

Thiol–Yne Photocurable Isosorbide-Derived Networks: Formulation and 3D Printing

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# Investigation about tribological behavior of ABS and PC-ABS polymers coated with graphene

**Authors:** Andrea Mura<sup>\*a</sup>, Federica Adamo<sup>a</sup>, Haozhe Wang<sup>b</sup>, Wei Sun Leong<sup>b</sup>, Xiang Ji<sup>b</sup>, Jing Kong<sup>\*b</sup>

<sup>a</sup>Politecnico di Torino, Department of Mechanical and Aerospace Engineering, C.so Duca degli Abruzzi 24 - 10129 Torino Italy.

<sup>b</sup>Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA, United States

\*E-mail: andrea.mura@polito.it; jingkong@mit.edu;

## Abstract

Graphene is an amazing material that finds application in many fields. In particular, graphene can be used as anti-friction material. Even if graphene has been already tested as lubricants additive, the use as friction reduction coating is not widely investigated. In this paper, the tribological performance of graphene-coated polymers has been investigated. In particular ABS (Acrylonitrile Butadiene Styrene) and PC-ABS (PolyCarbonate-Acrylonitrile Butadiene Styrene) have been investigated as polymers widely used in industrial field. Samples have been coated with graphene by means of a dedicated procedure. Tribological performance has been evaluated by ball on disk tests, taking into consideration different travelled distances in order to evaluate also the coating wear strength. Results show that graphene coat may reduce coefficient of friction of the tested materials although the wear strength of the coating is quite weak.

**Keywords:** graphene; coefficient of friction; plastic; polymers; wear

## 1. Introduction

Polymers are nowadays used in countless applications. The replacement of metal parts with polymeric ones in new technological devices and machines has become increasingly significant, and sliding parts of many components are made of plastic. The idea to use polymers in sliding system is arousing much interest in the field of tribology research due to its characteristics as low cost, vibration damping capacity, corrosion resistance and ability to work in the presence of contamination. However, it is known that polymers have lower mechanical strength and tribological performance than metals [1]. Furthermore, the same methods used to improve wear performance in metals, such as liquid lubricants, cannot be used with polymers, as they often degrade polymers and reduce their functionality [2].

There are many studies about improving tribological characteristics of polymers. A way to reduce the coefficient of friction and wear on polymers is to add solid lubricants as “fillers”. The presence of solid lubricants inside polymers decreases the stress needed for sliding, leading to a significant reduction of coefficient of friction and wear rate [3]. The most common solid lubricants used as filler for polymer are PTFE (poly-tetrafluoroethylene) [4-8], MoS<sub>2</sub> (molybdenum disulphide) [9-10], and graphite [11-15], but also nano-fillers such as alumina, carbon nanotubes and zinc oxide [16-18]. Another way to improve tribological performance is the surface modification. In fact, solid lubricants in the form of bonded coatings are used in a greater variety of applications promoting the reduction of friction and wear [19-23].

Recently, an innovative material has been added to the category of solid lubricants: graphene. Discovered in 2004 from Geim and Novoselov [24], it is well known for its excellent characteristics such as high mechanical, thermal and electrical properties [25]. Among all exceptional features, tribological one is also included. Recent studies investigated the possibility to use graphene as additive for liquid [26-29] and semi-solid [30, 31] lubricants, demonstrating its effectiveness in reducing friction. Graphene was also used as

a wear suppressant additive in polymers. In 2012, Kandanur et al. [32] used graphene as PTFE additive, achieving a higher wear strength and tribological performance of the graphene/PTFE composite compared with neat PTFE. As reported in literature [33-35], there are several other similar researches related to graphene-based polymers nanocomposites. Moreover, graphene has been also used as coating of metallic materials, demonstrating its capacity in improving the tribological behaviour and extending the life expectancy of these materials [36-38].

Up to now, many papers investigated graphene used to cover metallic materials, whereas very few studies are related to the use of graphene as polymers coating. Pan et al. [39] evaluated wear performances of PPS (Polyphenylene Sulfide) composite coatings reinforced by graphene, demonstrating its effectiveness in reducing wear and, consequently, in increasing over seven times the life of the composite coating. Chih et al. [40] investigated the frictional behavior of coatings based on graphene/ultra-high molecular weight polyethylene composites and sprayed graphene, obtaining a reduction of coefficient of friction in graphene coated material. In a more recent work, Puertolas et al. [41] tested poly ether ether ketone /graphene nanoplatelets composites finding out that GNP fillers provide a positive influence on both coefficient of friction and wear rate.

