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The 3D/4D Printing Defects and Their Influence on the Functional Behavior of the Achieved Items from Renewable Compounds. (I)

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Abstract: *The paper is part of a series in which the influence of the manufacturing defects on the functional behavior in biodegradation medium of some items obtained, both by 3D printing and by classical procedure (pressing), from an originaly renwable matrials based on polylatic acid will be presented. The first results regarding the correlation of the defects appeared at manufacturing into plates with the biodegradation behavior in an Aspergillus Niger(A.niger) medium, studied by SEM microscopy, are presented. These results demonstrated that the development of the A. Niger microorganism is related manly to the defects appeared at the melt processing of renewable polymeric material into finished product. A notable role in controlling the appearance of the manufacturing defects belongs both to the melt rheological properties which are responsible for the continuous or discontinuous flow and to the technical performance of the used equipement, 3D printer or classic hydraulic press. If the polymeric material melt has too high viscosity than the continuous flow is not possible and so the overlapped melt fronts are created which generate the voids formation, sometimes joined by small nano and/or micrometric channels. The rheological properties of the melts depend both on the material formulation and the seleted melt processing conditions.*

Keywords*: biodegradation, 3D printing, renewable compounds, surface and mass initial defects*

1. Introduction

Due to its functional properties, polylactic acid (PLA) is a renewable polyester successfully used instead of conventional polymers such as PP, PET which an be transformed into finished product considering both classical melt processing technologies and the revolutionary 3D printing methods. PLA is an ideal candidate for obtaining new materials for 4D printing, thnique which differs from 3D alternative by that the 4D printed item will change, in time, its shape, color, etc, the time becoming thus the 4th dimension, near the 3 known those, in the x, y, z directions [1-7].

Biodegradation is the capacity of a material to decompose completely under the microorganisms action, such as bacteria and fungi in a reasonable period of time and under particular conditions resulting in CO_2, CH_4 and biomass [8]. Biodegradation depends on the factors as shape, exposed surface area, thickness, the existence of both abiotic (temperature, atmospheric water/salt concentration, photo-degradation, hydrolysis) and biotic factors (presence of proper strains of microorganisms) [9,10]. Biodegradation of polyesters is a complex process that takes place in the following stages: biodeterioration (modification of the physical and chemical properties of the polymer [11,12]), depolymerization (transformation of the polymer into monomers and dimers by enzymatic cleavage [13]), bioassimilation (absorption of molecules by microorganisms [13]), mineralization (formation of oxidative metabolites after degradation [14]).

PLA is the material with the lowest biodegradation rate if compared to other materials but it can be composted both in industrial and domestic composters [15-20]. PLA has a molecular structure similar to fibroin, substrate of serine protease. As a consequence, first report on microbial degradation of PLA highlighted the role of serine proteinase K released by a strain of the mould *Tritirachium album* [18].

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Most of the PLA-degrading microorganisms phylogenetically belong to the family of Pseudonocardiaceae and related genera such as Amycolatopsis, Lentzea, Kibdelosporangium, Streptoalloteichus, and Saccharothrix. Several proteinous materials such as silk fibroin, elastin, gelatin, and some peptides and amino acids were found to stimulate the production of enzymes from PLA-degrading microorganisms. In addition to proteinase K from Tritirachium album, subtilisin, a microbial serine protease and some mammalian serine proteases such as alpha-chymotrypsin, trypsin, and elastase could also degrade PLA [15]. An efficient degrader of PLA is *Actinomycetes* belonging to *Amycolatopsis* genus, which might play an important role in PLA natural biodegradation [21-24]. Besides the ability for PLA degrading, the microbial secreted enzymes hydrolyze other substrates with the same constitutive units as PLA, α-amide and α-ester. There are reports on the environmental degradation of PLA by bacterial strains isolated from natural environment. A *Pseudomonas* sp. strain isolated from activated sludge samples produced an unique extracellular PLA depolymerase with applicative potential in biodegradation of plastic materials [25]. Two common bacterial strains isolated from digester sludge, *Pseudomonas* and *Bacillus,* where found to be active in PLA degradation, producing morphological changes evidenced by SEM and physical disintegration [26]. Several fungal species were also reported for degradation of lactic acid and its copolymers. *Aspergillus ustus* and *Penicillium verrucosum* were efficient in biodegradation tests carried out in dynamic conditions at 30°C for 10 days in a medium containing 0.1% of PLA foil as carbon source. Out of several fungi examined belonging to various genera like *Aspergillus, Trichoderma, Penicillium, Fusarium* and *Paecilomyces* tested, a *Fusarium culmorum* strain presented the better growth in presence of PLA as carbon source [27]. Species of *Aspergillus* genus were successfully used for the plastic biodegradation experiment [28-30].

As the authors' researches regards, the development of new polymeric materials based on renewable polymers designed for 3D and 4D printing-fused deposition modeling (FDM) method, it was necessary to find a method to identify the structural defects resulted from the printing procedure and to highlight the influence of the found defects on the behavior in use of the items thus obtained. The purpose of the paper was to estimate the extent in which the content of 3D printing defects seriously affects the-service life of the printed items. The first results regarding the correlation of the surface and mass defects of the 3D printed plates appeared at obtaining and the biodegradation behavior in Aspergillus Niger (A.niger), studied by SEM microscopy, in this paper are presented.

2.Methods and materials

Because of their widely usage in many application of practical interest, the items as plates were chosen for biodegradation study. This application was simulated by achieving (Figure 1), from a modified PLA according to an own formulation, both by 3D printing (Figure 1a, Figure1b) and classical method of thermoplastic pressing (Figure 1c), plates with selected dimensions (20 x10 x 2mm). The 3D printing was performed by depositing layers of material in the vertical (Figure 1a) and also in horizontal direction (Figure 1b) in classical melt flowing conditions.

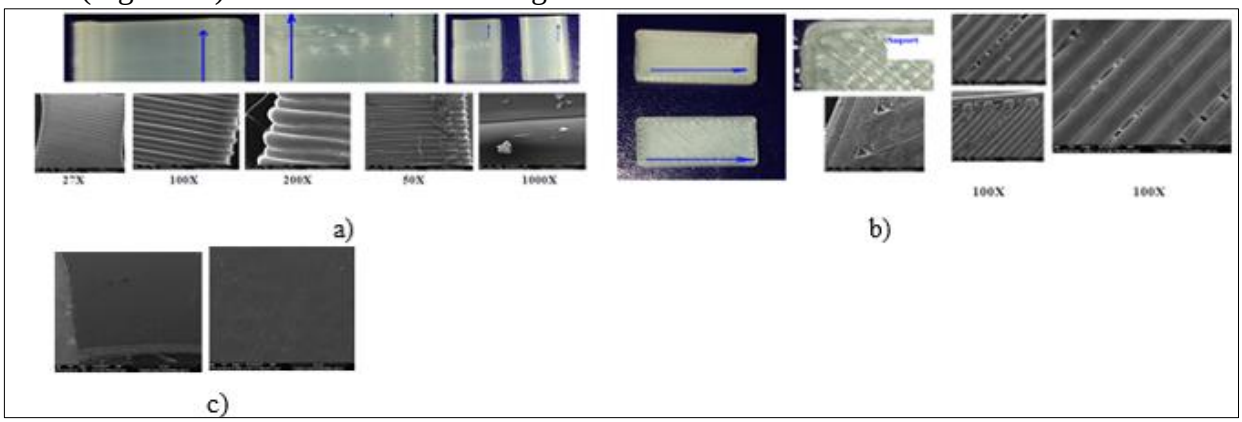

Figure 1. Plates made both by 3D printing with vertical (a) and horizontal (b) deposition of the layers of and by the classical pressing (c)

The 3D printing was made on a UP! Plus 2 3D Printer, Z SPOT MEDIA SRL, 10-100 cm^3 / h printing speed, 140x140x135 mm printing size, self-generated model support, 0.20-0.40 mm or 0.15-0.35 mm layer thickness, STL file input format. The plates were obtained on a hydraulic press using classical conditions (200 °C, 5min. /10 min.5 min., 200 kgf).

