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ADVANCES OF LASER SURFACE TEXTURINGON THE POL YAMIDE PARTS

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Abstract: Laser surface texturing (LST) technology improves the surface morphology and characteristics of materials by modifying their texture and roughness. The different behaviors during wettability test, depending on the texture pattern and number of passes suggest a complex dependence on the surface microstructure and the dynamics of surface energy change. Laser texturing significantly alters the coefficient of friction (COF) and wear behavior of the materials analyzed in this study PA6.6 and PA6.6 reinforced with glass microspheres. The increase in surface roughness after texturization is the main factor driving the higher COF values. Textured patterns have a functional role in the accumulation of wear debris, which contributes to the improvement of the wear behavior of textured surfaces. All tests showed a weight increase after degradation, suggesting incomplete degradation or chemical reactions with the test environment. The studied materials can be used in industrial applications such as functional coatings, components in the filtration industry, wear parts in the mechanical industry.
Key words: PA6.6, PA6.6 reinforced, COF, Wettability, degradadation.

1. INTRODUCTION

Laser surface texturing (LST) is an advantageous method for metal surface modification owing to its noncontact nature, rapid execution, exceptional precision, and ease of control, [1, 2]. This approach can improve metal–polymer adhesion by enhancing polymer wettability on metal or establishing a mechanical interlock between the two materials, [3, 4]. Prior research has investigated the influence of LST on metal–polymer interfaces. Liu et al. employed laser surface treatment (LST) to bond Ti6Al4V with carbon fiber-reinforced plastic (CFRP). The joint strength improved thrice relative to non-laser-textured Ti6Al4V-CFRP joints, attaining approximately 8.5 MPa, [5]. Lambiase et al. conducted laser texturing on AA7075 aluminium alloy and subsequently combined the laser-textured AA7075 with polyether ether ketone (PEEK) using friction-assisted joining. The highest joint strength was around 9.0 MPa, [6]. Liu et al. utilised the LST process on AZ31B magnesium alloy to link carbon fiber-reinforced thermoplastics (CFRTP) with the laser-textured AZ31B. This led to a joint strength nearly double that of non-textured AZ31B–CFRTP joints, with a maximum joint strength of 13.6 MPa, [7] Nonetheless, these tests demonstrated comparatively lower metal–polymer junction strengths than the 25 MPa standard for car structural adhesive bonding.

A group of researchers, [8], conducted an experimental investigation on the effects of laser texturing on the surface roughness and wettability of PAHT CF15 (polyamide composite reinforced with 15% carbon fiber) manufactured by fused deposition modelling. High-speed laser processing significantly alters the surface quality, wettability, and moisture absorption of FDM printed components, [8].

Glass microsphere reinforcement of polyamide (PA) is a commonly used technology to modify the properties of the material according to the desired application. The effects of this reinforcement are likely to include: density reduction: a material with lower density than pure polyamide is obtained by using glass microspheres. This can make the parts lighter, which is beneficial in applications where low weight is essential; improved stiffness: the presence of glass microspheres increases the stiffness of the module. The material becomes more resistant to breakage under load; Reduced shrinkage during injection molding: the material does not shrink as much during cooling due to the glass microspheres, which improves dimensional stability and allows tighter tolerances for injection molded components; Increased abrasion resistance: Polyamide can be made more resistant to abrasion by microsphere reinforcement, making it more suitable for components that are subject to continuous friction; Decreased elongation at break: the material is more brittle than pure polyamide due to the presence of microspheres. In applications that require greater flexibility, it is important to take this characteristic into account; Improved compressive strength - glass microspheres increase resistance to compressive stresses, making the material ideal for applications involving compressive-type loads; Improved isotropic properties - unlike other reinforcing materials such as glass fibers, microspheres help improve isotropic properties, meaning the material will have more uniform characteristics in all directions; Reduced water absorption: Polyamide's mechanical properties are affected by its high tendency to absorb water. Glass microspheres can reduce this absorption, improving performance in damp environments and dimensional stability; Thermal properties: reinforcement with microspheres can improve thermal stability and reduce linear thermal expansion, which is beneficial in applications where temperature variations are frequent. For example, higher brittleness may make the material more susceptible to cracking due to mechanical shocks - Additional costs: the introduction of microspheres makes the material more expensive, which may affect decision making depending on the application. Glass microsphere reinforcement makes polyamide a stiffer, lighter and more dimensionally stable material, but reduces its flexibility. It is a useful solution for technical applications where these characteristics are vital, [9-15].

This study aimed to assess the properties of two materials: PA6.6 and PA6.6 reinforced with glass microspheres. These were textured via the LST approach. The hypothesis posits that the pattern type, pass count, and substrate affect the surface physical and tribological properties of injected polymers. The conducted tests included wear, wettability, and degradation assessments. The findings suggest that several industrial applications may employ the textured polymers.

