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## Tribological characterization of modified polymeric blends

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### Abstract

The present work reports of a series of experimental tests with two polymeric materials, a thermoplastic polyurethane (TPU) and a polyamide (PA), modified with the inclusion of additives, in terms of their tribological properties of friction and wear. Many thermoplastic materials are in fact used in applications with sliding contact and friction (as in journal bearings, supports...) and, to improve their properties, the polymer is modified with additives having the capacity to change the surface properties.

Used additives are of several types: in this work a comparison is made between graphite, polytetrafluoroethylene, a silicone (siloxane), molybdenum disulfide, and carbon nanotubes. For each additive, different percentage in weight have been considered. All these materials can modify the surface properties of the base material exploiting different physical and chemical phenomena. Moreover, the presence of such additives can alter the mechanical properties of the materials sometimes reducing stiffness, strength, and strain limit.

The work reports of the experimental methods obtained with a typical tribological test (pin-on-disk method) to measure the tribological properties of the compounds in terms of friction and wear, together with mechanical tests. The analysis will show correlations between the composition, in terms of type and quantity of the additive, on the properties of the compounds.

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## 1. Introduction

Plastic materials are of paramount importance when dealing with the current widespread trend towards *lightweight design*. Their peculiar properties of low density, low cost, and flexibility in terms of both design and manufacturing, make them ideal for the process so-called of *metal replacement*, see Kerns (2016) or Platt (2003). Of course, total metal replacement is nonsense because not always convenient from many points of view. However, there is plenty of examples of efficient replacement of a more conventional material (mainly steel or other alloys) with a special polymer or a techno-polymer, see Lewis (1993). The process is not a straight and simple replacement of material: to exploit the advantage of plastics a re-design of the component is mandatory, together with a re-design of the whole manufacturing process, including assembly. Assembly can be sometimes simplified or even avoided with a smart re-design allowing to introduce internal joints or hinges.

One of the most interesting situations where a partial metal replacement can be efficiently carried out is in journal bearings and other connections where friction, and consequently wear, is involved. In these situations, one of the parts, more commonly the shaft, remains made of metal (typically a ferrous alloy) while the other will be in some plastic material with high strength and resistance to wear. Concurrently, reduction in the coefficient of friction is also highly welcome to decrease dissipation of energy that could induce problems due to heating and temperature increase but also losses of efficiency. Among the plastic materials with higher strength and wear properties, Sinha (2002) and Briscoe et al. (2002), there are PTFE (polytetrafluoroethylene), POM (polyoxymethylene or acetal resin), UHMWPE (ultra-high molecular weight polyethylene), PA (polyamide) and TPU (thermoplastic polyurethane), and secondarily, PES (polyester). As is well known, talking of a family of such polymers doesn't mean to represent a set of properties within a relatively small range: most properties (physical, mechanical, optical...) often vary of a large amount depending on the grade from the same manufacturer and between different manufacturers, and can also largely change depending on environmental influences (temperature, moisture...) and processing. Therefore, from selection of a plastic material to design, the freedom to search for a specific property is compensated by the uncertainty about the precise value of each characteristic.

Tribological systems are always very complex, even more when plastic materials are involved. In Zhang S.W. (1998) a review is made about different polymeric materials showing their peculiar problematic including lubrication, timing, frequency, and type of loading, composition and modifications by additives: all of these factors can be of different influence. Myshkin et al. (2005) also examined the influence of surface properties, contact mechanisms, temperature, speed and load, on wear and friction of some of the previously indicated polymers, showing a correlation between wear and strength.

TPU, a block copolymer consisting of alternating sequences of hard and soft segments or domains obtained by the reaction of diisocyanates with short-chain diols and diisocyanates with long-chain diols, is an important class of plastics because of the variable combination of good processability and flexibility that has demonstrated interesting properties of wear resistance, as shown by Yahiaoui et al. (2014). In that paper they examined the influence of load, velocity and temperature in the contact with steel under dry conditions of friction. Martínez et al. (2010) also examined the influence of load on the wear of TPU and correlated with the fatigue strength. The wear mechanisms in TPU were examined by Elleuch et al. (2007) confirming a correlation between friction and wear. The effect of additives has been studied by many authors: Akbarian et al. (2008) concluded that reinforcing with aramid fibers, despite increasing strength, was detrimental for wear resistance; on the contrary Tan et al. (2008) obtained improved abrasion resistance by adding ethylene-propylene-diene monomer rubber; Hill et al. (1996) and Bremner et al. (1996) showed that an increase in wear resistance up to 20% could be obtained with a small concentration of PDMS additive. TPU can also be used as an additive to other polymers such as in Pomali et al. (2008) who examined blends with PMMA, but the result is that TPU was detrimental for abrasion resistance.

Polyamides, the first engineering thermoplastics already used in the 1930s, see Rosato et al (2004), constitute another huge family of polymers with important technological applications. PA6 and even more PA66 are used in applications where load-bearing capacity is important as well as wear resistance, such as journal bearings, Feyzullahoglu et al. (2006). Consequently, the tribological properties of polyamides have been widely studied: Jia et al. (2007) studied the friction properties of PA66 against itself and the influence of some lubricants; Feyzullahoglu et al. (2006) studied the tribological properties of cast PA in contact with steel parts; Zhang Z.-Z et al. (1998) compared PA66 with other polymers in the oil-lubricated conditions against a chromium steel to confirm the interesting

tribological properties of polyamide; finally contact parameters were investigated by Pogačnik et al. (2017) to stress the importance of heat removal from the contact area. A countless number of additives has been considered to modify and improve the tribological properties of polyamides. Among these, the following are most significant: PTFE, examined by Rao et al. (1998) giving a reduction in terms of adhesional friction and consequently improvement in wear rate; UHMWPE, studied by Honggang et al. (2016) also obtaining and improvement in the wear resistance of the blend; similar results have been reported by Li et al. (2012) who also considered PTFE and UHMWPE; PI, investigated by Liu et al. (2010) obtaining improvements in the heat resistance, and reduction of the friction coefficient and wear rate; PVDF, studied by Wang et al. (2008) showing the good properties of the blend with PA for tribological applications; SEBS and maleic anhydride (MA) to obtain a ternary blend was introduced by Hu et al. (2009) obtaining improvements in toughness and wear resistance while HDPE with MA ternary blends were studied by Chen et al. (2005) with similar results; clay, recently studied and widely considered in many applications was studied by Mu et al. (2008) obtained a reduction in the wear rate with a 5% mass fraction of clay nano-particles; glass fibers (GF) were studied by Kim et al. (2013) who obtained improved friction and wear properties contrasting the negative effect of water absorption from PA66; again GF with PTFE for journal bearings was studied by Demirci et al. (2014) who obtained an optimal result with 20% GF and 25% PTFE content; carbon fibers (CF) were introduced by Nie et al. (2010) who also obtained an optimum result for 20% CF content; finally carbon nanotubes, Lee et al. (2014), and diamond nanoparticles, Karami et al. (2017), are the latest experimented additives: results are extremely important since in both cases an addition of only 1% in mass gave noteworthy improvements of the tribological properties. In general, most additives, by modifying the compatibility with the counterpart materials, decrease the adhesion properties of PA so decreasing the friction coefficient and the wear rate.

