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BIODEGRADATION BEHAVIOR OF POLY(VINYL ALCOHOL) – WOOD COMPOSITES

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Abstract

A study on the biodegradability of several formulations based on poly[vinyl alcohol] (PVA) and wood flour has been carried out. Basically, all formulations are based on PVA and wood flour, and the influence of starch, glycerol and/or polyvinyl chloride (PVC) incorporated in some of them was investigated. Biodegradation was performed by incubation of the composites with a selected *Aspergillus niger* strain able to act as a polymer biodegrading agent. The composites biodegradation was evaluated by using SEM observations, FTIR and TGA analysis before and after incubation with microorganism. The surface morphology obtained from SEM showed that fungal strain colonizes the polymer surface of samples VACW (supplemented with glycerol and PVC), and especially of samples VAA (supplemented with glycerol and starch), developing dense hyphae networks and conidia accumulations. The microbial attack on composites with more than two components has led to the increase of the peak around 1740 cm⁻¹, due to oxidation of PVA hydroxyl groups to carbonyl groups, proving in this way the beginning of the biodegradation process. TGA analysis demonstrated that the number of thermal decomposition steps depends on composition, from three steps for VA samples (only with the two basic components, PVA and wood flour), up to four steps for VAW samples (supplemented with glycerol) and VAA samples, and even five steps for VACW. The experiments confirmed the biodegradation process of the VAA and VACW samples that are more accessible to the fungal activity.

Keywords: *Aspergillus niger*, polymer biodegradation, poly(vinyl alcohol)-wood composites

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1. Introduction

Various types of synthetic polymers have been developed for everyday use. Due to the increase of polymer wastes and problems with their disposal there is a need for polymer compounds biodegradable in natural conditions. Poly[vinyl alcohol] (PVA), an environmental friendly and water soluble synthetic polymer with many hydroxyl groups, is a frequent component of biodegradable polymeric compounds (Chiellini et al., 2003; Imam et al., 2005; Vaclavkova et al., 2007). In last years, many efforts have been made to develop biodegradable materials containing

renewable raw materials. One of the most abundant sources of natural polymers, biomass is produced in large amounts by wood industry and agricultural activities. The wood flour can be added to plastics and resulted composites combine the best properties of individual components. There are some reports on the production and application of PVA-wood composites (Bana and Banthia, 2007; Lie et al., 2011; Ozaki et al., 2005).

The materials behavior at the end of their function is a feature to be studied and hence it is of interest to investigate their microbial degradation. Most of microorganisms involved in PVA

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biodegradation are aerobic bacteria belonging to *Pseudomonas* (Bharathiraja et al., 2013; Kawai and Hu, 2009; Leja and Lewandowicz, 2010; Matsumura, 2002) and *Bacillus* (Wu, 2008) genus. In last years, many studies were dedicated to fungal degradation of PVA (Guohua et al., 2006; Kim and Rhee, 2003; Mathur et al., 2011; Yun et al., 2008; Zhang et al., 2006), mainly as a consequence of involvement of fungal strains in organic materials degradation.

Aspergillus species which are among the most abundant fungi are suited for the biodegradation of plastic materials. In a previous work we reported an *Aspergillus niger* strain selected in our laboratory able to grow and degrade composites based on poly(vinyl alcohol) and natural polymers (Jecu et al., 2010; Stoica-Guzun et al., 2011). Our recent interest has further extended to the study of the biodegrading capacity of *A. niger* strain towards more complex PVA-based composites with high potential as packaging materials. In the present paper we present our researches on biodegradation of such materials, biodegradable films based on PVA-wood composites. Scanning electron microscopy (SEM) was applied to investigate the polymer surface after the fungal strain action. FTIR and TGA analysis were used to evaluate the polymers modification after the incubation with the selected *Aspergillus niger* strain.

2. Material and methods

2.1. Chemicals and reagents

The following reagents were used: water-soluble poly[vinyl alcohol] (PVA), (Du Pont, trade

name Elvanol 71-30), AMYZET 100 type corn starch (S) is produced by (AMYLUM – Romania), polyvinyl chloride plasticized with di-2-ethylhexylphthalate (Ongrovil, Hungary).

The chemicals used are: $MgSO_4 \times 7 H_2O$ (Merck, Germany); peptone (Oxoid, UK); D(+) glucose monohydrate (Loba, Poland); K_2HPO_4 (UCB, UK); NH_4NO_3 (Romania reagent); yeast extract (Difco, USA); maleic anhydride (Fluka); wood flour (a mixture of various woods; particle size of about 140 μm , specific volume of 8-8.5 dm^3/Kg , moisture content of 5-6 wt%) provided from a local unit of wood processing. The obtained films were cut into pieces of 2 cm x 2 cm and sterilized at UV light for 10 minutes. Each film was then aseptically transferred into sterile medium.

2.2. PVA/wood composites preparation

Several compositions based on PVA/wood materials obtained in laboratories of SC ICPE Bistrita SA were tested (Table 1). Samples with different compositions were obtained by melt blending of PVA and various components within Brabender Plastograph at 170°C and 45 rot/min, followed by pressing as films or sheets on Brabender Press, at 180°C and 500 bar. Wood flour was treated with maleic anhydride to increase the coupling capacity with PVA and starch. The preparation conditions (temperature, rotations/minute, time) mentioned in Table 1 are routine practices to ensure the miscibility of individual components (in various ratios) in composites. The use of these conditions should not be considered as a treatment of polymeric materials.

