Mechanical and tribological behaviour of PA6 and short aramid fiber composites

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Abstract: *This paper presents the results of mechanical and tribological characteristics for two composites: PA6 as matrix and 5% aramid whiskers as additive material and PA6 + 10% aramid whiskers, comparing them to those made of PA6 (polyamide 6). To improve the mechanical and thermal properties of polyamide (PA6), the composites were prepared via the Brabender lab mixer and mould forming under given pressure and temperature conditions. Test specimens made of pure PA6 and PA6 mixed with 5 wt.% and 10 wt.% aramid whiskers were subjected to mechanical tests (three-point bending and impact), thermo–mechanical test (HDT - heat deflection temperature), tribological test (block-on-ring) and analyzed from morpho-structural point of view. Compared to the PA6 samples, the mass concentrations of aramid whiskers improved the HDT deflection temperature values. In the case of samples with 5% aramid whiskers, the absorbed energy increased by 13% and for those with 10% aramid whiskers they increased by 30%. Aramid whiskers-doped materials performed much better on severe tribological testing as compared to PA6 samples. Increasing the deflection temperature, also improved their resistance from a tribological point of view.*

Key Words: *polyamide, aramid whiskers, block-on-ring, impact, heat deflection temperature*

1. INTRODUCTION

Polymeric matrix composites generally exhibit high specific strength, excellent ductility, and rather facile processing, advantages that make them excellent candidates for potential applications in aeronautics, aerospace, transportation, energy, electrical devices and even military fields [1-4]. Important attempts have been made to improve the properties of engineering grade polymers with the aid of different micro/nano-filler compounds and reinforcing agents, however due to the difficulties generated by the interphase issues, it is still a challenge to design highly thermostable, strong and durable polymer-based materials [5].

The current trends towards sustainable industry in various fields (from chemical industry to aerospace) require the increase in using materials with high capacity to be recycled and reused in order to diminish environmental impact to the minimum, therefore contributing to the growth of circular economy principles practice. This is the reason why thermoplastic polymers have gained a great interest from both research and industry directions in the last decade. Thermoplastics, such as polypropylene, polyamide, polyethylene terephthalates etc. represent engineering grade polymers that present high strength to weight properties, good impact properties, durability, good fatigue resistance, low dimensional stability, together with a facile processability and medium-low costs [6]. Among the mentioned thermoplastics, one of the well-known and most intensively used is polyamide (usually named after a trade mark, Nylon), a semi crystalline thermoplastic polymer with low density, excellent wear resistance, good coefficient of friction, very good chemical resistance (especially in contact with oils), very good strength and hardness and very good temperature and impact properties [7]. This excellent balance of properties makes polyamide a great candidate to replace metallic materials as well as non-recyclable thermosets in various applications in transport and high-tech industries where high strength, toughness and weight reduction are an important requirement [7, 8]. The thermoplastic nature of polyamides allows them to be processed by melt compounding at approximately 220-250°C and thermoformed into specific shapes for the target applications.

Often, polyamides are modified by adding different micro/ nanofillers or reinforcing fibers, such as carbon, glass or aramid.

Literature presents research studies regarding polyamide-short aramid fibers [9-12], however there are few using aramid whiskers, by Brabender melt compounding.

The current paper presents the development of polyamide 6 based composites with different aramid whiskers loadings, via melt compounding. The mechanical properties in terms of 3-point bending and impact testing, thermo-mechanical properties in terms of heat deflection temperature and tribological properties show an increase with aramid whiskers concentration increase.

2. MATERIALS

The materials developed for this experimental study were obtained using thermoplastic polymer as matrix (polyamide 6) added with a filling agent (aramid whiskers) in two concentrations, 5 wt.% and 10 wt.%. The technology of processing was by melt blending using the Brabender equipment followed by thermoforming in the mold by pressing in a hydraulic hot-platens press.

The matrix consisted of PA6 pellets, provided by SC MONOFIL SRL, and the filler was in the form of chopped fibers consisting of Twaron whiskers, with lengths of 250 μm and diameter of 8-10 μm, purchased from Teijin. The production process involved a preliminary step of establishing the parameters of processing in the Brabender mixer, respectively in choosing the pressing temperature and dwell time, using only the polymer, without fillers.

Table 1 – The obtained composites after mixing

	PA6	PA6+5%w	PA6+10%w
wt.% Twaron whiskers	0	5	10

Following the process, there were obtained samples of polymer without filler (control sample) and samples consisting of polymer added with aramid whiskers in various concentrations, presented in Table 1. The obtained plates had dimensions of 150 mm x 150 mm x 4 mm, from which specimens with specific geometries for impact testing, 3-point bending, HDT and tribology were cut, by milling.

