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Influence of Graphite Additives on Mechanical, Tribological, Fire Resistance and Electrical Properties in Polyamide 6

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Abstract: New types of polymers are usually produced with different additives. In this work, the effect of graphite addition (1.5wt%, 2wt%, 2.5wt%, 3wt% and 3.5wt%) on material's properties is analysed. Results of current investigation show that there are two possible subtypes (groups) of polyamide, containing 2% and 3.5% graphite, which reveal improved complex properties. By using graphite additives, the material becomes stiffer. In polyamide-2% graphite system, the abrasive wear tends to decrease while the fire resistance improves without significant changes in mechanical properties. In addition to improved tribological and fire resistance behaviour, polyamide with 3.5% graphite addition gains excellent antistatic properties. At the same time, in this material both the tensile and the Charpy impact strengths have decreased by 15% and 30%, respectively, whereas the Young's modulus increases by 6% as a result of dispergation/adhesion between the graphite and polymer.

Keywords: electrical behaviours; fire resistance; graphite; magnesium catalysed cast polyamide 6; mechanical-; tribological-;

1 INTRODUCTION

Generally, the cast polyamide 6 (PA6) has good mechanical and tribological properties. Traditional PA6 are made by polycondensation process. Researchers have come up with a new approach on casting which is based on the ring opening polymerization. The new casting process has two advantages under production: the process is faster and there is no water secession [1-5]. The sodium catalysed cast PA6 are being extensively used in the semi-finished material production such as bar, tubes, sheets. One of the earlier developments of the PA6 subtypes is the magnesium catalysed cast PA6 that has been used since 1990s. The magnesium catalysed cast PA6 has better impact strength and wear resistance at low load compared with sodium (natrium) catalysed cast PA6 [6]. Due to efficient production, and good behaviour, the cast PA6 is one of the most popular semi-finished engineering materials. In numerous equipment, cast PA6 was used in small- medium series by replacing metal parts, and these parts are generally manufactured using different cutting processes.

There are increasing requirements for special PA6 subtypes in addition to the traditionally used cast PA6. Enhancement of particular property is usually achieved by help of additives. In case of the traditional PA6 one of the most commonly used additives is the graphite. The graphite can be used to reduce the surface resistance [7-10], but in the case of cast PA6 the literature is limited. In other materials such as epoxy, the graphite additives can reduce the surface resistance until 109 Ω. The materials can be subdivided on the basis of surface resistance: antistatic between 1010-1012 Ω, and electrostatic dissipative (ESD) between 106-109 Ω [11, 12]. In PA, the graphite additives are traditionally responsible for better wear resistance [13-14]. The graphite is well known solid lubricant and widely used in different industrial applications to decrease the friction coefficient [15-18]. The graphite additives can result in better fire behaviour, which is generally not the main aim of the researches so there is only limited information about this effect [19].

Based on the literature the researchers study the effect of graphite additives partially. It is hard to see the complex effect of the additives, because different groups used different base material and different type of graphite. In case of magnesium catalysed cast PA6 (and generally also) there is no information on simultaneous changes in different parameters (mechanical, tribological, electrical, fire behaviour) due to graphite addition.

The aim of this study is to analyse the effect of PA6 behaviour with different graphite content. The goal is to specify the amount of additives, which improve a number of material's properties, suitable for specific applications where pure polymer does not show appropriate performance.

2 MATERIALS AND METHODS

The raw material used in the present research is magnesium catalysed cast polyamide 6 (DOCAMID 6G H – Quattroplast Kft., Hungary), whose material properties are shown in Table 1. The CR 5 995 graphite was used (Czech Republic), the size of the particles (at least 50%) are between 5,5-7 μm, specific surface area is 10 m^2/g.

Table 1 Magnesium catalysed cast polyamide 6 properties

Density	1,183 g/cm^3
Young's modulus	3300 MPa
Charpy impact strength	8 kJ/m^2
Oxygen index (OI)	22,5
UL-94 category (flammability)	HB

Table 2 Conditions of the mechanical tests

Test	Standard	Specimen	Test speed
Tensile test	ISO 527	1A	10 mm/min
Flexural test	ISO 178	60×10×4 mm	10 mm/min
Instrumented impact test	ISO 179	1eA	-
Shore-D hardness	ISO 868	25×150×5 mm	-
Surface resistance	IEC 60093	160×60×60	-
Abrasive tribological test	ASTM G132	⌀8×30 mm	80 mm/s
Fire resistance	UL-94	120×10×4	-

Based on the earlier experiments [20, 21], the contents of the graphite additives were the following: 0 wt% (reference), 1,5 wt%, 2 wt%, 2,5 wt%, 3 wt% and 3,5 wt%. The test samples were machined from the cast block for the tensile, flexural, Charpy, Shore-D hardness testing and the surface resistance measurement tribological tests and fire testing were also performed using the same material (Table 2).