In the current work a TPU and a polyamide PA66 were considered preparing a series of blends with different additives: molybdenum disulfide ( $\text{MoS}_2$ ), PTFE, silicone, graphite, and carbon nanotubes (CNT) were considered in different contents, to measure and evaluate their influence on the tribological properties of the two base polymers.

The experimental evaluation was carried out by means of the pin-on-disk method. The influence of the additives on the basic strength of the materials was also investigated by tension tests and impact tests.

The results show that most additives, except CNT, have an important influence in reducing friction and wear of the blends.

## 2. Materials and additives

### 2.1. Plastics

The two examined base materials are the following:

- Desmopan® DP 3059D (TPU)
- Radipol® A 45 D (PA6.6)

Desmopan® by Covestro is a TPU for injection molding, provided to guarantee excellent abrasion resistance and good wear resistance. Applications suggested by the producer are heel patches, rollers, and boot shells. Tensile strength measured with the methods in ISO 527-1-3 is 50 MPa at 400% strain at break; abrasion resistance according to ISO 4649 method A, is 18 mm<sup>3</sup>.

Radipol® A 45 D by Radici is a polyamide 6.6 with standard viscosity mainly proposed for compounding. It has a tensile modulus, measured by methods ISO 527-2/1A of 3200 MPa, a yield strength of 80 MPa, nominal strain at break of 40%; the technical data sheet does not provide any tribological data.

Samples of compounds based on these two plastics were manufactured by NEVICOLOR S.p.A. with the additives that will be described in the following section.

## 2.2. Additives

The additives considered in this work were as follows:

- Graphite (GR) FerroLube GR-4009 N masterbatch (black, with TPU)
- Polytetrafluoroethylene (PTFE) FLUON® FL1690ND (with TPU)
- Silicone (SIL) SiliconLube® MB EV-504 (with TPU and PA)
- Molybdenum disulfide (MoS<sub>2</sub>) MB 50% EVA (with TPU and PA)
- Carbon nanotubes (CNT) PLASTICYL™ PA1502 (with TPU)
- Carbon nanotubes (CNT) PLASTICYL™ PA1501 (with PA)

Graphite is a widespread, very common and cheap material known for its capacity to decrease friction due to its layered structure with slip planes weakly linked among themselves. As for other additives used in this work it's available as a masterbatch compounded with the base material before processing. This masterbatch is proposed as a 50% natural graphite mixed with a 50% LDPE carrier: compatibility with TPU has been positively verified.

PTFE also is well known for its peculiar properties of high mechanical strength, environmental resistance to many chemicals and solvents, and, due to its inertia to chemical reactions, having very poor adhesion capability is ideal to reduce friction and decrease wear. It is also used to decrease stick phenomena during injection processes.

SiliconLube® masterbatch EV-504 is composed of an ultra-high molecular weight siloxane in EVA resin (50%). Used also as a flow modifier in smaller concentrations, is used as lubricant and anti-wear in concentrations from 2% to 10%. The very low stickiness in the contact with most materials explains its low friction and the use to improve the tribological properties of the compounds.

Molybdenum disulfide is, with graphite, probably the most known material used as a solid lubricant. Similarly as to graphite, MoS<sub>2</sub> can form single layer stacked with very low interlaminar forces that can easily slip one with respect to the others. Therefore, it has many applications for this purpose. In the current work a masterbatch of 50% MoS<sub>2</sub> with 50% EVA was used for both TPU and PA.

GF

NANOCYL NC7000 CNT (9.5 nm average diameter, 1.5 μm average length) dispersed in PA12 (85±1%, PLASTICYL™ PA1502) or PA66 (85±1%, PLASTICYL™ PA1501) were then used as a last type of additives. CNT are receiving a large attention due to their remarkable properties of mechanical strength and stiffness, but because of their electrical properties and larger surface for unit volume, they are expected to improve the tribological properties of compounds. The expected advantage of CNT is that such improvement should be obtained with very low concentration of the additive (some 1-3%) much less than the usual concentrations typical of other additives (usually from 2% to even more than 10%) so only slightly affecting other properties of the modified plastic (for example without noticeable reduction in tensile and impact strength often found with some other additives).

Finally, to produce the various compounds, phenolic base antioxidants were added, IRGANOX 1010 (with TPU) and IRGANOX B225 (with PA). They are used to avoid thermal-oxidative degradation by linking to free radicals produced at high temperatures (during processing). They are included in very small quantities (typically 500-1000 ppm) so that they do not alter the typical properties of the materials.

## 2.3. Analyzed compounds

Compounds produced with double-screw extruders are listed in Table 1 for TPU and Table 2 for the PA. Percentage of IRGANOX is not reported being a negligible and constant quantity (0.25% or 250 ppm).

Table 1. TPU compounds for the tribological tests.

Compound	Material	Desmopan® 3059D	FerroLube GR4009	FLUON FL1690ND	SiliconLube EV-504	MoS <sub>2</sub> MB 50% EVA	PLASTICYL™ PA1502
TPU, natural		100%					
TPU + 4% GR		92%	8%				
TPU + 8% GR		84%	16%				
TPU + 10% PTFE		90%		10%			
TPU + 20% PTFE		80%		20%			
TPU + 1% SIL		98%			2%		
TPU + 2% SIL		96%			4%		
TPU + 4% MoS <sub>2</sub>		92%				8%	
TPU + 8% MoS <sub>2</sub>		84%				16%	
TPU + 1.5% CNT		90%					10%
TPU + 3% CNT		80%					20%

Table 2. PA compounds for the tribological tests.

Compound	Material	Radipol® A 45 D	FerroLube GR4009	SiliconLube EV-504	MoS <sub>2</sub> MB 50% EVA	PLASTICYL™ PA1501
PA, natural (66NAT)		100%				
PA + 2% GR (66GR2)		96%	4%			
PA + 4% GR (66GR4)		92%	8%			
PA + 8% GR (66GR8)		84%	16%			
PA + 2% SIL (66SI2)		96%		4%		
PA + 4% SIL (66SI4)		92%		8%		
PA + 8% SIL (66SI8)		84%		16%		
PA + 2% MoS <sub>2</sub> (66MS2)		96%			4%	
PA + 4% MoS <sub>2</sub> (66MS4)		92%			8%	
PA + 8% MoS <sub>2</sub> (66MS8)		84%			16%	
PA + 1.5% CNT (66CNT1.5)		90%				10%
PA + 3% CNT (66CNT3)		80%				20%

The compounds were then used to produce samples for testing in a Sandretto MICRO 65 injection molding machine in NEVICOLOR S.p.A. Molded pieces for tribological and mechanical testing specimen are shown in Fig. 1.

