

Branched Copolymer Based on Glycerol, Ethylene Glycol and Adipic Acid, Linear Copolymer Based on Lactic Acid, Ethylene Glycol and Succinic Acid: Thermal and Microbial Degradation Comparatives Studies

A. Benarbia^{1,*}, A. Elidrissi¹, Asehraou Abdeslam²

¹LCAE-URAC18: Laboratory of Applied Chemistry and Environment, Department of Chemistry, Faculty of Sciences, University Mohammed the First – Oujda, Morocco

²Laboratory of Biochemistry and Biotechnology, Faculty of Sciences, Mohammed Premier University, Oujda, Morocco

*Corresponding author: benarbia11@hotmail.com

Abstract In this work, we aim compare the thermal and microbial degradation of two copolyesters a Branched copolyester Based on Glycerol, Ethylene Glycol and Adipic acid COP B [27] and a linear copolyester based on Lactic Acid, Ethylene Glycol and Succinic Acid COP L [2]. The quantitative and qualitative biodegradation phenomenon of the prepared copolyesters studied using two selected strains of *Aspergillus sp* S1 and *Penicillium sp* S2. The mechanism illustrating this process was proposed. The mean of the apparent activation energy (Ea) of COP L is biggest than noted for COP B. In case of the biomass growth obtained for *Aspergillus sp* S2 and *Penicillium sp* S1 a high increase of biomass was observed for COP B. The branched biodegradable copolyester exhibit potential to replace linear biodegradable copolyester.

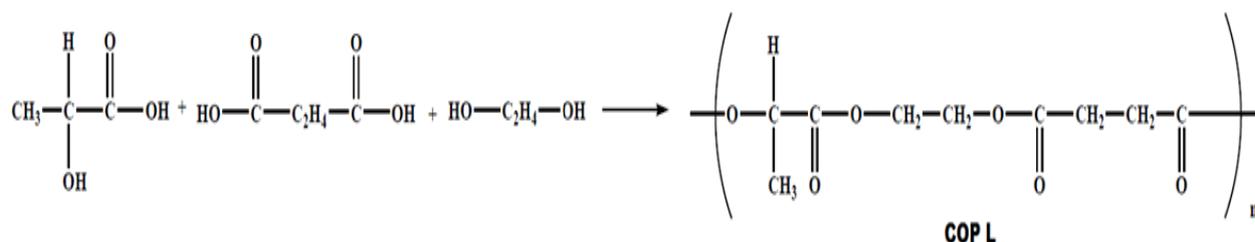
Keywords: copolyester, thermal degradation, biodegradation, *Aspergillus*, *Penicillium*

Cite This Article: A. Benarbia, A. Elidrissi, and Asehraou Abdeslam, “Branched Copolymer Based on Glycerol, Ethylene Glycol and Adipic Acid, Linear Copolymer Based on Lactic Acid, Ethylene Glycol and Succinic Acid: Thermal and Microbial Degradation Comparatives Studies.” *Journal of Polymer and Biopolymer Physics Chemistry*, vol. 6, no. 1 (2018): 1-12. doi: 10.12691/jpbpc-6-1-1.