2. MATERIALS AND METHODS

In order to manufacture the samples, the LST method was applied to texturize two different types of polymers. These polymers were poliamide 6.6 (PA6.6) and poliamide 6.6 reinforced with 5% glass microspheres. A SZ-600H injection machine was utilized by Shen Zhou, who is based in Zhangjiagang, China, in order to acquire the samples that were utilized for texturing. As the method of choice for mechanical finishing, laser micromachining has taken the place of the TERGAMIN-30 grinding-polishing equipment manufactured by Struers in Willich, Germany. The samples were mechanically planed and then polished in sequence with paper grain-size gradations of 500, 800, and 1200 grid/mm2 in time t = 4 minutes for each gradient. This was done before the samples were mechanically polished using polishing wheels with gradations of 9, 3, and 1 μm. During the surface texturing process, a diode-pumped solid-state picosecond laser with a wavelength of 335 nm was utilized. More specifically, an A-355 picosecond laser system was utilized, which was manufactured by Oxford Lasers Ltd. in Didcot, United Kingdom. This system generates pulses with durations ranging from 5 to 10 picoseconds and an energy of 120 µJ. These pulses are produced at a frequency of 400 hertz. Using a Gaussian distribution for the intensity of the laser beam, the texturing system had an average laser power of 24 milliwatts. It was the Cimita software from Oxford Lasers that was utilized in order to construct the laser pattern, which is also referred to as the filling method. This program is integrated into the micromachining equipment. It was used the following state-of-the-art analytical tools to characterize the coated samples' surfaces:

- The geometric structure of the sample’s surfaces and the wear tracks were analyzed using a Leica DVM6 digital microscope (DM).
- *Wettability test* - Contact angle measurements were carried out using the sitting drop method to determine the wettability of the tested samples surface. For this purpose, the Biolin Scientific Attension Theta Flex strain gauge was used. Drops of distilled water as measuring liquid in the volume of 2 µl were deposited on the surface of the tested samples, each time maintaining the minimum (same) height of the dispenser above the surface. Contact angle measurements were performed as a function of time (60 s) in a series of 3 measurements for each sample. The paper will present only the mean value of the contact angle. Measurements were carried out at room temperature 289 K (25°C).
- *Wear test* - The tribological properties of the tested samples were investigated using the ball-on-plate method using a CSM tribometer (CSM Instruments, Needham, MA USA). As a counter sample, an Al_2O_3 ceramic ball with a 6 mm diameter was used. Normal loads of 4 N were used. The stroke length was fixed at 6 mm and the frequency was 1 Hz creating a sliding speed of 1.2 cm/s.
- *Degradation test* was performed using WKL 100/40 - Weiss Climate chamber according to PN-EN 600068-14 standard. Test parameters were: T↓ - T=-5°C w t = 1 h; Aging: T= -5°C. t= 3 h; T↑ - T= 50°C. HD = 90%. t =1 h; Aging – T = 50°C. HD = 90%. t =3 h.

3. RESULTS AND DISCUSSION

3.1 Wettability test

In the wettability assessment of PA6.6 material, the average distilled water wetting angle for the samples in their original state was 64±2, indicating a hydrophilic surface characteristic, as illustrated in Figure 2(a). The contact angle is below 90°. Laser texturing altered the chemical properties of the samples' surface. For samples textured with four passes, the contact angle was approximately 35° for all texture patterns; however, after a certain duration, the value decreased to 0, as illustrated in Figure 1 and Figure 2(b) and (c). It can be noted that samples have superhydrophilic qualities following the initial wetting of the surface. In the set of samples subjected to 6 passes, a comparable wettability condition was noted, as illustrated in Figure 2(d) and (e). For the sample group with six passes and a square pattern, varying initial contact angles were recorded, contingent upon the measured area—33° or 101°. The heterogeneity of the sample's surface or the temporal fluctuations in surface energy may be indicated.