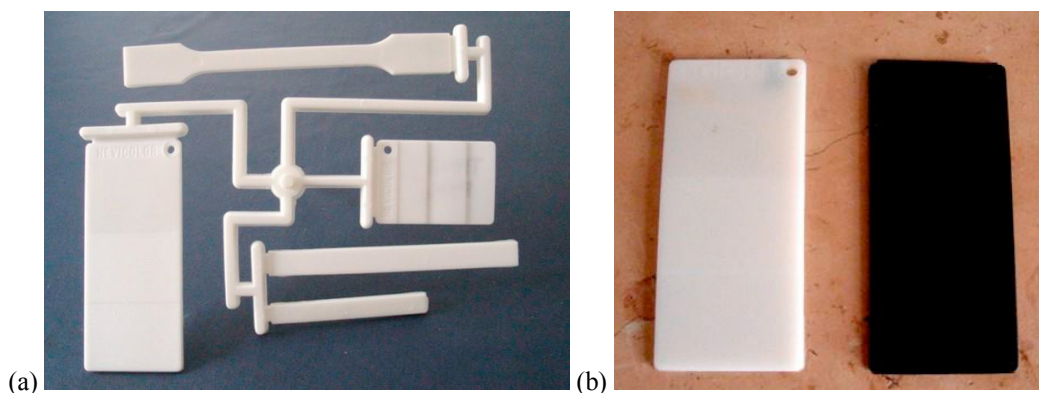


Fig. 1. Examples of injection molded pieces for the preparation of specimen for testing: (a) the part as molded; (b) rectangular sub-pieces to obtain the square specimen for the tribological tests

### 3. Testing methods

Tribological tests to evaluate the friction and wear properties of the examined compounds were performed using the pin-on-disk method according to ASTM

#### 3.1. Testing equipment

Tests were performed with a custom pin-on-disk tribometer (Fig. 2), made in the Alessandria material laboratory of Politecnico di Torino. The used tribometer can host different types of specimen, in dry or wet friction conditions, with a rotating speed of the disk ranging from 0 to 600 rpm, and with applied loads from 5 to 30 N. Forces are measured and recorded during the test with dedicated hardware and software.

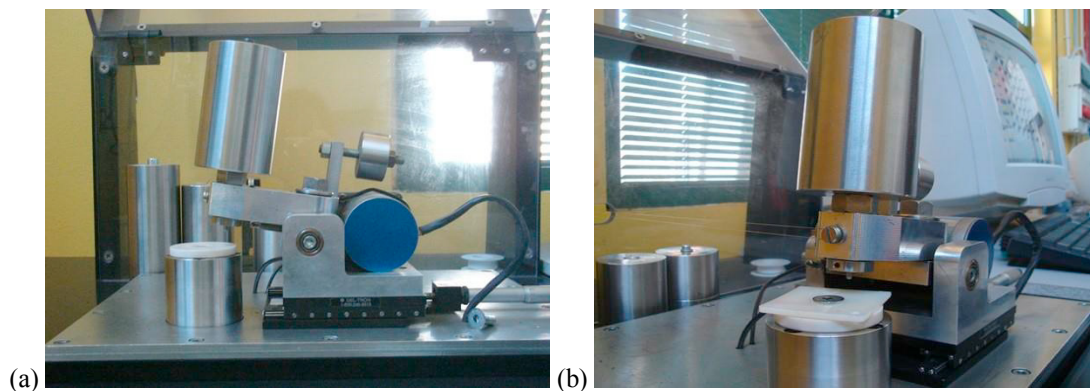


Fig. 2. Pin-on-disk tribometer used in the current work (a) and a detail with a sample mounted on it (b)

The volume loss at the end of the test was estimated by measurements of the eroded track with a HOMMEL tester T1000 profilometer. SEM analyses of the tracks were also performed.

Tensile tests were also performed with a general purpose electromechanical material testing machine Zwick Z100, and according to test method ISO 527-1, together with Charpy tests performed with a Zwick HIT 50 pendulum and according to ISO 179-1 method.

### 3.2. Testing specimen

Specimen used for tribological tests were 50 mm×50 mm square plates, 3 mm thick, obtained by cutting from injection molded pieces (Fig. 3). For tensile tests, the classical ISO 527-A specimen was used (cut from the pieces shown in Fig.1), and for the Charpy tests, the usual prismatic specimen was also obtained from the same pieces.



Fig. 3. Square specimen used for the tribological tests

## 4. Experimental results

### 4.1. TPU

The tests were performed with a pin load of 20 N, at a rotation speed of 300 rpm. The track diameter was 35 mm giving a tangential speed of 550 mm/s. The tungsten carbide pin, cylindrical with a diameter of 3 mm, generated an average normal pressure of 2.83 MPa.

Prior to testing, some SEM analysis with EDS spectroscopy analyses were performed on samples of the batch of the compounds. In the case of graphite, EDS examination does not help, Fig. 4(a), being all components mainly carbon, and only the morphological SEM examination help verifying the dispersion of the additive: despite some cluster, the dispersion seems good even if adhesion with the TPU is not optimal. PTFE bright particles are clearly visible, Fig. 4(b), appear not optimally dispersed but rather condensed in clusters, compatibility with TPU being not optimal. Examination of Fig. 4(c) reveals that despite a good dispersion, the adhesion of the silicone additive is also not optimal: this is revealed by the small black spot corresponding to voids, whereas bright areas are silicone particles. Molybdenum disulfide particles, Fig. 4(d) are evident as white spots: they appear well distributed and uniformly dispersed; adhesion can also be considered satisfactory. Another detail of a 4% MoS<sub>2</sub> sample, Fig. 4(e) show areas of poor adhesion, dark holes, of the particles to the polymeric substrate. Finally, for CNT, Fig. 4(f), a very high dispersion is observed even if not always homogeneous: this is clear from the dark area on the upper right area in the SEM image.

The wear tests were performed as described in §3.1, and are shown in Fig. 5 in terms of the friction coefficient measured during the test: even if at least 5 repetitions of each test were performed, in the graph only one curve is shown due to the good reproducibility of the experimental results. In general, natural TPU show an initial decrease in the coefficient of friction followed by a steady behavior. The influence of most considered additives, other than a considerable reduction except with CNT, is the elimination of this first peak usually followed by a steady response.