The purpose of this study is to investigate the use of graphene as a coating for polymers in order to improve their tribological characteristics. Non-polymer-on-polymer contact has been analysed, focusing in particular on ABS (Acrylonitrile Butadiene Styrene) and PC-ABS (PolyCarbonate-Acrylonitrile Butadiene Styrene) polymers rubbing against steel. ABS is one of the most widely used and versatile thermoplastic characterized by a wide range of properties such as toughness and rigidity, high tensile strength and stiffness and good chemical resistance. These characteristics make the ABS suitable for various applications as in electronic and automotive fields. PC-ABS is a thermoplastic polymer made of Poly

Carbonate and ABS; it offers the best properties of both materials as the superior strength and heat resistance of PC and the flexibility of ABS. The PC-ABS blends are commonly used in electronics, automotive and telecommunications applications.

In the present work, the potentiality of graphene as polymer coating has been evaluated. For this purpose, a set of pin-on-disk wear tests have been carried out. Coefficient of friction and average worn volume have been evaluated considering different sliding distances and compared with those of uncoated materials.

## **2. Materials and methods**

ABS used in this work, is known as SicoflexS460 and produced by Ravago Group Company, with density  $1.04\text{g/cm}^3$ . Concerning PC-ABS material (a blend of polycarbonate and acrylonitrile butadiene styrene), it is commercialized as Cycloy1200HF and produced by Sabic Company, with density  $1.15\text{g/cm}^3$ . Samples have been obtained by cutting from a bar and then coated with graphene layer. The sample dimensions are about  $10\times 10$  mm with 4 mm thickness. Tests have been performed on both coated and uncoated sample in order to compare the tribological performance.

### **2.1 Coating process**

Samples have been coated using the procedure described by Li et al. [42]. First of all, few-layer graphene flakes are produced using an electrochemical exfoliation method from graphite [43]. The electrochemical exfoliation has been performed using a platinum wire as grounded electrode and a graphite as bulk material to produce graphene flakes within an electrolyte solution. Applying 10V bias the graphite rod has been dissociated in flakes collected by filtration and then re-dispersed in dimethylformamide. The graphene flakes

solution has been further centrifuged to remove the unwanted side products and thick graphite particles, obtaining a narrowed thickness distribution.

The obtained product is added in ethanol with a mass concentration of  $1 \text{ mg mL}^{-1}$  and is injected on the surface of DI water. The graphene dispersion quickly spreads on the DI water surface due to the Marangoni effect. A self-assembly process of Ultrathin Graphene Film (UGF) on the surface of DI water follows: graphene flakes collide and tie with each other via  $\pi$ - $\pi$  interactions as ethanol evaporated. Then, the specimen is immersed in the solution and then take out, with the UGF covering the polymer surface. This follows by drying the coated samples at  $75^\circ\text{C}$ . With this process, it is possible to obtain graphene thickness of about 2.5nm corresponding to two or three atomic layers.

### **2.3 Tests description**

Tribological tests have been performed by means of an Anton Paar pin on disk tribometer, with two types of plastic materials: ABS and PC-ABS with and without the graphene coating.

Plastic samples have been tested using a stainless steel ball with diameter 6mm, applying a normal load of 5N. Sliding speed has been set constant in all tests (50mm/s). The maximum static contact pressure, calculated by the Hertz's theory is about 60MPa for both the ABS and PC-ABS samples (the materials parameters are: elastic modulus of the steel 210GPa with Poisson's ratio of 0.3; ABS elastic modulus 2.6GPa with Poisson's ratio of 0.35; PC-ABS elastic modulus 2.4GPa with Poisson's ratio of 0.35).

Tests have been performed with different sliding distances in order to evaluate the effect of the evolution of the coating layer conditions on tribological properties. In particular, tests have been performed at respectively 200m (Test 1), 1m (Test 2) and 0.5m (Test 3) total travelled distance. In Test 1, the sampling frequency for the coefficient of friction (CoF) has been set at 100Hz, while in Tests 2 and 3 it has been increased at 400Hz. The sampling

frequency for Test1 has been reduced respect to Tests 2 and 3 to allow smaller data files size.

Each test has been repeated three times in order to make sure the reliability and to give a statistical average to the obtained results.