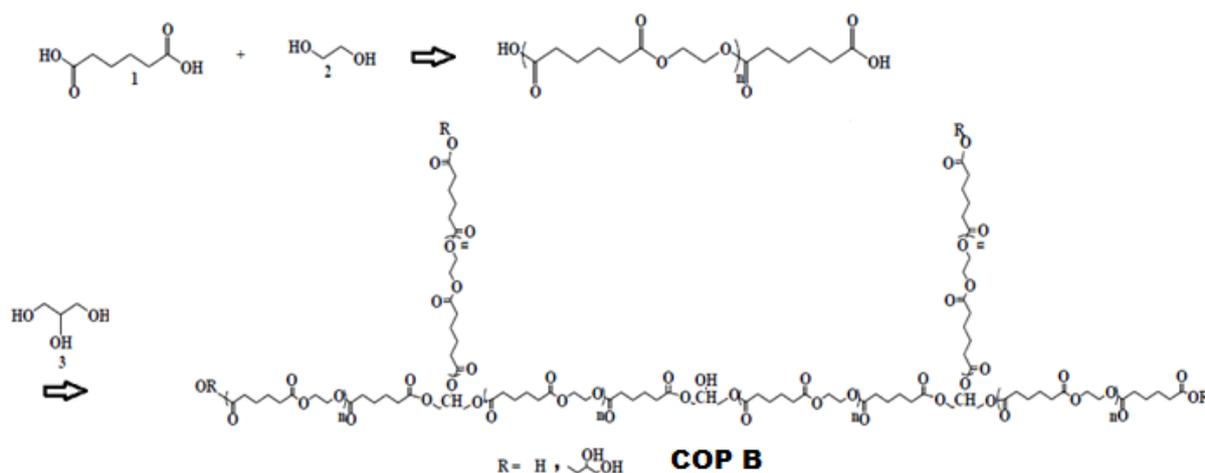
1. Introduction

Copolyesters attract more attention their hydrolysable ester bonds, especially aliphatic polyesters are considered to be susceptible to microbial attack. Their degradation is seen as a two step process: the first is depolymerization, the second is enzymatic hydrolysis. The enzymatic hydrolysis produces intermediates water soluble compounds that can be assimilated by microbial cells [1]. It's well known that the introduction of lactic acid in copolyester chain reduced its crystallinity [2], and to the increase rate of biodegradation. Recently, the architecture of copolyesters was investigated intensively to highlight their contribution

in thermal and microbial degradation. Branched copolymers attract more attention [3-8], particularly from glycerol and bifunctional acids [9-16]. Glycerol or glycerin is a viscous compound, obtained from natural resources. The glycerol presents three alcohols groups which are not equivalent, responsible of its solubility in water lead to hygroscopic nature, also can create three ethereal bonds. Furthermore, the glycerol is used in many drugs' compositions, because of its low toxicity. For example, polyester was synthesized by associating adipic acid and glycerol in the presence of dibutyltin oxide as catalyst [17]. The branched polyesters have opened new horizons especially in food, drugs and agriculture domains by the release of bio-active and non-human toxic substances such as pesticides and antibiotics [18-26].



Scheme 1. Linear copolyester based on Lactic Acid, Ethylene Glycol and Succinic Acid COP L



Scheme 2. Branched copolyester Based on Glycerol, Ethylene Glycol and Adipic acid **COP B**

In this work, we aim compare the thermal and microbial degradation of two copolyesters a branched copolyester based on Glycerol, Ethylene Glycol and Adipic acid COP B [27] and a linear copolyester based on Lactic Acid, Ethylene Glycol and Succinic Acid COP L [2]. The quantitative and qualitative biodegradation phenomenon of the prepared copolyester will be studied by using two selected strains *Aspergillus sp S1* and *Penicillium sp S2*. On the other hand, a mechanism illustrating this process will be proposed.

2. Experimental

2.1. Materials

Lactic acid, ethylene glycol, succinic acid, toluene, Tin (II) chlorides, Glycerol, ethylene glycol, adipic acid, toluene, paratoluene sulfonic acid, dichloromethane and diethyl ether were purchased from Sigma-Aldrich Chemical Co. All reagents were used as received.

2.2. Synthesis of Copolyesters

The synthesis of the linear copolyester is analogue to the preparation described [2]. First the copolyester was synthesized using lactic acid, succinic acid and ethylene glycol. Lactic acid (0.01mol), succinic acid (0.19mol) and ethylene glycol (0.19mol) were taken in three-necked round bottom flask and 20 ml of toluene was added. A thermometer was fitted to the neck, a stirrer to the other and Dean Stark was fitted to third neck. The temperature was kept at 120°C for 7 h to remove water by azeotropic. The organic solvent was extracted and 0.1% of SnCl₂ was added as a catalyst with constant stirring, the temperature was raised at 240°C under vacuum for another 5 h. The reaction mixture was dissolved in dichloromethane and precipitate in an excess of diethyl ether. The white copolyester was isolated by filtration and kept at 60 °C under vacuum for 24 hours. The synthesis of branched copolyester [27], based on adipic acid, ethylene glycol and glycerol, is carried out in two steps. The first step consists of the dehydration of reagents and formation of oligomers. In a flask of 500 ml we introduced a reaction mixture consisting of 0.123 mol of adipic acid, 0.099 mol of