Table 1. Composition and preparation of the PVA-wood composites materials

Sample	Components (w/w; %)					Preparation conditions		Visible characteristics
	PVA	Wood flour	Glycerol	Starch	PVC	T (°C)	Rot/min	
VA1	90	10	-	-	-	160	600	compact, white, with glassy surface and a roughly reverse
VA2	85	15	-	-	-	170	600	compact, rigid, white, a surface with cavities and a roughly reverse
VAW1	55	10	35	-	-	170	45	compact, flexible, white-yellow
VAW2	55	15	30	-	-	170	45	compact, flexible, sponge aspect, white-yellow
VAA1	55	10	25	10	-	170	50	compact, rigid, white
VAA2	55	15	20	10	-	170	50	compact, more flexible as VAA1, white-yellow,
VACW1	55	10	25	-	10	170	50	compact, flexible, white-yellow
VACW2	55	15	20	-	10	170	50	compact, more flexible as VACW1, white-yellow

2.3. Biodegradation tests of PVA-wood composites

Biodegradation tests were performed with an *Aspergillus niger* strain belonging to Microbial Collection of INCDCP-ICECHIM. The fungal strain was maintained at 4°C in tub test with dextrose-agar-potato medium. The composites biodegradation was performed in ¼ diluted Sabouraud medium with the following composition (g/L): 2.5 peptone; 10.0 D(+)glucose; mineral salts. The basic mineral medium contains (g/L): 1.0 NH₄NO₃; 1.0 K₂HPO₄; 0.5 MgSO₄ x 7 H₂O; 0.5 KCl; 2.0 yeast extract. The pH medium was adjusted to 6.0. The medium was autoclaved at 121°C for 20 minute. Aliquots of 50 mL sterilized medium were distributed in 300 mL Erlenmeyer flasks. Thereafter the polymeric samples were immersed in sterilized medium and the flasks were inoculated with a sporal suspension of *A. niger*. After inoculation, the cultures were incubated on a rotary shaker Heidolph Unimax 1010 at 120 rpm and 28°C for 30 days.

For each investigated polymer were prepared control flasks containing the liquid medium and the polymeric samples, without fungal cultures. After 30 days incubation, the pieces of polymer were taken out from the liquid culture, rinsed with distilled water and dried at 50°C. Experiments were carried out in Microbiology Laboratory of ICECHIM and all the microbiological tests were performed in duplicate.

2.4. Morphological analysis (Scanning electron microscopy)

The morphological analysis of the polymeric samples was carried out by Scanning Electron Microscopy (SEM) performed with a FEI-QUANTA 200 instrument in ICECHIM. The film samples resulted from the biodegradation experiments (see section 2.3.) were placed on metallic support, aluminum standard stub, using a double-sided adhesive carbon tape.

The SEM images were taken at an accelerating voltage of 12.5-15kV and 250-50 Pa using a gaseous secondary electron detector (GSED). Micrographs of the samples were investigated at different magnifications to identify changes on the surface during the degradation process. For each polymeric sample, 5-8 micrographs were performed and the relevant images were presented.

2.5. Fourier Transform Infrared Analysis

Fourier Transform Infrared (FTIR) analysis was carried out for evaluation of the biodegradation extent (Bhargava et al., 2003; Silva et al., 2008). The FTIR spectra were acquired using a FT-IR, Tensor 37 spectrometer (Bruker) with ATR Golden Gate in ICECHIM laboratory. All spectra were recorded from 400 to 4000 cm⁻¹. Each polymer sample was twice investigated.

2.6. Thermal stability

The thermal stability was investigated by thermogravimetric analysis (TGA). The determinations were conducted with a TGA Q5000IR (TA instruments) in ICECHIM. Samples (50 - 10 mg) were heated from 20 to 700°C at a 10°C/min scanning rate, under nitrogen atmosphere (flow rate about 200 mL min). The onset temperature (Ton) was determined as the temperature corresponding to the crossover of tangents drawn on both sides of the decomposition trace and the residue was evaluated as the residual weight at 700°C. The samples were investigated by TGA analysis before and after the incubation with the fungal strain. For each polymeric sample two TGA determinations were performed. Additionally, PVA was individually analyzed for the thermal stability.

3. Results and discussion

In present work, a total of eight selected formulations were prepared. Basically, all formulations were based on PVA and wood flour, and the influence of starch, glycerol and/or poly(vinyl) chloride incorporated in some of them was investigated. The composition and preparation conditions of the PVA-wood composites were summarized in Table 1. The ratios of individual components were chosen to confer hydrophilicity and to accelerate the microbial digestion. Each individual component incorporated added to the basic PVA and wood has a specific role in the features of tested samples.

Glycerol is a plasticizer used to improve compound processing characteristics, which also lowers the glass transition temperature for the plastics, providing them flexibility. The existing hydrogen bonds facilitate the compatibility between PVA and glycerol (Mohsin et al., 2011). Starch, as hydrosoluble natural polymer, enhances the biodegradative activity of the fungal strain which secretes amylases, the enzymes involved in starch hydrolysis. The influence of PVC on the biodegradability of the proposed composites was studied due to its importance in the polymeric wastes recycling (Hamad et al., 2013; Najafi, 2013; Sadat-Shojai and Bakhshandeh, 2011). The biodegradation extent evaluation was done by comparing the features of the polymeric samples before and after incubation with the fungal culture of *Aspergillus niger* strain.

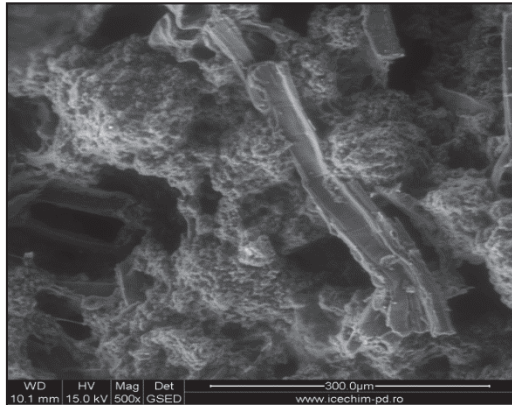
3.1. Microscopy studies

SEM technique was used in many studies on polymers biodegradation (Upreti and Srivastava, 2003; Sasek et al., 2006). The surface of starch/polyvinyl alcohol (PVA) blend films buried in compost for 30 days presented many changes in surface aspect, like: larger and deeper holes and cracks, and fungal filaments penetrating within polymer matrix (Maiti et al., 2012). Other

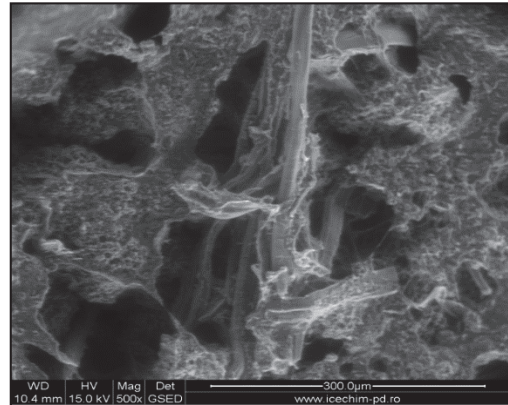
spectroscopic investigations revealed the bacterial colonization of polymeric films incubated with *Pseudomonas lemoignei* (Ashby et al., 2007). SEM analysis showed the increase of the porosity and fragility of the fungal degraded polythene surface (Raaman et al., 2012). In a recent study, Yoon et al. (2012) confirmed the deterioration of low-molecular-weight polyethylene sheets as a result of the degradation produced by a *Pseudomonas* isolated from a crude oil contaminated soil. The SEM images showed the adherence of the bacterial cells to the surface of the polymeric sheets. The SEM images of PVA-wood composites before and after

microorganism attack are presented in Figs. 1-4. From Fig. 1 it can be concluded that the polymeric samples containing only PVA and wood did not offer adequate nutrients for microbial growth.