3. EXPERIMENTAL PROCEDURES

Thermo-mechanical testing consisted of heat deflection temperature evaluation. The determinations of the deflection temperature values were made with the thermal stability under mechanical load QUALITEST Heat Deflection Tester (HDT 1), which operates in the range of ambient temperatures up to 300°C, with a temperature increase rate of 2°C/min. The thermal stability test was performed in accordance with ISO 75 [13] international standard.

Mechanical testing consisted of static and dynamic mechanical tests. The 3-point mechanical bending test was performed with the static mechanical test facility (INSTRON 5982), which uses the BlueHill Universal software. The testing was performed according to the ISO 178 [14] international standard, using a test speed of 2mm/min until the displacement of 1.5 x thickness of the tested specimen was reached. The span between the lower supports of the 3-point mechanical test accessory was 64 mm.

Low speed impact test was performed with the impact tower CEAST 9350. This equipment is a mechanical testing facility in dynamic regime with energy range between 0.59 J and 757 J, having an impact speed between 0.77 m/s and 4.65 m/s and with a free fall distance between 0.03 m and 110 m. The default energy for impacting the developed composites was 8 J, being sufficient to completely pierce the specimens.

Tribology testing. In order to evaluate the developed materials from a tribological point of view, tests were performed with the block-on-ring module of the Universal CETR UMT-3 Bruker tribometer. The testing process is described in the ASTM G77-98 [15] standard, specific to the block-on-ring test, mentioned above, the method that certifies the technique for determining wear after sliding tests, for a range of materials, including polymeric materials. Two of the objectives of the study are the evaluation of the additive influence in the polymeric material, but also their concentration, on the tribological behavior when sliding in dry regime against harden steel, using the block-on-ring tribometer. The parameters used to test the materials, simulate a severe regime, represented by a sliding speed of 1000 rpm (1.83 m/s), and a pressing force on the specimen of 50 N, 75 N or 100 N. The test time was relatively short, only 10 minutes (1099.21 m), but enough to bring the specimens to the glass transition temperature [16].

To record the coefficient of friction, the Universal CETR UMT-3 Bruker tribometer is equipped with a transducer that measures in real time the friction force and calculates the COF according to the normal force and the resistance force at a "t" moment of the test. The dedicated program of the tribometer allows for the visualization of the measured and calculated parameters.

For all the tests described above, at least 3 repetitions were performed to ensure the correctness of the recorded data. Samples that showed non-compliant values were excluded from the final average value.

Morphostructural analysis consisted of optical microscopy and scanning electron microscopy evaluation. Optical microscopy images were captured using Meiji 8520 microscopy, on the impact tested samples, while scanning electron microscopy investigations were performed on tribological tested samples using SEM QUANTA 250 equipment.

4. RESULTS AND DISCUSSIONS

Figure 1 shows displacement-temperature curves determined during the HDT measurement of the developed composites.

It can be observed the positive influence of aramid whiskers on the HDT deflection temperature values.

For specimens with 5 wt.% aramid whiskers, the values are improved by 13% and for those with 10 wt.% aramid whiskers, the results are improved by 30%.

For materials with short aramid reinforcement, the temperature at which the deformation begins is clearly higher compared to the temperature at which the simple PA6 begins to deform. The results obtained from the performed HDT tests are presented in table 2.

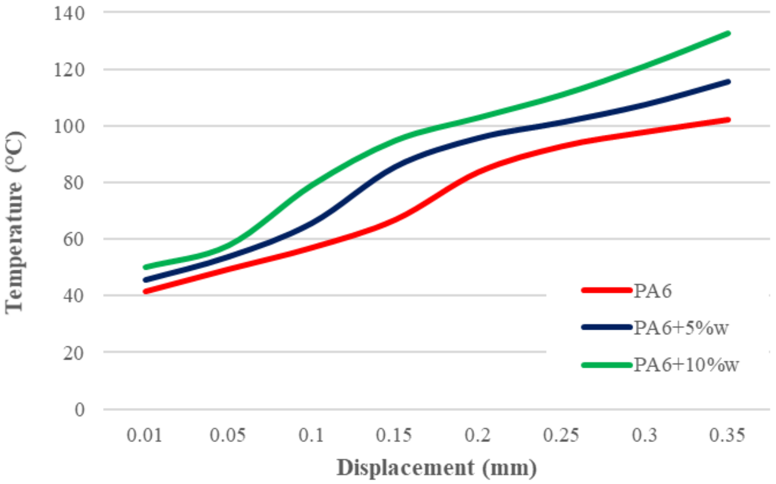

Fig. 1 – Displacement-temperature curves for HDT determination of PA6 samples and PA6 mixed with 5 wt.% and 10 wt.% aramid whiskers, respectively

The 3-point mechanical bending tests were performed for all the developed materials. From Figures 2, 3 and 4, it can be seen that the composites with aramid whiskers loadings have superior mechanical properties compared to the control material.