The abrasive tribological test was made in a special test rig corresponding to ASTM G132 standards (pin abrasion tester). The test speed was 80 mm/s, the surface pressure was 0.7 MPa, the abrasive paper was Vitex KK504XP60 and the sliding distance was 5200 mm. The cylindrical test sample has 8 mm diameter and 30 mm length. The measuring system comprises the data acquisition to record the forces in 3 directions (friction forces and normal force), moreover, a displacement sensor is separately accommodated for wear measurement. The abrasive test rig is shown in Fig. 1.

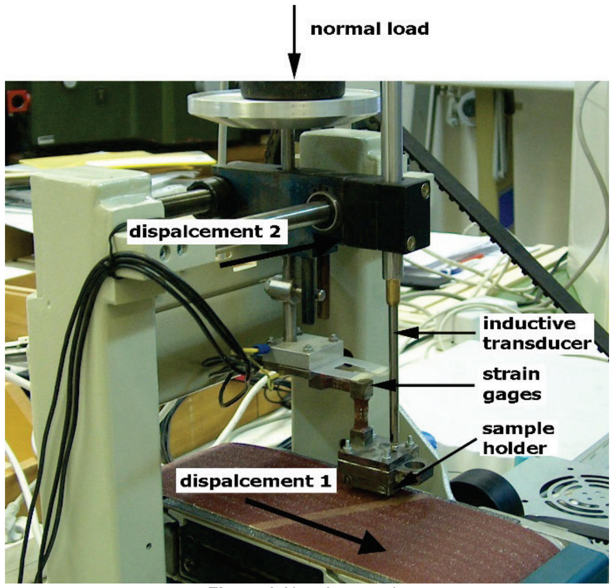

Figure 1 Abrasive test rig

The surface resistance measurement was used to define the antistatic behaviour based on the IEC 60093 standard. Based on the standard, 100 V was used, which can give surface resistance between 105 - 2×1011 Ω. This range is appropriate, because over 1012 Ω the materials are insulators, whereas for less than 106 Ω they are conductive polymers.

The fire behaviour test was made based on the UL-94 standard, the dimension of the samples was 120×10×4 mm as shown in Tab. 2. The flammability categories are HB, V-2, V-1 and V-0 depends upon the fire performance. HB materials have no fire resistance, and the V-0 materials do not burn in case of fire.

The polyamides can absorb the humidity from air, therefore the samples have to be conditioned. Generally all the measurements were made under dry condition (after casting the samples, they were in an exicator). Only the surface resistivity was measured in 3 different conditions, next to the dry condition (with no water absorption) and normal condition (20 °C, 50 RH), in wet condition as well (in water at 24 hours). The mechanical tests were carried out with at least 9 samples.

3 RESULTS AND DISCUSSION

This section presents the different tests results in order (mechanical, tribological, flammability). In case of the diagrams the error of $\pm 2\cdot\sigma$, which indicates 95% probability.

Mechanical characterization was made on the pure polymer and on the polymers with graphite additives (1.5-3.5%). The results show that the mechanical properties change linearly. The tensile strength decreases (Fig. 2) as a function of ratio of graphite additives. Tab. 3 shows the average result and the error ($\pm 2\sigma$) of the different mechanical properties.

Tab. 4 illustrates the change in mechanical properties because of graphite additives. The table includes the maximum measured difference from the pure material. The table also contains the relative errors, which refer to the repeatability. If the magnitude of the maximum difference and the relative error is the same, then the change is not vital.

Based on the measurements it is clearly seen that small amount of graphite additives (up to 2%) cause 5-15% changes of the mechanical properties. Generally, the graphite additives modify the base material properties, and the new material becomes more rigid. The rigid polymer has increased Young's modulus and flexural strength, however, the tensile strength decreases dramatically. The change in Shore-D hardness is almost negligible. The graphite has significant influence on the dynamic properties, causing a reduction in the Charpy impact strength with a higher rate than that of the change in the other mechanical properties. The variation of the Charpy impact strength with graphite content is shown in Fig. 3, which is over 30% when the graphite content varies between 0% and 3.5%. It is also well known that the dynamical test has bigger errors, almost 8% in the test under discussion.

