillers can improve the tribological properties of polymers depends on the requirement profile of the particular application, i.e. the friction coefficient and the wear resistance cannot be considered as real material properties, since they depend on the systems in which these materials have to function.

In particular, such applications as brake pads or clutches usually require a high friction coefficient and, at the same time, a low wear resistance; however, in other circumstances (like in the case of gears or bearings, acting as smooth metallic counterparts under dry sliding conditions) the development of polymer composites having low friction and wear properties is strongly needed.

The abrasion performances of polymeric materials depend on several factors, such as the wear mechanisms involved, the abrasive test method used, the bulk and surface properties of the tested specimens, ...

Many papers reported in the literature focus on the investigation on the physical processes involved in abrasive wear of a wide variety of polymers; the obtained results demonstrate that two very different mechanisms of wear may occur in polymers, namely cohesive and interfacial wear processes, as schematically shown in Figure 1.
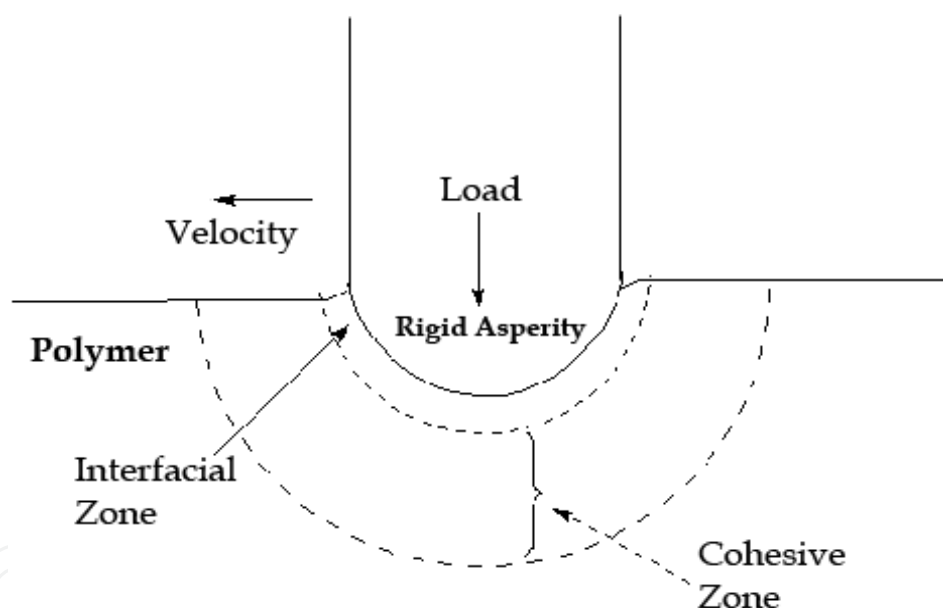

Fig. 1. Schematic representation of cohesive and interfacial wear processes (Adapted from Briscoe & Sinha, 2002)

In the cohesive wear processes, such as abrasion wear, fatigue wear and fretting, which mainly depend on the mechanical properties of the interacting materials, the frictional work involves quite large volumes close to the interface, either exploiting the interaction of surface forces and the consequent traction stresses or through the geometric interlocking exerted by the interpenetrating contacts. Contact stresses and contact geometry represent two key parameters that determine the extent of such surface zone.

On the other hand, the frictional work in interfacial wear processes (like transfer wear, chemical or corrosive wear) is dissipated in much thinner zones and at greater energy

density with respect to cohesive wear processes, so that a significant increase in local temperature occurs. Furthermore, the extent of wear damage can be substantially ascribed to the chemistry of the surfaces involved, rather than to the mechanical properties of the interacting materials.

As far as cohesive processes are concerned, *abrasion wear*, which is the most common type of wear encountered in polymer composites, can be divided into two-body and three-body abrasion wear. The former occurs in the presence of hard asperities that plough and induce plastic deformation or fracture of the softer asperities.

The latter relates to the presence of hard abrasive particles or wear debris in between the sliding bodies: such particles or debris derive from environmental contaminants or can be the consequence of two-body abrasion processes. In general abrasion wear depends on several factors, such as the hardness of the materials in contact, the applied load and sliding distance and the geometry of the abrasive particles as well.

Fatigue wear derives from surface fatigue phenomena, i.e. from the repeated stressing and un-stressing of the contacts, and can lead to fracture through the accumulation of irreversible changes, which determine the generation, growth and propagation of cracks. This kind of wear may also occur together with *delamination wear*, where shear deformations of the softer surface, caused by traction of the harder asperities, promote the nucleation and coalescence of subsurface cracks. As a consequence, the delamination (i.e. detachment) of fragments having larger size occurs.

Fretting wear is caused by relative oscillatory motions of small amplitude taking place between two surfaces in contact. The produced wear fragments can either escape from between the surfaces, thus promoting a fit loss between the surfaces and a decrease of clamping pressure, which may lead to higher vibration effects, or remain within the sliding surfaces, so that pressure increases and seizure eventually occurs.