Mechanical properties increase with whiskers content increase, the composites based on PA6 and 10 wt.% aramid whiskers present the highest results amongst the materials tested. The resistance values increase by 13% for the samples with 5 wt.% aramid whiskers and respectively 22% for the samples with 10 wt.% aramid whiskers. Also, the values of the modulus of elasticity increase by 10% for samples with 5 wt.% additive and by 16% for samples with 10 wt.% additive.

Table 2 – Effect of aramid whiskers content on mechanical properties of PA6 matrix

Aramid whiskers content (wt.%)	HDT (ºC)	Flexural Strength (MPa)	Absorbed Energy (J)
0	102.2	75.16	1.253
5	115.5	85.24	1.372
10	132.7	91.70	1.848

After performing the three-point mechanical bending tests, the mediated values of each group of tested materials were added in Table 2.

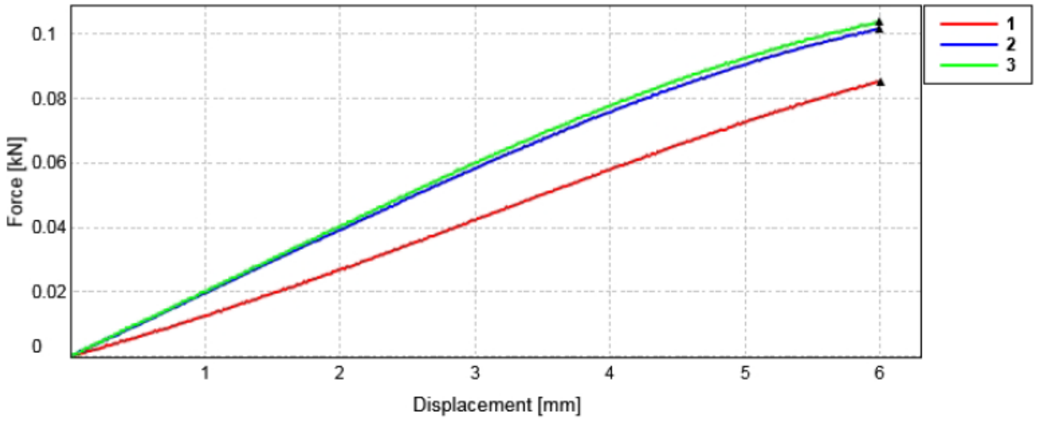

Fig. 2 – The force-displacement curves resulting from the bending test of the samples made of PA6

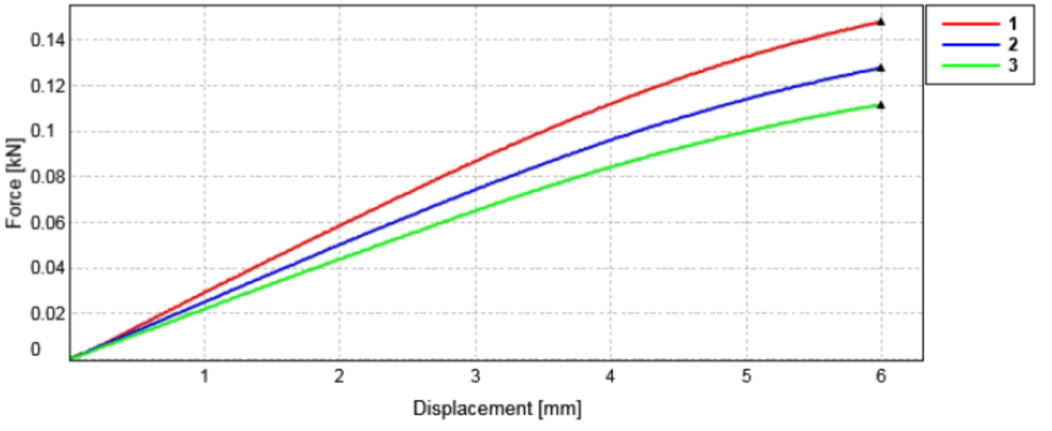

Fig. 3 – The force-displacement curves resulting from the bending test of the composite PA6 + 5% aramid whisckers