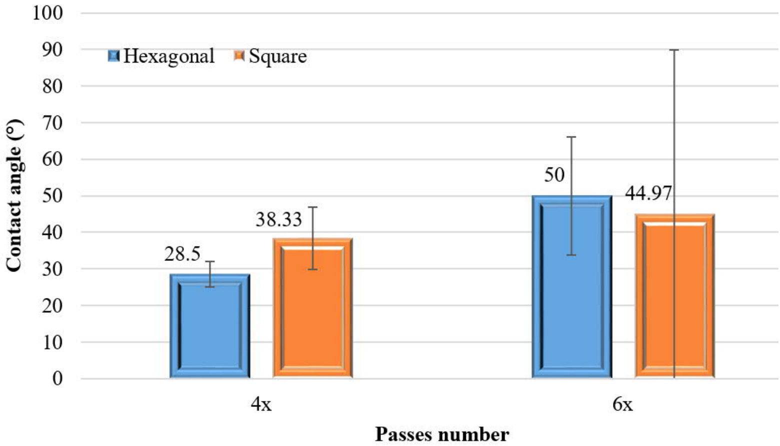
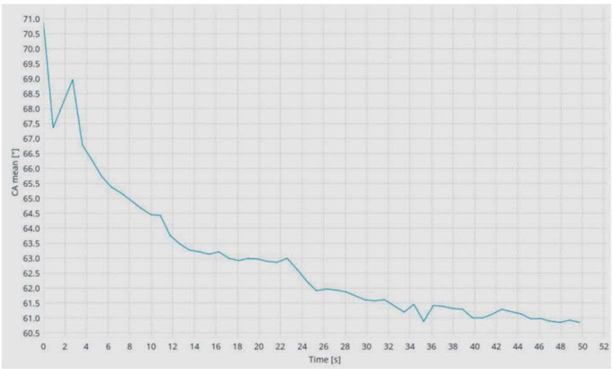
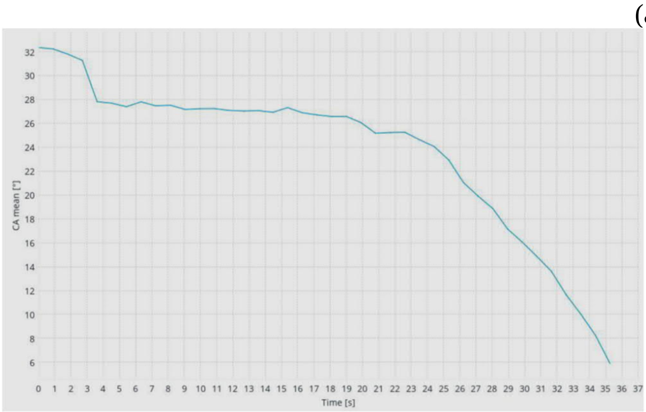


Fig. 1. Contact angle mesourements for the PA6.6 material



(a)



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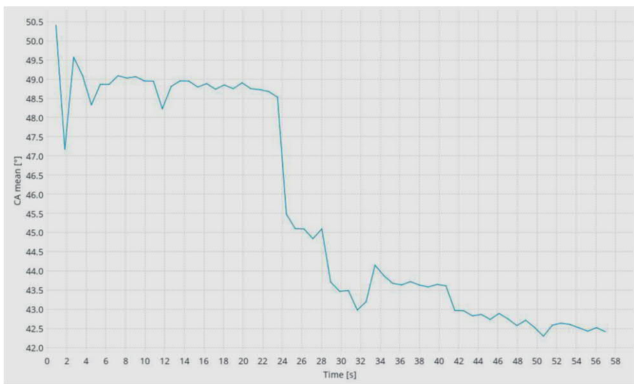

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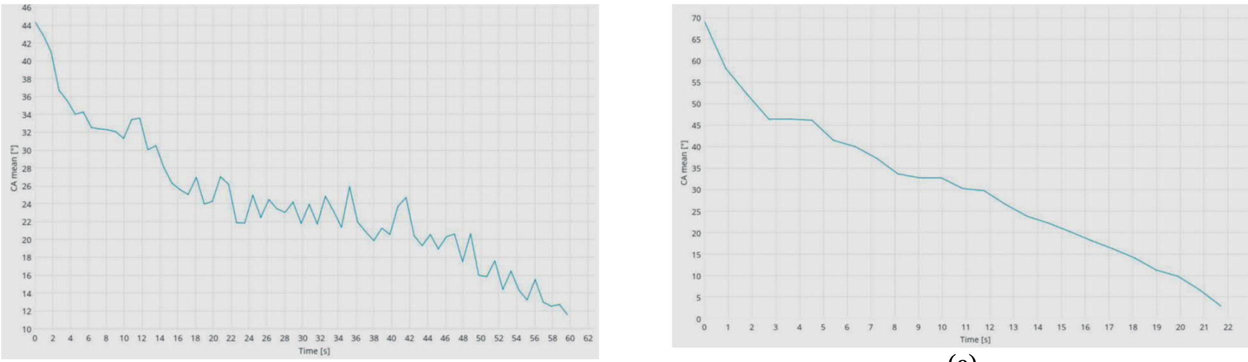


(d) (e)

Fig. 2. Contact angle diagram for PA6.6: (a) initial state; (b) 4 passes - square pattern; (c) 4 passes - hexagonal pattern; (d) 6 passes - square pattern; (e) 6 passes - hexagonal pattern

The mean distilled water wetting angle for Poliamide 6.6 reinforced with 5% glass microspheres in its initial form was 58±2°, signifying a hydrophilic surface (the contact angle is below 90°). Laser texturing for surface modification changed the chemical properties of the samples' surfaces. In the group of samples with a hexagonal texture pattern subjected to 4 passes, the initial contact angle was around 22°, which diminished to 0° after roughly 7 seconds, as illustrated in Figure 4(c). The samples demonstrated superhydrophilic characteristics following the initial surface wetting. In the group of samples with a square texture pattern subjected to four passes, a consistent behavior of the water droplet was noted throughout the testing period, as illustrated in Figures 3 and 4, with an average water contact angle of 63±1°. In the case of the six-pass sample group, irrespective of the texture pattern, the samples demonstrated complete hydrophilic qualities.