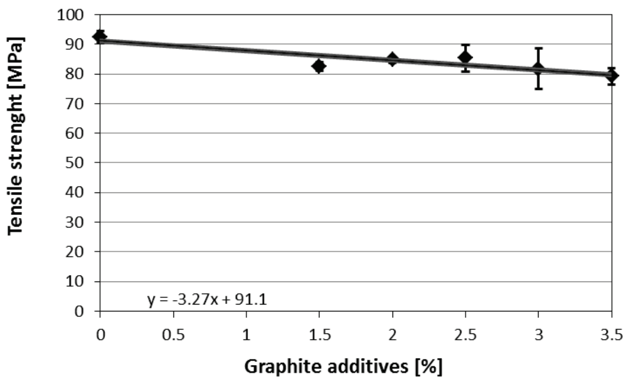

Figure 2 Tensile strength as function of ratio of graphite additives

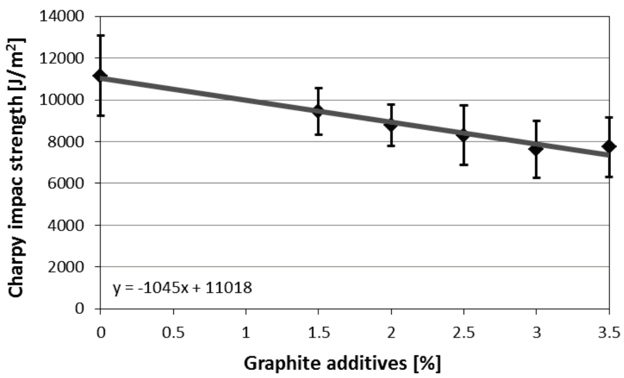

Figure 3 Charpy impact strength as function of the graphite content

Clearly seen are the graphite particles on the fractured surface after Charpy test, which means that there is no strong adhesion between the original base material and the additives (Fig. 4). The cracks can grow much faster next to the graphite particles without strong adhesion, which leads to smaller Charpy impact strength. Consequently, increasing graphite content gives decreasing impact strength.

Table 3 Result of the mechanical tests

Mechanical properties	0%	1.5%	2%	2.5%	3%	3.5%
Young's modulus (tensile) (MPa)	2018±133	2040±94	1968±55	2018±89	2095±69	2103±71
Tensile strength (MPa)	92±2.0	82±1.3	85±1.0	85±4.4	82±6.8	79±2.7
Flexural modulus (MPa)	2896±92	3067±174	3140±101	3284±179	3319±203	3161±175
Charpy impact strength (J/m^2)	11511±1926	9440±1100	8793±987	8293±1424	7636±1360	7736±1433
Shore-D hardness (-)	84.5±0.5	82.5±1.0	82.4±0.7	83.3±0.8	82.7±2.2	83.6±0.3

Table 4 Effect of the additives on the mechanical properties

Mechanical properties	Equation for the fitted curve	Max. difference (%)	Relative error (%)
Young's modulus (tensile) (MPa)	$22.3x + 1996$	6.4	3.3
Tensile strength (MPa)	$-3.27x + 91.1$	14.4	4.1
Flexural modulus (MPa)	$98.3x + 2923$	12.2	2.6
Charpy impact strength (J/m^2)	$-1045x + 11018$	32.8	7.9
Shore-D hardness (-)	$-0.31x + 83.8$	2.4	1.3

The graphite additives have very clear effect on the tribological properties. A small amount of graphite additives is sufficient to reduce the abrasive wear intensity. From 1.5% of graphite the wear intensity is reduced by 25% (Fig. 5.), which can significantly improve the lifetime of the machined parts. Higher graphite content cannot lead to better tribological properties. In practice, the minimum amount is recommended, which makes it more competitive than other solid lubricants.

