Review

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A review on tribo-mechanical properties of micro- and nanoparticulate-filled nylon composites

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Abstract: Nylon composites are of evolving interest due to their good strength, toughness, and low coefficient of friction. Various fillers like micro- and nanoparticulates of metals and metal compounds were used to enhance the mechanical and tribological properties of nylons for many years by researchers. In this paper, an overall understanding of composites, filler materials, especially particulate filler materials, application areas of polymer composites, wear of polymers, and the effect of various fillers on tribo-mechanical properties of nylons have been discussed. The detailed review is limited to micro- and nanoparticulate fillers and their influence on the mechanical and tribological properties of various nylon matrices.

Keywords: friction; mechanical properties; nylon composite; tribological properties; wear.

Nomenclature

ABS	Acrylonitrile butadiene styrene
Al ₂ O ₃	Aluminum oxide
CaF ₂	Calcium fluoride
CaO	Calcium oxide
COF	Coefficient of friction
CuF	Cuprous fluoride
CuO	Copper oxide
CuS	Copper sulfide
GRF	Graphite fluoride
GRP	Glass(fiber) reinforced plastic
HDPE	High-density polyethylene
HNT	Halloysite nanotubes
LDPE	Low-density polyethylene
MoS	Molybdenum sulfide
MoS ₂	Molybdenum disulfide

MWNT	Multiwalled carbon nanotube
PbS	Lead sulfide
PEEK	Polyether ether ketone
PTFE	Polytetrafluoroethylene
SiO ₂	Silicon dioxide
UHMWPE	Ultra-high-molecular-weight polyethylene
ZnF ₂	Zinc fluoride
ZnO	Zinc oxide
ZnS	Zinc sulfide
ZrP	Zirconium phosphate

1 Introduction

A composite is a material that consists of two or more chemically different constituents that are combined at a macroscopic level and are not soluble in each other to yield a useful material. Composite materials have been widely applied in various applications like aeronautical industries, biomechanics, public infrastructure, automobile industries, furniture. Composites have unique advantages over many monolithic materials, such as high strength, high stiffness, longer fatigue life, low density, and adaptability to the intended functions of the structure [1–8].

A few examples of composites are shown in Table 1.

There are several benefits of composites mentioned as follows:

- Light weight: composites can be made light in weight to replace any heavier material. Their lightness is important in automobiles and aircraft, for example, where less weight means better fuel efficiency. People who design airplanes are greatly concerned with weight since reducing an air craft's weight reduces the amount of fuel it needs and increases the speeds it can reach.
- High strength: composites can be designed stronger. Metals are equally strong in all directions, but composites can be engineered and designed to be strong in a specific direction.
- Strength to weight ratio: strength to weight ratio is a material's strength to how much it weighs. Some materials are extraordinarily strong and heavy, such as steel and other metals. Composite materials can be

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designed to be both strong and light. This property is why composites are used to build airplanes, which need a remarkably high strength material at the lowest possible weight. A composite can be made to resist bending in one direction.

- Corrosion resistance: composites resist damage from the weather and harsh chemicals. Composites can be used where chemicals are handled or stored. Composites can be used in humid areas. It can be used in an open rainy atmosphere.
- High-impact strength: composites can be made to absorb impacts like the sudden force of a bullet, for instance, or the blast from an explosion. Because of this property, composites are used in bulletproof vests and panels, and to shield airplanes, buildings, and military vehicles from explosions.
- Low thermal conductivity: composites are good insulators. They do not easily conduct heat or cold. They are used in buildings for doors, panels, and windows where extra protection is needed from severe weather.
- Durability: structures made of composites have a long life and need less maintenance. Composites can replace other materials where durability is the main issue.
- Nonconductivity: Most of the composites are non-conductive, meaning they do not conduct electricity. This property makes them suitable for such items as electrical utility poles and circuit boards in electronics. If electrical conductivity is needed, it is possible to make some composites conductive.
- Wear resistance
- Fatigue life
- Acoustic insulation
- Attractiveness
- Damping properties: composite materials can be engineered to get the desired damping properties.
- Temperature resistance.

And composites have many more advantages. Composites can be made to fulfill the requirements of properties that only one single material cannot fulfill. Current application areas of engineered composites are shown in Table 2.

Table 1: Natural and engineered composites.

Natural composites	Manmade/engineered composites
Wood (fibrous composite)	Concrete (particulate composite)
Bone (fibrous composite)	Plywood (fibrous composite)
Granite (particulate composite)	Fiberglass (short fibrous composite)

Apart from all these, composites are also used in consumer goods products, agriculture, computer hardware, and many more places.

Composites can be classified according to the:

- Matrix material used
- Reinforcing element used, and
- The orientation of fibers/particles and numbers of layers.

A few examples of available matrix materials are shown in Table 3.

Depending on the matrix material used, composites are classified as thermoplastic/thermoset matrix composite, metal matrix composite, and ceramic matrix composite.

A few general properties of matrix materials are mentioned in Table 4.

Following are the functions of matrix materials:

- Holds the fillers
- Protects the reinforcing particles/fillers from contamination
- Helps to maintain the distribution of fillers
- Distributes the loads evenly
- Enhances some of the properties of the resulting material and structural component (that filler alone is not able to impart) such as tensile strength, impact resistance
- Provides a better finish to the final product.
- Supports the overall structure.

Reinforcing elements may be in the form of particles, flakes, or whiskers. According to that, the following are the classifications of reinforcements:

- Fiber reinforced: in which, length to diameter ratio is remarkably high (of the order 1000). Continuous fibers are essentially characterized by one exceptionally long axis with the other two axes either often circular or near-circular. A composite with fiber reinforcement is called a fibrous composite.
- Particle reinforced: in which particles are used as reinforcement. These particles do not have any long dimensions. Generally, particles have neither preferred orientation nor shape. A composite with particles as reinforcement is called a particulate composite.
- Flake reinforced: flakes are small in length direction compare to continuous fibers.
- Whisker reinforced: whiskers are nearly perfect single crystal fiber. Whiskers are short, discontinuous, and have a polygonal cross-section.