### 3. Results and discussion

Figure 1 reports the surface characterization of the uncoated and coated samples. Optical images and SEM images have been collected in order to evaluate the effect of the coating. From the optical microscope images the presence of graphene flakes on the surfaces of both coated samples is revealed by a dispersion of small white particles (Figure1-b, d) absent on the uncoated samples (Figure. 1-a, c). The SEM images also confirm the presence of graphene flakes on the covered samples (Figure 1-f, h, l, n) revealing the structure of the graphene deposited on the surfaces; the flakes seem to be uniformly distributed on the surfaces of both ABS and PC-ABS samples.

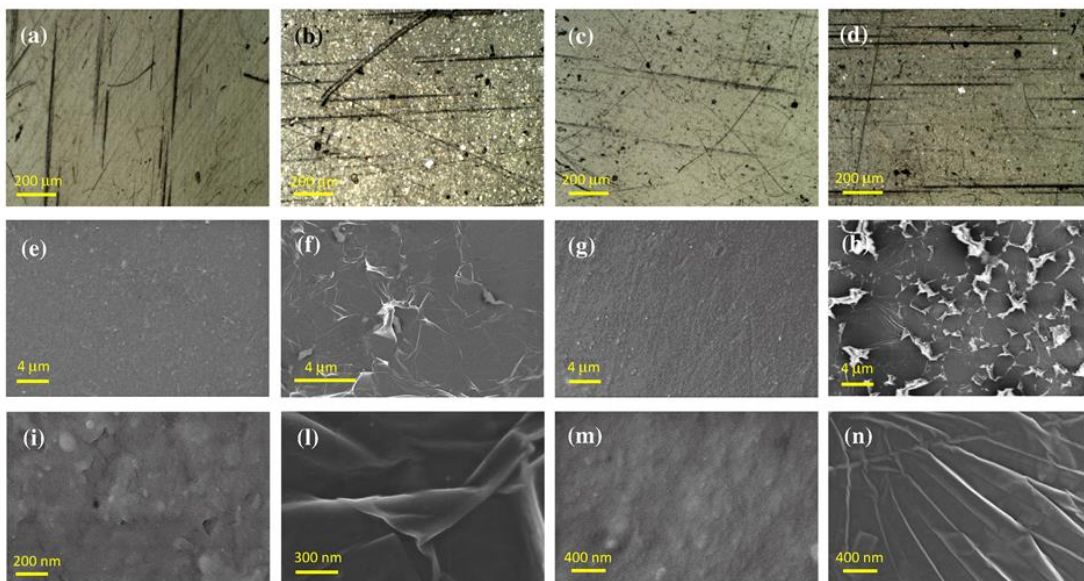


Figure 1. Surface images of the samples. Optical microscope of uncoated ABS (a), coated ABS (b), uncoated PC-ABS (c) and coated PC-ABS (d). SEM images of uncoated ABS (e), coated ABS (f), 6

uncoated PC-ABS (g) and coated PC-ABS (h). SEM images at higher magnitude of uncoated ABS (i), coated ABS (l), uncoated PC-ABS (m) and coated PC-ABS (n).

Concerning wear behavior, samples worn volume has been measured, according to ASTM G99 [44] standard, by measuring the track width at three different locations of the sample surface (at about 120° distance one from the other) and then averaged. Wear track width has been measured by means of an SM Metrology Systems PGS200 profilometer.

Figure 2 shows the average worn volume measured after tests at 200m (Test 1). Results show that, for both materials, graphene layer reduces wear strength as the worn volume measured in coated samples is higher respect to the one measured in uncoated samples. In particular, in coated PC-ABS samples the worn volume increases of about 72% and in ABS coated samples it increases of about 43%. Tests performed at shorter sliding distances (Tests 2 and 3) show negligible worn volume (it was not possible to measure the track width as the wear tracks were very weak).