Transfer wear belongs to interfacial wear processes and involves the formation of a transfer film (solid or liquid, depending on the interfacial temperature) in polymer-metal, polymer-ceramic, polymer-polymer sliding contacts. Such film invariably transfers from polymer to metal or ceramic, whereas the direction of transfer is not obvious in the case of polymer-polymer sliding contacts.

Several parameters can influence the formation of the transfer film and its role on the subsequent wear processes: thickness and stability of the film, cohesion features between the transfer layers, adhesion forces between the film and the sliding counterpart, chemical reactivity and surface roughness of the counterface slider, polymer structure (crystallinity, flexibility, presence of pendant groups or side chains, …), adopted sliding conditions (temperature, normal load, velocity, atmosphere, …) and presence of fillers.

Chemical wear involves a chemical reaction (oxidation, degradation, hydrolysis, …, which lead to polymer chain scission with the subsequent MW decrease) in between the sliding bodies or a material in itself or a material with the surrounding environment.

A schematic representation of the basic tribological interactions leading to wear particle generation is depicted in Figure 2.
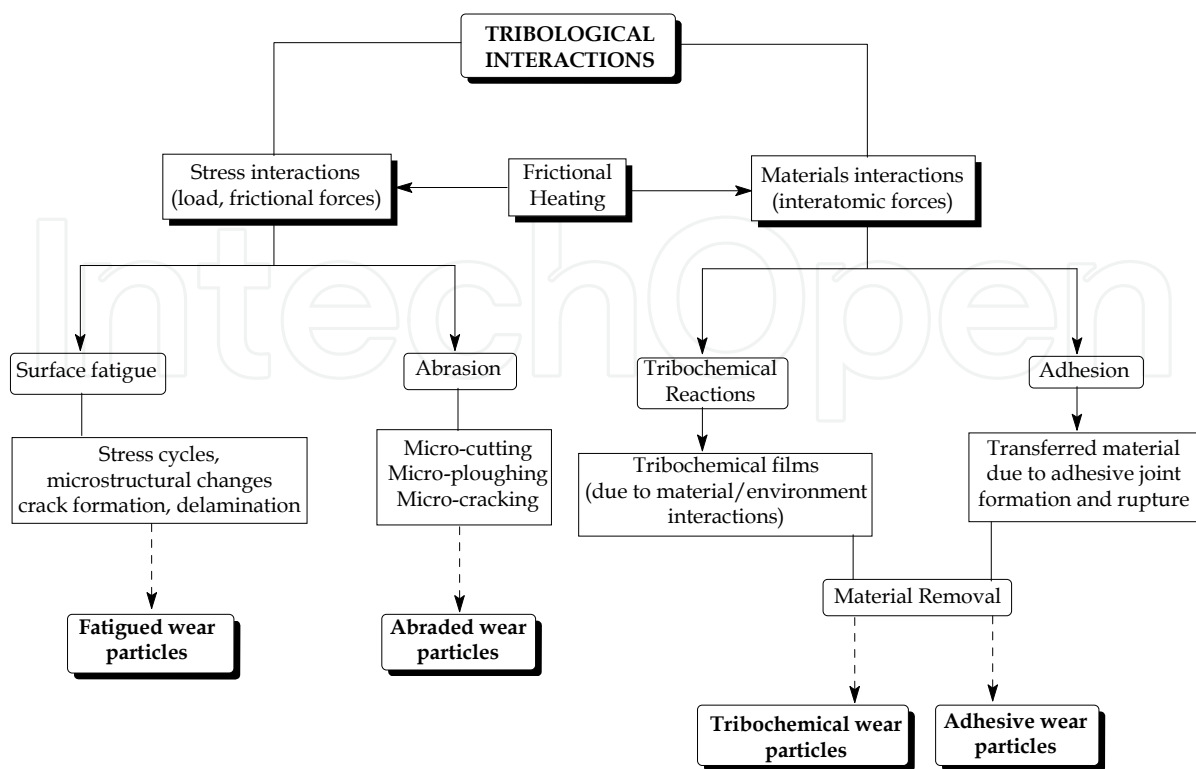
Fig. 2. Different wear processes leading to the formation of material particles (adapted from Czichos, 2001)

It is worthy to note that the wear mechanisms in polymer systems described above for macro- and micro-levels are quite different from those encountered at nano-level.

First of all, nano-level involves very low applied loads (from μN to nN); in addition, the wear particle generation is negligible and the original surface topography is more likely to be preserved for an extended period because of the adopted low wear rate.

Other differences concern the friction forces involved at the nano-level, since the ploughing factor and the inertial effect of the moving components are different, as well as the role exerted by surface forces (adhesion and electrostatic interactions), which become very important.

In the following paragraphs, a review on the recent studies on the tribological behavior of thermoplastic nanocomposites is presented. The role of the structure of the nanofillers and of their morphology (aspect ratio, effectiveness of dispersion within the polymer, …) and the possible interactions with the environment are widely discussed.

2. Tribology of thermoplastic nanocomposites

2.1 PEEK-based nanocomposites

Poly(ether ether ketone) (PEEK) is a high performance injection mouldable thermoplastic that can be widely used for many applications that require high mechanical strength and an outstanding thermo-mechanical stability.