ethylene glycol, 20 ml of toluene twice distilled and an amount of paratoluene sulphonic acid equal to 0.1% of the total mass of the reactant. The heating was maintained at refluxed for 5 hours with continuous stirring. The second step started, after removal of toluene by rotavapors. The titanium butoxide was added under vacuum; the glycerol is added 1ml/30 min using a micropipette at a temperature of 230°C. The reaction mixture was dissolved in dichloromethane and precipitated in an excess of diethyl ether; the yellow branched copolyester was obtained after filtration and stored under vacuum for 24 hours

2.3. Characterization

2.3.1. TGA/DTA Investigation

Thermogravimetric analysis was carried out with SHIMADZU TGA/DTA. Samples were placed in alumina crucibles, an empty alumina crucible was used as reference, and samples were heated from room temperature to 600°C in a 50 ml/min flow of N₂. Nominal heating rates of 10, 15 and 20 °C/min were used, and continuous records of sample temperature, sample weight, its first derivative and heat flow were taken.

The application of dynamic TG methods holds great promise as a tool for unraveling the mechanisms of physical and chemical processes that occur during solids state degradation. Thermal degradation is usually defined in terms of kinetic triplet: the activation energy E_a, pre-exponential factor A and the conversion function f(α) [28].

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f} \quad (1)$$

Where W_t, W₀, and W_f are time t, initial and final weights of the sample, respectively.

$$\frac{d\alpha}{dt} = k \times f(\alpha). \quad (2)$$

With the reaction constant k and f(α) is the function of converting α, the parameter k is dependent on the temperature T according to the Arrhenius law

$$K(T) = Ae^{-E_a/RT}. \quad (3)$$

The isoconversional method of Ozawa, Flynn and Wall (OFW) is in fact, a (model free) method which assumes that the conversion function $f(\alpha)$ does not change with the alteration of the heating rate for all values of α . It involves the measuring of the temperatures corresponding to fixed values of α from experiments at different heating rates β .

Therefore, plotting $\ln(\beta)$ against $\frac{1}{T}$ in the form of

$$\ln(\beta) = \ln\left(\frac{Af(\alpha)}{d\alpha/dT}\right) - \frac{E_a}{RT}. \quad (4)$$

Should give straight lines and its slope is directly proportional to the activation energy $\left(-\frac{E_a}{R}\right)$.

If the determined activation energy is the same for the various values of α , the existence of a single step reaction can be concluded with certainty. On the contrary, a change of E_a values with increasing degree of conversion is an indication of a complex reaction mechanism that invalidates the separation of variables involved in the OFW method. These complications are significant, especially in the case that the total reaction involves competitive mechanisms [2].

2.3.2. Biodegradability Testing Method

The biodegradation tests were performed in liquid culture medium under aerobic condition during a period of 28 days. These culture tests were carried out according to microbial invasion method [29]. For each test, blanks with microbial inoculums and without polyester samples were also performed for checking the micro-organisms activity.

2.3.2.1. Mineral Medium Preparation for Fungi

The mineral medium (M1) used in this study is composed of monopotassium phosphate (KH_2PO_4 : 0.7 g); di-potassium hydrogen phosphate (K_2HPO_4 : 0.7 g); magnesium sulfate heptahydrate ($\text{MgSO}_4/7\text{H}_2\text{O}$: 0.7 g); ammonium nitrate (NH_4NO_3 : 1 g); sodium chloride (NaCl : 0.005 g/l); ferrous sulfate heptahydrate ($\text{FeSO}_4/7\text{H}_2\text{O}$: 0.002 g); zinc sulfate heptahydrate ($\text{ZnSO}_4/7\text{H}_2\text{O}$: 0.002 g); manganese sulfate heptahydrate ($\text{MnSO}_4/7\text{H}_2\text{O}$: 0.001 g) dissolved in sufficient distilled water to make up 1000 ml. This medium was sterilized by autoclaving at 121°C for 20 min. After sterilization, the pH value was fixed at 6.3.