Table 2: Application areas of engineered composites.

Automotive sector	Aerospace sector	Sports	Transportation	Infrastructure	Biomedical industry
Car body	Nose	Tennis rackets	Railway coaches	Dams	Artificial legs
Brake pads	Aircraft, rocket, and missile body	Hockey sticks (glass fiber composite)	Ships	Bridges	Dentistry
Driveshafts	Doors	Bikes	Trucks		Artificial joints
Fuel tank	Struts	Boats			
Hoods/bonnet	Trunnion	Golf			
Spoilers	Fuel tanks				
	Satellite frames and other structural parts				
	Antenna (smart materials)				

Table 3: Matrix materials.

Thermoplastics	Thermosets	Metals	Ceramics
Polypropylene	Polyesters	Aluminum	Carbon
Polyvinyl chloride (PVC)	Epoxies	Titanium	Silicon carbide
Nylon	Polyimides	Copper	Silicon nitride
Polyurethane		Tin	
Poly-ether-ether ketone (PEEK)			
Polyphenylene sulfide (PPS)			

Table 4: General properties of matrix materials.

Thermoplastics/thermosets	Metals	Ceramics
Operating temperature range <300 °C	Higher use operating temperature range (>200 °C up to 1500 °C and more)	Extremely high-temperature range >2000 °C (most cases)
Lighter	Heavier	Heavier
Low moisture absorption	No moisture absorption	Low moisture absorption
Low-cost processing	High-cost processing	High-cost processing
Heat resistance is less	Good heat resistance	High heat resistance
Cold and hot moulding	Hot moulding	Hot moulding
Low cost	High cost	High cost
Mechanical strength is less	Good mechanical strength	Good mechanical strength
Average chemical resistance	Average chemical resistance	High chemical resistance

Depending on the reinforcing element used, composites are classified as fiber reinforced composite, particle reinforced composites, flake reinforced composite and whisker reinforced composite. Reinforcing constituents in composites, as the word indicates, provide the strength that makes the composite what it is. But they also serve certain additional

purposes of heat resistance or conduction, corrosion resistance, and provide rigidity. Reinforcement can be made to perform all or one of these functions as per the requirements. A reinforcement that embellishes the matrix strength must be stronger and stiffer than the matrix and capable of changing the failure mechanism to the advantage of the composite. Briefly, it must

- Contribute desired properties
- Be load-carrying
- Transfer the strength to the matrix.

Figure 1 shows the classification according to the orientation of fibers/particles and the layers.

1.1 Classifications of particulate fillers

Various metals and metal compounds are used as the filler materials for enhancing the tribo-mechanical properties of polymers.

- (1) Metals: metal particles like aluminum, copper, iron, boron, lead, bronze are used as the fillers in polymer matrices to enhance the required properties of polymers.
- (2) Metal compounds: metal compounds like oxides, nitride, carbides, and fluorides are generally in application to enhance the properties of matrix polymer materials. Metal carbides tend to increase the COF but ultimately reduce the wear rate due to their abrasive nature. Various metal compounds are used as solid lubricants as they develop a smooth transfer layer on the counterparts which decreases COF as well as the wear rate of the polymer part. Solid lubricants are classified as:

- a) *Inorganic lubricants with lamellar structure*: the crystal of these materials has a layered structure that consists of hexagonal rings and forms thin parallel planes. Within the plane, each atom is

bonded strongly while the planes are bonded by weak Van der Waals forces to each other. The layered structure gives the sliding movement of the parallel planes. Weak bonding between the planes gives low shear strength and lubricating properties to the materials. The commonly used inorganic solid lubricants with lamellar structure are graphite, molybdenum disulfide (MoS_2), and boron nitride (BN). Other examples are sulfides, selenides and tellurides of molybdenum, tungsten, niobium, tantalum, titanium (e.g. MoSe_2 , TaSe_2 , TiTe_2), monochalcenides (GaS , SnSe), chlorides of cadmium, cobalt, lead, zirconium (e.g. CdCl_2 , CoCl_2 , PbCl_2 , CeF_3) and some borates (e.g. $\text{Na}_2\text{B}_4\text{O}_7$) and sulfates (Ag_2SO_4).

- b) *Oxides*: examples: boron trioxide (B_2O_3), molybdenum dioxide (MoO_2), zinc oxide (ZnO), and titanium dioxide (TiO_2).
- c) *Soft metals*: due to their low shear strength and high plasticity these soft metals provide lubrication properties, e.g., lead (Pb), tin (Sn), bismuth (Bi), cadmium (Cd), and silver (Ag).
- d) *Organic lubricants with the chain structure of the polymeric molecules*: polytetrafluoroethylene (PTFE) and polychlorofluoroethylene are examples of such kinds of materials. The molecular structure

of these materials consists of long-chain molecules parallel to one another. The bonding strength between the molecules is weak so they slide on each other at low shear stresses while the strength of molecules along the chains is high because of strong bonding between the atoms within a molecule.

Table 5 represents the merits and demerits of polymers with the additives and their effects on the mechanical as well as on the tribological properties of polymers. The main question with the use of solid lubricants is to maintain a continuous supply of solid lubricants between two sliding surfaces. The best answer to this question is to introduce the solid lubricant as reinforcement into the matrix. A self-lubricating material is one whose composition facilitates low coefficients of friction and wear. Composites reinforced by solid lubricants become self-lubricating due to the lubricant film which prevents direct contact between the mating surfaces. This lubricant film is not present at the beginning, it forms due to the surface wear of solid lubricant reinforced composite material.

Self-lubrication can be produced by:

- Interface sliding of anisotropic materials such as graphite, molybdenum disulfide, or diselenides
- Inter-chain sliding in linear thermoplastics like polytetrafluoroethylene or polyolefins
- Surface melting of fusible elements like lead, tin, or polyethylene
- Surface thermal decomposition of metal-containing chemical compounds like oxalates of metals.