This polymer has a high glass transition temperature (Tg≈143°C) and a high melting point (Tg≈343°C) and it is also regarded as one of the most promising polymer materials for tribological applications in aqueous environments.

Nevertheless, it seems that neat PEEK exhibits relatively poor wear resistance with water lubrication in some cases, so that different types of fillers (and nanofillers) have been incorporated into this polymer, aiming to facilitate more applications by enhancing its anti-wear features. In particular, short carbon fibers (SCFs) are currently used in PEEK-based composites for improving its wear resistance, even at elevated temperatures and under aqueous conditions (water lubrication).

Very recently, Zhong investigated the tribological properties of PEEK/SCF/zirconia composites under aqueous conditions, using a three-pin-on-disc configuration (Zhong et al., 2011). A synergistic effect of SCFs with zirconia nanoparticles was assessed: indeed, the composites showed excellent wear resistance under aqueous conditions; SCFs were found to carry the main load between the contact surfaces and to protect the polymer matrix from further severe abrasion of the counterpart. Nano-ZrO_2 efficiently inhibited SCF failure either by reducing the stress concentration on the CF interface through reinforcement of the matrix or by lowering the shear stress between the sliding surfaces via a positive rolling effect of the nanoparticles between the material pairs.

Werner et al. investigated the influence of vapour-grown carbon nanofibres (CNFs) on the wear behaviour of PEEK (Werner et al., 2004). To this aim, unidirectional sliding tests against two different counterpart materials (100Cr6 martensitic bearing steel and X5CrNi18-10 austenitic stainless steel) were performed on injection moulded PEEK-CNF nanocomposites. CNFs were found to reduce the wear rate of PEEK very significantly, as compared to a variety of commercial PEEK grades. This behaviour was attributed to CNFs, which act as solid lubricants; in addition, the roughening effect on the counterpart exerted by CNFs, because of their small size, was minimised with respect to conventional fibre fillers (carbon fibres, PAN-based carbon fibres, glass fibres).

McCook and coworkers investigated the role of different micro and nanofillers on the tribological properties of PEEK in dry sliding tests against 440C stainless steel counterfaces (McCook et al., 2007). To this aim, microcrystalline graphite, carbon nano-onions, single-walled carbon nanotubes, C60 carbon fullerenes, microcrystalline WS_2, WS_2 fullerenes, alumina nanoparticles and PTFE nanoparticles were jet-milled with PEEK and the friction coefficients and wear rates of the obtained composites were measured in open laboratory air (45% R.H.) and in a dry nitrogen environment (less than 0.5% R.H.).

Both wear rate and friction coefficient were reduced in the dry nitrogen environment: in particular, the more wear resistant coatings also had lower friction coefficients. On the contrary, in open air environments the more wear resistant coating exhibited the higher friction coefficients. Furthermore, the polymeric nanocomposites investigated showed similar environmental responses, regardless of the type of micro or nanofillers used.

Hou and coworkers performed tribological ball-on-flat sliding wear tests on PEEK-based nanocomposites incorporating inorganic fullerene-like tungsten disulfide nanoparticles (Hou et al., 2008). The friction coefficient was found to decrease about 3 times in the presence of 2.5 wt.% nanoparticles, with respect to the neat PEEK: this behaviour was attributed to the lubricating capability of the nanofillers.

Zhang et al. investigated the effect of nano-silica particles on the tribological behaviour of PEEK: silica nanoparticles were compounded with the polymer by means of a ball milling technique (Zhang et al., 2008). The wear resistance of PEEK was significantly improved after incorporating nano-SiO$_2$ and at a rather low filler loading (1 vol.%), the composites showed the optimum wear resistance, which was ascribed to the reduced perpendicular deformation of PEEK matrix and to the decreased tangential plastic flow of the surface layer involved in friction processes. Furthermore, the nanocomposites evidenced much smoother surfaces with respect to neat PEEK.

Pursuing this research, the role of the same nano-silica particles on the tribological behaviour of SCF-reinforced PEEK was also investigated (Zhang et al., 2009). To this aim, 1 vol.% (1.51 wt.%) nano-SiO$_2$ particles were compounded with SCF/PTFE/graphite filled PEEK in a Brabender mixer; the obtained composite materials were tested using a block-on-ring apparatus at room temperature (counterpart: 100Cr6 steel ring), in extremely wide pressure and sliding velocity ranges. Under all the conditions investigated, nano-SiO$_2$ particles remarkably reduced the friction coefficients; above 2 MPa pressures, the nanoparticles were found to reduce the wear rate: this behaviour was attributed to a protection effect of SCF/PEEK interface exerted by the nanoparticles, which are able to reduce the stress concentration on SCFs taking place in the surface layer involved into friction.

Zhang also investigated the effect of different amounts of nano-silica particles on the tribological behavior of SCF-reinforced PEEK composites. The nanoparticle loading was varied from 1 to 4 vol.% (Zhang et al., 2009).