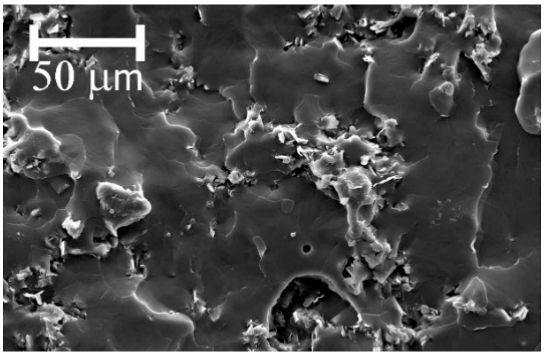

Figure 4 Fractured surface of PA- 2% graphite

Apart from wear intensity, the friction coefficient also decreases by 8-10% for polymers with graphite additives, having tendencies similar to abrasive wear. Thanks to the two effects, the energy balance of the operation and the extended lifetime (33%) are requirements in case of abrasive environment like bearing, cam, ways application at mines, agricultural machines and excavators.

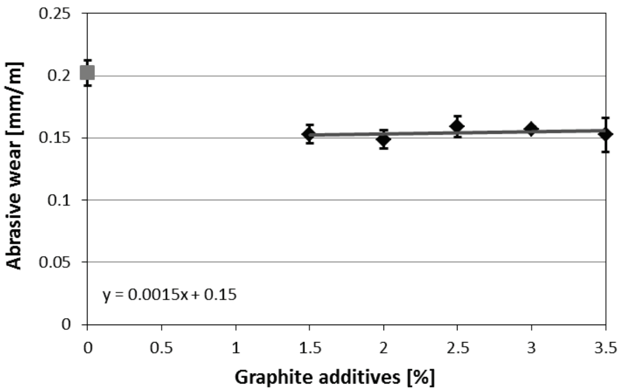

Figure 5 Wear intensity as a function of the graphite content

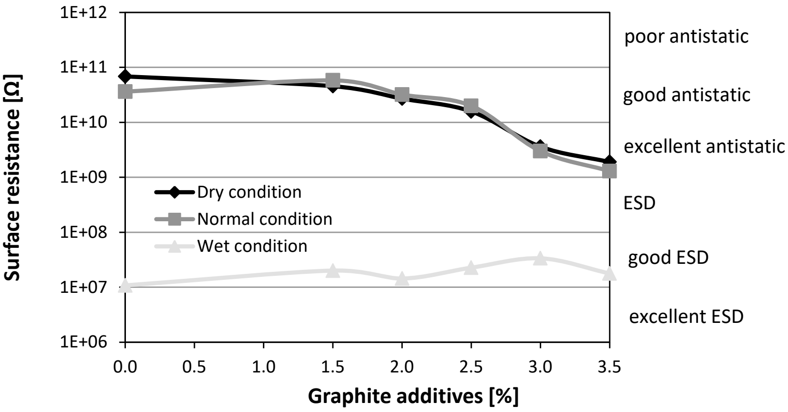

Figure 6 Surface resistance as function of the graphite content

Originally, the diverse polyamides are insulator materials, but with the additive, they gain good antistatic properties. Fig. 6 shows the result of the surface resistivity measurement at the three different conditions. More than 2.5% additives are needed to achieve excellent antistatic properties at dry and normal conditions. More additives further decrease the surface resistivity, which means that the material has better antistatic properties.

In Fig. 6 it is obvious that there is no big difference between the dry and normal conditions, which are the most typical application conditions. The graphite particle, which has good electrical conductivity, is on the base matrix

(PA6), and more additives lead to get smaller distance between the graphite particles. If the distance is decreasing linearly, the surface resistance also decreases, but with increasing intensity. At wet condition, the PA6 absorbs water at the top layer of the surface. In this layer, the electrical charges can move much easier. In wet condition more graphite additives cannot improve the electrical behaviour (107 Ω), because the absorbed water originally responds to the requirement of better conductivity.

The flammability was also studied on these samples. The results of the UL-94 test are in Tab. 5.

Table 5 Fire behaviour function of the graphite content

Graphite contents (%)	Mark of the group	Comments
0	HB	dropping every 2 sec
1.5	V-2	stop burning after dropping
2	V-2	stop burning after dropping
2.5	V-2	stop burning after dropping
3	V-2	stop burning after dropping

The pure polyamide is dropping during the burning process. The graphite additives cannot modify this behaviour, however more energy is needed to create the fire (more time is required). After lighting the fire, the dropping behaviour ensues with the melt drop, and thus a substantial part of the energy is dissipated from the burning system. A relatively smaller energy is not enough to sustain the fire and consequently the samples stop burning. Although the samples cannot burn along the measuring section, the dropping can spread the fire for the environment, which means that the samples cannot be in a flammability category better than V-2.