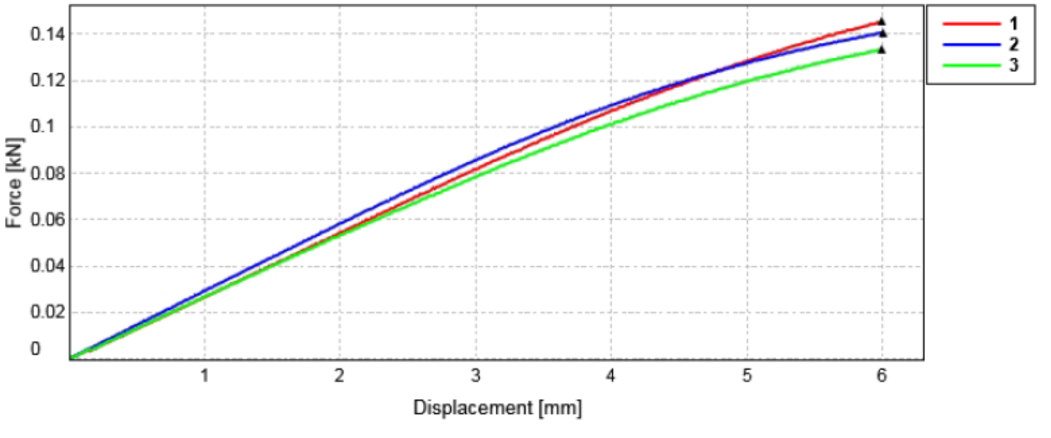

Fig. 4 – The force-displacement curves resulting from the bending test of the composite PA6 + 10% aramid whisckers

Images 5 and 6 show the sample and additivated PA6 specimens with 10% aramid whiskers, tested on impact by free fall before and after testing.

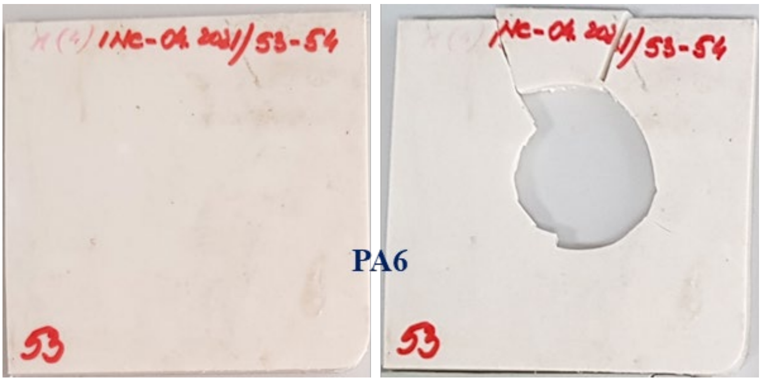

Fig. 5 – Images of PA6 samples before and after testing on impact by free fall

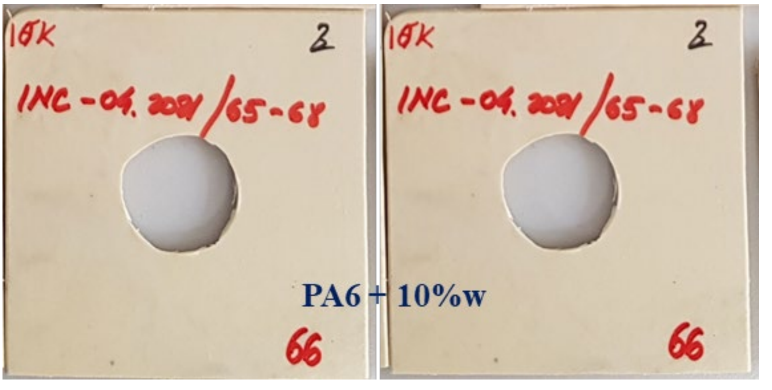

Fig. 6 – Samples made of PA6 + 10% aramid whiskers, before and after testing on impact by free fall

For the aramid fiber reinforced specimens, both mass concentrations of whiskers showed improved values of absorbed energy after impact, as compared to control PA6 samples.

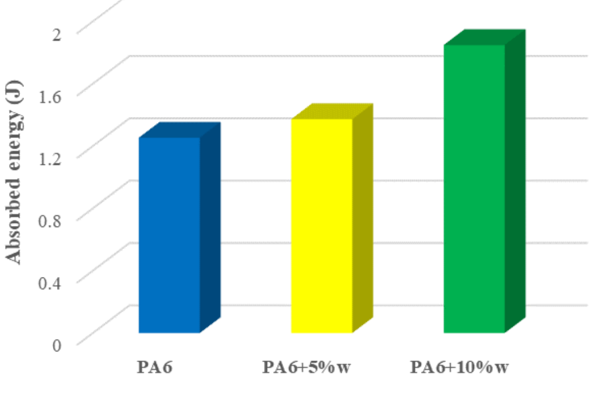

Fig. 7 – Impact absorbed energy diagram for PA6 and PA6 + aramid whiskers composites

The average value of the absorbed energy for the samples additivated with 5 wt.% aramid whiskers showed increases of 9.5% compared to the average value of the absorbed energy of the control samples. The samples with 10% filler showed an increase of 47% absorbed energy compared to PA6.