The variation of nanoparticle content from 1 to 4 vol.% did not significantly affect the friction coefficients of the nanocomposites; in addition, operating with low pressure-sliding velocity (pv) factors, the nanoparticles turned out to worsen the wear rate of the composites, because of the abrasion on SCFs exerted by nanoparticle agglomerates. On the contrary, with a high pv factor, such agglomerates were crushed into tiny ones, so that nano-silica particles were capable to protect SCFs reducing their failures. Similar wear rates were found for the nanocomposites tested at very high pv factors.

2.2 Polyolefin-based nanocomposites

Thermoplastic polyolefins like poly(ethylene)s (PEs) and poly(propylene) (PP) are well-established polymers available at the market, each having a different structure and very different behaviour, performances and applications (Feldman & Barbalata, 1996). Several papers deal with their tribological properties, in the presence of different types of nanofillers.

High density poly(ethylene) (HDPE) was used as matrix for preparing nanosilica coatings, the wear resistance of which was measured using a rotative drum abrader (Barus et al., 2009). It was found that this parameter, despite a significant increase in the mechanical properties of the nanocomposites (stiffness, yield strength and fracture toughness), exhibited lower values with respect to the neat polymer.

Johnson and coworkers manufactured and tested the wear behaviour of HDPE/multi-walled-carbon-nanotubes composites (Johnson et al., 2009). Different weight percentages of

nanotubes (1, 3 and 5%) were used for preparing the samples, which were tested on a block-on-ring apparatus. Wear resistance and frictional properties of HDPE were found to improve in the presence of the nanofillers; furthermore, the addition of multi-walled-carbon-nanotubes to HDPE turned out to bring wear rates down to the level seen in ultra-high molecular weight poly(ethylene) (UHMWPE).

The effect of the presence of Alumina nanoparticles (5 wt.%) was exploited for investigating the abrasion resistance of low-density poly(ethylene) (LDPE)-based nanocomposites (Malucelli et al., 2010). The abrasion resistance of the nanocomposites increased in the presence of the nanofillers, as indicated by the decrease of the Taber Wear Index with respect to the neat polymer.

Very recently, Xiong and coworkers investigated the effect of the presence of nano-hydroxyapatite (nano-HAP) on the tribological properties of non-irradiated and irradiated UHMWPE composites, prepared by using a vacuum hot-pressing method (Xiong et al., 2011). The friction coefficients and wear rates were measured by using a reciprocating tribometer (counterface: CoCr alloy plates). The presence of 7 wt.% nano-HAP in the polymer matrix resulted in lowering both the friction coefficients and wear rate, irrespective of using irradiated or non-irradiated samples, whereas filling 1 wt.% nano-HAP reduced friction coefficients and wear rate of the non-irradiated UHMWPE only.

Misra and coworkers investigated the tribological behaviour of polyhedral oligomeric silsesquioxanes (POSS)/poly(propylene) nanocomposites (Misra et al., 2007). The relative friction coefficient of the samples turned out to strongly decrease from 0.17 for neat PP to 0.07 for the nanocomposite containing 10 wt.% POSS: this behaviour was ascribed to the increase of the surface hardness and of the modulus, due to the presence of the nanofiller.

2.3 Fluorinated-based nanocomposites

Fluorinated polymers usually exhibit many desirable tribological features, including low friction, high melting temperature and chemical inertness. However, their anti-wear applications have been somewhat limited by their poor wear resistance, which has led to the failure of anti-wear components and films.

Therefore, many researchers have tried to reinforce fluorinated polymers using different fillers, such as glass fibres, carbon fibres, ceramic powders, non-ferrous metallic powders: unfortunately, these fillers induced a large frictional coefficient and abrasion. Quite recently, nanometer size inorganic powders have been chosen as fillers capable to enhance the wear behaviour of fluorinated polymers.

Poly(tetrafluoroethylene), PTFE, is the most common fluorinated polymer used for tribological purposes.

Lee and coworkers added carbon-based nanoparticles, synthesized by heat treatment of nanodiamonds, to PTFE, in order to prepare fluorinated nanocomposites (Lee et al., 2007). The wear resistance, measured through ball-on-plate wear tests, was found to depend on the heat treatment, which nanodiamonds were subjected to: in particular, wear resistance turned out to increase when nanodiamonds were heated at 1000°C. Beyond this temperature, carbon nanoparticles became aggregated and therefore the wear coefficient of

the obtained nanocomposites increased: this failure in the wear behaviour was ascribed to the formation of carbon onions that promoted the aggregation of carbon nanoparticles.

Single-walled carbon nanotubes have been exploited for lowering the wear rates of PTFE (Vail et al., 2009). A linear reciprocating tribometer was exploited for performing the tests (counterface: 304 stainless steel) on nanocomposite samples containing up to 15 wt.% nanotubes. The obtained results clearly indicated that, in the presence of low nanofiller loadings (5 wt.%), PTFE wear resistance is improved by more than 2000% and friction coefficient increased by ≈50%.

Shi and coworkers have studied the effect of various filler loadings (from 0.1 to 3 wt.%) on the tribological properties of carbon-nanofiber (CNF)-filled PTFE composites (Shi et al., 2007). The friction and wear tests were conducted on a ring-on-ring friction and wear tester. The counterface materials was steel 45.