Figure 1: Classification of composites according to orientation of fibers/particles and numbers of layers.

Table 5: Polymer merits, demerits, additives, and their effects [9].

Merits	Demerits	Additives	Effects
Low friction & wear	Low strength	PTFE	Reduce friction & wear
No tendency to seizure	Low thermal conductivity	Lamellar solids	
Easily fabricated	High thermal expansion	Inorganics	Reduce wear
Less costly	Poor dimensional stability	Fibers	Improve mechanical properties, reduce wear
Varieties available	Poor chemical stability	Metals	Improve mechanical & thermal properties
Blending of polymers is possible (not all)	Some polymers absorb moisture from the environment		

Graphite and polyethylene form lubricating layers of friction transfer on the mated surfaces during friction and due to this, it provides low resistance to relative motion and high wear resistance. At temperatures above 100 °C local meltings of polyethylene takes place, and it functions as a highly viscous lubricant [10]. Self-lubricating polymer composites are widely used in space applications where timely preventive maintenance is not possible [11]. Also, they are widely used in cryogenic bearings where liquid lubrication of parts is not possible. The application areas are increasing day by day because of its unique ability of self-lubrication which will eliminate the usage of external lubrication requirements.

2 Wear of polymers

The wear of polymers is influenced by three groups of parameters in which the first group includes the sliding contact conditions like surface roughness and contact kinematics. The second group includes the bulk mechanical properties of the polymer and the effect of temperature and environmental conditions on these properties. The third group involves the role and properties of the ‘third body’ i.e. the transfer film and loose degraded polymer particulates. The wear mechanism and its magnitude are defined by the contract conditions, mechanical properties of the bulk polymer, and how these parameters lead to the subsequent transfer film formation and debris production. The following Figure 2 represents the wear classification based on generic scaling, phenomenological, and material response approaches [12].

Few studies show that polymer wear in the presence of external lubricants will depend primarily upon the interaction between the fluid phase and the polymer and on their counter face. Except where there is sorption of the lubricant by the polymer surface, generally, polymer wear

has been seen high in the presence of an external fluid. According to one study, the friction force is proportional to the normal applied load i.e. $F_f = \mu F_n$. Where F_f is friction force, μ is the coefficient of friction and F_n is the normal force or normal load. The friction coefficient remains constant in the range 10–100 N load. It was noticed that in the range of 0.02–1 N load, the friction coefficient decreases with increasing the load [13], and the friction coefficient increases with increasing the load on the other side. This is due to the plastic deformation of asperities that are in contact. Polymers are viscoelastic materials and extremely sensitive to frictional heating. Due to friction, mechanical energy is converted into heat which raises the temperature at contact and makes an influences the wear of polymers. It was observed that many polymers sliding against steel exhibit minimum wear rates at characteristic temperatures. The product of the elongation to break (ϵ) and the breaking strength (S) are important parameters in the wear of polymers. $1/S\epsilon$ varies with temperature in the same way as the wear rate varies. In abrasive wear, the wear rates of many polymers show an approximately linear correlation with $1/S\epsilon$ [14]. The most common types of wear of polymers are abrasion, adhesion, and fatigue. The wear mechanisms of the polymer composites show that micro composites tend to suffer from abrasive wear while nanocomposites suffer from adhesive wear while observing the wear tracks on scanning electron microscopy (SEM) [15].

To provide lubrication, the material must be able to support dynamic stresses induced by the applied load and the tangential friction stresses. If the polymer/polymer composite cannot support these stresses then it will plastically deform, undergo brittle fracture, and ultimately wear quickly. To provide the best lubrication, a thin shear layer must develop between the sliding surfaces. This shear layer is important to reduce the adhesive and the ploughing interactions which take place between surfaces moving relative to each other. A thinner shear layer is found to be better in general compared to a thick layer. Table 6 represents some self-lubricating composites and their possible uses in space [16]. Table 7 shows some commercially available materials for bearings [17].

Figure 2: Classification of the wear of polymers.

Table 6: Some self-lubricating composites and their uses in space.

Composite type	Use
PTFE and glass fiber	Bearing cages
PTFE, glass fiber and MoS ₂	Bearing cages and gears
Polyacetal homopolymer and copolymer	Bearing cages and gears
Reinforced phenolics	Bushings and brakes
Polyimide and MoS ₂	Bearing cages and gears etc.

Table 7: Commercially available materials for bearings.

Thermoplastics	PTFE/bronze-filled polyacetal
	Moulded or cast MoS ₂ -filled nylons
	Porous (oil-filled) or solid (MoS ₂ -filled) nylon
	Oil-filled nylons
	Oil-filled polyacetal
	Steel-backed porous bronze with oil-filled polyacetal
	PTFE/glass fiber/oil-filled thermoplastics
Thermosets	Graphite/MoS ₂ -filled thermoset
	Asbestos fiber reinforced thermoset
	Cotton fabric reinforced thermoset

In one research, glass fibers were used to reinforce an epoxy to which additives of PTFE, graphite, and molybdenum disulfide were used to produce a self-lubricating material. The composite of glass fibers reduced the coefficient of friction value to as low as 0.02 [18]. Graphite in epoxy composite reduced the coefficient of friction and improved the wear resistance of the material to a good extent in Xiubing Li et al.'s experimentation [19]. In another experiment, 16 MnNb steel-PTFE composite (A) containing 60% area proportion of PTFE composite and C86300 bronze-PTFE composite (B) containing 35% area proportion of PTFE composite were developed for a comparative investigation. As the result, composite A exhibited a much low coefficient of friction and high wear resistance as compared to composite B had been found due to the area proportion of solid lubricant for composite A reached 60%, which provided sufficient lubrication during the whole tests [20]. According to the study of Debnath et al., increasing the strength of the bond between filler and matrix will not improve the mechanical properties of particulate-reinforced composites compare to fiber reinforced composites [21]. Also, the wear rates of materials, in general, are related to the ratio of the indentation hardness (H) to elastic modulus (E). The lower the ratio H/E, the greater the rate of wear. Fibers and particle reinforcements are generally advantageous in reducing friction coefficient and wear rate in dry conditions rubbing with the smooth surface while in the case of abrasive wear, these reinforcements generally increase it. One research stated that the carbon, graphite, molybdenum disulfide (MoS₂), polytetrafluoroethylene (PTFE) and short glass fibers increased the abrasive wear of polymers [22]. One study revealed that the 10 wt% of h-BN resulted in a minimum specific wear rate of polyether ketone while 3 wt% of neodymium oxide addition enhanced the microhardness by 17% and resulted in lower abrasion [23, 24].