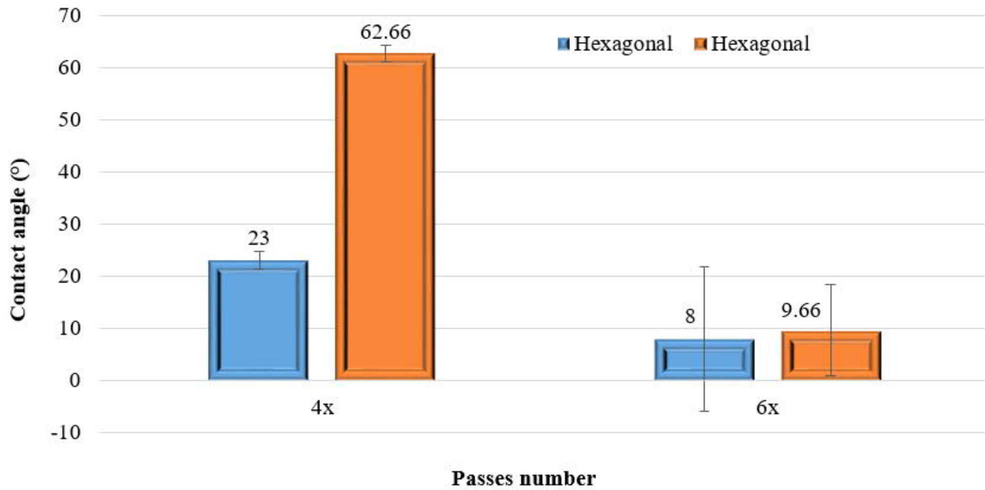
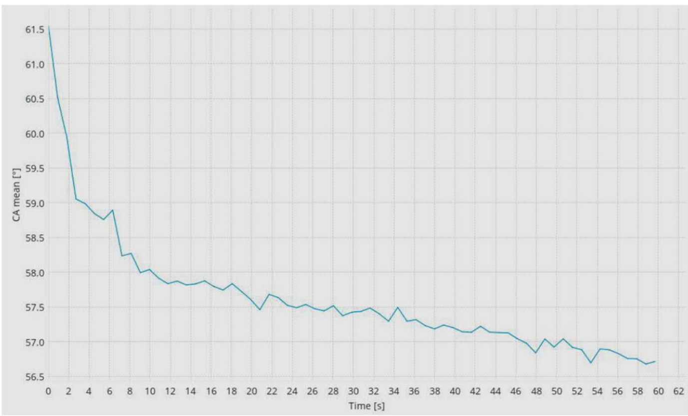
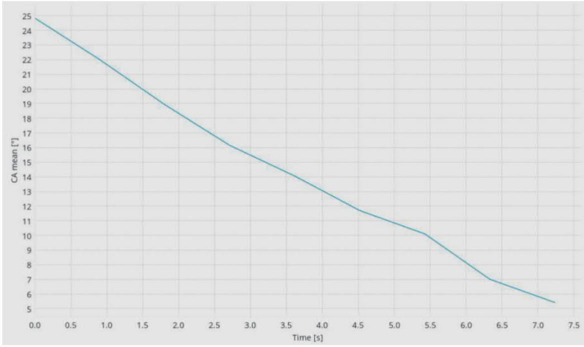


Fig. 3. Contact angle mesourements for the Poliamide 6.6 reinforced with glass microspheres



(a)



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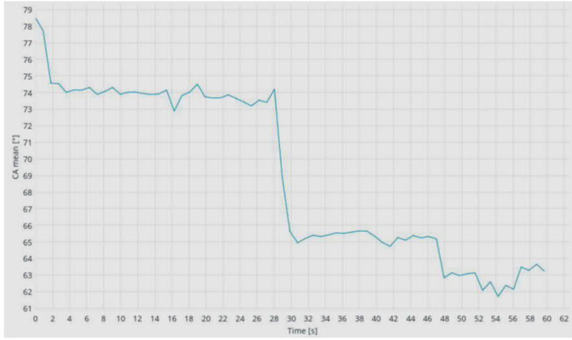

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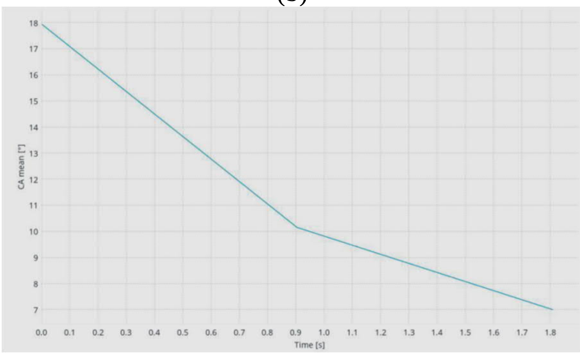