These results are in line with the expectations and values obtained in HDT and 3-point mechanical bending tests and taking into account the high tenacity of aramid fibers, which recommends them for ballistic applications.

Analyzing the results presented in table 2 a considerable increase can be observed for all mechanical performances of the composites with 10% aramid whiskers.

After performing tribological tests for all developed materials, the test specimens were weighed, and based on the data obtained, the average weight loss was determined depending on the material and test parameters, as shown in Figure 8.

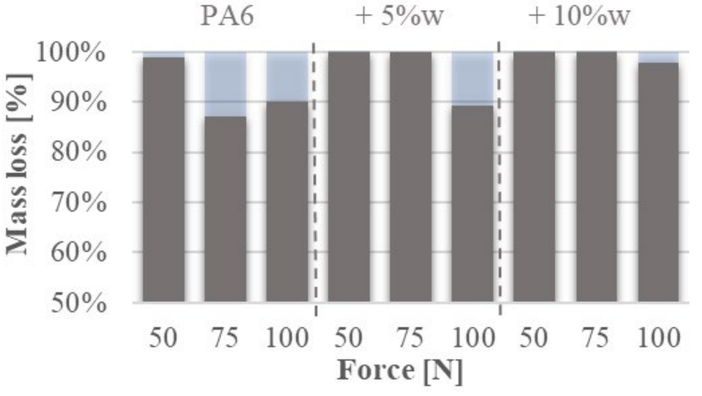

Fig. 8 – The average values of the material losses of the specimens, as a result of the dry friction tests

Analyzing Fig. 8 it can be seen that in the case of aramid whiskers based materials, at least for the used conditions, the mass loss is significantly reduced, except for the concentration of 5 wt.% aramid whiskers, where the mass loss is higher compared to the control material, tested under the same conditions.

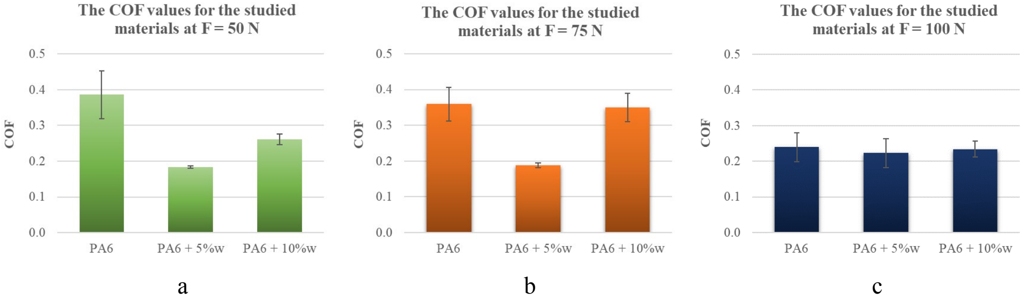

Fig. 9 – The average values of the the friction coefficients, as a result of the dry friction tests

In Fig. 9 (a, b and c), the average values of the friction coefficients are represented for each developed material and also their standard deviations. For the tests performed at a force of 50 N (Fig. 9a), a major increase of the coefficient of friction for the non-additivated material can be observed, but also a large deviation. This means that the glass transition temperature is reached more easily, which leads the material to thermo-mechanical degradation. Also, the abrasive and adhesive wear increased. At a force of 50 N, the lowest coefficient of friction, below 0.2, is showed by the material added with 5 wt.% aramid whiskers, which improves the coefficient of friction by about 50% compared to the non-additivated material.

The tests performed at 100 N (Fig. 9c) show that the influence of the additive is no longer significant, the values of COF being close of each other for all the tested materials.