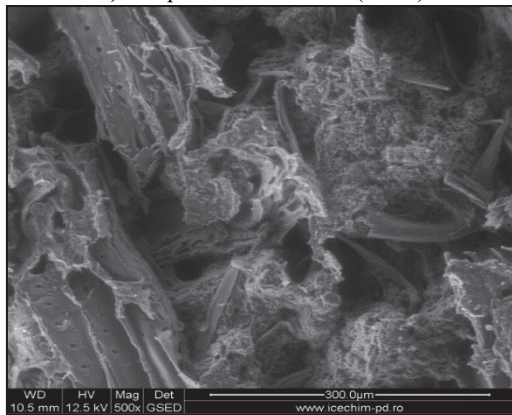
No evidence of fungal growth was observed on these samples indicating a low accessibility to microbial attack. Practically, no changes in the morphology of these samples after exposure to the microorganism were observed. The voids from SEM photos may be formed as air holes (gaps) during melt processing or they can arise due to plasticizer migration through polymer to its surface and leakage in the liquid culture medium.



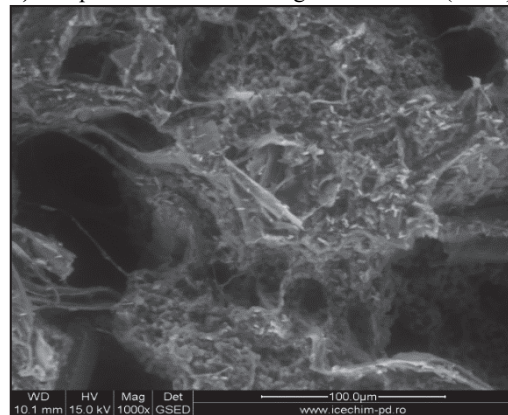
a) Sample VA1 as control (x 500)



b) Sample VA1 after microorganism contact (x 500)

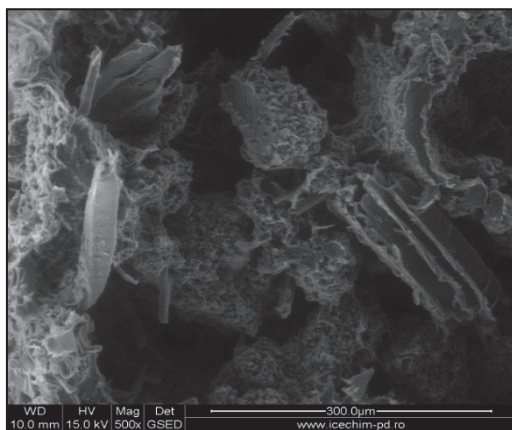


c) Sample VA2 as control (x500)

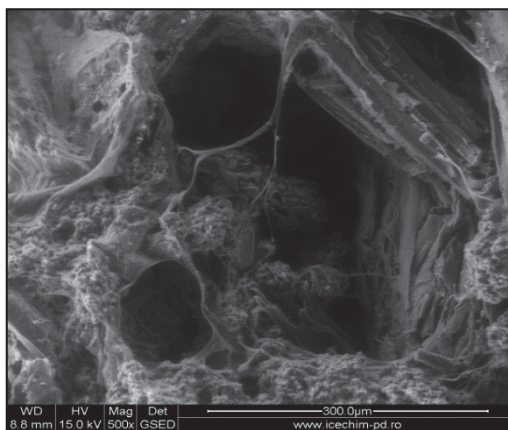


d) Sample VA2 after microorganism contact (x 500)

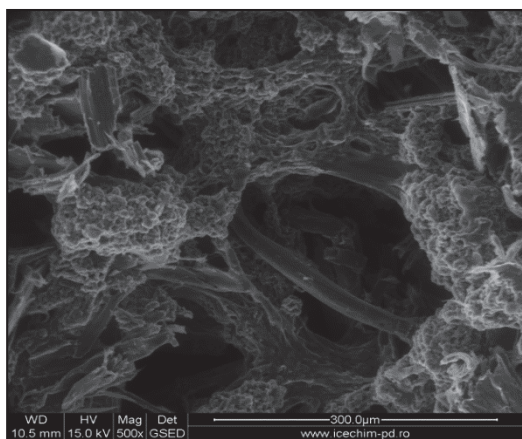
Fig. 1. Scanning electron micrographs from surfaces of VA1 and VA2 polymeric samples before and after 30 days of incubation with *Aspergillus niger*



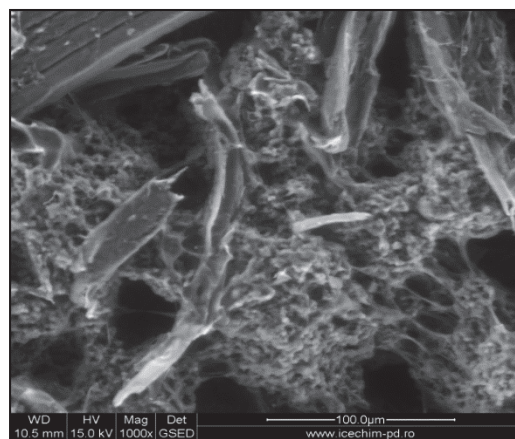
a) Sample VAW1 as control (x500)



b) Sample VAW1 after microorganism contact (x500)

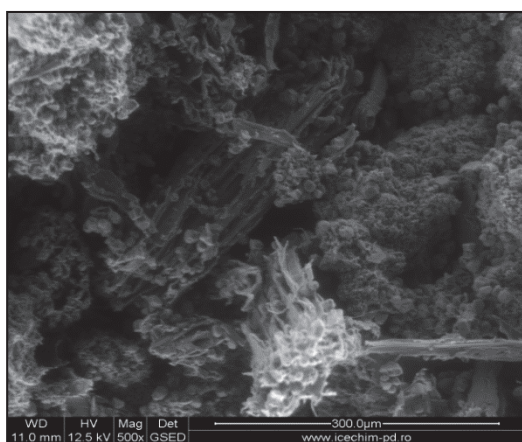


c) Sample VAW2 as control (x500)