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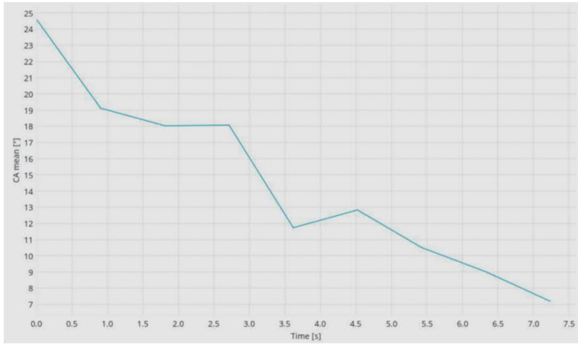
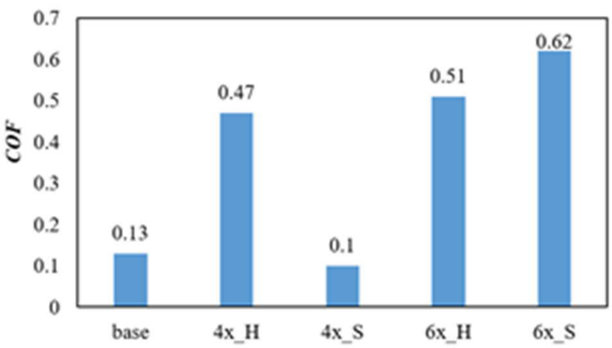


(e)

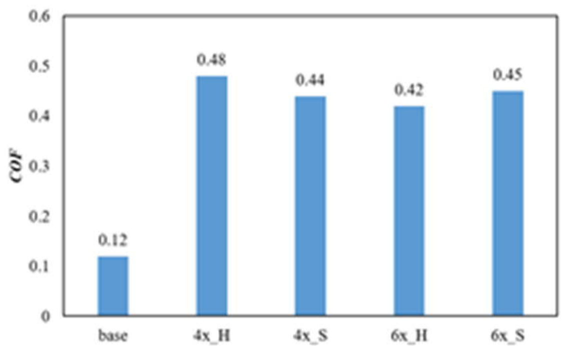
Fig. 4. Contact angle diagram for Poliamide 6.6 reinforced with glass microspheres:
(a) initial state; (b) 4 passes - square pattern; (c) 4 passes - hexagonal pattern; (d) 6 passes - square pattern; (e) 6 passes - hexagonal pattern

3.2 Wear test

The average coefficient of friction (COF) for the PA6.6 sample group in the starting state was 0.13, as depicted in Figure 5(a). Surface modification using laser texturing resulted in a modification of the wear behavior of the PA6.6 material. Only the PA6.6 sample group with four passes and a square texture pattern exhibited a recorded coefficient of friction (COF) comparable to that of the initial state, as illustrated in Figure 5(a). Furthermore, for the PA6.6 in its initial form and the PA6.6 subjected to four passes in a square pattern, the coefficient of friction remained constant throughout the testing duration. An elevation in the COF value was seen for additional samples. For samples exhibiting a hexagonal-textured pattern, irrespective of the number of laser passes, a mean coefficient of friction value near 0.5 was observed. The maximum coefficient of friction (COF) was recorded for the PA6.6 sample group with six passes and a square texture pattern, yielding a mean value of 0.62. Furthermore, for the samples, the coefficient of friction (COF) exhibited an increase throughout the initial phases of the wear resistance assessment. For samples exhibiting a hexagonal-textured pattern, the coefficient of friction remained constant after approximately 5 meters, irrespective of the number of laser passes. For the sample with six passes and a square textured pattern, the coefficient of friction stabilized after approximately one meter. Microscopic examination of wear track morphology revealed that the textured pattern remained intact for all samples following the laser texturing procedure during the wear test under the specified conditions, as illustrated in Figure 6.



(a)



(b)

