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Graphene and polytetrafluoroethylene synergistically improve the tribological properties and adhesion of nylon 66 coatings

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ABSTRACT

In this work, we exploit the bidimensional structure and high stiffness of graphene to improve the tribological response of nylon-based composites. Graphene nanoplatelets, coupled with polytetrafluoroethylene microparticles, synergistically improve the friction coefficient and wear rate, as well as the adhesion to the substrate. The enhancement, as high as threefold for both friction and wear rate at the optimal graphene concentration (0.5% in weight), depends upon the formation of a continuous, robust transfer film with the steel rubbing counterpart, as shown by Raman measurements. The graphene-nylon coating also shows three-fold improved adhesion to the underlying substrate, attributed to the high surface energy of graphene.

1. Introduction

The use of polymers and polymer nanocomposites is increasingly growing in a number of tribology related components, such as bearings, gears, seals, vacuum pumps as well as components for prosthesis and implants in biological or medical applications, to name a few [1,2]. Their increased usage is observed particularly in areas where traditional fluid lubricants cannot be used, or the formation of hard debris must be avoided [3]. Good resistance to sliding contact, together with strong adhesion to the underlying substrate, are also desirable when surface coverage is involved, with coatings as paints and varnishes [4], in microelectronic systems [5] or machine parts [6], etc. Polymeric coatings are a class of the family of solid lubricants, alternative to the spraying of solvent-suspended particles [7–9] when the application of the latter is hindered by incompatible substrate, unadapt environment, danger of contamination. Indeed, the elimination of harmful solvents is one of the objectives of Green Tribology, a growing field within the broader one of Green Chemistry, dedicated specifically to reduce the environmental impact of tribological systems [10,11].

Aliphatic polyamides are extensively used as sliding parts in food packaging, automobile parts, engineering products and bearings [12–14]. Among various polyamides, nylon 66 has been widely used in industry due to its excellent physico-chemical properties, such as high melting point, low permeability, low melting viscosity, ductility, heat resistance, etc. [15]. However, despite the good mechanical and tribological properties of polyamides as bulk components [16], their use as coatings is limited by their poor adhesion to substrates, due to their low surface energy and weak mechanical interlocking mechanism [17]. A possible approach to the improvement of adhesion is based on the addition of different fillers, exploiting their stronger interaction with the substrate or the improved formation of anchor points for mechanical interlocking [18,19]. Yet the main purpose of fillers is to improve the mechanical properties of polymeric materials, and, among them, their tribological response. The most common fillers to reduce friction and wear include hard ceramics such as alumina, polytetrafluoroethylene (PTFE), molybdenum-disulfide (MoS_2) and carbon based materials, often prepared in nanometric size [20,21]. However, these fillers have some limitations, for instance PTFE is well-known for low friction, but has poor wear resistance [22], MoS_2 performs poorly in the presence of humidity [23,24] and graphite has restriction of operating in dry or vacuum environment [25]. Compared to such conventional fillers, graphene has gained great attention in recent years because of its exceptional electrical [26], mechanical, thermal, structural properties and has already shown promising results in tribology as a lubricant additive [27]. As an additive, graphene can have a strong effect on the mechanical

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properties of a composite material, owing to its high strength (~130 GPa) and elastic modulus (0.5–1 TPa) [28,29]. Graphene has been employed as a filler for different polymers, among which Lahiri et al. incorporated graphene nanoplatelets (GNPs) as a reinforcement element in ultrahigh molecular weight polyethylene to improve its fracture toughness and tensile strength [30], Xu et al. reported the enhancement of tensile strength and Young's modulus by the in situ polymerization of graphene nylon 6 polymer [31], Cataldi et al. studied the improvement in modulus of stiff and soft polymers by the addition of graphene with different thermal treatments [32]. Apart from effect on bulk properties of a composite material, graphene has unique characteristics of interfacial interaction with different substrates, such as silica, copper and nickel [33,34].

Despite the physical properties that make graphene a promising candidate as a solid lubricant or as an additive, such as its bidimensional structure, high strength and low permeability to gases [35], its use in the field of tribology is relatively unexplored, if compared to other carbon-based materials [36]. Graphene nanoplatelets have been proposed as a thin solid lubricant [37,38] and have shown high wear resistance especially at nanoscale [39,40], but only in few works its performance in macroscopic solid materials has been investigated [41,42]. Notably, Kandanur et al. reduced the wear rate of PTFE by addition of 10 wt% graphene platelets [43]. A limiting factor to the widespread use of graphene as a tribological material is its friction coefficient (0.1–0.2) [44] which is still higher than that of the best performing materials, such as PTFE (<0.05).