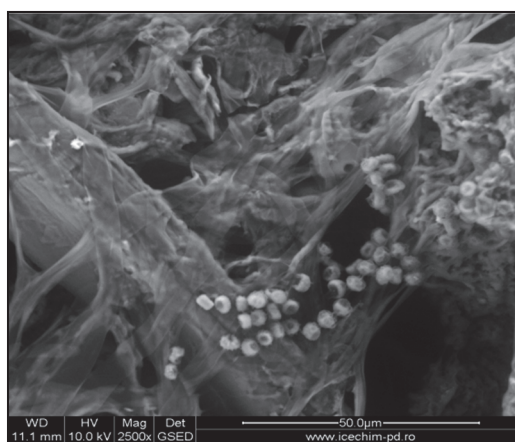


d) Sample VAW2 after microorganism contact (x1000)

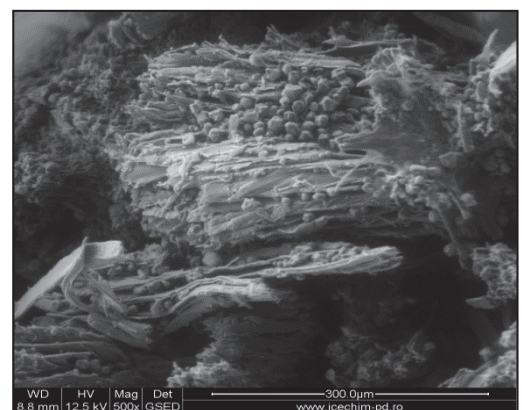
Fig. 2. Scanning electron micrographs from surfaces of VAW1 and VAW2 polymeric samples before and after 30 days of incubation with *Aspergillus niger*



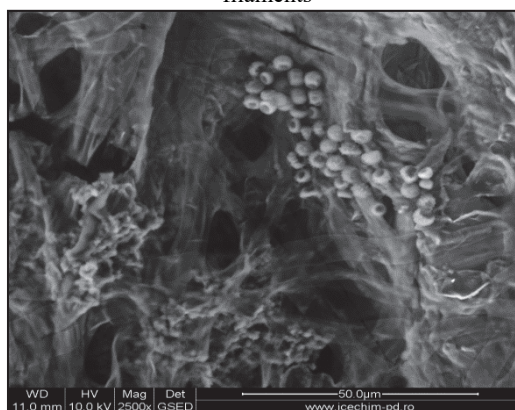
a) Sample VAA1 as control (x 500)



b) Sample VAA1 after microorganism contact (x2500); white arrow – conidia; black arrow – network of ribbon filaments



c) Sample VAA2 as control (x500)



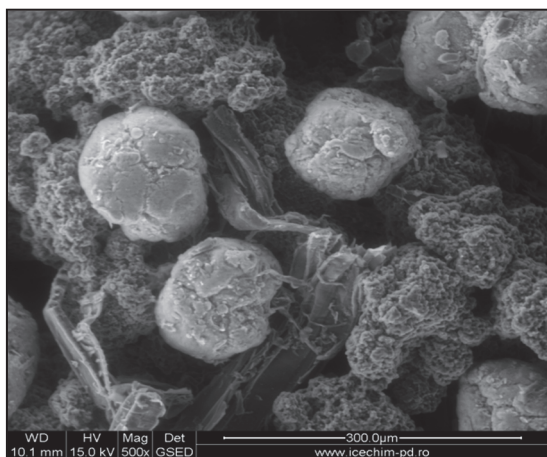
d) Sample VAA2 after microorganism contact (x2500); white arrow – conidia; black arrow – ribbon filaments

Fig. 3. Scanning electron micrographs from surfaces of VAA1 and VAA2 polymeric samples before and after 30 days of incubation with *Aspergillus niger*

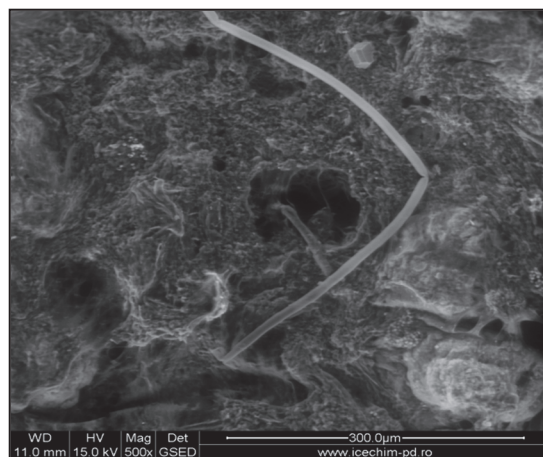
The same results were obtained with VAW1 and VAW2 samples that contain, comparing with VA1 and VA2, apart from the same percentage of wood flour, 30% and 35% glycerol, respectively. Fig. 2 shows that glycerol addition did not facilitate the biodegradation process, no microbial growth being observed on surface of these samples. Despite of this fact, an increase of the number of the cavities on the

polymer surface was observed. These cavities may initiate the microbial propagation, colonization and adhesion of microorganism, which represents a fundamental prerequisite for polymer biodegradation.

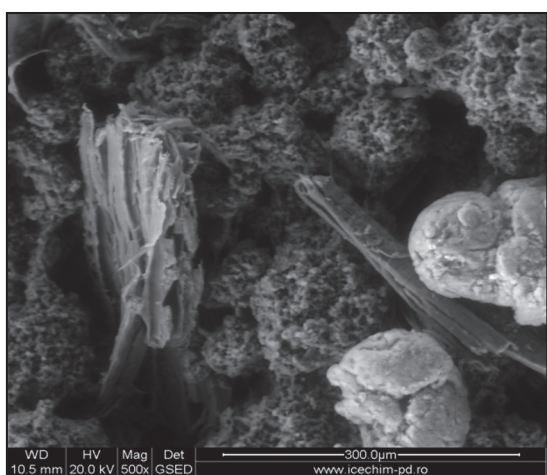
The third set of samples VAA1 and VAA2 contains 10% of starch, the same percentage of PVA (55%), 10 or 15% wood flour and 25 or 20% glycerol, respectively.