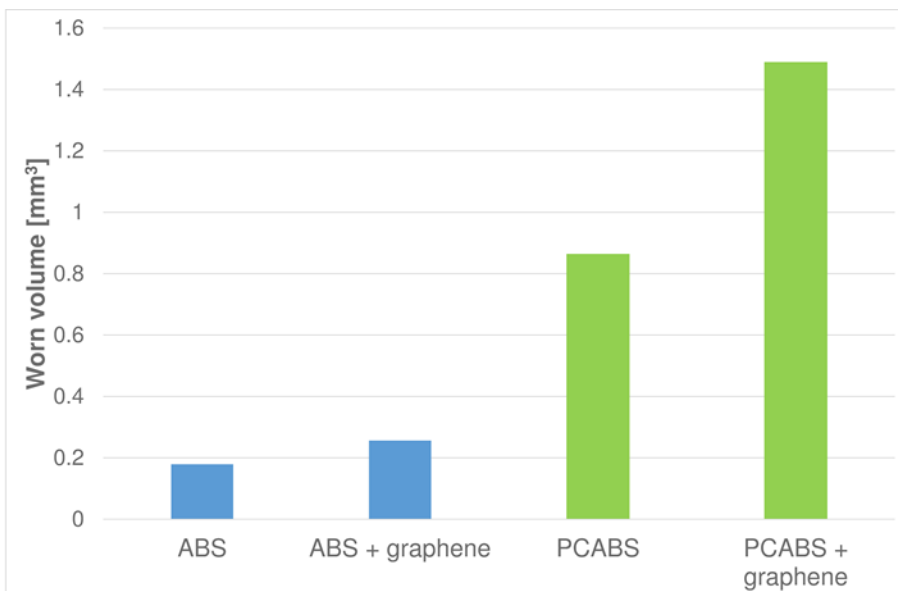
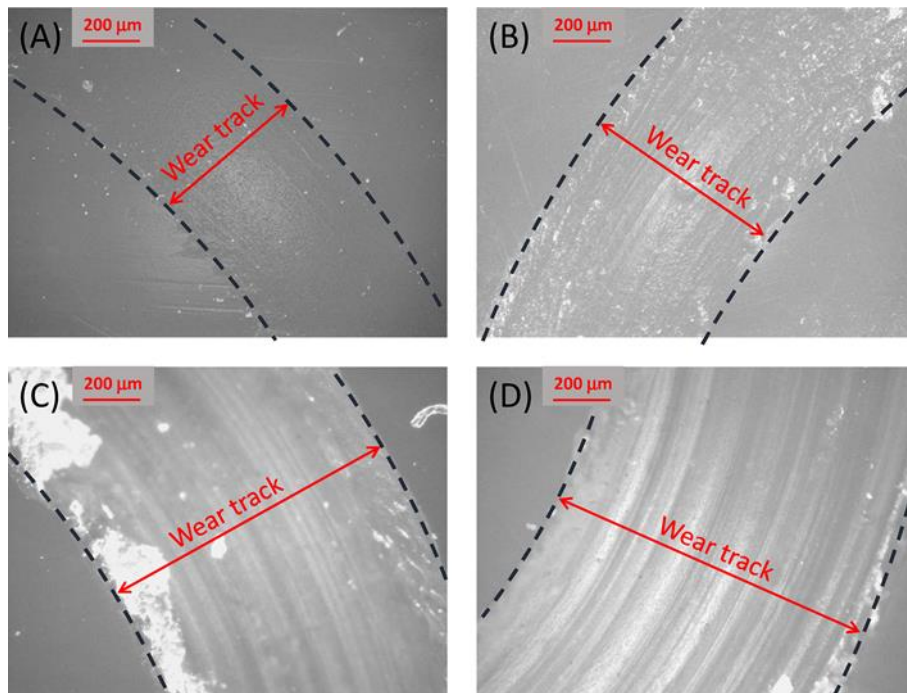


Figure 2. average worn volume in coated and uncoated samples after 200m sliding distance.

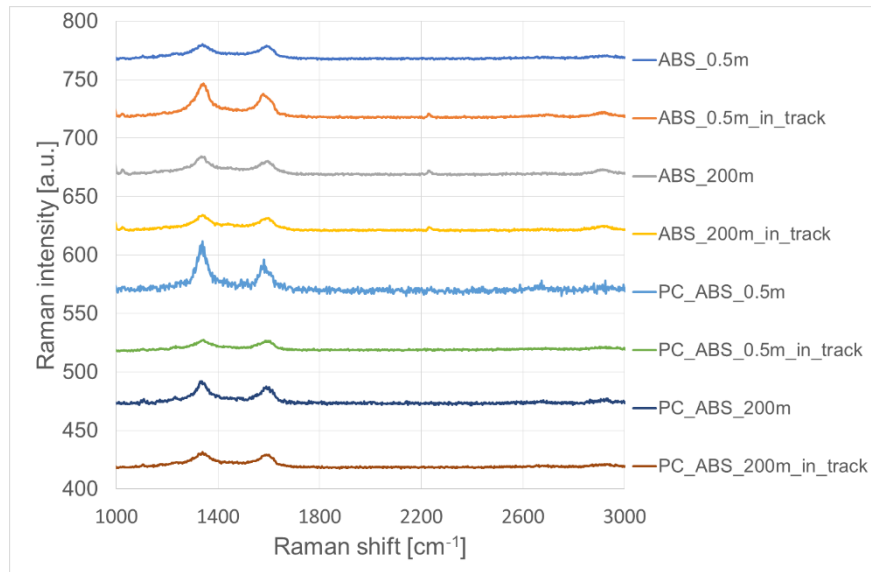
Figure 3 shows the samples surfaces after 200m travelled distance. The track width appears to be different between the four kind of analyzed samples. There is an important difference between the coated samples and the uncoated samples: the width track of the ABS with graphene coating appears to be larger than the ABS without coating; the same occurs for the PC-ABS samples.