Fig. 5. (a) PA6.6 material; (b) PA6.6 + glass material

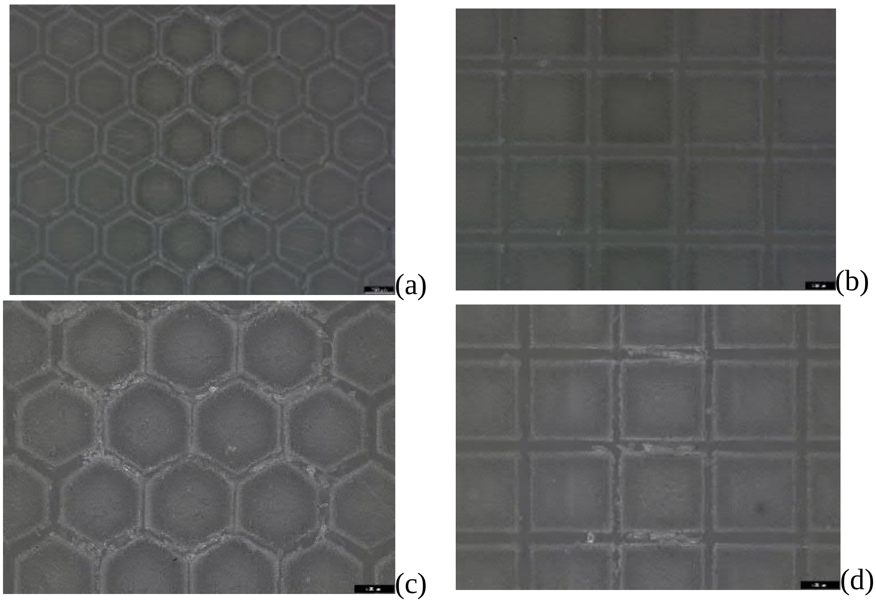


Fig. 6. Wear track morphology of PA6.6 samples group: (a) 4x_H, x300; (b) 4x_S, x400; (c) 6x_H, x300; (d) 6x_S, x300

The average coefficient of friction (COF) for the initial samples of Poliamide 6.6 reinforced with glass microspheres was 0.12, as shown in Figure 5(b). Surface modification using laser texturing resulted in a modification of the wear characteristics of the base material. All examined samples exhibited an increase in the coefficient of friction (COF) value, ranging from 0.42 to 0.48, following the laser texturing process, irrespective of the process parameters and texture pattern. The COF remained constant only for the samples in their initial state throughout the testing period. Following surface modification, the coefficient of friction (COF) exhibited an increase during the initial phases of the wear resistance assessment. For samples textured with four laser passes, irrespective of the texture pattern, the coefficient of friction stabilized after roughly 1 meter. Augmenting the number of laser passes from 4 to 6 resulted in an extension of the distance at which the steady state of the coefficient of friction (COF) was attained – 5 m. Microscopic examination of wear track morphology revealed that the textured pattern remained intact for all samples following the laser texturing procedure during the wear test under the specified conditions, as illustrated in Figure 7.

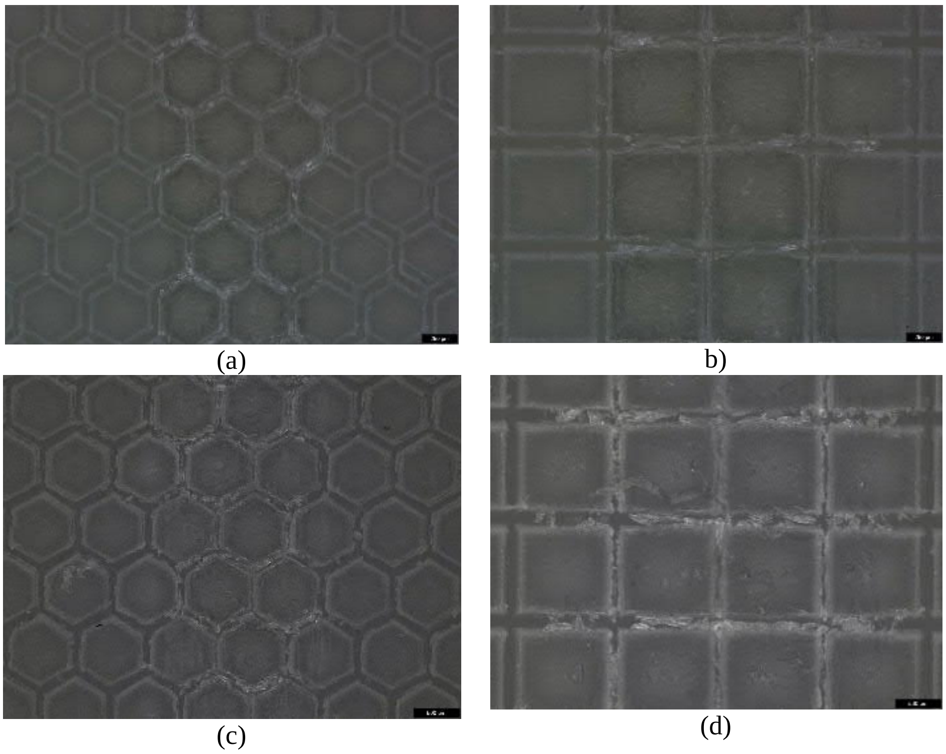


Fig. 7. Wear track morphology of Poliamide 6.6 + glass samples group: (a) 4x_H, x300; (b) 4x_S, x400; (c)6x_ H, x200; (d) 6x_S, x300

In all examined sample groups, it was noted that wear debris produced during the wear process might become caught within the micro-groove structure. This results in diminished wear detritus on the surface, ultimately enhancing wear performance. The elevated COF values observed in samples post-laser texturing can be ascribed to the enhanced surface roughness relative to the base material.