CNT compounds did not give satisfactory performance so that the tests had to be stopped prematurely (at around 300 m of traveled distance). Important adhesion wear was observed resulting in the removal of large particles: after only 300 m 151 mg of material was removed (for comparison the natural TPU after 1900 m traveled distance had a mass loss of only 52.3 mg). A SEM analysis (Fig. 6) also showed the important damage with a huge track, much larger than in the other cases.

The volume loss at the end of the test is finally reported in Table 3 for the examined compounds with the exception of CNT samples for which it was not even possible to exactly measure it because of the excessive material removal as noted above.

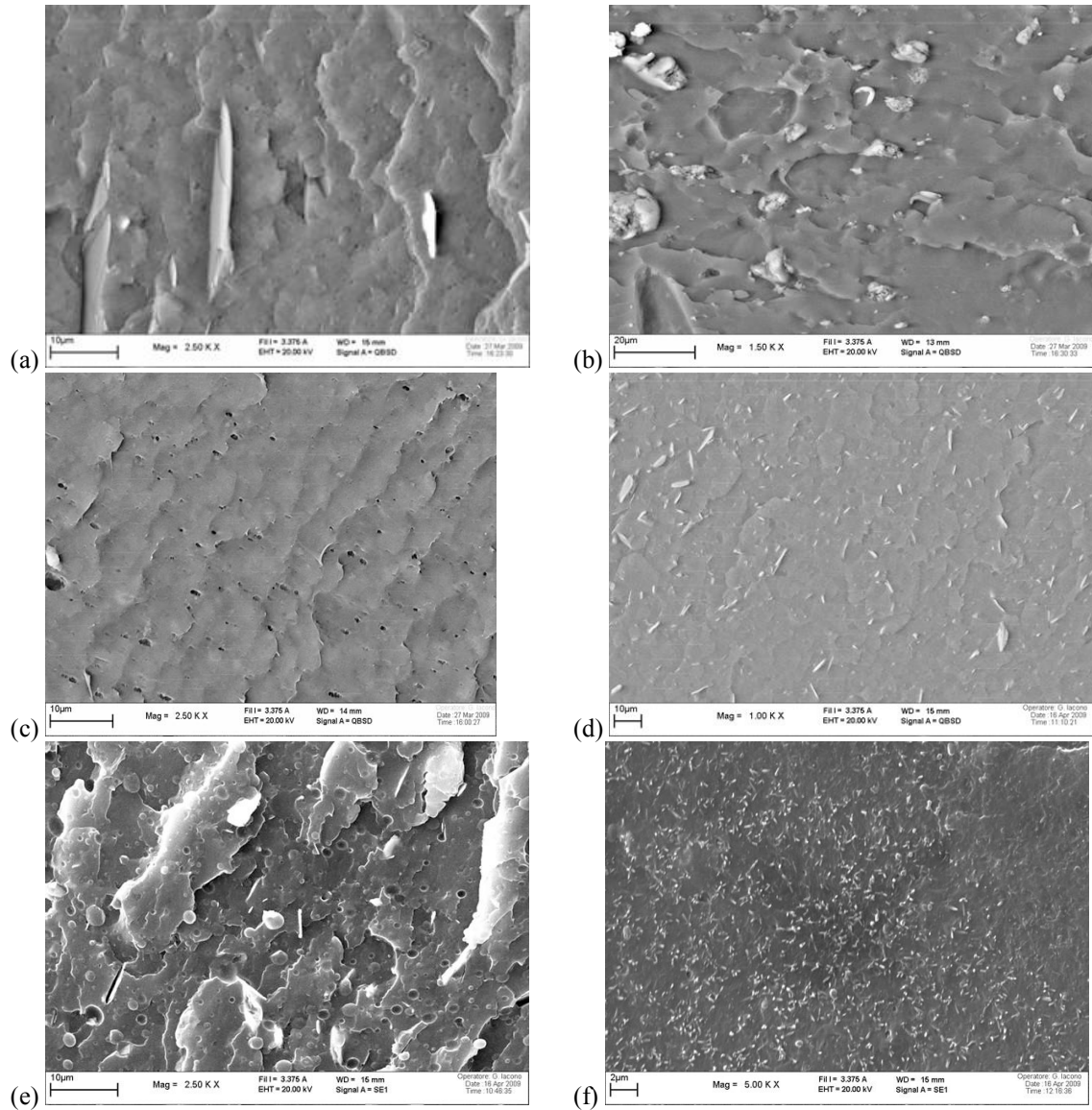


Fig. 4. SEM images of the TPU compounds: (a) 4% GR, 2500 $\times$ ; (b) 10% PTFE, 1000 $\times$ ; (c) 2% Silicone, 2500 $\times$ ; (d) 8% MoS<sub>2</sub>, 1000 $\times$ ; (e) 4% MoS<sub>2</sub>, 2500 $\times$  (f) 3% CNT, 5000 $\times$ .