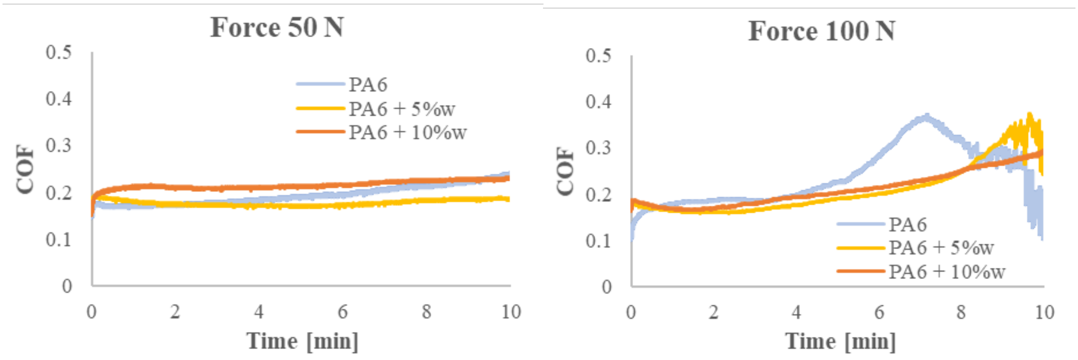

Fig. 10 – Variation of the COF in time at forces of 50 N and 100 N

Analyzing the variation of the COF over time, presented in Fig. 10, all the materials developed show a good stability during the whole test.

The exception is the test with 100 N applied force in which the COF variation for all materials increases towards the end of the test.

After performing the tribological tests, the mediated values of coefficient of friction for all of developed materials were added in Table 3.

Table 3 – Effect of aramid whiskers content on tribological properties of PA6 matrix

Aramid whiskers content (wt.%)	**Force (N)**			
	50	**75**	**100**	
0	0.3860	0.3594	0.2395	COF
5	0.1832	0.1883	0.2232	
10	0.2618	0.3500	0.2340	

The behavior of materials when subjected to mechanical stress, either in static or in dynamic regime, is very important for evaluating the properties and, consequently, the performance of the tested materials, for certain applications.

In addition to numerical values and mechanical curves, post-test light microscopy (Fig. 11 and Fig. 12) provides important information about how the material withstood the applied mechanical load and possible failure mechanisms.

Figure 11 illustrates areas of one of the controls PA6 test specimens after impact testing. Area 1 illustrates a crack captured on the surface of the material.

Although macroscopically, the material does not appear completely torn, microscopic images captured at 40x magnifications illustrate the penetration of the crack into the depth of the material.

The images captured in area 2 illustrate the edges of the rupture zone, observing the specific rupture mode of a ductile polymer, such as polyamide 6.

Zone 3 illustrates an area marginal to the rupture zone, observing numerous superficial cracks (scratches) on the surface material.

The PA6 sample shows no gaps or traces of unprocessed polymer (pellets).

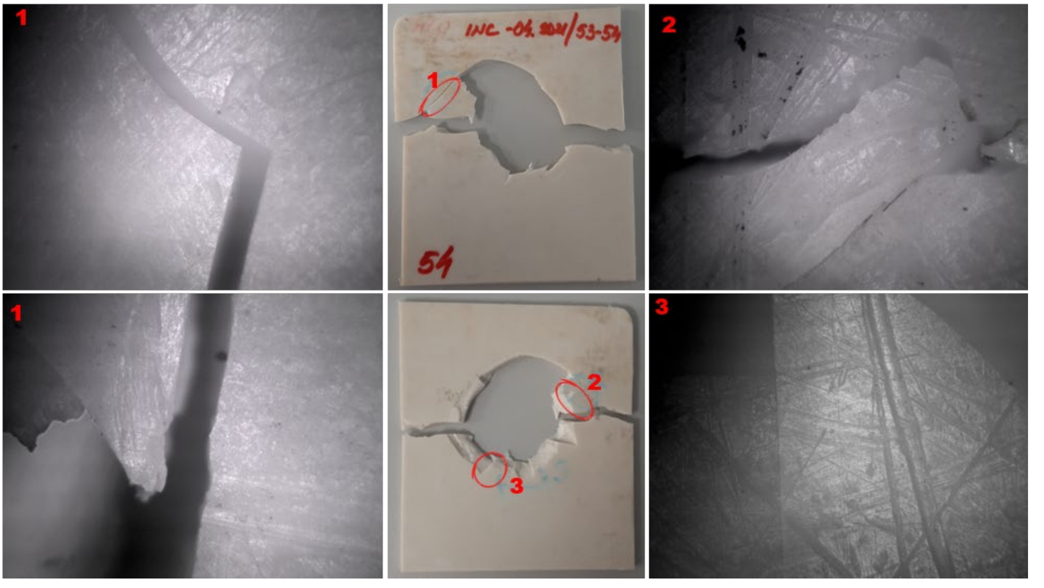

Fig. 11 – Micrographs captured in various areas of the PA6 sample after impact testing
(40x magnification)