In the first stage, the plate's defects generated by the obtaining procedure (3D printing or pressing) were identified by SEM microscopy and then the plates whose surface or mass defects were identified were immersed in the biodegradable medium. Biodegradation was achieved by culturing in a liquid medium, under controlled conditions of temperature and stirring, a selected strain of A. Niger 105 which previously demonstrated the ability to degrade polymeric materials. 50 mL of ¼. dilute liquid Sabouraud medium were distributed in 100 mL Erlenmeyer flasks. The composition of the medium was (w / l): 10, glucose; 2.5, peptone; distilled water, 1L; *p*H 5.6. The plates were inserted into the flasks with culture medium, which were subsequently inoculated with 1 mL of fungal suspension of A. Niger 105UFC / mL; except for chemical controls which does not contain the microbial agent. The flasks were incubated at 280°C, 120 rpm for 540 days.

2.1.Characterization

Biodegradation was followed by periodic analysis, after 10 days, 90 days and 540 days of immersion into the microorganism medium of the appearance of the plate's surfaces (face and verso) and fractures (SEM microscopy), of the variation of chemical changes (FTIR), and by measuring the weight and the size of the plates (length, width thickness) which were immersed into the biodegradation medium. The first results regards the SEM studies on the morphological changes with the biodegradation time, which was performed using a scanning electron microscope Quanta INSPECT F equipped with electron field emission gun - EFG with a resolution of 1.2 nm.

3. Results and discussions

3.1. Defects of the obtained plates

3.1.1. 3D printed plates by horizontal deposition of material layers

If the printing was done by horizontal deposition of the material layers then on the surface of the resulted plates a small number of defects are observed mainly as voids between the 3D printed overlapped layers (Figure 2a). The voids number is relatively higher on the 3D printed plate surface which was in contact with the printer surface. For this reason, this side of the plates has a rough appearance, visible at image's magnification of X 1000 (Figure 2b). The fracture of these plates shows that although the 3D printing was performed at temperatures selected according to the flow index method [31] there is still a significant number of defects, probably generated by many reasons. A possible reason can be the lack of printer performance and so the melted material layers have not always been deposited one over the other to ensure a good contact between them. It is also possible that the polymeric material did not have the necessary fluidity for an optimal 3D printing behavior.

The fracture's SEM micrografies (Figure 2c) indicate a number of voids appeared most likely due to the improper valus either of the printing speed or of the melt temperature or because of the both these parameters. For these reasons, probably the melt viscosity was too low and therfore, the melt flow was no longer continuous but through overlapping layers and therefore with voids formation. All these results suggest that the final defect number of the achieved plates depends on: technical performance of the used 3D printer, material's formulation and the fluidity of the melt during the 3D printing.

If the material layers wre vertically deposeted then the connection defects between the layers are more frequent. These defects are visible even from the smaller magnification of X500. From figure 3a which shows the defects of the surface of the vertically 3D printed plate, it is very clear that the material discontinuities between the deposited layers through 3D printing are also present in this case too, as for the horizontal 3D printing. The plate outside in contact with the printer surface is also rough (Figure 3b). The SEM micrographies in the fracture proves defects both as sites where there is no contacts between the deposited layers or even as voids into the material of component layers (Figure 3c). The defects

between the deposited layers are more frequent than for the horizontal 3D printing (Figure 2c, Figure 3c).

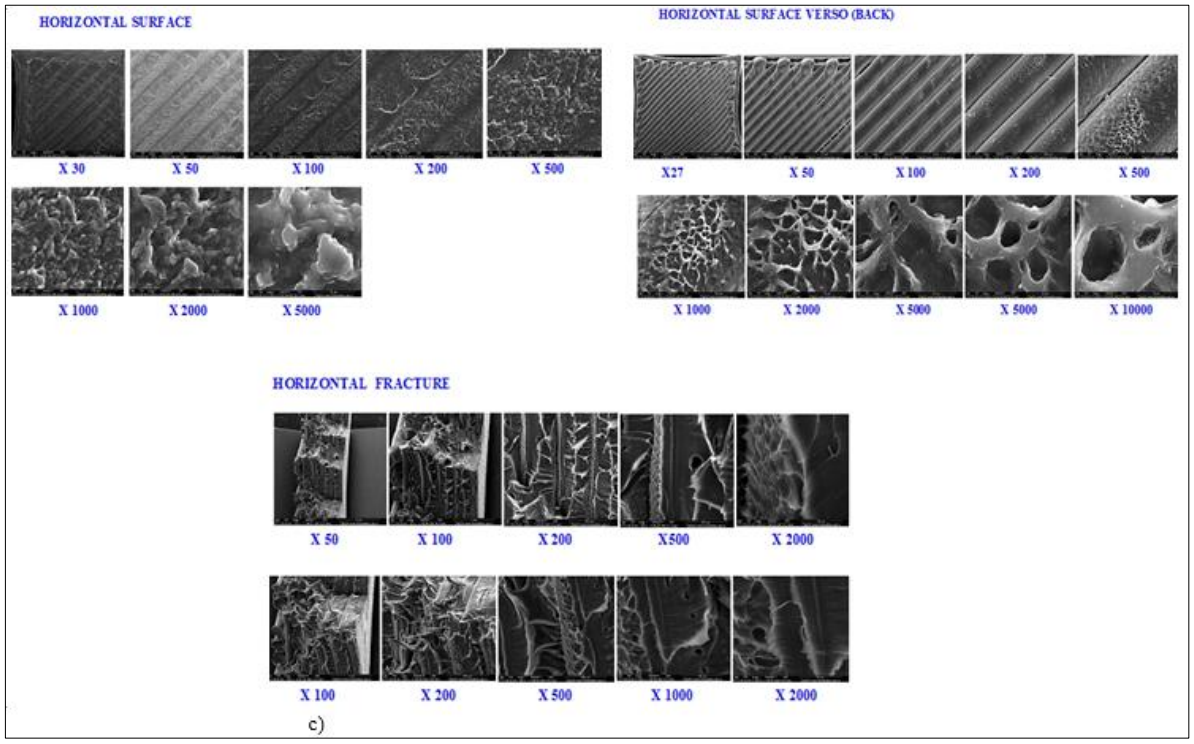

Figure 2. The fracture SEM micrographs of plate achieved by horisontal 3D printing with horizontal deposition of material layers (face, verso, fracture-up and down)