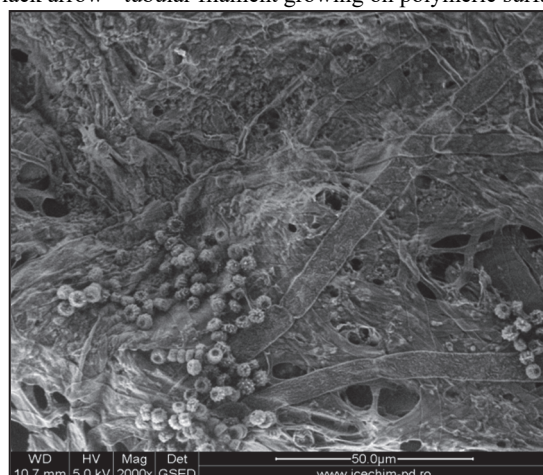
a) Sample VACW1 as control (x500)



b) Sample VACW1 after microorganism contact (x500); black arrow - tubular filament growing on polymeric surface



c) Sample VACW2 as control (x500)



d) Sample VACW2 after microorganism contact (x2000); white arrow – conidia growing on surface; black arrow – ribbon filament

Fig. 4. Scanning electron micrographs from surfaces of VACW1 and VACW2 polymeric samples before and after 30 days of incubation with *Aspergillus niger*

The presence of starch induced a relative increase of polymer biodegradability revealed by elements of fungal growth, such as conidia and hyphae filaments (Fig. 3).

Extensive networks of fungal hyphae and agglomeration of conidia covered the surface of VAA1 and VAA2 composites (Figs. 3b and 3d). Also, the disappearance of starch granules due to the hydrolytic activity of amylases secreted by *Aspergillus niger* can be observed.

Dense networks of ribbon and tubular filaments and agglomeration of conidia were revealed by SEM micrographs of VACW1 and VACW2 samples. A long and tubular fungal filament may be observed in Fig 4b. Photo 4d reveals that *A. niger* created a complex networks of ribbon filaments, some of them penetrating the polymer matrix. Also many reproductive units (conidia) are present on sample surface. From SEM observations, it can be concluded that the VACW samples and, especially, the VAA samples allowed an abundant fungal growth. The higher accessibility to microorganism attack for the

VAA samples is due to the presence of the starch in its composition.

3.2. FTIR studies

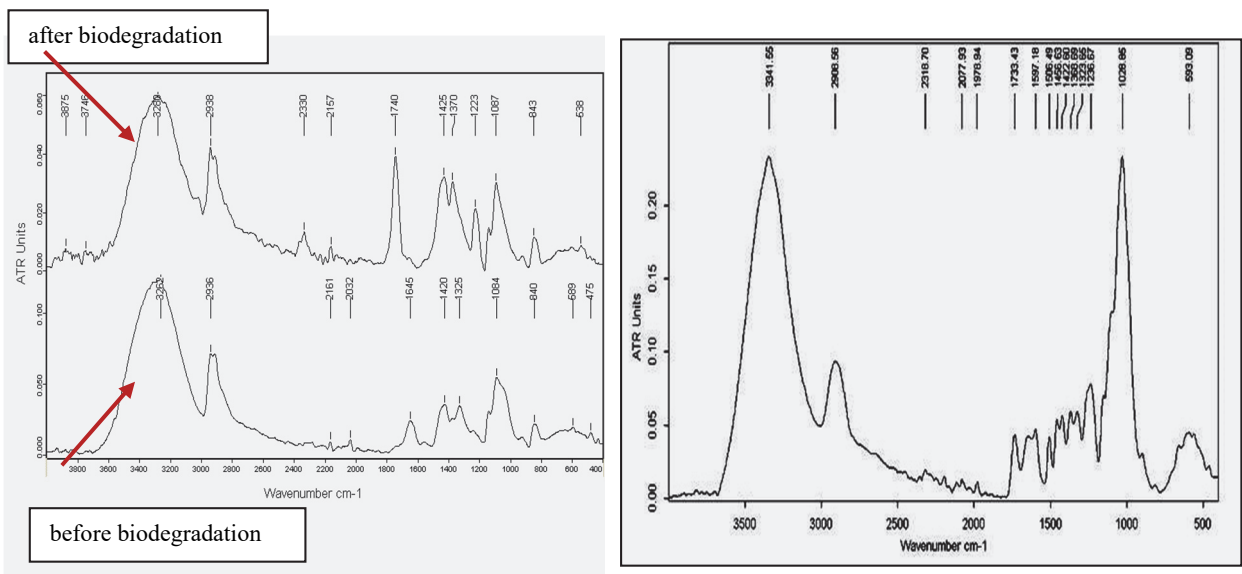
FTIR spectroscopy has been used to show the modifications in sample structure induced by microorganism attack. By comparing the spectra of degraded and non-degraded composites and taking into account the assignment of bands from literature (www.science-and-fun.de/tools/), some changes in their structure can be observed.

FTIR results of the investigated samples are presented in Figs. 5 - 6. Fig. 5 shows the spectra of components, PVA and wood fibers. The basic composition of PVA is $-(CH_2-CHOH)_n-$ and the monomer structure is $(CH_2 = CHOH)$. From this structure, the following chemical bonds are present: C-H, C-O, O-H and C=C. The peaks are identified according to these type of bonds: 2939 cm^{-1} due to C-H group, 1424 cm^{-1} due to O-H group, 1740 cm^{-1} due to C=O, and 1088 cm^{-1} associated with C-O specific

to secondary alcohol. Hydrogen intermolecular bonds are present in the domain 3200 - 3400 cm^{-1} (Vasques et al., 2007; Wolkers et al., 2006). Starch and PVA molecules are in general associated with inter- and intramolecular hydrogen bonding in the composites.