Two-dimensional materials generally have higher elastic properties when used in small amounts in comparison to the corresponding bulk quantity. And because of that,

the mechanical properties of 2D materials have been found to decrease with increasing content of it [25]. Boric anhydride is used by many researchers to improve the mechanical properties of materials. For example, 5 wt% of boric anhydride improved micro-hardness and strength of hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) which is used in human hard tissue implants [26]. In one research, 10 mol% of boric anhydride improved bending strength and Rockwell hardness of diamond composite [27]. While the mechanical properties of the phosphate-based glass fibers continuously increased with increasing boric anhydride content [28].

3 Nylon and nylon particulate composites

Nylons are an especially important part of the thermoplastic polymer family and having different subtypes like nylon 6, nylon 66, nylon 11, nylon 1010. Nylons are also known as polyamides (PA) due to their repeating units linked by amide links. Nylons are tough, possessing high tensile strength, as well as elasticity and luster. They are wrinkle-proof and highly resistant to abrasion and chemicals such as acids and alkalis. Some nylons can absorb up to 2.4% of water, although this lowers tensile strength. There are various fabrication techniques developed by the researcher to make nylon composites in which two methods as follows are widely known and effective.

3.1 Fabrication of nylon particulate composites

The dispersion of micro-/nanoparticulates in a nylon matrix is an important step in the synthesis of nylon composites. A well-dispersed filler ensures a good surface area which affects the properties of nylon matrices. Generally, two methods are widely used for the compounding purpose and these are *in situ* polymerization and melt blending.

3.1.1 *In situ* polymerization

In situ polymerization is a widely used technique for the compounding of micro- and nanoparticulate-filled nylon composites. Other widely used polymers in this method are, for example, epoxy, polystyrene, acrylic, polyurethane, polyethylene, polyimide. There are two steps in this method, First, the fillers are mixed with the monomers, and then in the second step, a suitable initiator is diffused in for polymerization at adjusted temperature for a suitable

time. *In situ* techniques are more popularly used for nanocomposite fabrication with nanoparticulate fillers like graphene, graphene oxide. In this method there are two routes, one is ionic ring-opening polymerization and the second one is hydrolytic polymerization. Xu et al. have prepared nylon 6/graphene oxide composite with the help of *in situ* polymerization technique. Graphene oxide was first dried and then thermally reduced to graphene and they found improvement in the mechanical properties of composite compare to pure nylon 6 [29]. Liu et al. fabricated nylon 6/functional graphene composite by this method. Nylon 6 chains were grafted on functional graphene and enhancement in mechanical properties of the composites was found compare to pure nylon 6 [30]. Ding et al. prepared nylon 6/graphene oxide nanocomposite by *in situ* technique. Graphene oxide was reduced to graphene at 250 °C and it improved the thermal conductivity of the base matrix material [31].

3.1.2 Melt blending

Melt blending is a more commercially used method for compounding micro- or nanoparticulates with thermoplastic polymers. Various thermoplastic polymers are used in melt blending like nylon, PEEK, LDPE, HDPE, polystyrene, polyurethane, polyethylene, polypropylene. It is the most suitable method for mass production. In this method, fillers are initially mixed mechanically with the matrices and then fed into the single screw or twin-screw extruder or directly injection moulded with the help of an injection moulding machine. Screw speed, temperature, and time of extruder or injection moulding machine are selected according to the matrix materials and fillers used.

3.2 Tribo-mechanical properties of nylon composites

Nylons are used in many commercial & industrial applications like bearings, gears, slides, toys, ropes, toothbrushes, household equipment, food packaging. But it cannot be used where excessive loads are applied and excessive wear are the main causes of failure due to low strength, hardness, and high wear rates compared to metals [32]. To achieve better mechanical and tribological properties, various micro- and nanoparticulate fillers have been used by the researchers like, copper, copper oxide, copper fluoride, graphite, molybdenum disulfide, silica, lead sulfide, copper sulfide, calcium sulfide, calcium oxide, long carbon nanotubes, silicon carbide, graphite fluoride, fluorographene,

almond skin powder, magnesium hydroxides, boric anhydride, aluminum oxide, halloysite nanotube, nanotitanium dioxides [33–50]. Various fibers were also used to improve the tri-mechanical properties of polymers. Basalt, bamboo, pineapple-like natural, and glass & carbon fiber-like man-made fibers were used by the researchers to improve the tribo-mechanical properties of the base polymer material [51–54]. In one research, 1 wt% diamond nanoparticles improved the friction coefficient and wear resistance by 60 and 30%, respectively of nylon 6 [55]. Haoyang Sun et al. used alpha-zirconium phosphate nanoplatelets and in their result, they found improvement in mechanical and tribological properties of nylon 66 up to several percentages [56]. Nylon 66/Al₂O₃ micro-composites were fabricated with the help of a twin-screw extruder by Lalit Guglani and TC Gupta. Filler % varied from 2 to 8 wt% in their study. In their results, they found that the friction coefficient and wear rates reduced with the filler addition and found the lowest for the 2 wt% Al₂O₃ reinforcement. Tensile strength, elastic modulus, flexural strength, and flexural modulus were also found to improve and the best values were found for 6 wt% Al₂O₃ filler reinforcement. Compressive and impact strength were enhanced and found maximum for the 6 wt% filler [57]. Nylon 6/Al₂O₃ nanocomposite was prepared with the *in situ* polymerization by Li-Yun-Zheng et al. Tensile strength of 3 wt% nanocomposite was found 52% more than the pure nylon 6 [58]. CaO nanoparticles of 0.5 wt% were introduced in the nylon 6 matrix by W. S. Mohamed et al. by the extrusion process. The tensile strength of the composite was investigated for the materials and it found a 57.35% increase for the composite material compare to pure nylon 6 [59]. Nylon 6/SiO₂ nanocomposites were fabricated with the help of single screw extrusion by Hasan et al. Nanoparticles with the wt% of 1 & 2 were introduced into the nylon 6 matrix and 26% enhancement in tensile strength was observed for the composite material compare to pure nylon 6 [60]. Nylon 6 composites with different fillers like kaolin, talc, glass beads, and wollastonite at 10–30 wt% were fabricated with an injection moulding machine by Unal et al. These composites were fabricated with individual fillers as well as with the mixing of two. Tensile strength and flexural strength were found to improve as the content of filler increased in the matrix. Maximum tensile strength, flexural strength, and impact strength were found for 20 wt % talc and wollastonite fillers mixture in the nylon 6 matrix [61]. Nylon 6/clay nanocomposite was fabricated using the melt intercalation technique by Mohanty and Nayak. In their result, they found the optimum performance for nylon 6 composite with 5 wt% nano clay loading [62]. Nylon 6/MWNT composite was prepared by Wei De Zhang et al. with the help of a twin-screw extruder and they found