3.3 Degradation test

As can be seen in Table 1, the results of weight measurements that were carried out both before and after the deterioration test reveal that there was an increase in weight for all of the samples that were evaluated. Following a degradation test, an increase in the weight of polymer materials may indicate that the degradation process was not carried out correctly. If the degradation process was not carried out correctly, residues from polymer molecules that were only partially destroyed may persist, which would result in the overall weight increase. Figures 1 and 2 show that a microscopic analysis of all of the samples after the degradation test revealed that there were no obvious degradation products. Polymer-based materials may be exposed to degrading conditions, which can cause chemical reactions that result in weight gain. These reactions may be induced by the interaction of the materials with the testing environment. There are several circumstances in which degradation processes can result in the cross-linking of polymer chains, which ultimately results in an increase in the weight of the material.

Table 1. Results of degradation test

Name		Weight (g)		Difference (g)
		Before	After	
PA6.6	4x	32.898	33.113	+0.214
	6x	33.287	33.499	+0.212
PA6.6+glass	4x	32.680	32.891	+0.211
	6x	33.168	33.377	+0.209

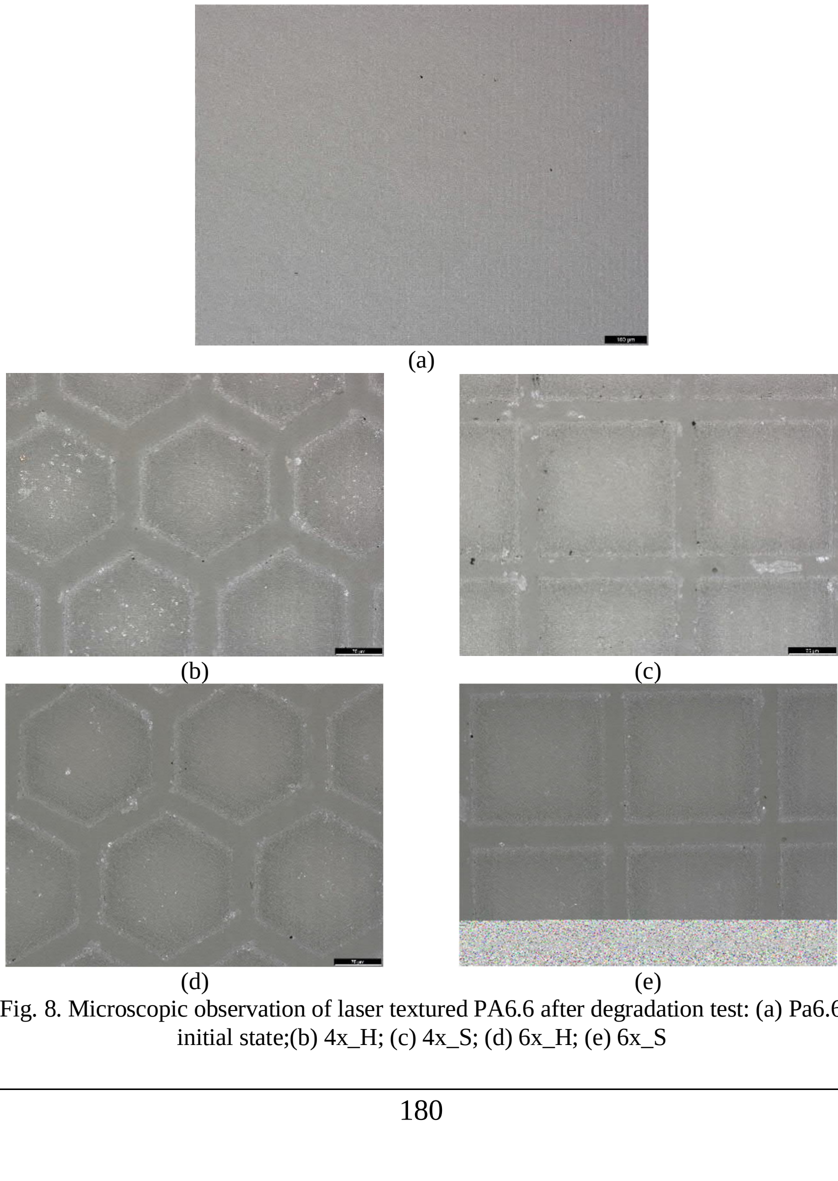
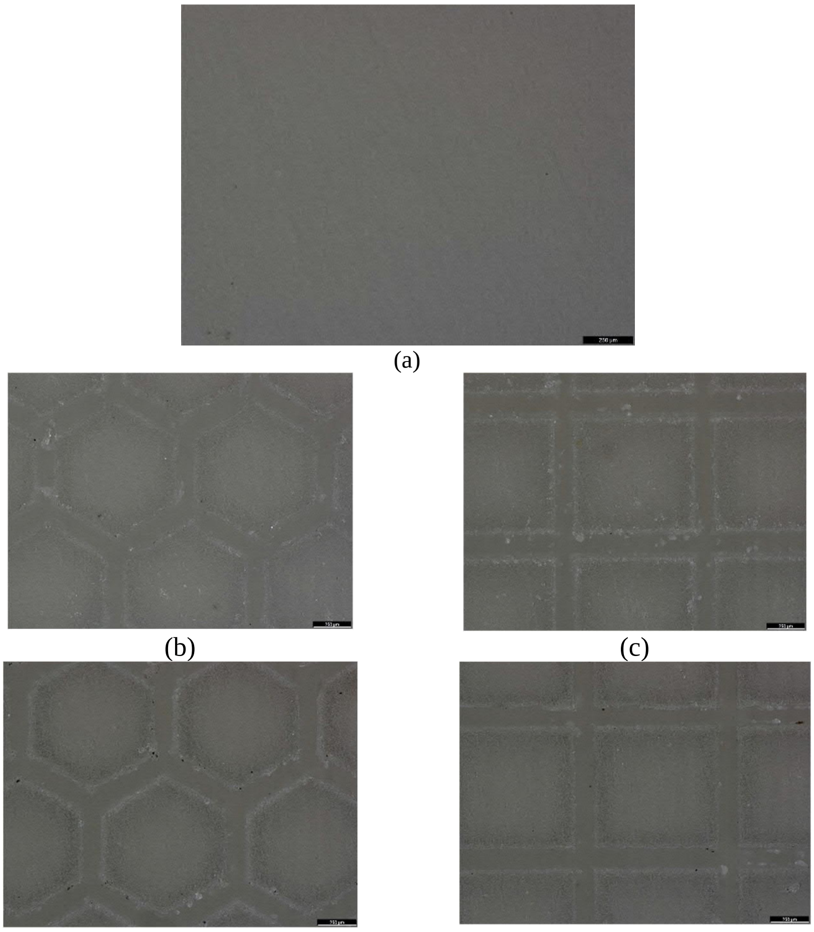