2.3.2.2. Fungi Preparation

Two strains of *Penicillium* sp S1 and *Aspergillus* sp S2 were isolated from the lixivia of the landfill of Oujda (Morocco) and previously selected for their biodegradation capacity of the polyester [30]. The microorganisms were previously purified and stored in YEG medium (yeast extract + Glucose).

2.3.2.3. Biodegradability Investigation by Invasion Method

The biodegradation of polyesters was carried out using 200 mL bottles containing tested polyester (powder 1.5g/L) as a sole carbon source. The strain (*Penicillium* sp S1 or *Aspergillus* sp S2) was inoculated at 2×10^6 cells/ml as initial inoculum in 150 ml of mineral medium M. The cultures were incubated at 30°C during 28 days under

stirring conditions. The development of biomass was evaluated at regular intervals (typically twice a week). For each assay, samples of 2 ml were collected and the cells were counted by cell Thoma cell counter (hematimetre). The tests were repeated three times to check the reproducibility. The results of these studies are presented as cell growth curves.

2.3.2.4. IR Spectroscopy

The FTIR spectrum of the linear and branched polyester synthesized were recorded before and after biodegradation using FTIR B8400S SHIMADZU between 4000 and 600 cm^{-1} at resolution of 4 cm^{-1} .

2.3.2.5. Crystallinity Investigation

The crystallinity investigation was carried out with shimadzu XRD 6000 using Cu $\text{k}\alpha$ radiation ($\lambda=15$) at 40KV and 30 mA with scan of $4^\circ/\text{min}$.

As reported in Figure 1 the copolyesters COP B and COP L are semicrystallins. In Figure.1.a, the COP B, exhibited some diffraction peaks which appeared around $2\theta = 21^\circ, 22^\circ$ and 24.5° indicating different size of crystallites and attributed to the order arrangement of the polyester chains. Moreover, we noted the presence of others peaks at $44.65^\circ, 64.60^\circ$ and 78° which are assignable to (010), (110) and (100) plans. The COP B presents more amorphous areas (Figure.1.a). Also as reported in Figure.1.b, the COP L exhibited more diffraction peaks which appeared around $2\theta = 20^\circ, 23^\circ, 24^\circ, 26^\circ, 31^\circ, 38^\circ$ indicating different size of crystallites and attributed to the order arrangement of the COP L chains at $44.65^\circ, 64.60^\circ$ and 78° which are assignable to (010), (110) and (100) plans. The COP L exhibited more crystallites areas (Figure 1.b).

3. Results and Discussion

Thermal degradation of the copolyesters COP L and COP B was studied by determining their mass loss during heating. In (Figure 2 and Figure 3) are presented the mass loss (TG mg % and %) and their derivative mass loss (DTG mg/min and %/min) curves. From the thermogravimetric curves TGA % the copolyester COP L under heating rates $10^\circ\text{C}/\text{min}$ (Figure 2), it can be seen that the copolyester presents a relatively good thermostability, consequently no significant weight loss occurred until 158.52°C , and the weight loss (%) was 3.35 % at $T = 165^\circ\text{C}$. Studies showed that polyethylene succinate is stable until $T = 300^\circ\text{C}$ [31], the succinic acid degrades at a temperature equal at 200°C and the ethylene glycol degrades at a higher temperature up to 300°C [32]. The introduction of lactic acid significantly reduces thermal stability in the case of the copolyester COP L. In Figure 2.a, showing the variations of instantaneous reaction in DrTGA (% / min) with heating rate $\beta = 10^\circ\text{C}/\text{min}$, it is noted that two peak rates can be identified, the first peak at $T = 214.11^\circ\text{C}$ may be caused by small volatile molecules, the catalyst residue and unreacted monomers [33]. The second peak showed rapid deterioration of the copolyester at $T = 361.38^\circ\text{C}$. An early comprehensive overview about the mechanism of the thermal decomposition of polyesters was reported by Buxbaum, but only for aromatic polyesters like poly