In this work, we aim to study polymer composites, containing GNPs as solid lubricants. Nylon 66 is chosen as the polymer matrix, due to its wide use in the industry. Nylon 66 is usually processed by extrusion or hydraulic press to form bulk specimens, or dissolved in solvents like formic and hydrochloric acids or cresol [45,46] resulting in porous membrane with poor mechanical properties, unsuitable for use where tough mechanical parts are needed. Recently, a new solution-based method was developed [47] to produce nonporous films with good mechanical properties, which were further improved by the addition of GNPs. Here, we propose this novel route for the study of nylon 66/GNPs as a coating incorporating also PTFE for tribology application. The GNPs/nylon 66/PTFE composites show strong adhesion and a three-fold reduction in friction and wear rate, compared to the pure nylon 66. The best performance was obtained for an amount of GNPs of 0.5% in weight.

2. Materials and methods

Nylon 66 (PA66) was purchased from Sigma-Aldrich (molecular weight MW = 120,000; degree of polymerization DP = 531; density $\rho = 1.14$ g/mL). Grade Pure G+ Graphene nanoplatelets (GNPs), with lateral dimension of a few micrometres and a thickness of a few nanometers [48], were kindly provided by Directa Plus (Lomazzo (CO) – Italy). Polytetrafluoroethylene (PTFE) with nominal particle size of 1 μm, aluminum oxide nanoparticles with nominal particle size of 13 nm and Ethyl Cyanoacrylate (Permabond 105) were purchased from Sigma-Aldrich.

Reagent grade solvent trifluoroacetic acid (TFA), dimethyl sulfoxide (DMSO) and acetone were purchased from Sigma-Aldrich and used as received.

2.1. Sample preparation

Composite coatings of nylon 66 were prepared using different GNPs concentrations while keeping constant the concentration of PTFE with respect to the nylon 66. The preparation of the nylon 66 is described in detail in Ref. [47]. Briefly, nylon 66 was first dissolved in solution of TFA and acetone with 1:1 vol ratio to obtain 7 wt% polymer in solution. After the nylon 66 pellets were completely dissolved, PTFE was added to the solution at concentration ratio of 5 wt% with respect to nylon 66. GNPs were then added at different weight fractions, ranging from 0 wt% to 3 wt% with respect to nylon 66. Solutions were bath sonicated at 40 Hz for 3 h and at 59 Hz after 24 h to get homogeneous dispersion of both PTFE particles and GNPs. The choice to include PTFE in all composites was taken after screening tests (not reported) showed significantly higher friction when it was not added.

Glass substrates were cut to a rectangular shape, cleaned with acetone and bath sonicated for 60 min for the removal of residues. A simple dip coating method was used for the deposition: the substrates were dipped in the solution for 10–15 s and left in fume hood for the solvent to evaporate. All the samples prepared and their labels are presented in Table 1.

Additional samples were fabricated with the same technique substituting GNPs with alumina nanoparticles, as a reference for the tribological tests. Details on these samples are reported in the supporting information, Table S1. Samples of Ethyl Cyanoacrylate (ECA) were also deposited with the same technique starting from a solution of dimethyl sulfoxide (DMSO) and acetone, as a reference for the adhesion tests.

2.2. Morphological characterization

The morphology of the films was studied by Optical Microscopy (Leica DM 2500 M) and Scanning Electron Microscopy (SEM, JEOL JSM-6490AL operating at 10 kV and JEOL JSM 7500FA operating at 5 kV). Films were sputtered with a thin layer of gold or graphite before observation to improve conductivity.

Grazing Incidence X-ray Diffraction (GIXRD) analysis was performed on a Rigaku Smartlab equipped with a 9 kW CuKα rotating anode, operating at 40 kV and 150 mA. A Göbel mirror was used to convert the divergent X-ray beam into a parallel beam and to suppress the Cu Kβ radiation, while a 0.5° Parallel Slit Analyzer was employed in the receiving optics. The diffraction patterns were collected with a fixed grazing incidence angle ω of 3° and over a 2θ angular range from 7° to 60°, with a step size of 0.05°. The specimens were placed on a zero-diffraction quartz substrate and measured at room temperature. GIXRD data analysis was carried out with the PDXL 2.1 software from Rigaku.

2.3. Mechanical characterization

The Young's modulus and hardness of the samples were characterized by nanoindentation on an Anton Paar UNHT equipped with a diamond Berkovich tip. Maximum load was 1 mN, loading and unloading time 30 s, with a dwell time at maximum load of 30 s to allow viscous relaxation. Young's modulus E and hardness H

Table 1
Labels and PTFE and GNPs concentration of the prepared samples.

Sample label	Concentration (Nylon 66 to 100%)	
	PTFE wt.%	GNPs wt.%
P0G0	0	0
P5G0	5	0
P5G0.1	5	0.1
P5G0.2	5	0.2
P5G0.3	5	0.3
P5G0.4	5	0.4
P5G0.5	5	0.5
P5G1	5	1.0
P5G2	5	2.0
P5G3	5	3.0