The IR spectrum of the wood fibers shows the characteristics band in the region of 1733 cm^{-1} and 2940 cm^{-1} due to carbonyl stretching and C-H stretching (Fig. 5b). The IR spectrum of the wood shows the absorption band at the region near 1627 cm^{-1} . A characteristic peak of wood fibers appears at 3341.55 cm^{-1} for OH stretching. Peaks at around 2900 cm^{-1} correspond to C-H stretching in cellulose and hemicellulose present in wood fibers. Peak at 1733.43 cm^{-1} is for C=O in hemicellulose or lignin. The CH_2 bending vibration around 1420 cm^{-1} is due to the presence of lignin. Also, for wood a specific absorption band is present at 1028.85 cm^{-1} (cellulose

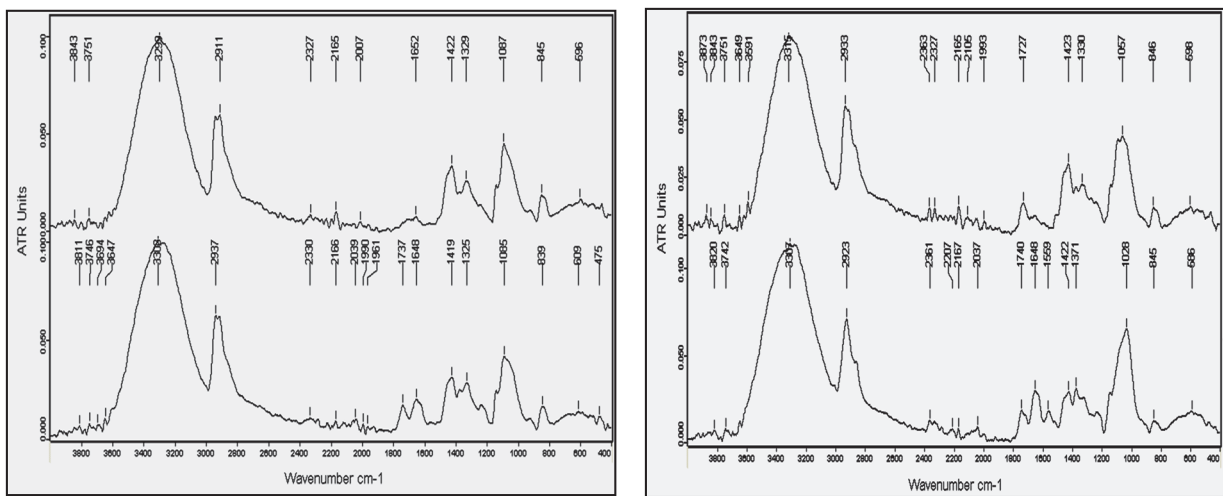
C-O stretch) (Lee et al., 2010). Fig. 6 shows the FTIR spectra of wood - PVA composites. For VA1 and VA2, there are not significant differences between samples before and after microorganism incubation, only a small increase of absorption band around 1740 cm^{-1} may be observed (Figs. 6a and 6b). These samples contain a lower percentage of wood and the spectra are almost similar to PVA. Samples VAA1 and VAA2 (Figs. 6e and 6f) have the same spectra shape with a small increase of the absorption band around 1740 cm^{-1} . After incubation with *A. niger*, the samples VAW (Figs 6c and 6d) and VACW (Figs. 6g and 6h) present a significant increase of the peak around 1740 cm^{-1} . This may be attributed to the CH-OH oxidation to C=O in PVA after incubation with the fungal strain. This modification could be considered as the beginning of PVA degradation (Jayasekara et al., 2003).



a) PVA sample

b) Wood fibers (before)