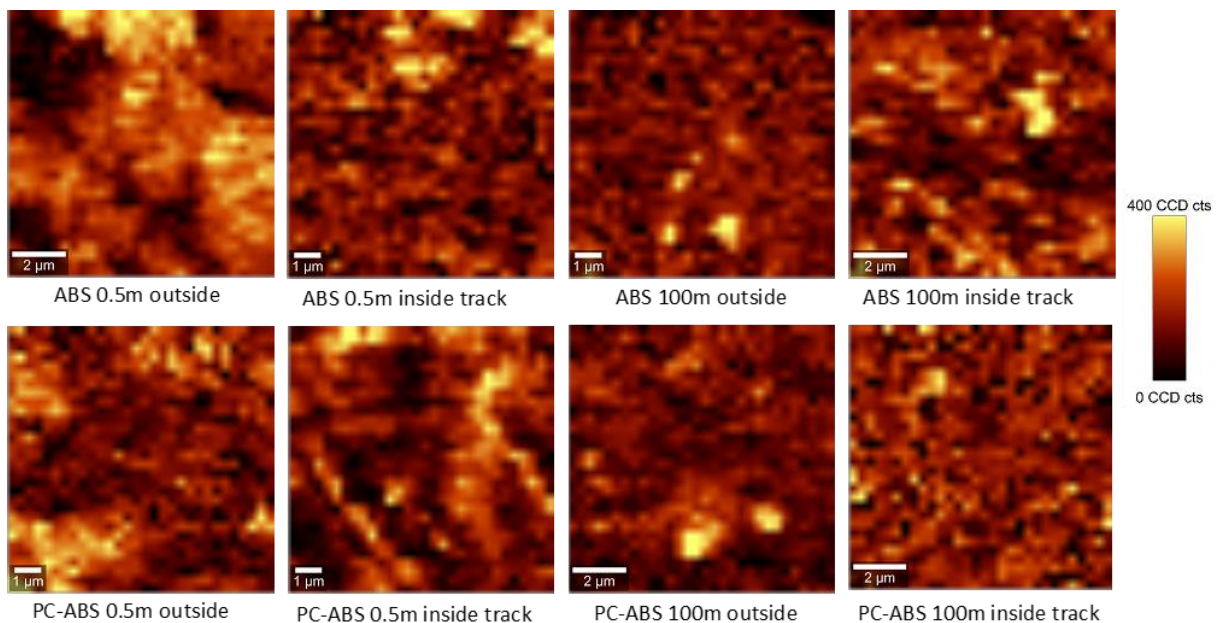
**Figure 3. Optical microscope images of samples after test 1(200m travelled distance): (A) uncoated ABS; (B) coated ABS; (C) uncoated PC-ABS; (D) coated PC-ABS. The scale bars are all 200µm**

Raman analysis performed on all samples, confirmed the presence of percolative graphene inside the track. As can be seen in Figure 4, similar graphene signals were captured inside and outside the track, for both ABS and PC-ABS samples, while no Raman signals were detected on uncoated ABS and PC-ABS substrates. This confirms that although wear damage is clearly visible on the samples and therefore the coating layer is damaged, graphene is still present inside the worn area, affecting tribological behavior of materials.

In addition, for each sample, 900 Raman spectra was collected over an area of 10 $\mu$ m\*10 $\mu$ m and the G band intensity map (that corresponds to the Raman peak at 1580  $\text{cm}^{-1}$ ) is represented in Figure 5. The presence of G band intensity everywhere in the mapped region shows that percolative graphene exists inside the track universally, similar to that outside the track.