4 EVALUATION

Relying only on the mechanical test results, it is hard to decide which additive content can be efficient. At first relative values were calculated, based on the pure material properties. The relative flexural modulus was calculated by the following Eq. (1):

$$relE_{g}\% = \frac{E_{\%}\%}{E_{0}\%} \quad (1)$$

where the $E_0\%$ is the flexural modulus of the pure material, the $E_g\%$ is the flexural modulus of the samples with graphite additives. The results of the calculation are shown in Fig. 7.

Table 6 Factorization of mechanical properties for two different applications

Mechanical properties	Agricultural sliding bearing	Holder in an assembly tool
Young's modulus (tensile) (*EY*)	0.1	0.3
Tensile strength (σ)	0.0	0.2
Flexural modulus (*EF*)	0.3	0.2
Charpy impact strength (*C*)	0.3	0.2
Shore-D hardness (*S*)	0.3	0.1
Summa	1.0	1.0

For all results from mechanical tests, relative values were defined and calculated similarly. In order to evaluate the results, the relative values are added to each other to obtain a general tendency. The importance of the mechanical parameters is related to the application where the material will be used. Tab. 6 contains two possible factorizations (where sums should be 1) for two different engineering applications.

Suitable calculation for the application can be made based on the factors. For example, in case of holder (2):

$$\begin{aligned} relM_{g}\% &= 0.3 \cdot relEY_{g}\% + 0.2 \cdot rel\sigma_{g}\% + \\ &+ 0.2 \cdot relEF_{g}\% + 0.2 \cdot C_{g}\% + 0.1 \cdot S_{g}\% \end{aligned} \quad (2)$$

where $relM_g\%$ is the relative mechanical properties for different values of graphite content. The results of the calculation are provided in Fig. 8.

Based on the calculation there is no vital difference according to the factorization. Although the factors are significantly different the mechanical properties exhibit limited changes. Generally, the material becomes stiffer with graphite additives, which gives little lower values. Generally, the relative mechanical properties decreased with a maximum of 5%. These changes cannot limit the traditional applications of the polyamide 6.

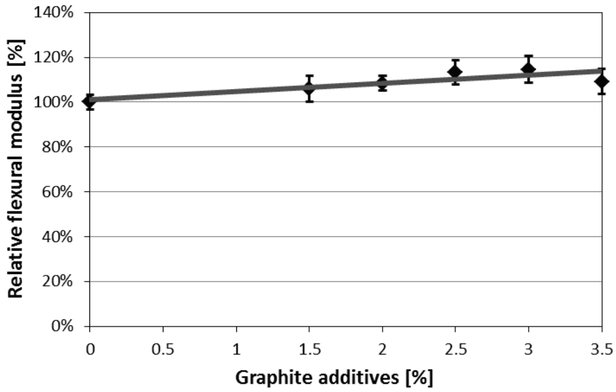

Figure 7 Relative flexural modulus as function of the graphite content

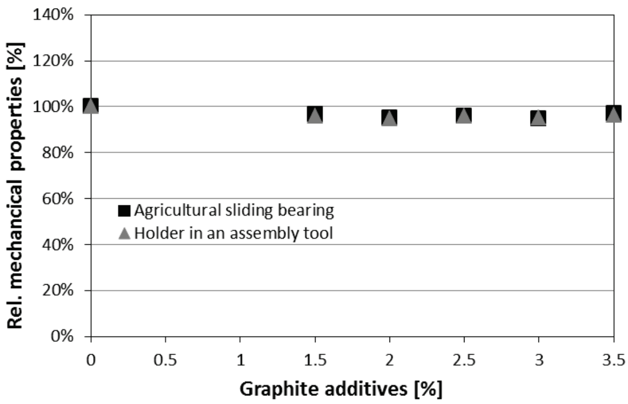

Figure 8 Relative mechanical properties as a function of graphite content

Table 7 Factors for the different application in case of different properties

Properties	Agricultural sliding bearing	Holder in an assembly tool
Mechanical properties	0.2	0.5
Tribological properties	0.5	0.2
Electrical properties	0.2	0.2
Fire behavior	0.1	0.1
Summa	1.0	1.0

Based on material development, the target properties were the antistatic behaviour, better tribology and the better fire resistance. By applying the same mathematical method we can compare the different additives (Tab. 7 and Fig. 9).