Fig. 8. Microscopic observation of laser textured PA6.6 after degradation test: (a) Pa6.6 initial state;(b) 4x_H; (c) 4x_S; (d) 6x_H; (e) 6x_S



(a)

(b) (c)

(d) (e)

Fig. 9. Microscopic observation of laser textured PA6.6 + glass after degradation test: (a) Pa6.6 + glass initial state;(b) 4x_H; (c) 4x_S; (d) 6x_H; (e) 6x_S

4. CONCLUSIONS

The textured polymeric materials, PA6.6 and PA6.6 reinforced with glass microspheres, show promising characteristics for use in industrial applications due to their versatile behavior, influenced by the type of texturing and process parameters. The analysis revealed the following relevant aspects:

The PA6.6 material and the PA6.6 material reinforced with 5% glass microspheres exhibited a hydrophilic character in the initial state, with average contact angles below 90° (64±2° for PA6.6 and 58±2° for the reinforced material). These values confirm the natural tendency of the surface to attract water. The laser texturing modified the chemical character and surface energy of the samples, leading to improved hydrophilic properties: for 4 passes, irrespective of the texture pattern, the contact angle decreased significantly, reaching values close to 35°. Over time, the surfaces became superhydrophilic (contact angle of 0°). 6-pass samples showed similar behaviors, demonstrating superhydrophilic properties. For the textured samples with 6 passes and square pattern, different values of the initial contact angle (33° or 101°) were recorded, indicating: surface heterogeneity due to texturing; dynamic changes in surface energy over time. Samples of PA6. 6 reinforced with 5% glass microspheres showed varied behaviors depending on the texture and the number of passes: at 4 passes with hexagonal texture, the initial angle was 22°, becoming 0° in about 7 seconds, indicating superhydrophilic properties; at 4 passes with square texture, the water droplet behavior was stable during the test, with an average contact angle of 63±1°; at 6 passes, regardless of the texture pattern, the surfaces showed absolute hydrophilic properties.

For PA6.6 in the initial state, the mean COF value was 0.13, and for PA6.6 reinforced with glass microspheres, the mean value was 0.12, indicating low friction behavior for both materials before surface modification. Laser texturing led to increased COF values for all samples compared to the material in its original state. This increase is attributed to the increased surface roughness after texturization. For all textured samples, the COF increased in the early stages of the wear test, but reached a steady state after a certain test distance. Microscopic analysis showed that the textured patterns created by laser texturing were not removed during the wear tests, which confirms their resistance to the imposed conditions. During the wear process, wear debris accumulated in the micro-grooves created by texturing, reducing the wear debris on the surface and thus improving the wear behavior.

All samples showed an increase in weight after the degradation test, indicating possible incomplete degradation or chemical reactions with the test medium. Microscopic observations revealed no degradation products on the surface of the samples, suggesting internal degradation mechanisms or subtle reactions. The increase in weight can be attributed to: residues of partially degraded molecules; chemical reactions between the material and the test medium; cross-linking of polymer chains, a phenomenon that can occur under certain degradation conditions. PA6.6 and PA6.6 reinforced with 5% glass microspheres, due to their hydrophilic and superhydrophilic properties obtained by laser texturing, as well as their wear and degradation resistant behavior, can be used in industrial applications such as functional coatings for self-cleaning surfaces, components in the filtration industry (where interaction with water is essential), wear parts in the mechanical industry and equipment for corrosive or controlled degradation environments.

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