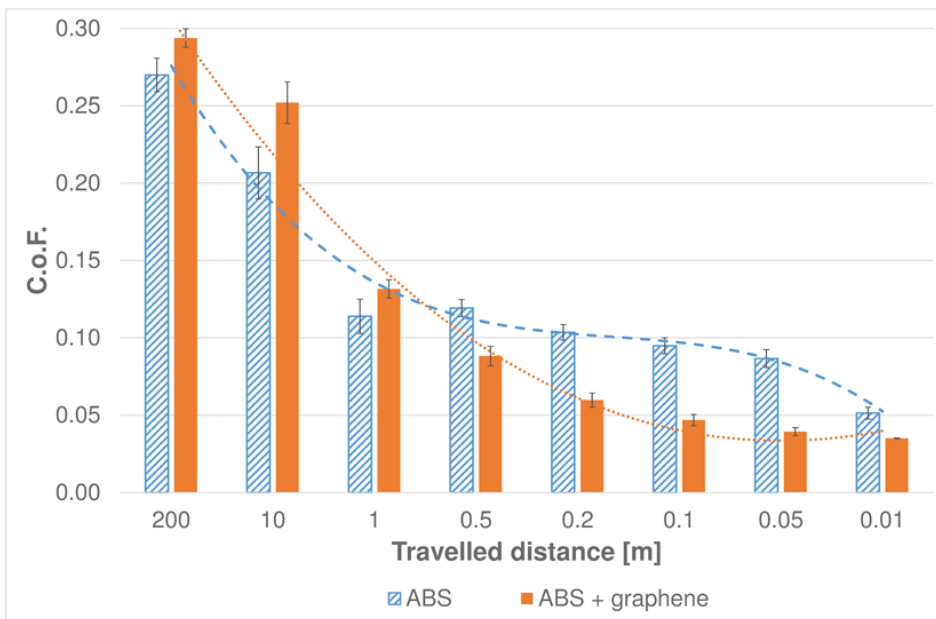
**Figure 4. Raman spectra graph**



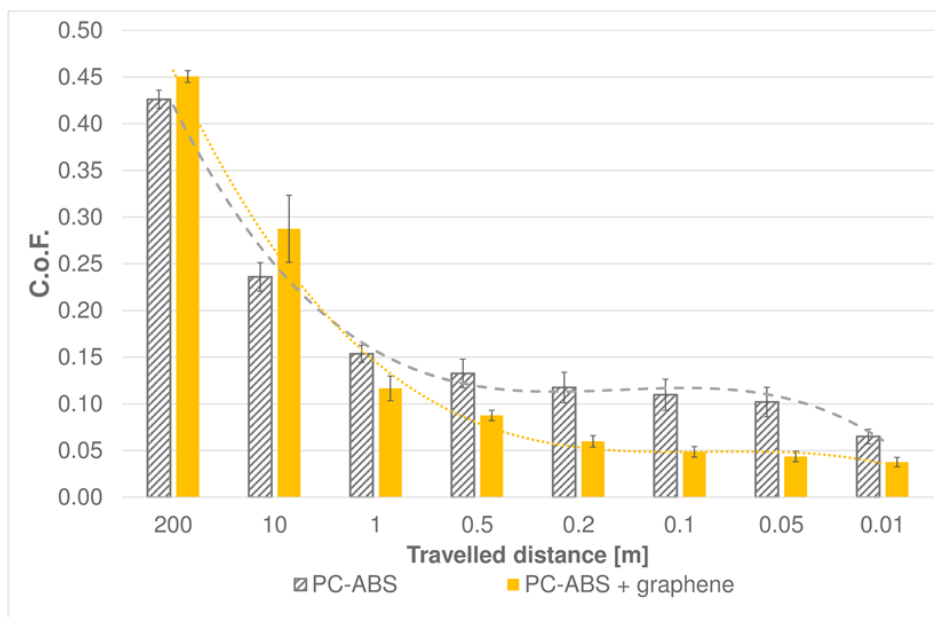
**Figure 5. G band intensity maps.**

The coefficient of friction has been evaluated calculating the average value after different travelled distances, in order to better understand the graphene coating behavior and its wear damage evolution while the testing is evolving.

Figures 6 and 7 show the CoF trend of respectively ABS and PC-ABS samples at different travelled distances (from 0.01m to 200m) together with the standard deviation.