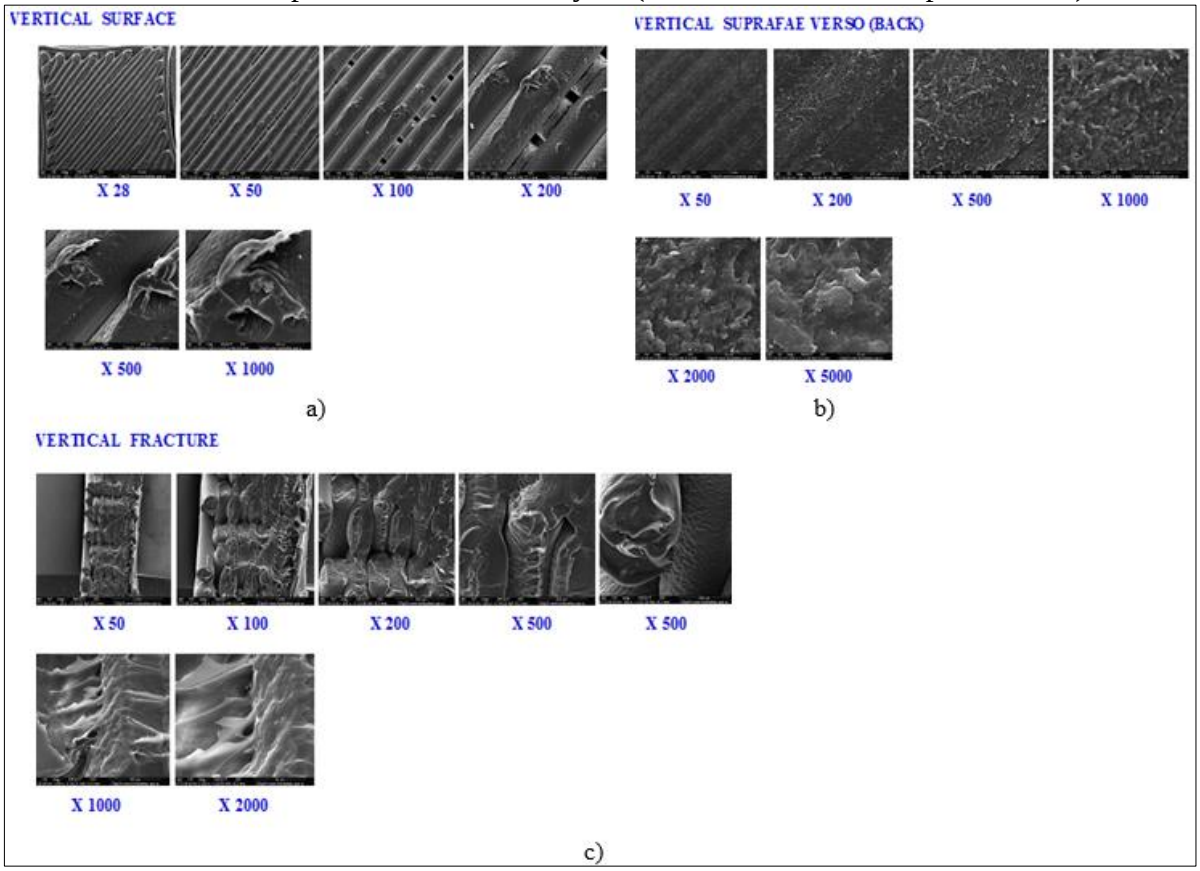

Figure 3. SEM micrographs of plates made of renewable materials by 3D printing with vertical deposition of polymeric layers (front (a), back (b), fracture (c)

In case of the plates achieved by pressing (Figure 4), the defects seems to be mainly concentrated in the fractures (Figure 3) and appear to be the result of the unproper melting flow. The seleted conditions probably do not provide the melt fluidity necessary for a continuous flow and therefore the dynamic viscosity which represent the melt flow resistance [32], is still high enough. No defects were observed on the surface of the pressed plates (Figure 4a) just as it is not observed on the other side of thes plates (Figure 4b). However, in the fractures (Figure 4c) it can be seen the melting flow fronts freeze in positions in which the material flow had no continuity resulting therefore many voids. This behavior is possible if the viscosity of the melt was too low and, for this reason, the melt did not flow as a whole. Under pressure, the material that flowed in unequal fronts, remains discontinuous, irregularly arranged.

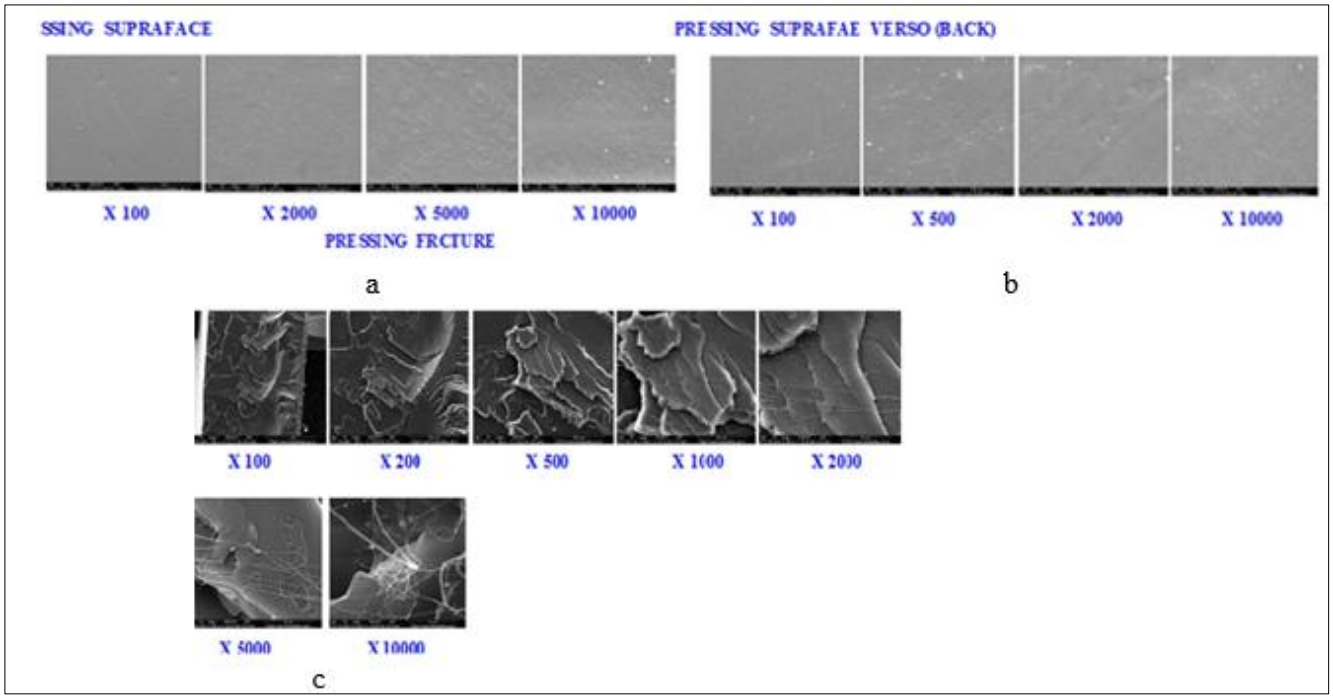

Figure 4. SEM micrographs of plates made of renewable materials by classical pressing (face, verso, fracture)

The above presented results demonstrate that at polymeric material processing into finished product via new technology as 3D printing or by using classical methods, defects of the new items surface or in mass can appear. These defects can be generated by issues as the performance of the equipment, (ex. 3D printer), the materials formulation and last but not least, the materials melt flow properties. The melt flow properties depend of several parameters but also on the accuracy of selection of the melt processing conditins into finished product. An inappropriate choice of these parameteres controles the characteristics of the melt flow and therefore can generate the flow in overlapped layers which favor the formation of voids. In addition to formulations, the controlling of the melt rheological properties of the polymeric materials are critical points in guide the material performance including the defects number appeared at melt processing into finished product.