The obtained results showed that the friction coefficients of the PTFE composites decreased initially up to a 0.5 wt.% filler concentration (during sliding, the released CNFs transfer from the composite to the interface between the mating surfaces, acting as spacers and thus preventing direct contact between the two surfaces and lowering the friction coefficient) and then increased, whereas the anti-wear properties of the materials increased by 1-2 orders of magnitude in comparison with those of PTFE. Finally, the composite having 2 wt.% of CNFs exhibited the best anti-wear properties under all the experimental friction conditions.

The tribological investigation on fluorinated polymers has been also extended to PTFE-based blends, as described by Wang and coworkers (Wang et al., 2006). In particular, Xylan 1810/D1864, a commercially available PTFE blend for dry lubricant and corrosion resistant coatings, has been blended with alumina nanoparticles at different loadings (from 5 to 20 wt.%). The wear resistance was measured using a Taber Abrasion Tester and was found to decrease with increasing the content of the embedded alumina nanoparticles in the polymer matrix. The minimum wear rate was achieved when the nanoparticle loading was 20 wt.%.

Another paper from Burris and Sawyer reports on the role of irregular shaped alumina nanoparticles on the wear resistance of Al_2O_3/PTFE nanocomposites (Burris & Sawyer, 2006). A reciprocating pin-on-disc tribometer was used for testing the wear and friction of the samples (counterface: AISI 304 stainless steel plates). It was found that the inclusion of irregular shaped alumina particles is more effective in reducing PTFE wear than spherical shaped particles (the wear resistance of PTFE was increased 3000x in the presence of 1 wt.% former nanofiller), but also determines an increased friction coefficient.

Another fluorinated polymer, namely poly(vinylidene fluoride), was used as matrix for preparing nanocomposites containing a phyllosilicate (organoclay) by Peng and coworkers (Peng et al., 2009). The friction and wear tests were conducted on different loaded nanocomposites (clay content: 1 - 5 wt.%), using a block-on-ring wear tester (mated ring specimen: carbon steel 45, GB 699-88). The nanoclay at 1-2 wt.% turned out to be effective for improving the tribological properties of neat PVDF, since such filler may act as a reinforcement to bore load and thus decrease the plastic deformation.

Tribological studies were also performed on PTFE-based fabric composites (Sun et al., 2008; Zhang et al., 2009). In particular, Sun and coworkers prepared polyester fabric composites, in order to study the influence of alumina nanoparticles and PTFE micro-powders

embedded in an epoxy matrix on the tribological properties of the fabric composites. The excellent tribological performance of the fillers significantly turned out to enhance the wear resistance of the fabric polyester composites.

Zhang et coworkers were able to improve the wear resistance of PTFE/phenolic/cotton fabric composites, by dispersing functionalized multi-walled carbon nanotubes in the phenolic resin (Zhang et al., 2009). Sliding tests were performed on a pin-on-disc tribometer (flat-ended AISI-1045 pin). The high homogeneity of dispersion of the nanofiller allowed to achieve an improved wear resistance in the fabric composites; furthermore, the tribological properties of the obtained systems were found to strongly depend on the carbon nanotubes content: 1 wt.% nanofiller was the optimum loading for maximizing the wear resistance of the fabric composites.

2.4 Poly(amide)-based nanocomposites

Poly(amide) 6 and 66 (Nylon 6 and Nylon 66) have been widely used as engineering plastics in different applications, such as bearings, gears or packaging materials. They possess an outstanding combination of properties such as high toughness, tensile strength and abrasion resistance, low density and friction coefficient and quite easy processing. Indeed, their abrasion resistance is a key factor for their widespread applications.

Aiming to further improve their mechanical properties and tribological behaviour, nylons were reinforced with some micro-particles or fibres, such as CuS, CuF_2, CuO, PbS, CaO, CaS and carbon fibres: they were effective in reducing the wear rate of polyamides (Bahadur et al., 1996).

In quite recent years, as for other thermoplastic matrices, several nano-materials were served as suitable fillers of poly(amides) for improving their integrated properties, particularly referring to their tribological behavior.

Garcia and coworkers found that nano-SiO_2 could reduce effectively the coefficient of friction and wear rate of nylon 6: in particular, the addition of 2 wt.% nano-SiO_2 determined the lowering of the friction coefficient from 0.5 to 0.18 (Garcia et al., 2004). This was possible since the surface of nylon 6 nanocomposites was well protected by the transfer film on the surface of the metal counterface. At the same time, the low silica loading led to a reduction in wear rate by a factor of 140, whereas the effect of higher silica loadings was less pronounced.

Dasari and coworkers reported on the role of nanoclays on the wear characteristics of nylon 6 nanocomposites processed via different routes (Dasari et al., 2005). They demonstrated that aggregated nanoclay particles result in the worst wear resistance of the nanocomposites, whereas the systems, which exhibit a good interfacial adhesion of clay to polymer matrix, together with an homogeneous clay dispersion, determine substantial improvements of wear resistance.