(ethylene terephthalate) [34]. It was shown that esters containing at least one β -hydrogen decompose via a cyclic intermolecular transition state to an olefin and acid end groups. Tomonaga et coll [35] investigating the random scission and chain-end scission in the thermal degradation of polyethylene and showed that the direct scission and one-step-radical transfer increased with the temperature, indicating that β scission occurs on the chain end before the radical transfer because the rate of the β scission becomes faster as the temperature rises. In our case the polyester is aliphatic chain but at least two carbons are nearest which indicate that probability of random scission

is very low. Bikiaris et coll have investigated the thermal degradation mechanism of poly (propylene succinate) using pyrolysis - gas chromatography- mass spectrometry (Py-GC-MS) and TGA analysis [36]. They have concluded that the decomposition of polyester begins by the decomposition of its hydroxyl and carboxylic end groups, also it was noted that in similar aliphatic polyesters similar polycaprolactone (PCL), at the same temperatures given, a sharp decrease molecular weight while water, carbon dioxide and 5-hexanoic acid were the main evolved gases [37]. These gases are produced from the decomposition of hydroxyl and carboxylic end groups, respectively.

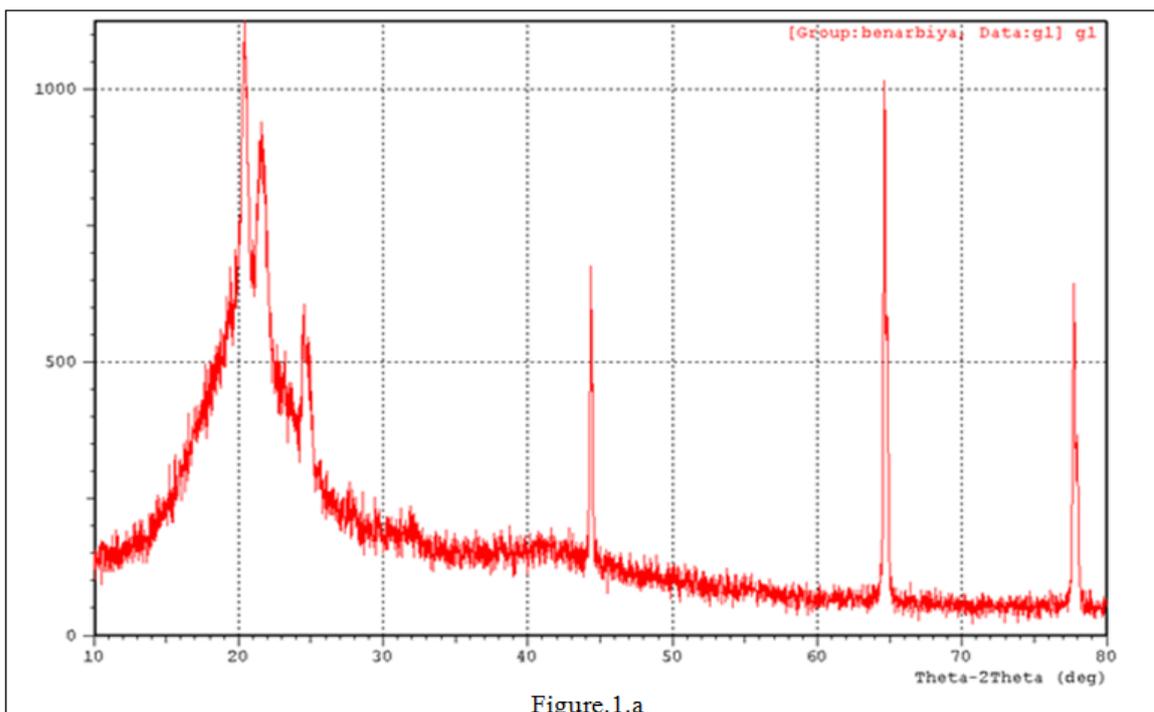


Figure.1.a

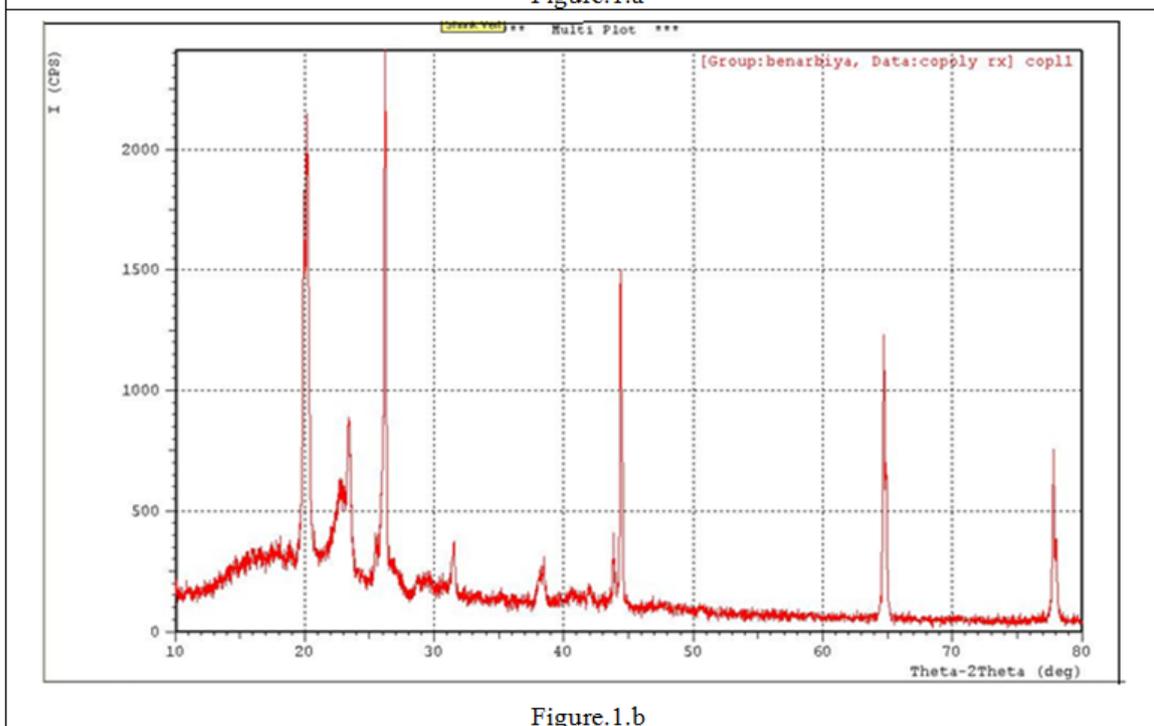


Figure.1.b

Figure 1. X-ray diffraction patterns of COP B Figure.1.a and COP L Figure.1.b

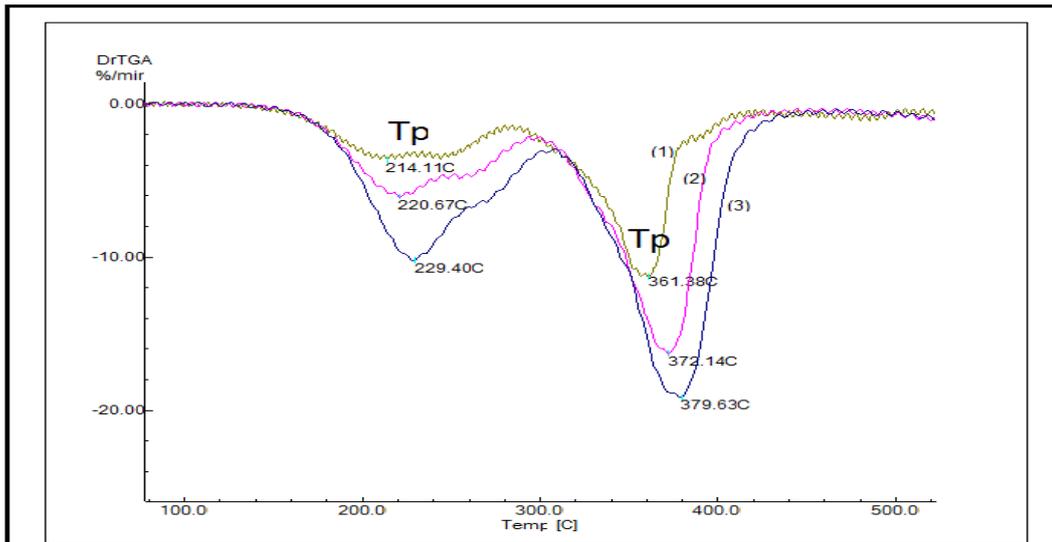


Figure.2.a

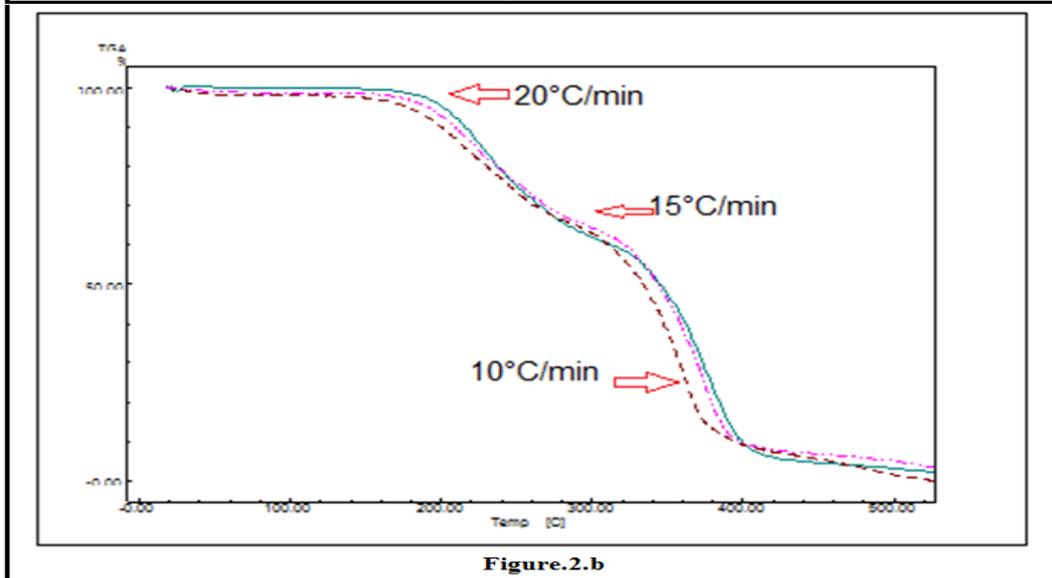


Figure.2.b

Figure 2. Thermal analysis of the COP L, at heating rate β : 1) 10 °C/min, 2) 15 °C/min and 3) 20 °C/min