3.2. Behavior at biodegradation - SEM analysis

3.2.1. After 10 days

After 10 days of testing, the results show an extremely interesting dependence of the biodegradation behavior on the achieving method of the plates. The immersion of the plates into the A. niger culture caused a differentiated development of the pathogen, conditioned by the characteristics of each immersed plate (Figures 5, 6, 7). The formation of mycelial filaments (hyphae) and conidiophores with columnellas of A.niger in different evolution degrees characterising each type plates, in all cases, was obsered.

If the plates were obtained by horizontal 3D printing than, the fungal growth was observed at the joints between the printed layers with mycelial filaments passing over these layers (Figure 5-up). The fungal development on the surface of these plates was zonal, on each of them being small parts where the mycelial filaments are even underdeveloped and others where, at magnification of X1000 or X2000, are visible conidiophores with columnellas of A.niger (Figure 5 up).

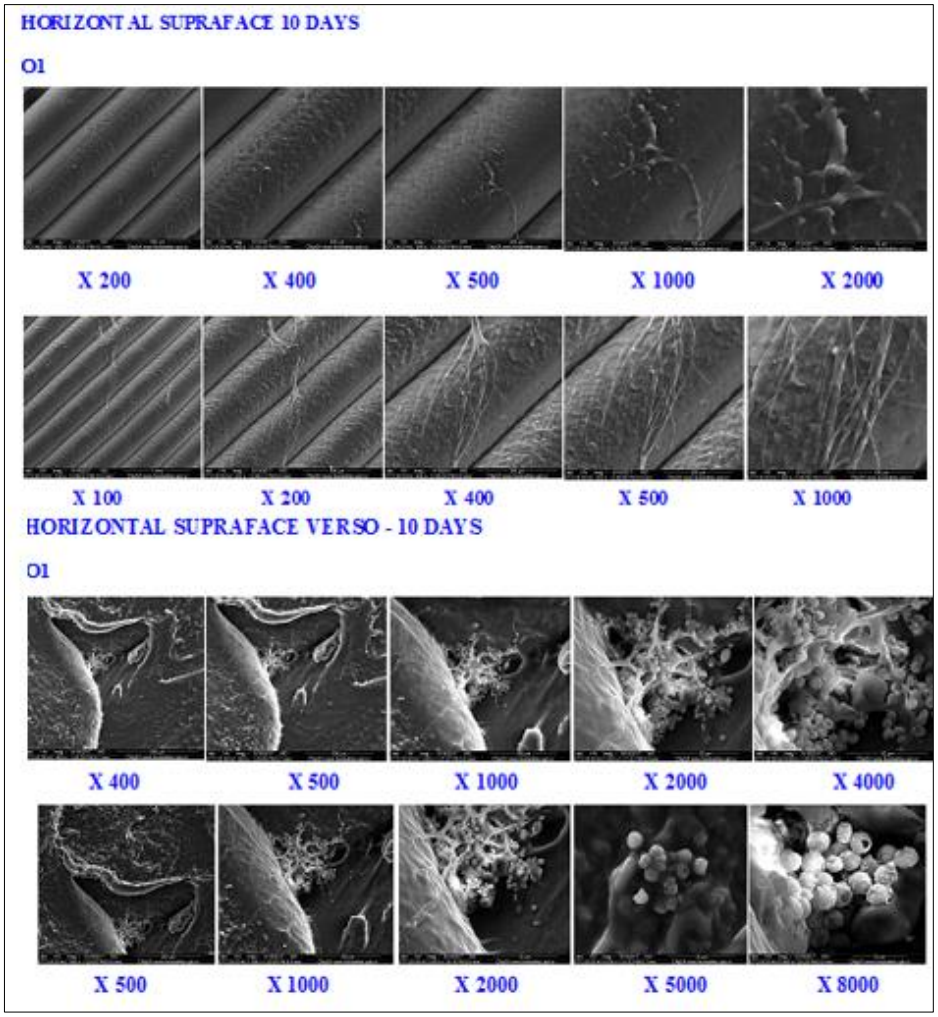

Figure 5. The SEM micrographs of the plates made by horizontal deposition of the 3D printed layers, biodegraded 10 days in A. Niger culture (face, verso)

However, the micellar growth is much stronger on the opposite side of the plates (Figure 5 below). On this part appear, at magnifications between X1000 and X8000, especially in the range of X5000 - X8000, not only the mycelial filaments but, well visualized and spreaded, conidiophores with columns of A.niger (Figure 5 below). The explanation of the differences between the fungal development on the two surfaces of these plates can be related to the much numerous defects of the surface in contact with the support on which the 3D printing was done.

If the plates were achieved by vertical 3D printing than an abundant micellar development was remarked between the printed layers and also on the plates edges (Figure 6). The existance of the micellar filaments and of the conidiophores with columnellas, are visible even from a smaller magnification, starting with X1000 (Figure 6-up). In the four situations presented in Figure 6-down, frequent conidophores with the columns of A.niger are visible even in the range of magnification of X1000 - X4000. It is obvious that if the initial plate had quite a lot of defects then the fungal development will be very abundant.

The fungal growth can be found on the plate obtained by pressing mainly on the edges of the plates and less on their surface. The growth is less abundant than in the case of plates made by vertical 3D printing and is especially as mycelial filaments (hyphae). The presence of the conidiophores with columnellas of A.niger are visible only at magnification higher than X1000, up to X10000. No essential difference was remarked between the fungal development on the two surfaces of the plates (face and verso). The fungal expansion is moreover related to the defects of the plates appeared during the achieving process of th plates.