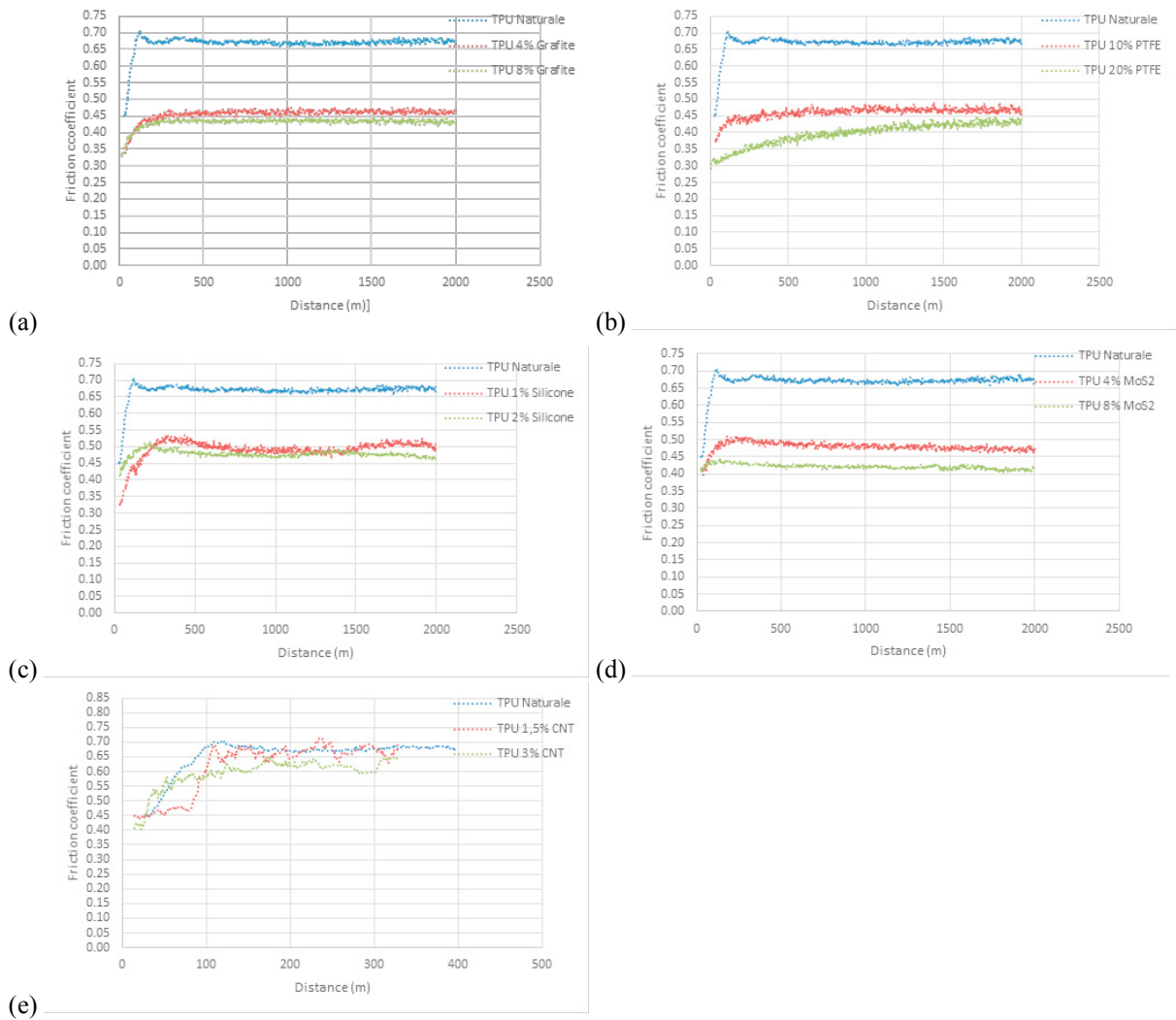


Fig. 5. Friction coefficient measured during the tests on TPU compounds as a function of the distance travelled by the pin: (a) GR; (b) PTFE; (c) Silicone; (d) MoS<sub>2</sub>; (e) CNT.

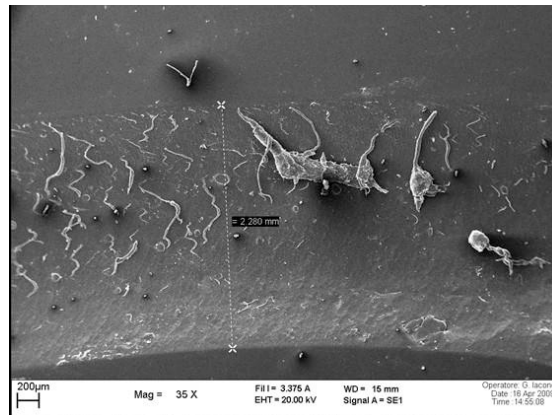


Fig. 6. SEM analysis of the eroded surface on the track in a 3% CNT sample after the pin-on-disk test.

Table 3. Results in terms of volume loss for TPU compounds.

Compound	Volume loss (mm <sup>3</sup> ) @ 2000 m
TPU, natural	4.703
TPU + 4% GR	1.613
TPU + 8% GR	3.574
TPU + 10% PTFE	1.157
TPU + 20% PTFE	0.607
TPU + 1% SIL	1.204
TPU + 2% SIL	1.148
TPU + 4% MoS <sub>2</sub>	2.774
TPU + 8% MoS <sub>2</sub>	3.816

#### 4.2. PA66

The tests were performed in almost the same conditions with the exception of the track diameter being 40 mm, thus giving a slightly higher tangential speed of 628 mm/s.

SEM analysis of the PA compounds were also carried out. For graphite it can be observed that exfoliation of lamellar graphite is not very effective as lamellas stack of several micrometers of thickness were seen, Fig. 7(a). For silicone it can be seen that even if there is good dispersion and distribution, Fig. 7(b), the compatibility between is poor as there are fractures and lack of adhesion with the substrate, as visible in the detail of a large silicone particle in Fig. 7(c). For MoS<sub>2</sub> good dispersion and distribution can be seen. There is also good compatibility because good interface is visible: some MoS<sub>2</sub>, Fig. 7(d), particles have a thickness smaller than 0.1 μm so that they can be considered as in a nanocomposite.

The wear tests performed as described in §3.1, give the results shown in Fig. 8 in terms of the friction coefficient measured during the test. In general, natural PA show an increasing value of the coefficient of friction followed by a steady behavior. Constant values of the coefficient of friction are also observed in almost all compounds with the exception of some case with lower contents of graphite: at 4% and 8% GR content, the coefficient of friction has an increase followed by a decrease to an almost constant value. This is probably because of an imperfect dispersion of the large lamellas observed in the SEM inspection. Differently from TPU, PA with added CNT does not reveal the same catastrophic behavior: it appears, however, that in this case also the effect of CNT is negligible.

Finally, in Table 4 the volume loss at the end of the test is reported for the examined compounds.