Zhou and coworkers investigated the tribological behaviour of Nylon 6/Montmorillonite clay nanocomposites: the poor abrasion resistance exhibited by the nanocomposites was attributed to the presence of defects at the clay/polymer interface, resulting in lower wear resistance of the polymer matrix as the nanofiller content increased (Zhou et al., 2009).

Sirong and coworkers studied the tribological behaviour of Nylon 66/organoclay nanocomposites, in the presence of styrene-ethylene/butylene-styrene triblock copolymer grafted with maleic anhydride (SEBS-g-MA) as a toughening agent (Sirong et al., 2007). A pin-on-disc friction and wear testing apparatus was used in sliding experiments (counterface: 65 HRC steel disc). It was demonstrated that the use of SEBS-g-MA allows to obtain significant improvements as far as the wear resistance of the nanocomposite is concerned: this behaviour was ascribed to the toughening effect of SEBS-g-MA, which favours the transfer of a uniform, continuous and smooth thin film to the steel counterface, thus avoiding the direct contact of this latter with the nanocomposite.

Poly(amide) 66 was also chosen as matrix for preparing nanoparticle-filled composites (Chang et al., 2006). Different fillers, such as TiO_2 nanoparticles (5 vol.%), short carbon fibres (15 vol.%) and graphite flakes (5 vol.%), were added to the polymer and the obtained composites tested on a pin-on-disc apparatus (counterface: polished steel disc). It was found that nano-TiO_2 could effectively reduce the frictional coefficient and wear rate, especially under higher pv conditions. In order to further understand the wear mechanisms, the worn surfaces were examined by scanning electron microscopy and atomic force microscopy; a positive rolling effect of the nanoparticles between the material pairs was proposed, which contributes to the remarkable improvement of the load carrying capacity of polymer nanocomposites.

Quite recently, Ravi Kumar and coworkers studied the synergistic effect of nanoclay and short carbon fibers on the abrasive wear behavior of nylon 66/poly(propylene) nanocomposites (Ravi Kumar et al., 2009). A modified dry sand rubber wheel abrasion tester was employed for performing the three-body abrasive wear experiments. The obtained results clearly indicated that the addition of nanoclay/short carbon fiber in PA66/PP significantly influences wear under varied abrading distance/loads. Furthermore, it was found that nanoclay filled PA66/PP composites exhibited lower wear rates with respect to short carbon fiber filled PA66/PP composites.

2.5 Poly(oxymethylene)-based nanocomposites

Poly(oxymethylene) (POM) is an engineering polymer that has been widely used as self-lubricating material for many applications, such as automobile, electronic appliance and engineering. This polymer exhibits good fatigue resistance, creep resistance and high impact strength. Its low friction coefficient derives from the flexibility of the linear macromolecular chains; in addition, its high crystallinity and high bond energy result in good wear resistant properties. Some papers report on the preparation of polymeric nanocomposites based on POM.

Various fillers or fibers, such as graphite, MoS_2, Al_2O_3, PTFE, glass and carbon fibers, have been incorporated into POM matrices as internal lubricants or reinforcements to further enhance the tribological properties of such a polymer.

Kurokawa et al. investigated the tribological properties of POM composites containing very small amounts of silicon carbide (SiC) and/or calcium salt of octacosanoic acid (Ca-OCA), as well as PTFE (Kurokawa et al., 2000). It was found that the incorporation of Ca-OCA into POM/SiC composites drastically lowered their friction coefficient; furthermore, the wear rate was also lowered because of the nucleating effect of SiC and Ca-OCA.

Wang and coworkers prepared POM/MoS$_2$ nanocomposites by in situ intercalation polymerization: the intercalated composites showed a significant decrease of friction coefficient, together with an improved wear resistance, especially under high load, while the heat resistance of the composites decreased slightly (Wang et al., 2008).

The same research group also prepared POM/ZrO$_2$ nanocomposites, which evidenced better wear resistance with respect to neat POM, whereas the change in friction coefficient of the nanocomposites was very limited. (Wang et al., 2007)

Sun and coworkers studied the tribological properties of POM/Al$_2$O$_3$ nanocomposites (Sun et al., 2008). The friction and wear measurements were conducted on a friction and wear tester, using a block-on-ring arrangement (counterface: HRC50-55 plain carbon steel ring). It was found that alumina nanoparticles were more effective in enhancing the tribological properties of Poly(oxymethylene) nanocomposites in oil lubricated condition rather than in dry sliding experiments. Indeed, the former environment allows to form a uniform and compact transfer film on the surface of the counterpart steel ring, whereas the transfer film under dry sliding condition is destroyed by the agglomerated abrasives residing between the friction surfaces. The optimal nanoparticles content in POM nanocomposites was 9% under oil lubricated condition, below which alumina nanoparticles between the friction surfaces were still under saturation.