Fig. 5. FTIR spectra of major components, as wood fibers and PVA



a) VA1 sample

b) VA2 sample

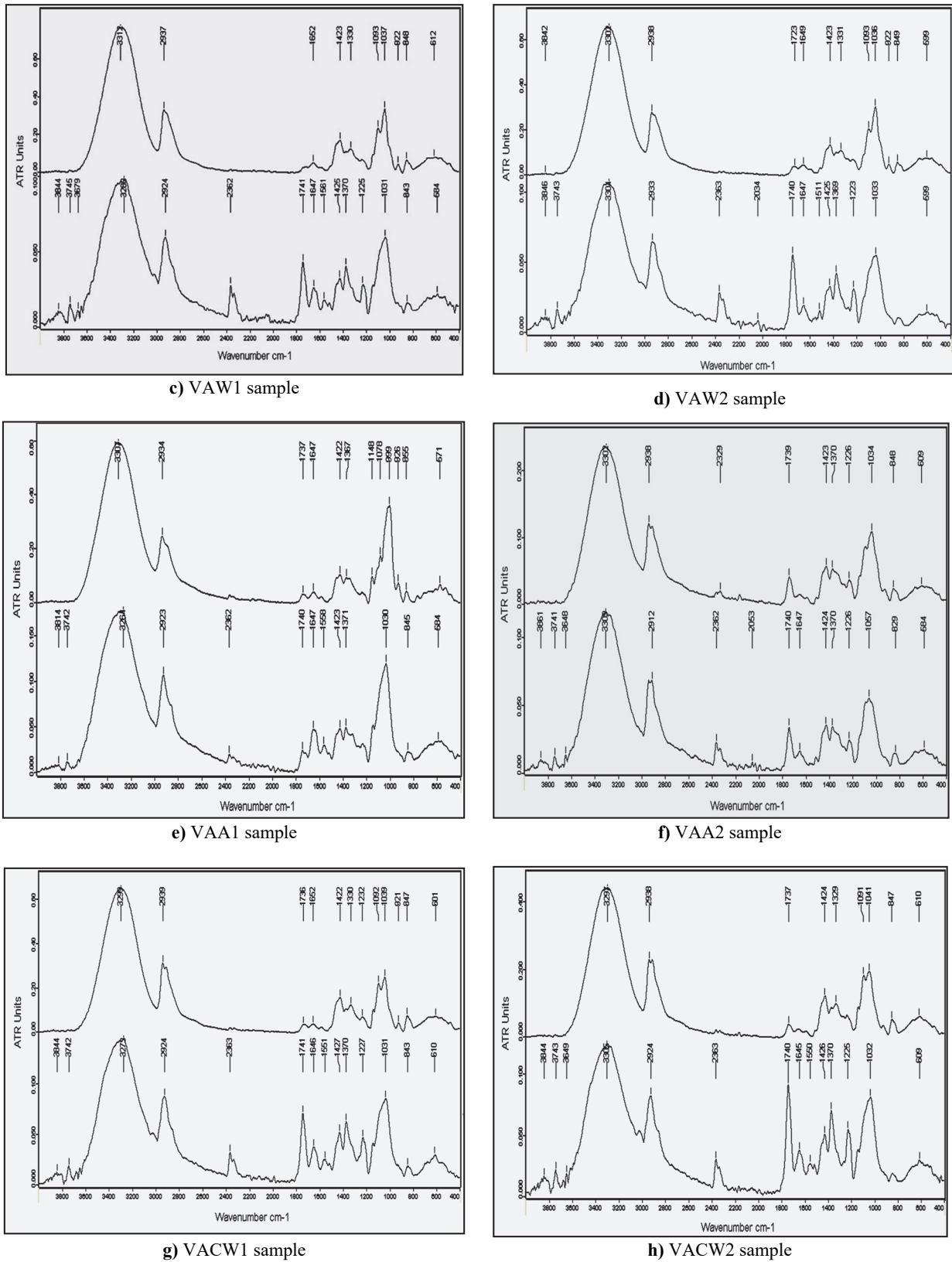


Fig. 6. FTIR spectra of wood - PVA composites before and after 30 days of incubation with *Aspergillus niger* in agitated liquid culture (upper line – before microorganism contact; lower line – after microorganism contact)

3.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of the samples was performed to define the thermal stability of the tested materials. The profile of thermal

degradation of PVA - wood composites is presented in the Fig. 7. Molecules of polymeric materials are stable only up to a certain temperature range. Their stability depends on the characteristics of the samples and on the specific interactions between the different

macromolecules or molecules present in the polymer, such as hydrogen bonds, dipole-dipole interaction, van der Waals etc. (Sreedhar et al., 2006).

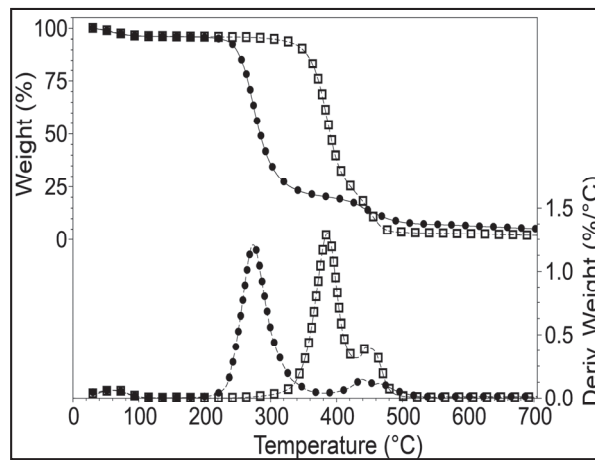
PVA decomposed in three steps with the main weight loss at 273.5°C (75.88%), and 386.33°C (74.42 %) respectively after biodegradation (Fig. 7a). The C-C bonds from polyene structure of PVA are broken at 439.05°C and respectively at 463.26°C after biodegradation, indicating an increase of the thermal stability. Starch and glycerol as individual components were not investigated through TGA. In composites, each of these compounds exhibited a single decomposition peak, at 277°C for starch, and respectively at 170°C for glycerol. Wood fibers decomposed in three steps at 47°C (4.78%), 285°C (24%), and the main weight loss of 49.06% at 358°C. The influence of microorganism attack upon wood component was not performed. The obtained data are in agreement with results reported previously by other authors (Follain et al., 2005; Imam et al., 2005; Negim et al., 2014; Taghizadeh and Sabouri, 2011). Figs. 7 (b-i) shows a comparison of the thermograms of wood - PVA composites before and after incubation with the fungal strain. The composite samples presented the main weight loss in the range 300°C - 400°C, more precisely 350-391°C, without taking into account PVC.

The number of thermal decomposition steps depends on sample composition. For samples VA the

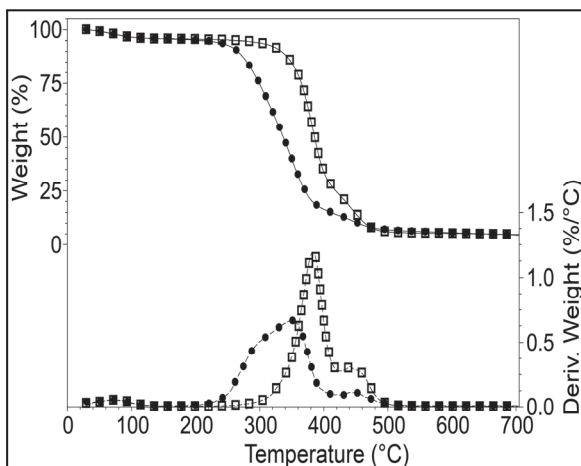
decomposition occurred in three steps, in four steps for VAW and VAA samples and for VACW composite types in five steps. The additional step at 280-282°C is due to PVC presence. All the samples showed an initial weight loss (around 3-5%) in the range 40 °C – 100°C attributable to water evaporation.

The thermal decomposition data showed an increasing trend in stability for all specimens. With the exception of VACW1 and VACW2 samples, the temperature values for all the biodegraded samples increased over 20°C. It is noteworthy that for VAW and VAA biodegraded composites, the thermal decomposition produces an increase of weight losses up to 8-15%, as comparative with untreated samples, possible due to the decomposition intermediates with higher thermal stability.

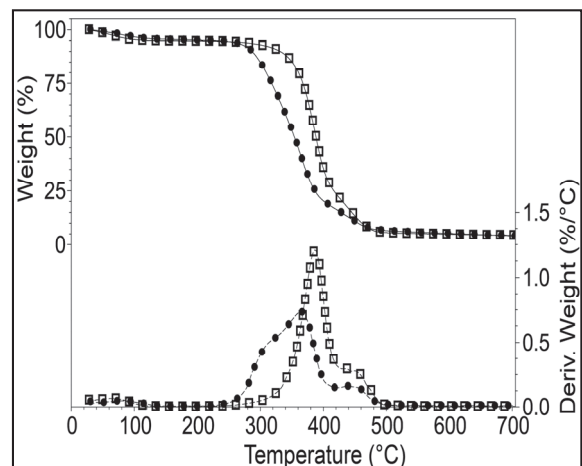
The experiments confirmed the biodegradation process of the VAA and VACW samples that are more accessible to the fungal activity. A correlation between the biodegradation level and samples composition was found, but nevertheless, from our measurements it is premature to classify the samples according to their biodegradability. The degradation of the investigated PVA based composites may be considered not sufficiently relevant, but we have to take in consideration that a period of 30 days for a complete biodegradative process is too short to demonstrate the ability of *A. niger* to use these composite materials as sole carbon source.