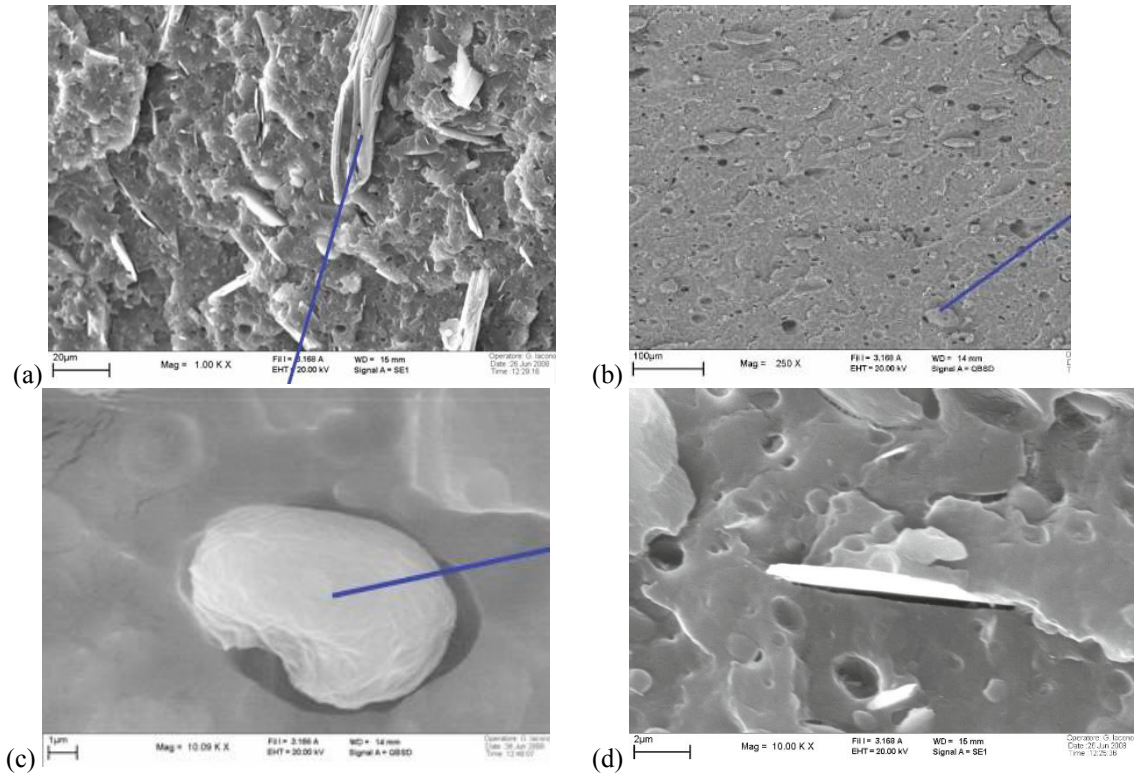


Fig. 7. SEM images of the PA compounds: (a) GR, 1000×; (b) Silicone, 250× and (c) at 10k× detail of a silicone particle; (d) MoS<sub>2</sub>, 10k×.

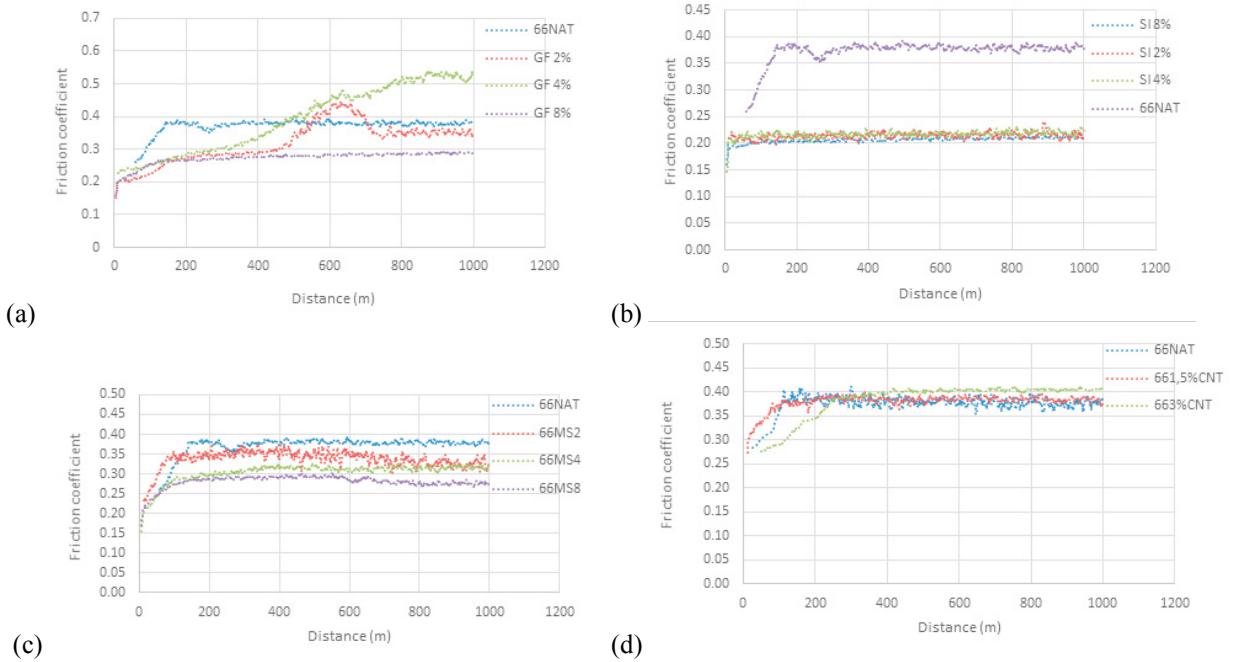


Fig. 8. Friction coefficient measured during the tests on TPU compounds as a function of the distance travelled by the pin: (a) GR; (b) Silicone; (c) MoS<sub>2</sub>; (d) CNT.

Table 4. Results in terms of volume loss for PA66 compounds.

Compound	Volume loss (mm <sup>3</sup> ) @ 300 m
PA, natural	0.378
PA + 2% GR	1.125
PA + 4% GR	0.617
PA + 8% GR	0.018
PA + 2% SIL	0.119
PA + 4% SIL	0.171
PA + 8% SIL	0.306
PA + 2% MoS <sub>2</sub>	0.336
PA + 4% MoS <sub>2</sub>	0.293
PA + 8% MoS <sub>2</sub>	0.289
PA + 1.5% CNT	0.029
PA + 3% CNT	0.049

## 5. Analysis of the experimental results and discussion

Table 5 aims at collecting friction coefficient results at different traveled distance of the pin. As already observed from Fig. 5 the variation at different distances is almost always negligible. For this reason, in Fig. 9, the trend of variation of the friction coefficient is reported for the lower value of around 200 m to keep all results included that of CNT. The volume loss as a function of the composition is instead illustrated by Fig. 10.

Table 5. Results in terms of volume loss for TPU compounds.

Compound	Distance travelled (m)			
	200 ± 50	500 ± 50	1000 ± 50	1900 ± 50
TPU, natural	0.673	0.674	0.667	0.677
TPU + 4% GR	0.442	0.457	0.461	0.461
TPU + 8% GR	0.429	0.434	0.436	0.432
TPU + 10% PTFE	0.439	0.457	0.469	0.471
TPU + 20% PTFE	0.345	0.379	0.406	0.430
TPU + 1% SIL	0.481	0.512	0.489	0.507
TPU + 2% SIL	0.501	0.481	0.471	0.469
TPU + 4% MoS <sub>2</sub>	0.495	0.490	0.481	0.471
TPU + 8% MoS <sub>2</sub>	0.434	0.423	0.421	0.413
TPU + 1.5% CNT	0.669			
TPU + 3% CNT	0.625			

The analysis of Figs. 9-10 suggests graphite with a content around 5% as the best solution in terms of both reduction of the friction coefficient and wear rate. Molybdenum disulfide gives similar results, but the effect is slightly less marked. The use of silicone is also interesting because it can give an important reduction in the friction coefficient in very small concentrations, less than 5%, but the effect seems to remain for higher concentrations. To further reduce both friction coefficient and wear rate PTFE appears to be a valid alternative, but with much higher contents of the additive material. However, this seems not to be a problem in terms of modification of other compound properties: as shown in the following Fig. 11, adding a relatively high content of PTFE (and of most other additives) does not affect

the tensile strength of the TPU. The only important exception is again with CNT that, even in small concentrations, largely affect the strength and maximum strain of the TPU compounds.