Based on the calculation it is clearly seen that for the two kinds of application using graphite additives gives better properties. For example, in an agricultural sliding bearing the tribological properties mean the most important factor, which justifies using 1.5% graphite additive. At 1.5% the value of relative material properties is 122%, whereas at 3.5% this value increases to 130%. The last value becomes greater due to the great antistatic behaviour, which can also increase the bearing lifetime (less dust on the bearing surface). In case of the holder the relative values are smaller, but still greater than 100%. This application traditionally depends upon the mechanical properties, which do not change dramatically. In case of this application the wear resistance and the antistatic properties also have influence on the operation and maintenance (no charging effect, easier to clean).

The additives change the material properties, but the measurements are not comparable mathematically. Using the relative values and the factorization, better material can be chosen based on the numbers and not on the intuition. These two examples showed the method of the calculation. If the engineers/researchers know the application field, then they can choose the correct factors.

5 CONCLUSION

In the newly developed magnesium catalysed cast polyamide 6 (PA6), the graphite additives improve the tribological, electrical and fire behaviour. Fig. 10 shows the relative changes in case of different properties. The change in mechanical properties is closely linear, while the other properties show complex trends.

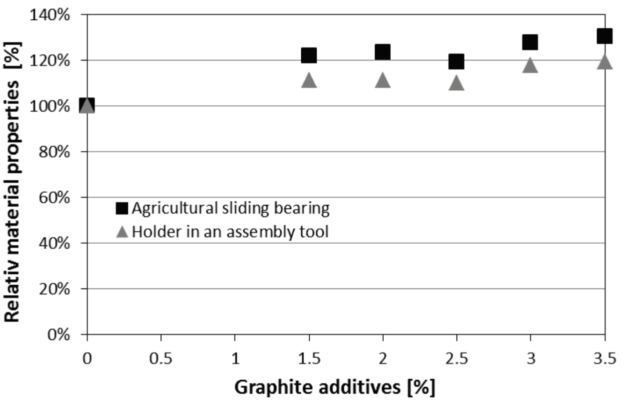

Figure 9 Relative material properties as a function of graphite content

The abrasive wear decreased by 25%. The PA6 inhibits excellent antistatic properties in case of 3% of graphite additives. The flammability is better from 1.5% additives, V-2 category is better than the original HB. Moreover, the mechanical properties also change the stiffness of pure PA6 increases due to the graphite additives. The flexural strength increases by 10% but the Charpy impact strengths and tensile strengths decrease by 30% and 15% respectively.

Based on this study, 1.5% graphite additive is sufficient to provide better tribological, fire and electrical properties without losing much of the mechanical strengths. 1.5% additives cannot limit the original application range but provide extra application fields. With 3 % of graphite additives, the samples become antistatic. The fire and tribological properties remain the same as those of 1.5% additives. At 3% the sample becomes more rigid, the Charpy impact strength decreases by 30%. An application range has been narrowed due to the rigid behaviour; however, the composition can be used in new applications, because of the improved antistatic properties.

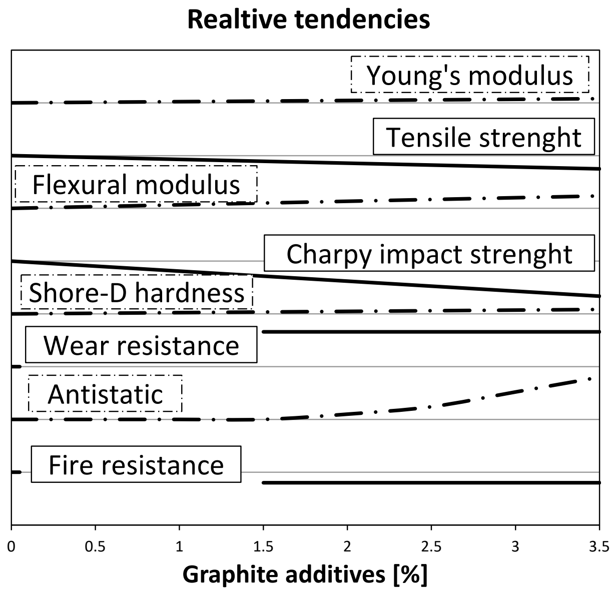

Figure 10 Relative tendencies of different properties

The relative values help to choose the optimal additive content for the specific application. In case of agricultural bearing 1.5% graphite additive is sufficient to get 20% better material; 3.5% additive can provide 30% relatively better material properties than those of pure PA6.

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