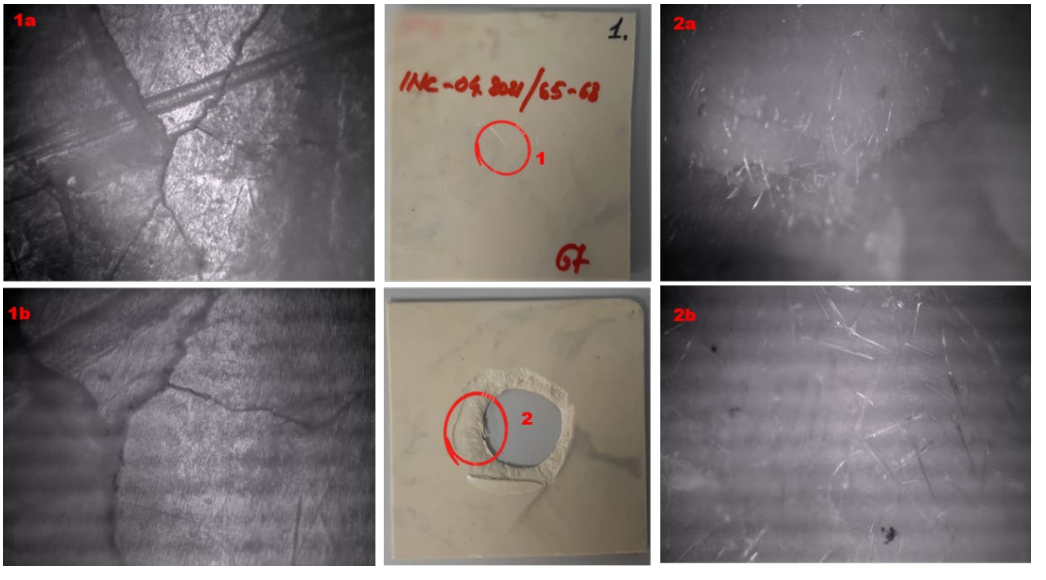

Fig. 12 – Micrographs captured in various areas of the PA6 + 10 wt.% aramid whiskers after impact testing
(a - 40x magnification, b - 100x magnification)

Figure 12 illustrates areas from two of the PA6 + 10 wt.% aramid whiskers specimens after impact testing. Following the impact test, the first specimen showed only the radial crack around the impact zone, the figures illustrating area 1 emphasize the radial propagation of the cracks. The second test piece showed the complete breaking and detachment of the impacted area, behavior shown by all the other test pieces.

In the breaking section (area 2) the absence of gaps is noticed along with a very important aspect, namely the presence of short aramid fibers, whose distribution has a uniform appearance on the visualized areas, even at this concentration of 10 wt.%w compared to the polymer.

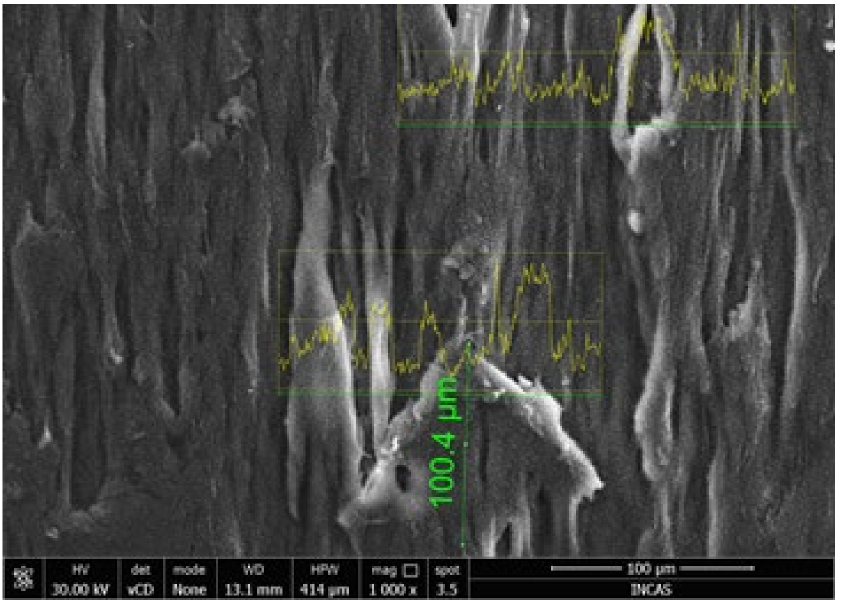

Fig. 13 – SEM Micrography of PA6 material tested at 100 N force (1000x)

Microscopic analysis of polymer samples with added fillers was performed in order to observe the changes induced in the structure of the polymer but also the morphology of the specimens after mechanical testing at different loads.

The values of the friction coefficients as well as the values of the stress-deformation curves are completed by the SEM morpho-structural images and the fractographic analysis.