Table 8: Various polymers, reinforcement, and reinforcements' effects.

Polymer matrix	Reinforcement		Fabrication process	Effect on the mechanical properties	Effect on COF & wear rate	Any other effect
	Type	wt%				
Nylon 66	Al ₂ O ₃ microparticles	2, 4, 6 & 8 wt%	Twin screw compounding	Up to 6 wt% increased then decreased	Lowest found at 2 wt%	–
LDPE	Al, Cu, Fe, bronze microparticles	10 wt% (anyone)	Single-screw compounding	Reduction in strength	–	Increased thermal diffusivity
HDPE	Al flakes	5, 10, 15 & 20 wt%				
ABS	SS microparticles	10, 15 & 23 wt%	Fused deposition modeling	Up to 15% same as pure then decreased	–	Enhancement in glassy behavior up to 15%
Nylon	Iron particles	– (increasing order)	Single screw extrusion and FDM	–	–	Increase in thermal conductivity
Polystyrene	Nickel	0 to 25 wt%	Brabender mixer	–	–	Improved melting point
	Iron			Improved		Improved electrical properties
Nylon 6	Al particles	0 to 80 wt%	Compression moulding	Decrease initially then increased	–	–
Epoxy	Silicon carbide particles	–	–	Continuous increment in hardness	–	–
Nylon 11	Silica nanoparticles	2, 4 & 6 wt%	Selective laser sintering (SLS)	Decrease in compressive modulus at 2% and then it increase	–	–
Nylon 6	CaO nanoparticles	0.5 wt%	Twin screw compounding	Tensile strength increased	–	–
Nylon 6	SiO ₂ nanoparticles	0, 1 & 2 wt%	Single screw extrusion	Ultimate tensile & yield strength, hardening modulus increased	–	More thermally stable
Nylon 6	Al ₂ O ₃ nanoparticles	3 wt%	<i>In situ</i> polymerization	Tensile strength increased	–	Glass transition temperature increased
Nylon 6	Wollastonite, kaolin, talc & glass beads	10 to 30 wt%	Twin-screw compounding	Tensile & flexural strength improved but impact strength decreased	–	–
Nylon 6	Nano clay particles	5 wt%	Melt intercalation technique	Tensile & flexural strength improved	–	–
Nylon 6	Carbon nanotubes	1 wt%	Twin-screw compounding	Tensile strength & modulus, hardness improved	–	–
Nylon 6	Graphene	0.1, 0.3, 0.5, 1, 3 & 5 wt%	Twin screw compounding	–	–	Improved thermal properties
Nylon 6	SiC & Al ₂ O ₃ microparticles	–	Single screw extrusion & FDM	Tensile & yield strength, Young's modulus improved	–	–
HDPE	SiO ₂ microparticles	2, 4 & 6 wt%	Twin screw compounding & extrusion	Increased Young's modulus	–	–
Nylon 6	Pristine α -zirconium phosphate nanoplatelets	1, 3 & 5 wt%	Single screw extrusion & injection molding	Increased tensile modulus	–	–

Table 8: (continued)

Polymer matrix	Reinforcement		Fabrication process	Effect on the mechanical properties	Effect on COF & wear rate	Any other effect
	Type	wt%				
Nylon 6	Carbon nanotubes	1 wt%	Twin-screw compounding & injection molding	Increased tensile strength	–	–
PTFE	Boric oxide	–	Compression molding	–	Reduction in COF & wear	–
PTFE	Serpentine	10 wt%	Compression molding	–	Reduction in COF	–
Epoxy	Graphite	Less than 30 vol%	–	–	Reduction in COF & wear	–
	MoS ₂				Reduction in wear rate but COF unchanged	
	Graphite + MoS ₂				Reduction in COF & wear	
Epoxy	Woven carbon fiber	30 vol%	Resin transfer molding process	Increased bending strength	Reduction in COF & wear	–
Polyester	Glass fiber	50 vol%	–	–	Reduction in COF & wear	–
Polyphenylene sulfide	Carbon fiber	50 vol%	–	–	Reduction in wear	–
Polystyrene	MoS ₂	0.3, 1.6 & 4.5 wt%	Compression molding	–	Reduction in COF & wear as filler % increases	Improvement in thermal stability
PEEK	Carbon fiber	30 wt%	Injection molding	Increase in tensile strength	Reduction in COF	–
	Glass fiber	30 wt%		Decrease in tensile strength	Reduction in COF	
	Carbon fiber + Graphite + PTFE	10 wt% each		Decrease in tensile strength	Reduction in COF but increased wear rate	

improvement in tensile strength and hardness with 1 wt% loading of fillers [63]. Nylon 6/Hytrel blends and MWNT composites were fabricated with the help of melt-mixing by Jogi et al. 15 wt% loading of hytrel blends shown tensile strength of 40 MPa and 1 wt% modified MWNT blend shown the tensile strength of 65 MPa in their experimentations [64]. These different reinforcing fillers were also used in other polymer matrices like LDPE, HDPE, ABS, polystyrene, polyester, PEEK, Epoxy, PTFE to improve different properties of polymers as shown in Table 8 [65–76].