All these observations do not clearly correlate with the morphological observation made by SEM: it seems that the peculiar properties of the additives alone, as for example the solid lubricant graphite and MoS<sub>2</sub>, are the most influencing factors.

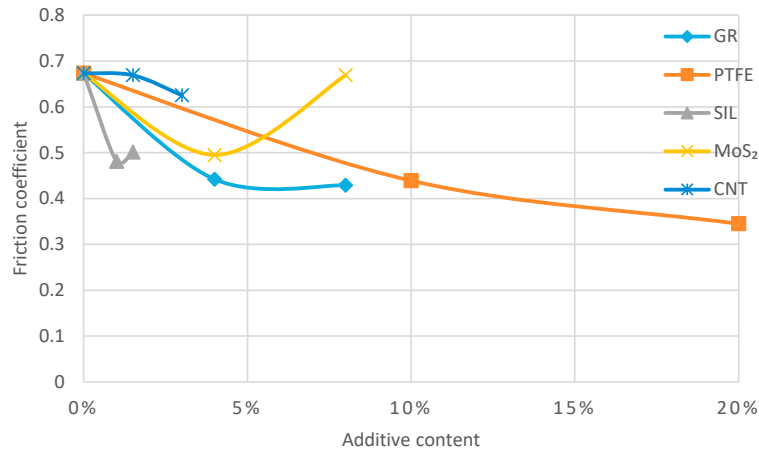


Fig. 9. Effect of additives content on TPU compounds, coefficient of friction

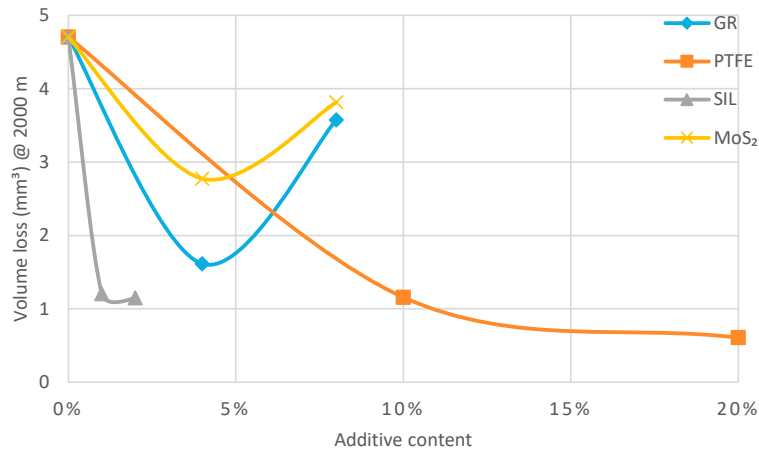


Fig. 10. Effect on wear of additives content on TPU compounds (CNT case not indicated as not measurable)