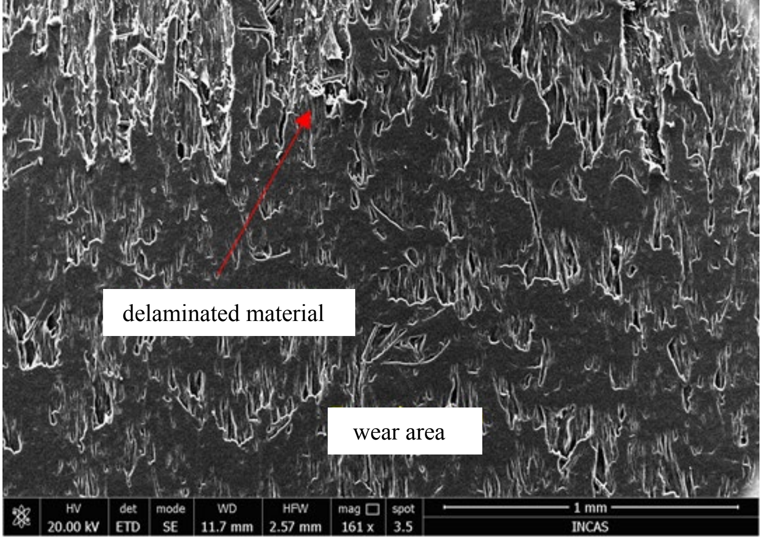

Fig. 14 – SEM Micrography of PA6 material tested at 100 N force (1000x)

Figures 13 and 14 show the micrographs of the control specimen after tribological testing. There is a specific morphology of the material in this type of test, with areas of material torn in the marginal areas and those on the direction of flow in the contact area. At the beginning of the contact area there are no discontinuities or detached material.

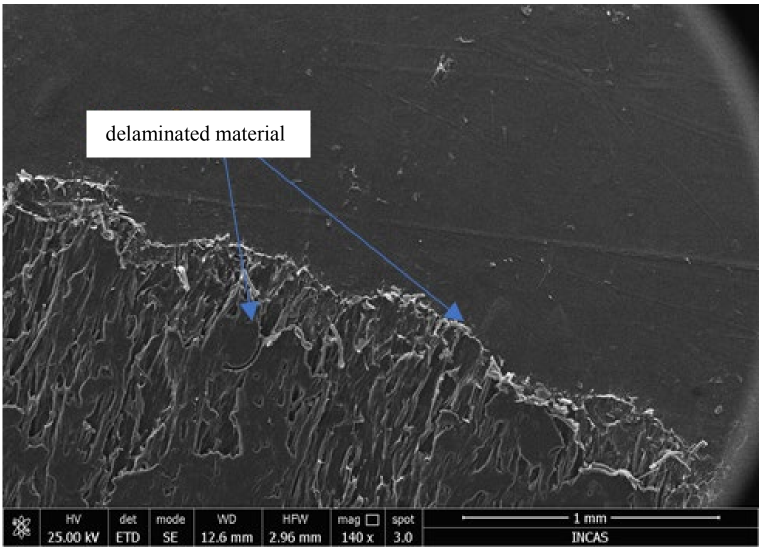

Fig. 15 – SEM Micrography of PA6 material tested at 100 N force (1000x)

Figure 15 illustrates the SEM micrographs of sample PA6+10%w after tribological testing at 100 N load. In the contact area, at the edge of contact zone of the block, a delamination of the material is highlighted. The central zone of the tested sample, shows a wear area with material detachments.

Optical microscopy as well as SEM investigations prior testing (impact and tribological respectively), corroborated with the thermo-mechanical, mechanical and tribological test results indicate the existence of a strong fiber-matrix interphase in the developed materials, indicating that the melt compounding processing was a suitable method to manufacture these samples.

5. CONCLUSIONS

For composite specimens with aramid whiskers as reinforcement, both mass concentrations of 5 wt.% and 10 wt.% whiskers, showed improved values of mechanical properties, regardless of the testing methods used, as compared to control PA6 specimens.

The mediated value of the absorbed energy for the samples with mass addition of 5% showed an increase by 9.5% compared to the mediated value of the absorbed energy of the control samples, and in the case of samples with mass addition of 10% fillers, these values increased up to 47% as compared to values obtained for samples made of PA6.

Wear tests reveal that in the case of materials with aramid whiskers, at least for the used test conditions, the mass loss is significantly reduced.

Samples with a concentration of 5% and 10% aramid whiskers, respectively, have a much better wear resistance, as compared to control sample materials, a fact supported by the decrease of the contact area illustrated in the presented micrographs.

These results indicate that the composites with aramid whiskers have a better response to impact, as they absorbed more energy. The corroboration of the experimental results indicates the positive effect of aramid whiskers on the evaluated properties, suggesting that high quality materials with a strong matrix-fiber interphase were developed through the melt compounding processing.

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