Some research on COF and wear analysis described in Table 8 is discussed here for brief detailing. In one research, boric oxide particles were added in PTFE material which reduced the wear rate of the overall composite. This lubrication effect results from the replenishment of lubricous boric acid lamella solid provided to the sliding interface. Regarding PTFE based composite filled with serpentine

powder, the normal contact pressure has a significant effect on the friction and wear properties of the composite. With an increase in applied load, the anti-friction performance of the nanocomposite increased gradually, and the wear resistance of the composite was gradually decreased. Sliding velocity is also found as an influencing parameter on the wear performance of the composite. The specific wear rate decreased first and then increased with the increasing rate of sliding velocity. This was due to the decline in mechanical properties under the frictional heat on the contact surface area. PTFE-serpentine nanocomposite showed good self-lubricating property due to compact and uniform transfer film generated on the counter face which acted as an excellent solid lubricant. It was also found helpful to reduce the frictional coefficient of the composite. In the case of graphite and MoS₂ in the epoxy matrix in dry conditions, it had been found a very impressive effect on reducing the

friction coefficient and increasing wear resistance when the composite was contacted with A36 steel. Graphite reduced the friction coefficient from 0.48 to 0.25 and the wear volume of the composite drop down about two orders of magnitude. It found to be effective when added less than 30 vol%. In the case of MoS_2 , the wear rate decreased but the friction coefficient remained unchanged. In the case of both graphite and MoS_2 were present in the composite, the friction coefficient can be as low as 0.25 and the wear volume dropped effectively. Another study reveals that the increased volume fraction of carbon fibers was found effective in tribological properties of epoxy composite reinforced with woven carbon fiber. It led to a decrease in the coefficient of friction and wear loss and the tribo-surfaces became smoother. The coefficient of friction decreased due to carbon fibers acted as a solid lubricant between surfaces. In one study of glass fiber reinforced polyester and a carbon fiber reinforced polyphenylene sulfide, it reveals that the glass fiber reinforced polyester had self-lubricating ability without additional lubricant and carbon fiber reinforced polyphenylene sulfide had a self-protecting ability. Self-lubricating ability was found dependent on the load and speed while the self-protecting ability was found independent of load and speed. In the case of glass fiber reinforced polyester, there was a lubricating polymer film which reduced the abrasive nature of the glass fibers while carbon fiber reinforced polyphenylene sulfide created its self-protecting film which was found independent of the applied load and applied speed, resulted in protection and the composite did not found the wear loss. In another study, glass fibers were used to reinforce an epoxy to which additives of PTFE, graphite, and molybdenum disulfide were used to produce a self-lubricating material. The composite of glass fibers reduced the coefficient of friction value to as low as 0.02. One research on polystyrene (PS) and MoS_2 in oleylamine composites which were prepared by the solvent blending method showed better tribological properties than pure PS. The friction coefficient and wear loss of PS composites decreased with the addition of MoS_2 in oleylamine. The MoS_2 in oleylamine nanosheets separation and extrusion out of the matrix were found responsible for the friction coefficient reduction. PTFE + MoS_2 + glass fibers and PTFE + bronze particle composites were tested for friction coefficient and wear rate in one study. The PTFE with additive MoS_2 composite had shown a good coefficient of friction compared to the other one. Unfilled PEEK exhibited a relatively high wear resistance compared with carbon fiber (30%), glass fiber (30%) and carbon fiber (10%) + graphite (10%) + PTFE (10%) composites. However, it showed the highest friction coefficient of 0.38 in the study when it was contacting with an oscillating chromed steel shaft.

Composite reinforced by carbon fiber and modified by graphite and PTFE as internal lubricants, did show the best self-lubricating behavior under all operating conditions, including varying speeds and loads. However, it significantly reduced its wear resistance. Carbon fiber reinforced PEEK composite showed the best overall tribological characteristics among four test materials. Carbon fibers were superior to glass fibers in enhancing sliding wear resistance.

Table 9 represents the influence of particulate fillers on the mechanical properties of nylon matrices in detail. From Table 9, one chart is drawn for comparing the tensile strength of nylons and nylon particulate composites. It is visible that the micro/nano particulate filler reinforcement increases the tensile strength of nylon matrices by several percentages as shown in Figure 3.

Many researchers have enhanced the tribological performance of nylons by various fillers. Few of the results are shown in Table 10 after COF & wear resistance testing of materials. Table 10 represents the study of wear rates of different nylon composites. It includes nylon type, reinforcement, test environment (i.e. dry or wet), and the effectiveness of reinforcement on the wear rate of the material. Some symbolic representation of Table 10 is described below:

- ⁺ The wear rate of copper-acetate-filled nylon was high because the composite transfer film had poor adhesion to the counterface.
- Φ Transfer film was absent.
- Δ Some CaS decomposed during sliding and FeS and FeSO_4 were produced. No such decomposition was found for CaF_2 . The bonding strengths of the compounds that decomposed were lower than that of CaF_2 which did not decompose. FeS and FeSO_4 formation were responsible for increased adhesion between the composite transfer films.
- ^{*}In most of the cases, where reinforcement was not effective this was due to the large, aggregated particle formation in the matrix material.
- $\#$ The addition of clay affected the crystallinity of the nanocomposites, which in turn affected the plasticization. Plasticization of the surface by water caused an increase in wear and decreases the coefficient of friction.
- $\$$ The wear rate of nylon 1010 increased while the friction coefficient decreased in water compare to dry sliding. The hydrolyzation of amide groups and the decrease in bonds of hydrogen between the molecules of nylon 1010 resulted in a high wear rate of nylon in water.