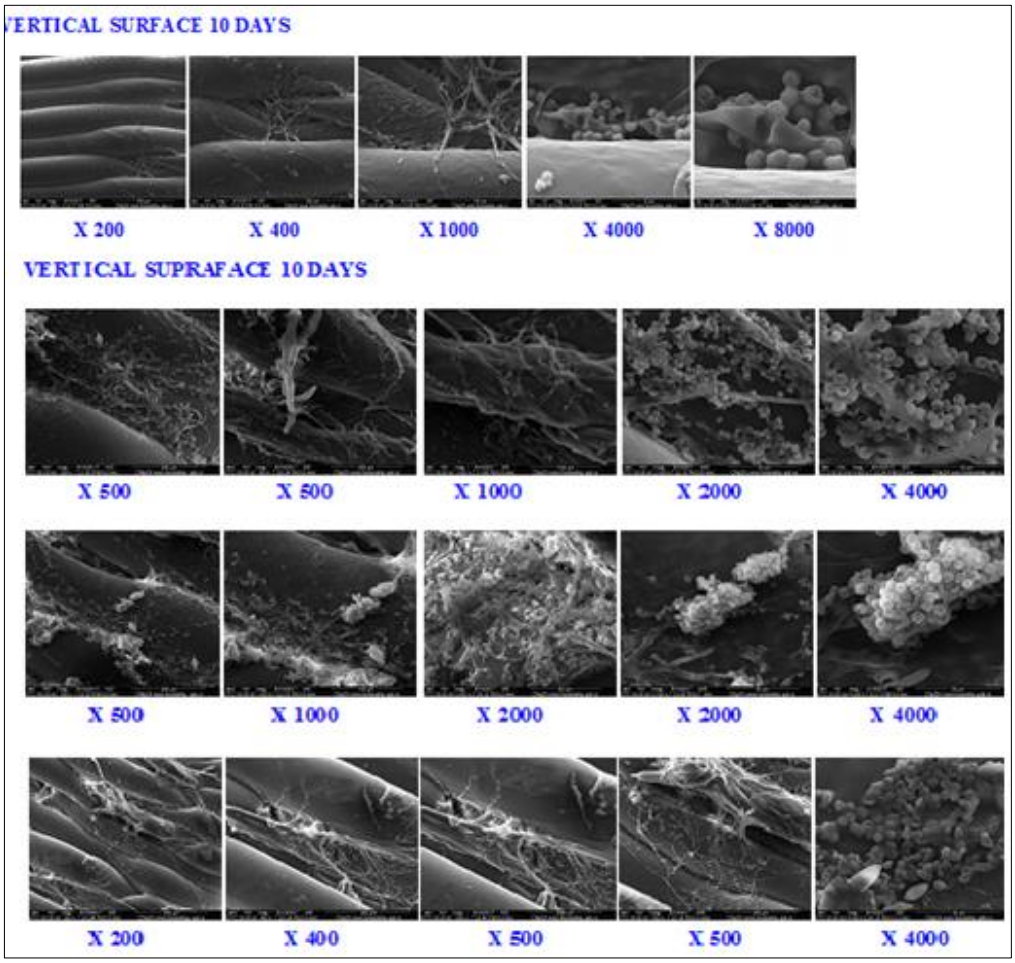

Figure 6. SEM micrographs of plates made of by ertial 3D printing that have been immersed into the biodegradation medium for 10 days (face, verso, fracture)

3.2.2.After 90 days

On the surface of the horizontal 3D printed plates that have been imersed in the biodegradation medium for 90 days (Figure 7 – 12) have been developed micellar filaments and conidia with columnellas of A.niger vizible even from small magnification of X100 (Figure 7). In the 4 different situations presented in Figure 7 which represent diverse areas of the same platewas observed, even from X100 magnification, microbial development, placed as in the case of the plates imersed for 10 days, mainly at the joint between the printed material layers (Figure 7). It can be remarked that, on the plate surface there are zones where the micellar filaments pass from one layer to the next layer of material (Figure 7d). At higher magnification, starting with X800 – X1000 and above up to X10000, the conidia formations with columella was seen, but without a spectacularly developement, if it is compared with the one raised after 10 days of biodegradation, visible from mgnification of X400.

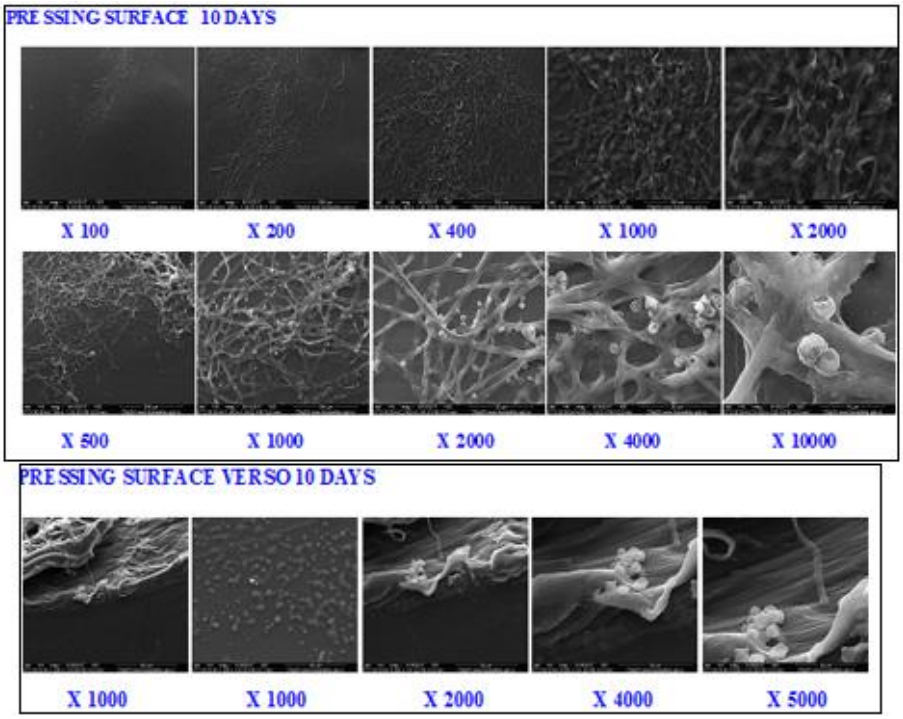

Figure 7. SEM micro-graphs of the plates made by classical pressing that have been in the bio-degradation medium for 10 days (face, verso)

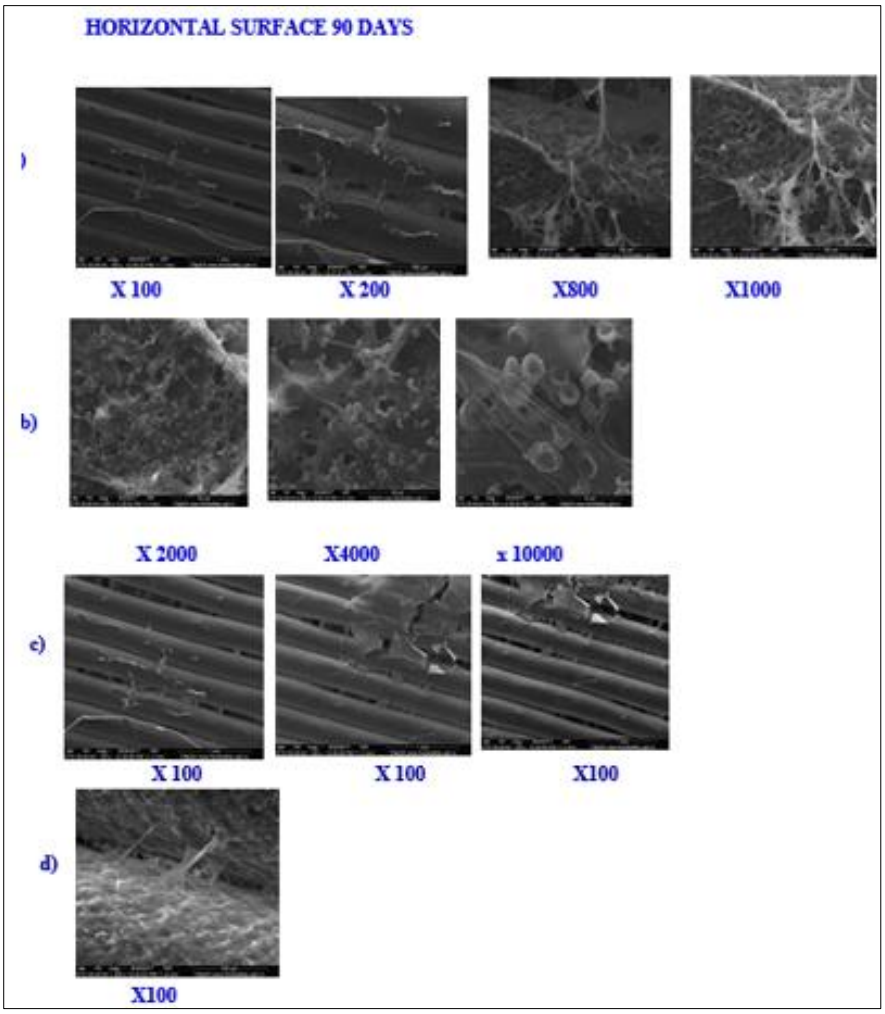

Figure 8. Development of A. Niger on the surface of the plates obtained by horizontal 3D printing, after 90 days of immersion in biodegradation mdium