Sun and coworkers have also investigated the tribological behaviour of Poly(oxymethylene) (POM) composites compounded with nanoparticles, PTFE and MoS$_2$ in a twin-screw extruder (Sun et al., 2008). The tribological tests were performed on a friction and wear tester using a block-on-ring arrangement under dry sliding and oil lubricated conditions, respectively. The better stiffness and tribological properties exhibited by POM nanocomposites with respect to POM composites were attributed to the high surface energy of the nanoparticles; the only exception was represented by the decreased dry-sliding tribological properties of POM/3%Al$_2$O$_3$ nanocomposite, ascribed to Al$_2$O$_3$ agglomeration. Furthermore, the friction coefficient and wear volume of POM nanocomposites under oil lubricated condition decreased significantly.

2.6 Poly(methylmethacrylate)-based nanocomposites

Poly(methylmethacrylate), PMMA, is an important engineering polymer, which finds application in many sectors such as aircraft glazing, signs, lighting, architecture, and transportation. In addition, since PMMA is non-toxic, it could be also useful in dentures, medicine dispensers, food handling equipment, throat lamps, and lenses.

Unfortunately, this polymer shows poor abrasion resistance with respect to glass, thus limiting its potential use in other fields. Despite several efforts, attempts to improve the PMMA scratch and abrasion resistance have induced other drawbacks, such as a decrease of the impact strength, so that researchers focused on the preparation of PMMA nanocomposites.

Avella and coworkers studied the tribological features of PMMA-based nanocomposites filled with calcium carbonate (CaCO$_3$) nanoparticles, exploiting in situ polymerization (Avella et al., 2007). In order to improve inorganic nanofillers/polymer compatibility, poly(butylacrylate) chains have been grafted onto CaCO$_3$ nanoparticle surface.

CaCO$_3$ nanoparticles, regardless of the presence of the grafting agent, turned out to significantly improve the abrasion resistance of PMMA also modifying its wear mechanism: indeed, the nanoparticles induced only micro-cutting and/or micro-ploughing phenomena, thus generating a plastic deformation and consequently increasing the abrasion resistance of the polymer matrix.

The same research group also investigated the tribology of PMMA-based nanocomposites containing modified silica nanoparticles, obtained through in situ polymerization approach (Avolio et al., 2010). The high compatibility between silica nanoparticles and the polymer allowed to significantly improve the abrasion resistance of PMMA, because nanoparticles were able to support part of the applied load, thus reducing the penetration of grains of the rough abrasive wheel into PMMA surface and contributing to the wear resistance of the material.

Dong and coworkers prepared Poly(methyl methacrylate)/styrene/multi-walled carbon nanotubes (PMMA/PS/MWNTs) copolymer nanocomposites by means of in situ polymerization method (Dong et al., 2008). The tribological behavior of the copolymer nanocomposites was investigated using a friction and wear tester under dry conditions: with respect to pure PMMA/PS copolymer, the copolymer nanocomposites showed not only better wear resistance but also smaller friction coefficient. MWNTs were found to strongly improve the wear resistance property of the copolymer nanocomposites, because of their self-lubricating features, their homogeneous and uniform distribution within the copolymer matrix and their help in forming thin running MWNTs films that slide against the transfer film (developed on the surface of the stainless steel counterface).

Very recently, Carrion and coworkers exploited single-walled carbon nanotubes modified with an imidazolium ionic liquid for preparing PMMA nanocomposites and studying their dry tribological performances as compared to neat PMMA or to the nanocomposites containing pristine carbon nanotubes without ionic liquid (Carrion et al., 2010). The tribological behavior of the obtained nanocomposites, studied against AISI 316L stainless steel pins, resulted in a significant wear rate decrease with respect to PMMA/carbon nanotubes (-58%) and neat PMMA (-63%).

2.7 Other thermoplastic-based nanocomposites

Some other thermoplastic engineering and specialty polymers have been considered as far as tribological issues are concerned. In the following, we will summarize the recent progress in understanding wear and friction in nanocomposite systems based on these polymers.

Bhimaraj and coworkers studied the friction and wear properties of poly(ethylene) terephthalate (PET) filled with alumina nanoparticles (up to 10 wt.% nanofiller), using a reciprocating tribometer (Bhimaraj et al., 2005). The obtained results showed that the addition of alumina nanoparticles can increase the wear resistance by nearly 2x over the unfilled polymer. Furthermore, the average friction coefficient also decreased in many cases. This behavior was attributed to the formation a more adherent transfer film that protects the sample from the steel counterface, although the presence of an optimum filler content could be ascribed to the development of abrasive agglomerates within the transfer films in the higher wt.% samples.

Another paper from the same research group reports on the effect of particle size, loading and crystallinity on PET/Al$_2$O$_3$ nanocomposites (Bhimaraj et al., 2008). The nanocomposite samples were tested in dry sliding against a steel counterface. The tribological properties were found to depend on crystallinity, filler size and loading; in addition, wear rate and friction coefficient were very low at optimal loadings that ranged from 0.1 to 10 wt.%, depending on the crystallinity and particle size.

Wear rate were found to lower monotonically with decreasing particle size and crystallinity at any loading in the range tested.

Poly(etherimide)s (PEIs) are high-performance thermoplastics with high modulus and strength, superior high temperature stability, as well as electrical (insulating) and dielectric properties (very low dielectric constant). These polymers perform successfully in aerospace, electronics, and other applications under extreme conditions. Nevertheless, pure PEIs show such disadvantages as brittleness and high wear rate, which limit their applications. Therefore, appropriate modifications of PEIs with nanofillers have been proposed, in order to widen their industrial applications.