PTFE & UHMWPE complex solid lubricants improved both frictions and wear behaviors of nylon due to the lower

Table 9: Effect of particulate fillers on mechanical properties of nylons.

Matrix material	Filler(s)	Max. tensile strength (MPa)		Max. flexural strength (MPa)		Max. Rockwell hardness		Max. Izod impact-notched (kJ/m ²)	
		Matrix	Composite	Matrix	Composite	Matrix	Composite	Matrix	Composite
Nylon 66	Al ₂ O ₃ microparticles	75	79 for 6 wt%	111	119 for 6 wt%	97	105 for 8 wt%	5.1	6.02 for 6 wt%
Nylon 6	Al ₂ O ₃ nanoparticles	60	93 for 3 wt%	–	–	–	–	–	–
Nylon 6	Talc and wollastonite microparticles	65	78 for 20 wt%	40	90 for 20 wt%	–	–	10.2	12 for 20 wt%
Nylon 6	Clay nanoparticles	70	91 for 5 wt%	115	146.52 for 5 wt%	–	–	90	91 (J/m) for 5 wt%
Nylon 6	MWNT nanocomposite	20	42 for 1 wt%	–	–	60	100 for 1 wt%	–	–
Nylon 6	Hytre blends, MWNT	39	40 for 15 wt% hytre blends, 65 for 1 wt% MWNT	–	–	–	–	–	–
Nylon 6	Boric anhydride microparticles	52.7	62.9 for 2 wt%	–	–	116	123 for 8 wt%	48.4	45.7 (J/m) for 6 wt%
Nylon 11	HNT nanoparticles	41	44.6 for 1 wt%	–	–	–	–	5.5	3.8 for 1 wt%
Nylon 66	ZrP nanoplatelets	72.7	82.8 for 3 wt%	–	–	–	–	–	–
Nylon 66	GRF	70.21	73.62 for 1 wt% GRF	–	–	–	–	–	–

Figure 3: Comparison of the tensile strength of nylons and nylon composites.

friction coefficient [116]. Also, internally lubricated glass-fiber filled nylon gears showed better performance than nylon gears [117]. Nylon 66 composite exhibited less friction and wear compared to unreinforced when running against steel and aluminum counter faces but when tested against brass, pure nylon 66 exhibited lower wear than the composite had been noted [118]. The characteristics of the different counterface metallic materials and the surface treatment greatly control the wear behavior of nylon 66 and its composites. In one experiment, PTFE filler was found effective on the friction and wear properties of nylon than MoS₂ and the main wear mechanisms were fatigue and abrasion had been noted [119].

Nowadays to avoid the use of external lubrication due to several reasons like contamination, degradation of mechanical properties & absorption, self-lubricated composites are in trends [120–122]. The self-lubrication property of polymer and polymer composite eliminates the requirement of any other external lubrication. Self-lubrication property is advantageous where one cannot use traditional liquid lubrication and where it is almost impossible to reach and do lubrication in a definite time interval. Liquid or grease lubricants are used to minimize friction and wear in the case of metals. When there is an extreme environmental condition like extremely high or low temperatures, vacuum, extreme contact pressure, and absorption (in the

Table 10: Effect of fillers on tribological properties of nylons.

Matrix	Reinforcement	Test environment	Test result	References
Nylon 6	Nano SiO ₂ (2 wt%)	Dry air	Effective (reduction in COF and improvement in wear resistance)	[77]
Nylon 66	PTFE (15 wt%)	Dry air	Effective (reduction in COF and improvement in wear resistance)	[78]
		Water	Reduction in COF	
Nylon 11	CuS, CuO, CuF (35 vol% each)	Dry air	Effective (reduction in wear rate)	[79]
	Copper acetate (35 vol%)		Not effective ⁺	
Nylon 6	Wax (4 wt%)	Dry air	Effective (reduction in wear rate)	[80]
Nylon 11	Nano silica (15 vol%)	Dry air	Effective (35% in scratch and 67% in wear resistance)	[81]
Nylon 11	ZnF ₂ , ZnS (35 and 40 wt%)	Dry air	Not effective ^o (increased specific wear rate 11 times and 15 times respectively and COF increased 15–20%)	[82]
	PbS (<35 wt%)		Effective (reduction in specific wear rate but COF increased 15–20%)	
Nylon 11	CuS (35 vol%)	Dry air	Effective (reduction in wear rate)	[83]
Nylon 11	CaS, CaO (35 vol% each)	Dry air	Effective (reduction in wear rate)	[84]
	CaF ₂ (35 vol%)		Not effective ^Δ (increased wear rate)	
Nylon 66	Long carbon nanotubes (1 wt%)	Dry air	Effective (reduction in COF but wear rate was increased beyond 110 °C)	[85]
Nylon 6	Glass fiber (10, 20 & 30 wt%)	Dry air	Effective (reduction in specific wear rate, lowest @ 30% fillers)	[86]
Nylon 1010	ZnO whiskers (10% & 15 wt%)	Dry air	Effective (reduction in COF & wear)	[87]
Nylon 6	Wollastonite particles (5% & 10 wt%)	Dry air	Effective (reduction in material weight loss due to wear)	[88]
Nylon 66	Fly ash and silica fume (5–25 wt%)	Dry air	Effective (reduction in wear rate, best @ 15% fly ash fillers)	[89, 90]
Nylon 6	Copper (2%)	Dry air	Effective (reduction in COF & wear)	[91]
Nylon 66	Titanium dioxide (TiO ₂)	Dry air	Effective (reduction in COF & wear)	[92]
Nylon6/TiO ₂ (95/5)	PTFE (15 wt%)	Dry air	Effective (reduction in COF & wear)	[93]
	UHMWPE (15 wt%)		Effective (reduction in COF & wear)	
	MoS ₂ (15 wt%)		Not effective (increasing COF and wear rate)	
Nylon 66	SGF (35 wt%)	Dry air	Effective (reduction in specific wear rate)	[94]
	SGF (35 wt %) + MoS ₂ (2 wt%)			
Nylon 6	Pristine clay (60 wt%)	Dry air	Not effective* (worst wear resistance)	[95]
Nylon 6	Al ₂ O ₃ (30%), graphite (20%)	Dry air	Effective (reduction in COF & wear)	[96]
Nylon 66	Nano calcium carbonate	Dry air	Effective (reduction in wear rate)	[97]
Nylon 6	Multiwall carbon nanotubes (1 wt%)	Dry air	Effective (33.8% reduction in penetration depth)	[98]
Nylon 6	Nano Cu/Si (0.5%)	Dry air	Effective (reduction in COF and wear till 0.5% fillers, after that it increases)	[99]
Nylon 6	Nano clay	Dry air	Effective	[100]
Nylon 6	Glass fiber (30 wt%)	Dry air	Effective (reduction in COF and wear till 30% fillers, after that it increases)	[101]
Nylon 6	VGCF (5 wt%)	Dry air	Effective (COF decreasing for a small amount of VGCF and then increasing, wear resistance increasing as the filler content increasing)	[102]
Nylon 6	SiC (10 wt%) – Al ₂ O ₃ (40 wt%)	Dry air	Effective (reduction in wear rate)	[103]
Nylon 6	Carbon fibers (20 wt %)	Dry air	Effective (reduction in specific wear rate)	[104]
Nylon 6	Graphite (5, 10, 15 wt%)	Dry air	Effective (reduction in specific wear rate)	[105]
Nylon 66	Fly ash (15 wt%)	Dry air	Effective (reduction in specific wear rate)	[106]
	Silica fume (15 wt %)			
Nylon 1010	Carbon fibers (20 vol%)	Dry air	Reduction in COF but the increasing wear rate	[107]
		Water [§]	Reduction in COF and wear rate	
Nylon 6	Polypropylene (30%)	Dry air	Effective (reduction in COF and wear rate)	[108]