**Figure 6. Trend of CoF for ABS samples**



**Figure 7. Trend of CoF for PC-ABS samples**

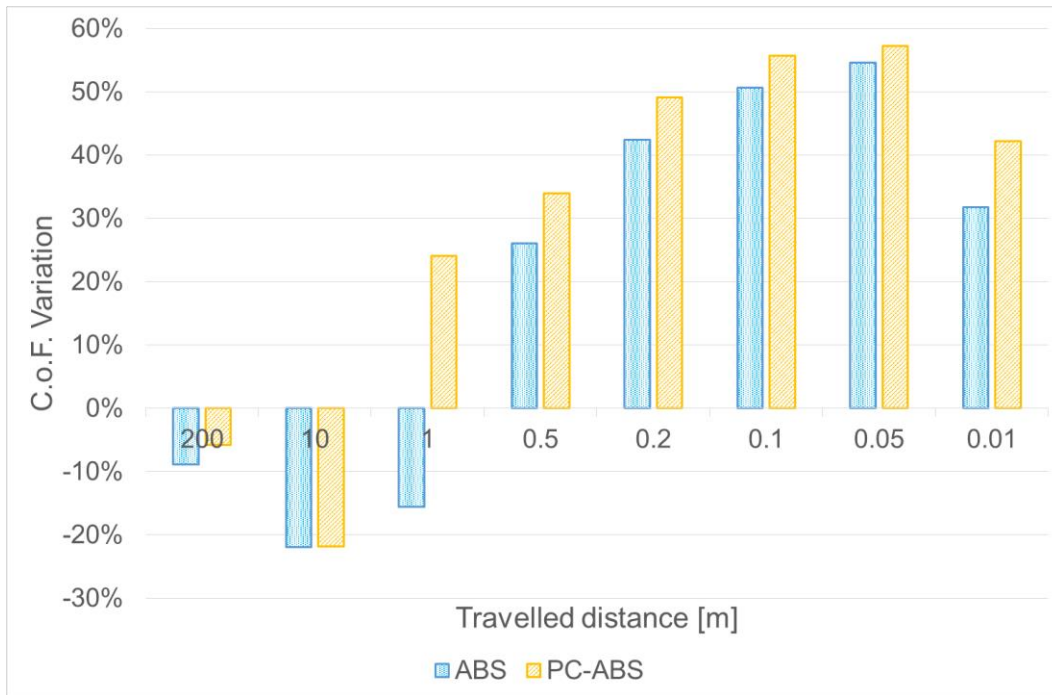
The average CoF of the uncoated ABS samples (Figure 6) varies from 0.051 to 0.270 for respectively 0.01m tests to the 200m tests. The trend is similar for the ABS + graphene samples characterized by a minimum value of CoF equal to 0.035 (at 0.01m of sliding distance) and a maximum value of CoF equal to 0.294 (at 200 m of sliding distance).

Results of the PC-ABS (Figure 7) samples for the 200m sliding distance tests, show higher values of average CoF for coated samples respect to uncoated ones (CoF = 0.426 in uncoated PC-ABS and CoF = 0.451 in coated PC-ABS). In addition, in this case the minimum values of average CoF have been obtained at 0.01 m tests: 0.065 for uncoated PC-ABS and 0.038 for PC ABS + graphene.

It is interesting to highlight that for both materials, the CoF values in coated samples are smaller respect to uncoated samples, up to a certain sliding distance and then they increase. In particular, for ABS samples, the benefit of grafene coating is appreciable up to 0.5 m sliding distance and in PC-ABS up to 1m sliding distance. This behavior could be explained with the failure of grafene layer due to wear process, as also reported in [40] where graphene/ultra-high molecular weight polyethylene composites heave been tested.

Figure 8 resumes the CoF variation for the coated materials respect to the uncoated materials. The behaviour of the two different materials is similar and the trend appears characterized by two regions: the first one in which the CoF variation is negative (indicating an increase on CoF) and the second one in which the values are positive (indicating a decrease of CoF). More in detail, in case of the tests at 200 m and 10 m of travelled distance, the CoF undergoes an increase in values respect to the uncoated materials up to 20%. Indeed, in all the tests at 0.5m or less of sliding distance the variation of CoF is positive, showing a decrease in the CoF respect to the uncoated materials. The maximum decrease of CoF occurs for the test at 0.05 m of sliding distance and it is equal to 55% and 56% for