Chang and coworkers reinforced PEI with titania nanoparticles, in the presence of short carbon fibres (SCFs) and graphite flakes as well (Chang et al., 2005). Wear tests were performed on a pin-on-disc apparatus, using composite pins against polished steel counterparts, under dry sliding conditions, different contact pressures and various sliding velocities. SCFs and graphite flakes turned out to remarkably improve both the wear resistance and the load-carrying capacity. Nevertheless, the addition of nano-TiO$_2$ further reduced the frictional coefficient and the contact temperature of the composites, especially under high pv conditions.

The same research group investigated the role of the presence of nano- or micro-sized inorganic particles (5 vol.% nano TiO$_2$ or micro-CaSiO$_3$) on the tribological behavior of PEI matrix composites, additionally filled with SCFs and graphite flakes (Xian et al., 2006). The influence of these inorganic particles on the sliding behavior was assessed with a pin-on-disc tester at room temperature and 150°C.

The obtained results showed that both micro and nano particles could reduce the wear rate and the friction coefficient of the PEI composites under the experimental adopted conditions, but in a different temperature range: indeed, the microparticles filled composites showed improved tribological features at room temperature, whereas the nano-titania-filled composites possessed the lowest wear rate and friction coefficient at elevated temperature. The tribological improvements evidenced by the nano-particles were attributed to the formation of transfer layers on both sliding surfaces together with the reinforcing effect.

Very recently, Li and coworkers dispersed carbon nanofibers (from 0.5 to 3 wt.%) in a PEI matrix through a melt mixing method and tested the tribological properties of the obtained nanocomposites (Lee et al., 2010). The composites containing 1 wt.% CNFs showed very high wear rates comparable with that of pure PEI; nevertheless, higher CNF loadings promoted a significant reduction in wear rate at steady state wear.

Like PMMA, also poly(carbonate) (PC), an amorphous engineering thermoplastic, which combines thermal stability, good optical properties, outstanding impact resistance and easy

processability, shows poor scratch and abrasion resistance with respect to glass, thus limiting its potential use in fields other than medical, optics, automotive, ….

Carrion and coworkers prepared a new polycarbonate nanocomposite containing 3 wt.% organically modified nanoclay by extrusion and injection moulding, and its tribological properties were measured under a pin-on-disc configuration against stainless steel (Carrion et al., 2008). The obtained nanocomposites showed 88% of reduction in friction coefficient and up to 2 orders of magnitude reduction in wear rate with respect to the neat polymer. Such good tribological performances were attributed to the uniform microstructure achieved and to the nanoclay intercalation.

3. Conclusion

The significant spreading of research activities concerning the tribology of thermoplastics and thermoplastic-based nanocomposites demonstrates that this topic is very up-to-date. Indeed, several low-loading, low-wear polymer nanocomposites are being prepared and evaluated in tribology laboratories.

In many cases, nanocomposite systems result in outperforming traditional macro- and micro-composites by orders of magnitude with substantially lower filler loadings (often less than 5 wt.%), provided that the tribological features strongly depend on the homogeneity of dispersion and distribution of the nanofillers within the polymer matrix.

Past macro and micro models, which have been always exploited for estimating the mechanical behavior of composite materials seem to be quite inadequate to describe the phenomena occurring at a nanoscale level, particularly referring to wear and friction.

The standard tools applied for characterizing nanomaterials need to be implemented more in tribology studies to help clarify the obtained experimental results. This means that tribology should always be considered as an important issue of the materials science.

In particular, regardless of the effectiveness of the nanofiller dispersion within the polymer matrix, some issues become very crucial and should be consequently deeply investigated. First of all, the chemistry and chemical reactions, which may occur in between the mating surfaces, have to be considered, and the influence of the by-products resulting from such reactions or during wear as well.

Indeed, the effect and dynamics of the development of the transfer film during low wear sliding, together with the evolution of its physico-chemical and mechanical properties should be thoroughly investigated. Consequently, the mechanisms, through which removal of abraded materials occurs, should be deeply investigated, so that proper mechanics models for the design of high wear resistant nanocomposites can be developed.

Finally, synergies between materials science and tribology have to be developed, aiming to better understand the complex tribological phenomena taking place in polymeric nanocomposites.

This approach will surely contribute to design more efficient nanomaterials for tribological applications.

4. Acknowledgment

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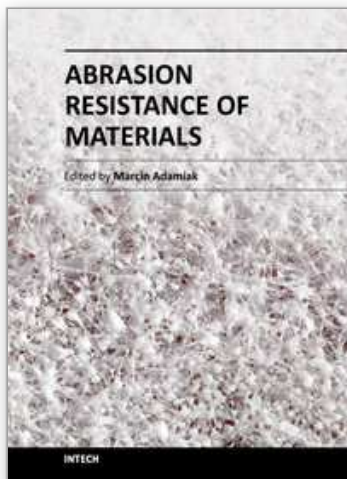
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