Table 10: (continued)

Matrix	Reinforcement	Test environment	Test result	References
	Nano clay (2.5, 5 & 7.5 wt %)		Reduction in COF but increased wear rate due to agglomeration)	
GFN (30% glass fibers)	Graphene oxide (0.03%)	Dry air	Effective (~60% reduction in COF and wear rate)	[109]
Nylon 11	Halloysite nanotube (1, 3, 5 wt%)	Dry air	Effective (19% reduction in COF @ 3 & 5% fillers, 49% reduction in specific wear rate @ 3% fillers)	[110]
Nylon 66	Graphene nanoplatelets (1 wt%)	Dry air	Effective (reduction in wear rate)	[111]
Nylon 6	Glass fibers	Dry air	Effective (reduction in wear rate)	[112]
Nylon 6	Organo nano clay (5%)	Dry air	Effective (30% reduction in COF, reduction in specific wear rate)	[113]
Nylon 66	Short glass fibers (20 wt %)	Dry air	Effective (28% reduction in COF, 74% reduction in specific wear rate)	[114]
	Short carbon fibers (20 wt%)		Effective (28% reduction in COF, 45% reduction in specific wear rate)	
Nylon 6	Nano clay (1, 3 & 5 wt%)	Water	Not effective [#]	[115]

Symbols: ⁺, Poor adhesion of composite transfer film to counterface; ^Φ, Transfer film was absent; ^Δ, Poor adhesion of composite transfer film; ^{*}, agglomeration; [#], Plasticization of the surface by water; ^{\$}, Hydrolyzation of amide groups.

case of some polymers), liquid lubricants may not be a good choice for tribological applications. Liquid lubricants should not be used where contamination by a liquid is a problem, at low temperatures where it freezes or become too viscous to pour, and at high temperatures where it thermally breaks down. At such conditions, solid lubricants may be the only choice and can help to reduce friction and wear. Solid lubricants function in the same way, as they made a low shear strength layer that can shear easily between two surfaces and avoid direct contact between surfaces. Solid lubricants can provide low friction and reduce wear damage between the sliding surfaces.

4 Conclusions

It is visible that the mechanical and tribological properties of nylons are enhanced by the various micro- and nano-particulates fillers. The coefficient of friction of nylons is further improved and wear rates are decreased by the particulate filler reinforcements. Tensile strength, hardness, and impact strength of nylons are improved by a small number of particulate fillers. There are few cases where particulate fillers were not effective that was due to the clustering of particles in the nylon matrix or due to the excessive humidity and processing temperature effect or due to the improper compounding of matrix and filler materials. Micro- and nanoparticles are having a large surface area to volume ratio i.e., the smaller the particles, the greater will be the surface area to volume ratio. Particle dispersion

and distribution play a vital role in determining composite properties. To fabricate a good quality particulate composite, the particle agglomerates must be broken down during processing. A twin-screw extruder is having the advantage of better compounding of thermoplastic polymers and fillers over a single screw in this matter. The clustering of particles is a major issue in the case of nanoparticles. The clustering will result in empty spaces in the matrix and the final composite material can be failed due to mechanical forces. An optimum number of particulate fillers in the composite is desired. The highly filled polymers generally suffer from the clustering of particles, the low adhesive strength of matrix with the particles due to the high amount of fillers and ultimately results in the failure of final composite materials. Metallic fillers in nylons are generally useful in improving a few of the mechanical properties, thermal properties, and wear rates. Metallic compounds like oxides and nitrides are beneficial in enhancing the tribological properties of nylons. Still, the results may vary according to the process and process parameters used for the fabrication of composite. Nylon composite's fabrication process requires special attention to the environmental humidity as it can absorb moisture from the environment which can deteriorate the properties of the final product. Drying of nylon is essential before the compounding of matrix and fillers as well as before injection moulding of products.

The effect of filler particles' size on the tribological behavior of nylon composites is the less explored area. Humidity effect on the tribological behavior of nylon composites is also an important aspect and to understand

that more research in this area is required. So still there are vast research possibilities available in the area of polymer composites.

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