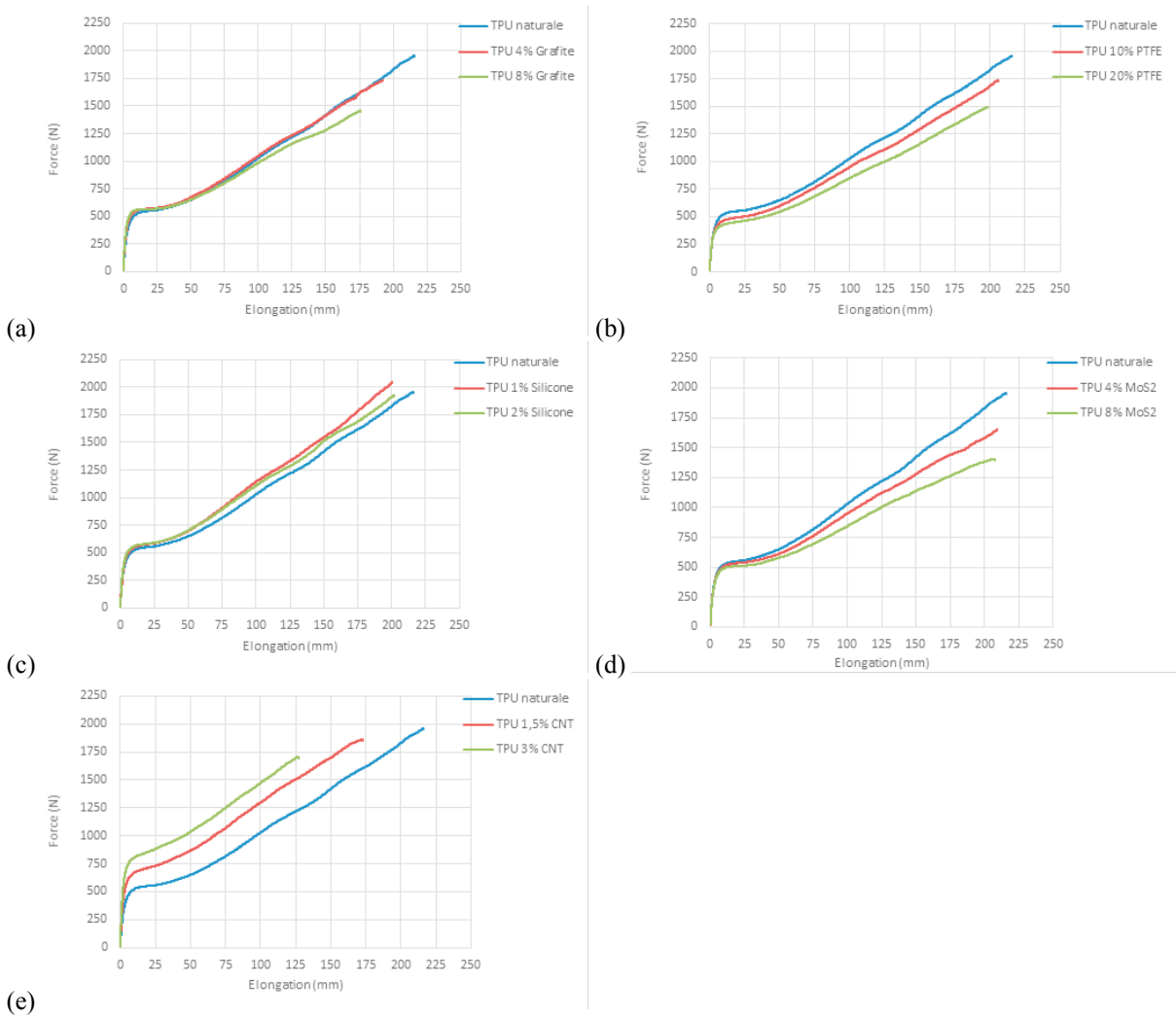


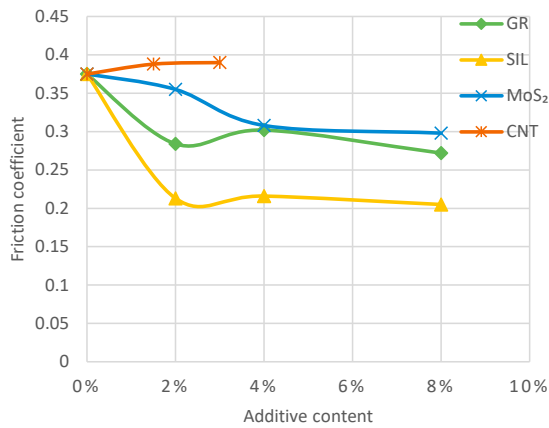
Fig. 11. Comparison of tensile tests performed on the TPU compounds: (a) GR; (b) PTFE; (c) Silicone; (d) MoS<sub>2</sub>; (e) CNT.

For the polyamide compounds the results are quite different in many aspects. First of all, the effect of CNT is not as detrimental as it is for the TPU. Table 6 again reports the results in terms of volume loss at two different distance traveled by the pin.

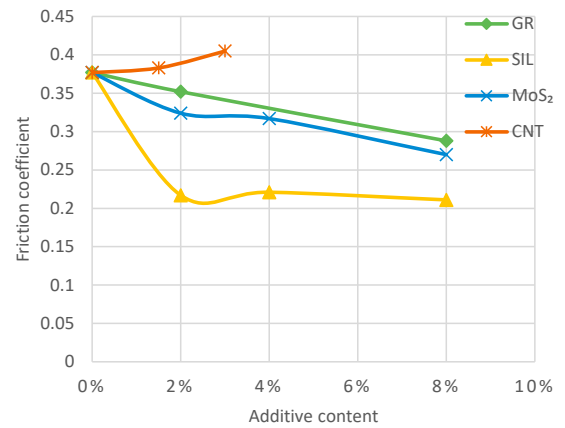
In this case values of the coefficient of friction were evaluated at two values of the distance traveled by the pin: even in the variation are not large, in Fig. 12 the friction coefficient measured in the two cases is reported. As a matter of fact, similar conclusions can be obtained: for the examined polyamide, the best additive in terms of friction reduction is silicone in relatively small concentrations, around 2%. More content of almost any additive does not seem to give further improvements. Additionally, as visible in Fig. 13, silicone is also mostly beneficial in terms of wear reduction, in concentrations of 2-3%. Curiously, CNT seems to be the best in reducing wear even if slightly increasing the coefficient of friction of the material. This unexpected result is not easily explained and needs further investigations. As a final remark, graphite appears to be not suitable for this polyamide to improve the tribological properties: at low concentrations it increases the wear rate without modifying effectively the friction coefficient. Even worse, from tensile tests (not reported here) it comes out that the strain at failure of the compounds with graphite is greatly reduced.

Table 6. Results in terms of volume loss for PA compounds.

Compound	Distance travelled (m)	
	300 ± 50	900 ± 50
PA, natural	0.375	0.377
PA + 2% GR	0.284	0.352
PA + 4% GR	0.302	0.526
PA + 8% GR	0.272	0.288
PA + 2% SIL	0.213	0.217
PA + 4% SIL	0.216	0.221
PA + 8% SIL	0.205	0.211
PA + 2% MoS <sub>2</sub>	0.355	0.324
PA + 4% MoS <sub>2</sub>	0.308	0.317
PA + 8% MoS <sub>2</sub>	0.298	0.270
PA + 1.5% CNT	0.388	0.383
PA + 3% CNT	0.390	0.405



(a)



(b)

Fig. 12. Effect of additives content on PA compounds, coefficient of friction at distance traveled (a) 300 m; (b) 900 m

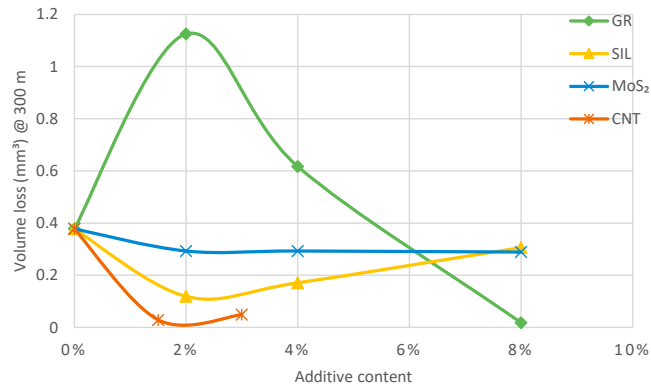


Fig. 13. Effect on wear of additives content on PA compounds

Similarly to TPU silicone is very effective in decreasing friction and wear. Graphite, instead, due to the formation of large stack of lamellas does not contribute to the improvement of friction coefficient: it is probably the additive itself contributing to the volume loss during the test. Probably, to obtain a beneficial effect it is necessary to improve the dispersion so to obtain better adhesion of the graphite particles to the polymer.

## 6. Conclusions

In the present work experimental results on the tribological properties of two polymers, and the effect of various additives were reported. The base polymers were thermoplastic polyurethane and polyamide, two thermoplastic materials widely used in technical applications as supports with sliding contact. Several additives commonly used as solid lubricants or modifier to change the surface properties of materials were used: namely graphite, polytetrafluoroethylene, silicone, molybdenum disulfide, and carbon nanotubes. The latter are of particular interest due to the attention given to such innovative materials for various applications.

Compounds of the different combinations of substrate materials and additives were obtained, then samples of the compounds were tested in a pin-on-disk apparatus. Measurements of wear rates, coefficient of friction, together with SEM and EDS analyses were then carried out. Some tensile tests and Charpy tests to check for possible influences of the additives on the mechanical properties were also performed.

The results show some beneficial effects both in terms of reduction of the friction coefficient and wear rates with some additives. Silicone appears to be an interesting added material both for polyurethane and polyamide. On the contrary graphite has some problems in the combination with the polyamide: probably due to some incompatibility with the material, it can even worsen the situation. PTFE is also interesting for the application with the thermoplastic polyurethane giving important improvements in the tribological properties not affecting strength and toughness.

Opposite results were obtained with the carbon nanotubes. In both cases the influence is either negligible, as for the polyamide, or strongly detrimental, as for the thermoplastic polyurethane: in this case the CNT promote the formation of small debris that increase wear and damage the surface prematurely. If CNT are to be used as additive for wear, it requires further investigation and improvements in the processing methods.

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