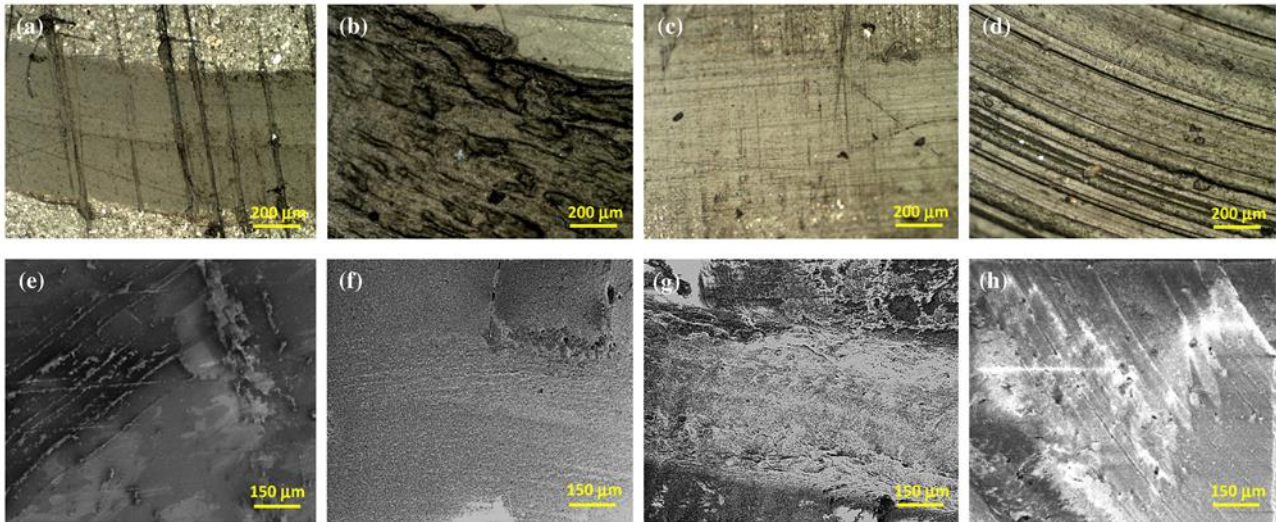
ABS and PC-ABS respectively. The decrease in CoF of PC-ABS appears to be slightly higher than the ABS for all travelled distances. Moreover, the CoF variation starts to be negative at 1m of travelled distance for the ABS and at 10 m for the PC-ABS.



**Figure 8. Comparison of CoF values variation at different sliding distances (negative value means increase of CoF in coated samples, positive value means decrease of CoF in coated samples).**

Figure 9 shows optical microscope images and SEM images of the worn surfaces of the two coated samples (coated ABS and coated PC-ABS). As expected, the wear track of both kind of samples appears to be smaller and smoother in case of 0.5 m of total travelled distance (Figure 9-a, c, e, g) respect to the 200 m wear track. Analyzing the wear track at the end of the test (Figure 9-b, d) a different wear mechanism appears to afflict the samples. In particular, the coated ABS wear track (Figure 9-b, f) is characterized by furrows and spalling, typical of an adhesive wear form. Otherwise, the wear track of the coated PC-ABS after 200m travelled distance (Figure 9-d, h) results to be more defined: in the whole wear scar,

several scratch lines along the sliding direction are present, indicating an abrasive wear form. The difference on the wear mechanism affecting the two different materials confirms the results of the tribological tests, in which the PC-ABS is characterized by better results in terms of CoF reduction compared to the coated ABS sample.



**Figure 9: Surface images of the tracks of the coated materials at different sliding distances. Optical microscope of the coated ABS sample after 0.5 m (a), coated ABS after 200 m (b), coated PC-ABS after 0.5 m (c) and coated PC-ABS after 200 m (d). SEM images of coated ABS after 0.5 m (e), coated ABS after 200 m (f), coated PC-ABS after 0.5 m (g) and coated PC-ABS after 200 m (h).**

#### **4. Conclusions**

In this paper, the effect of graphene layer on coefficient of friction of PC-ABS and ABS plastics has been investigated. After coating, samples have been tested by means of pin on disk test and the behavior of CoF vs the total sliding distance has been acquired. Results show that graphene layer reduces the CoF of both materials, but when wear damage increases, the benefits of graphene layer are reduced until the CoF increases compared to uncoated samples.

Wear tracks have been analyzed by means of both optic microscope and SEM to better understand the wear phenomena. Both adhesive and abrasive wear damage have been found in the samples, in different amount depending on both the total travelled distance during the test and the kind of the sample material. Raman analysis has been performed inside the wear track showing the presence of graphene even when the wear phenomena damages the graphene coatings.

## 5. **Aknowledge**

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