a) PVA sample



b) VA1 sample



c) VA2 sample

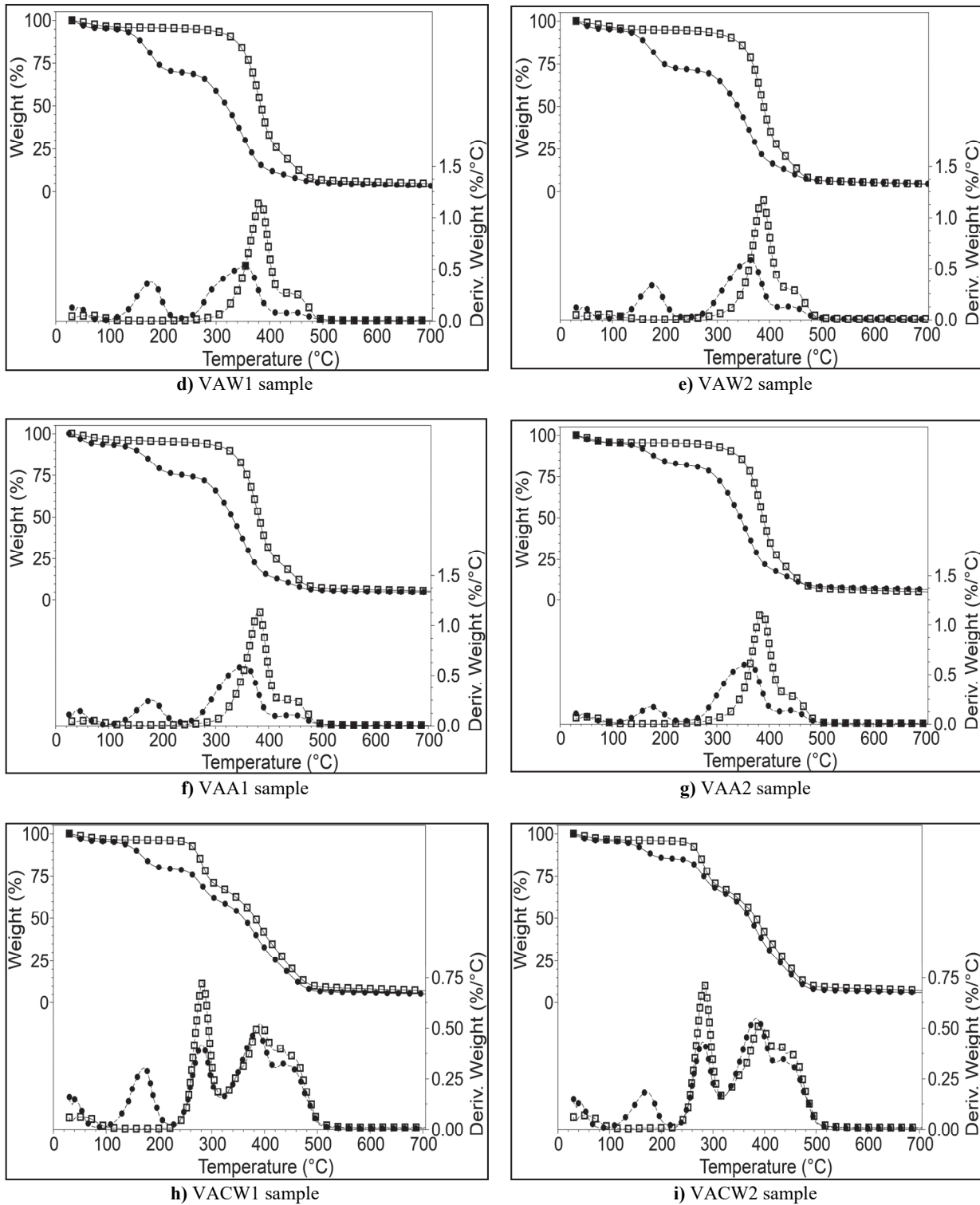


Fig. 7. Thermogravimetric measurements of wood - PVA composites (black circles – before microorganism contact; empty squares – after microorganism contact)

An exposure to microbial activity for a prolonged period of six months was applied to an environmentally friendly material composed of waste wood and poly(vinyl alcohol). In correlation with composition, after testing by soil burial, some composites showed a weight loss of 12% (w/w). The buried samples were colonized by soft rot fungi belonging to *Trichoderma*, *Chaetomium*, *Penicillium*, *Hemicola* and *Botryotrichum* genera (Ozaki et al.,

2005). A contact of 126 days with selected *Aspergillus* and *Lysinibacillus* strains has determined a 29.5% biodegradation percentage of low-density polyethylene films (Esmaili et al., 2013). Biodegradability of methylated-cornstarch/poly(vinyl alcohol) blend films (50/50; w/w) was evaluated by the weight loss after soil burial for over seven months. The films displayed a higher degradation, from 50 to 75% percentage, depending on the degree of

substitution in methylated starch (Guohua et al., 2006).

4. Conclusions

In the present study, several composites based on waste wood and PVA were subjected to the biodegrading activity of a selected fungal strain, *Aspergillus niger*. The SEM images of samples show the level of microbial colonization of samples, in accordance with materials composition. Samples VACW (55% PVA, 10-15 % wood flour, 25-20 % glycerol, 10% PVC), and especially, samples VAA (55% PVA, 10-15 % wood flour, 25-20 % glycerol, 10% starch) present dense hyphae networks and conidia accumulations.

FTIR spectra of composites with more than two components indicate the increase of the peak around 1740 cm⁻¹, due to oxidation of PVA hydroxyl groups to carbonyl groups. This modification proves the beginning of the biodegradation process.

From TGA data it can be concluded that the number of thermal decomposition steps depends on the material composition. Therefore, samples VA were degraded in three steps, samples VAW and VAA in four steps and samples VACW in five steps. All the PVA - wood composites displayed an improvement of thermal stability. An increasing of temperature values over 20°C was recorded for the composites with the exception of VACW samples.

Further researches could be undertaken to investigate the biodegradability of PVA - wood composites in natural environment, by composting or soil burial test. Also, an important point would be to determine the influence of wood species composition, as lignin, hemicelluloses and cellulose content upon composites biodegradability in order to reach a rational use of renewable resources.

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