After 90 days of biodegradation, the microbial development on the fracture of the plate achieved by horizontal deposition of the layers, from magnification of X1000 was visible (Figure 9). However, the existence of conidiophores with the columnellas was seen only from magnification higher than X4000 - X5000, which means that the microbial development, after 90 days, is not spectacular as at the beginning of the experiment. It seems that the microorganism grow speed no longer increases but, on the contrary, is stationary or has begun to decrease. The finding of the microorganism in the fracture of these plates can be explained in those it found ways to penetrate the structure of the plates, most likely with the help of the voids detected before immersion in the biodegradation medium. The quasi-uniform spread of the microorganism into the plate mass suggests possible fine connections between the voids that could probably be visualized at larger magnification of the initial plate. This way of connections between the voids of the plates allowed the microbial development in the mass, even up to the level of conidiophores with the columnellas.

On the plates achieved by vertial 3D printing grew up in those 90 days of immersion, mycelial filaments, conidia with columnellas of A Niger (Figures 9, 10). Figure 9 shows fungal development, especially on the surface of the plate, in the areas of the assembly between the printed layers, or at the plate corners where the printer nozzle has changed the deposition direction (Figure 9b, left). At higher magnification of X 4000 or of X 8000 the colonies of conidia with columnellas of A. Niger also are observed (Figure 10c). These colonies are widespread, especially if they are compared with the microbial development after 10 days (Figure 5).

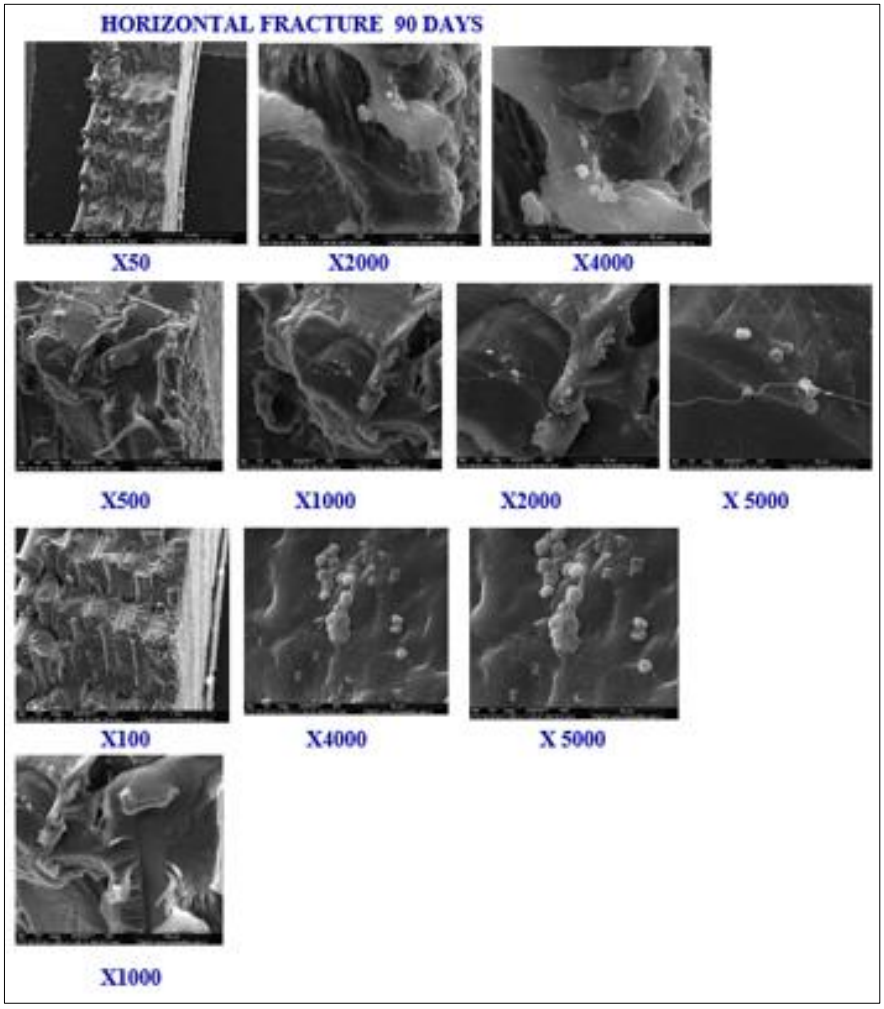

Figure 9. Development of A. Nigel, after 90 days, in fracture of the plates with horizontal deposited layers

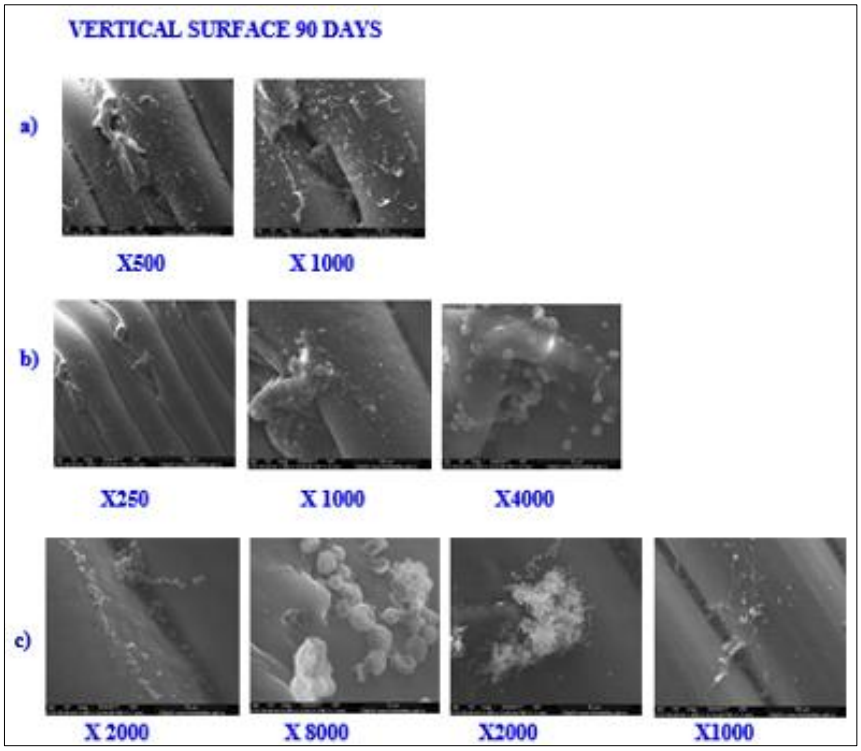

Figure 10. Development of A. Nigel, on the surface of the plates obtained by vertically 3D printing, (a, b, c visualization at different magnification in distinct place on the plate)

It seems that during the 90 days of immersion into the biodegradation medium the microorganism has penetrated the mass of the plate but only with a very small number of micellar filaments and much smaller of conidia with columnellas (Figure 11). Accordingly to the SEM images of the fractures, on the vertically printed plates there are areas where there is no traces of fungal development, even if the image has been magnificated up to X 10000 (Figure 11). It can be asserted that, in this situation too, the fungal development is related to the defects as voids of the plates appeared at their obtaining.

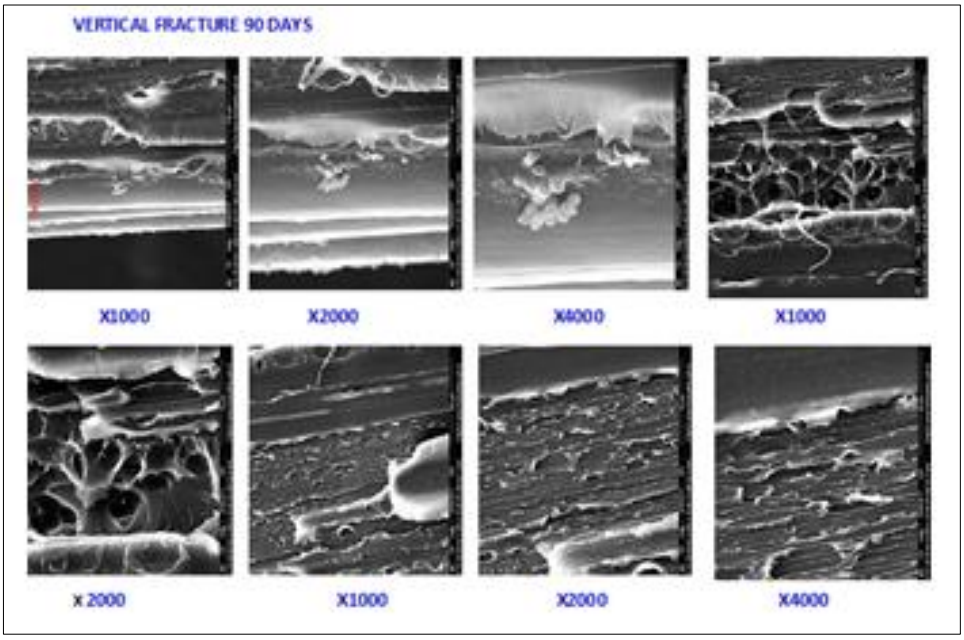

Figure 11. Development of Aspergilius Nigel, for 90 days, in the fracture of the plates achieved by vertical 3D printing

The biodegradation behavior of the plates achieved by pressing depends also on the number of defects appered during their obtaining (Figure 12). Surprisingly, these plates showed developments of the microorganism on their surface, possible in tiny, nanometric cracks that could not be seen at the initial control of the surface (Figure 12). According to the fracture SEM images, the development of the A. Niger has continued into the volume of the plates. However, the fungal development is visible only at a very high magnification of X10000 or of X16000 (Figure 12 left). This means that the growth of the microorganism was not abundant but, on contrary, was quite slow, takeing into consideration that the plates were immersed into the biodegradation medium for 90 days.

The plates obtained by pressing present in the fracture an inhomogeneous structure with discontinuous, overlapped material fronts, visible from the magnification of X1000 or X2000 (Figure 12 right). It is possible that the too high dynamic viscosity of the melt during pressing to generate the ditosition of the melt in overlapped layers, and so to be possible to appear voids and a networks of very fine, nanometric or microetri connected channels in which the filaments of the microorganism grew up. The high values of the dynamic melt viscosity can be the consequence either of formulation or of the incorrectly setting of the pressing parameters or boh of these two reasons. There, where the spaces from the channels were wider, sporadically small colonies of conidia with columella of A.niger have developed (Figure 12 right). The microbial development was additionally observed on the edges of the plates.

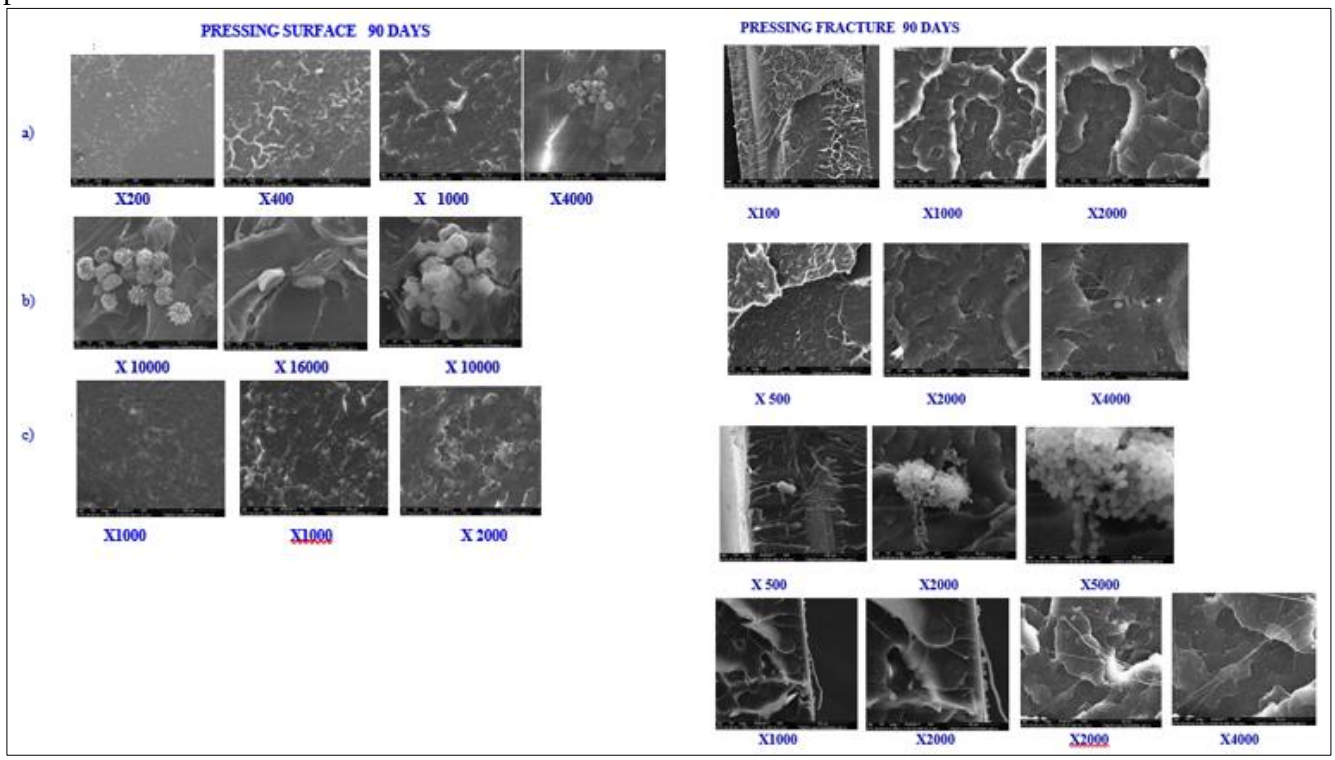

Figure 12. Development of A. Niger, on the plates obtained by pressing, for 90 days:
Left. surface; Right - fracture

The biodegradation behavior of the pressed plates demonstrates that, in this case too, the rheological properties in the molten state of the used polymeric materials must be better controlled, considering the adjustmant of the formulation and / or a better selection of the melt processing conditions.

3.2.3.After 540 days

After 540 days of immersion in the biodegradation medium, the microbial development is quite low, sometimes as a netting of micellar filaments, found only in certain areas, both on the surface or in the fractures of the plates, more on the 3D printed plates (Figure 13). The plates removed from the biodegradation medium, cleaned and sterilized, are whole and did not crumble or fracture.

From the SEM analysis of the microbial evolution on the different plates immersed in the biodegradation medium for 10, 90 and 540 days, the following stages of the microbial development were identified:

-initial, almost explosive, in the first 10 days, especially on the surface of the plates;

-with a much slower growth rate, so that after 90 days the microbial development seems to decreses, without haveing the expansion possible if it had follow a similar rate similar to those of the first 10 days;

-final, after 540 days of immersion in the biodegradation environment when the microorganism existance is few visible, with a tendency towards a complete disappearance.

As long as all the plates did not show essential dimensional changes at the end of the testing period, it seems that the microorganism had consumed in those 540 days of immersion, the components of the biodegradation medium and not the polymeric support. The material changes resulted after immersion in the biodegradation medium will be presented in a future paper focused on the time evolution of the biodegradation analysis through FTIR spectroscopy and other measurements.

The rigorous control of the initial surfaceand mass defects can lead to differences between the biodegradation behavior of the items made from renewable polymeric materials considering various melt processing techniques, as a new one as 3D printing and the other pressing classical.

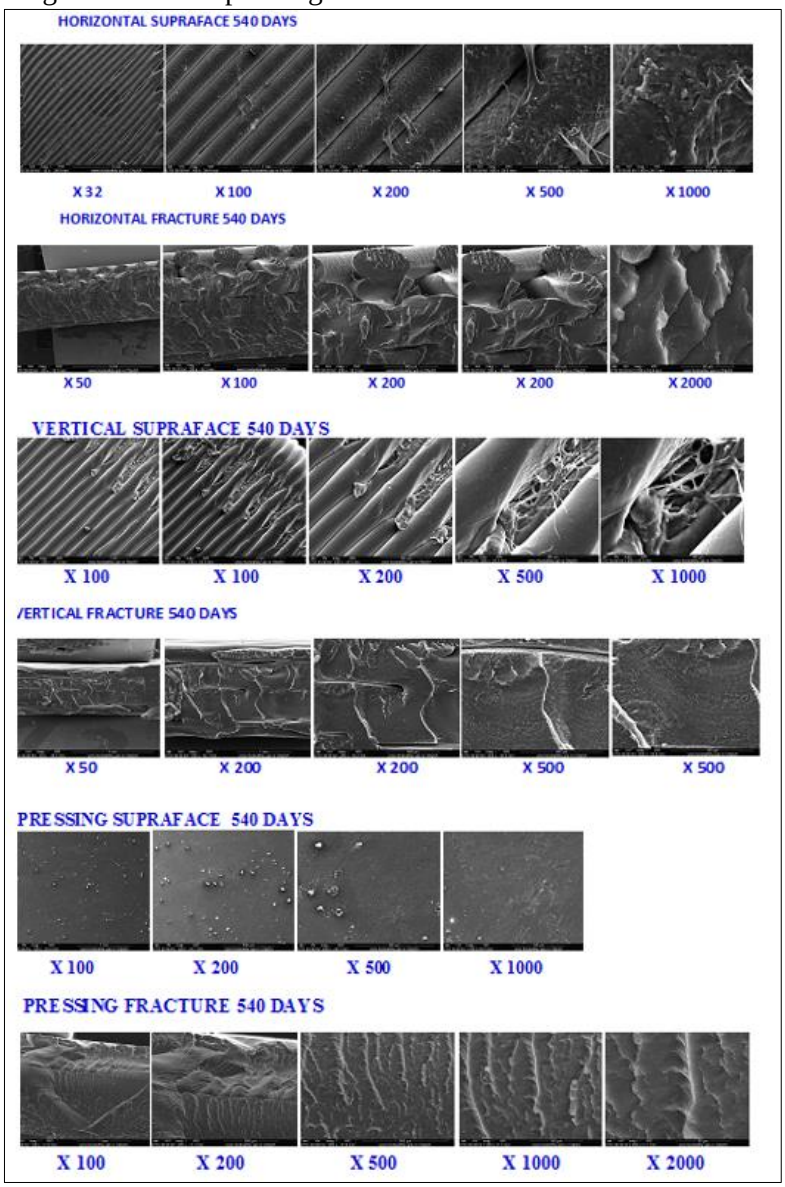

Figure 13. Fungal development on the surface and in the fracture of the plates immersed for 540 days in biodegradation environment. Plates obtained by horizontally and vertically 3D printing, and by classic pressing

From the analysis of the microbial evolution on the different plates types immersed in the bio-degradation medium for 10, 90 and 540 days, the following stages of the microbial development were identified:

-initial, almost explosive, in the first 10 days, especially on the surface of the plates;

-with a much slower growth rate, so that after 90 days the microbial development seems to decreses, without haveing the expansion possible if it had follow a similar rate similar to those of the first 10 days;

-final, after 540 days after immersion in the biodegradation environment when the microorganism existance is few visible almost, with a tendency towards a complete disappearance.

As long as all the plates did not show essential dimensional changes at the end of the testing period, it seems that all the obtained results demonstrate that the microorganism had consumed in those 540 days of immersion, the components of the biodegradation medium and not the polymeric support. The material changes resulted after immersion in the biodegradation medium will be presented in a future paper focused on the time evolution of the biodegradation analysis through FTIR spectroscopy and other measurements.

The rigorous control of the morphological defects can lead to differences between the biodegradation behavior of the items made from renewable polymeric materials considering various melt processing techniques, a new one as 3D printing and the other by classical types as pressing

4. Conclusions

The paper is part of a series in which the influence of the manufacturing defects on the functional The paper is part of a series in which the influence of the manufacturing defects on the functional behavior in biodegradation medium of some items obtained both by 3D printing and by classical pressing using an original renewable matrials based on polylatic acid will be presented. The first results regarding the SEM microscopy study on the correlation of the surface and the mass defects appeared at manufacturing into plates through the two techniques and the biodegradation behavior in Aspergillus Niger medium are presented in this article.

The obtained results demonstrated that the development of the A. Niger microorganism is related to the defects appeared at the melt processing of renewable polymeric material into finished product. The 3D printing has generated more defects because of many reasons including the technical performance of the 3D printer. A valuable role in controlling the manufacturing defects belongs to the rheological properties of the melts because these properties are responsible for how the flow is performed. If the polymeric material melt has too high viscosity than the continuous flow is not possible and so the overlapped melt fronts which are created generate the voids formation, sometimes joined by small nano and/or micrometric channels. The rheological properties of the melts depend both on the formulation and the setted conditions at achieving finished product

It seems that all the obtained results demonstrate that the microorganism had consumed in the 540 days of immersion, the components of the biodegradation medium and not the polymeric support.

The chemical changes of the regenerable material resulted after immersion in the biodegradation medium will be presented in a future paper focused on the time evolution of the biodegradation through FTIR and other measurements.

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