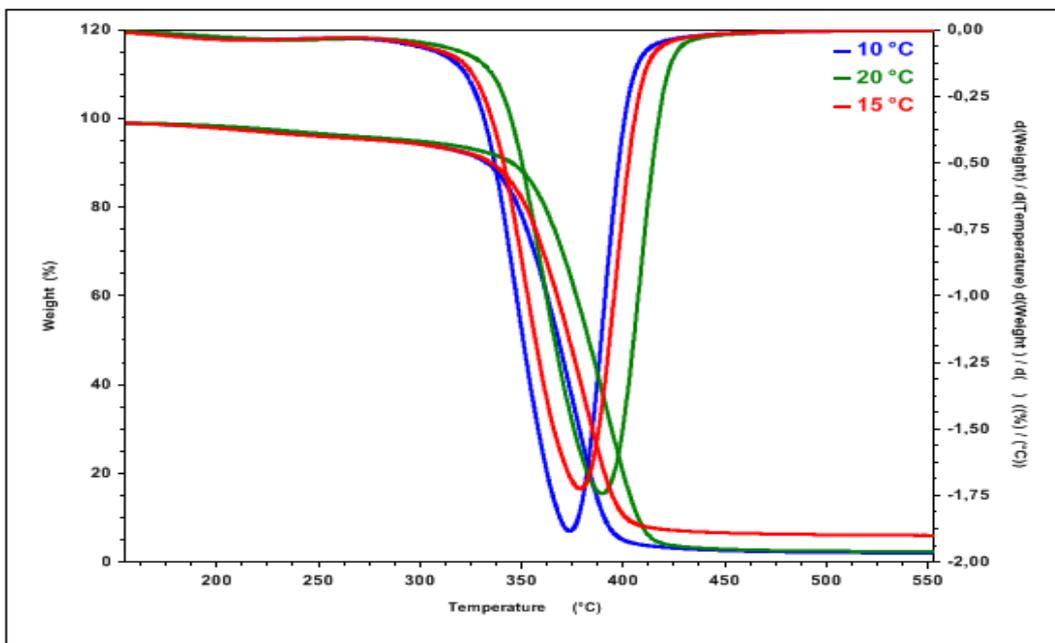


Figure 3. Thermal analysis of the COP B, at heating rate β : 1) 10 °C/min, 2) 15 °C/min and 3) 20 °C/min

Thermal stability and thermal degradation traces of the branched copolyester (COP B) were also measured, Figure 3 illustrates the noted thermogravimetric traces TGA/DTG at heating rate of $\beta = 10, 15$ and 20 °C /min. We noted that the polyester presents a good thermal stability, since there is no significant weight loss until $T = 226.93$ °C which corresponds to a weight loss of 2.92 %. Two peaks are identified in the TGA curve, the first peak is barely distinguishable, but it is very apparent in the corresponding DTG curve. At the heating rate $\beta = 10$ °C/min, the first peak started at $T = 162.5$ °C and finished at $T = 275$ °C and the second peak started at $T = 276$ °C and finished at $T = 475$ °C. These two peaks indicate the existence of two thermal reactions. The presence of more than one reaction indicates the existence of a very complex mechanism governed by the transition states.

To simplify calculates our approach will study the principle reaction by using Ozawa method. The results are summarized in Table 1.

Table 1. The apparent activation energy E_a of COP B and COP L Ozawa method

Conversion α	E_a (KJ /mol) Ozawa method			
	COP B	R^2	COP L	R^2
0.1	149.24	0.815	84.54	0.986
0.2	158.84	0.902	220.97	0.934
0.3	156.88	0.912	518.86	0.996
0.4	157.71	0.926	168.4	0.338
0.5	156.31	0.939	206.19	0.996
0.6	156.36	0.951	163.36	0.997
0.7	155.04	0.960	160.02	0.999
0.8	154.75	0.975	153.76	0.994
0.9	154.67	0.994	143.80	0.990
Mean	155.53		202.22	

The apparent activation energy (E_a) previously determined (Table 1) were evaluated utilizing the classical Ozawa methods, all process was described. It can be seen that in the case of COP L there is two important steps (Figure 4): the first step E_a increases between $0.05 \leq \alpha \leq 0.3$; the second step E_a decreases and becomes relatively stable between $0.4 \leq \alpha \leq 0.85$. In the case of COP B the apparent activation energy (E_a) previously determined (Table 1) is relatively stable in all processes and the lowest value. The mean of the apparent activation energy (E_a) of COP L 202.22 KJ /mol is biggest than these noted for COP B 155.53 KJ /mol. These phenomena can be explained by carbonaceous residue. It is important to note that works reported that the activation energies of the thermal degradation process depend largely on the polymerization methods which determine the nature of architecture. María Angeles et coll [38] demonstrated that while the combustion progresses a carbonaceous residue is slowly forming. This carbonaceous residue limits the diffusion of the decomposed volatile products and, as a consequence, the activation energy increases. These phenomena are noted in the case of linear copolyester COP L between $0.1 \leq \alpha \leq 0.4$ but very slightly in the case of branched copolyester witch meaning that the branched copolyester inhibits the formation of carbonaceous residue.

Quantitative tests show an effective and simple way of biodegradation of the copolyester COP B and COP L by their simple contamination with drops of leachate landfill Oujda north Morocco. Three Tests were performed. The three tests are positive, and the results are reported in Figure 5.

The evolution of biomasses of *Aspergillus sp* S1 and *Penicillium sp* S2 in mineral medium M1 without copolyester is already reported [27]. The results indicate the impossible growth of *Aspergillus sp* or *Penicillium sp* in mineral medium (M1) without carbon source. The strain *Penicillium* S1 was more sensitive to the absence of carbon source than *Aspergillus*.

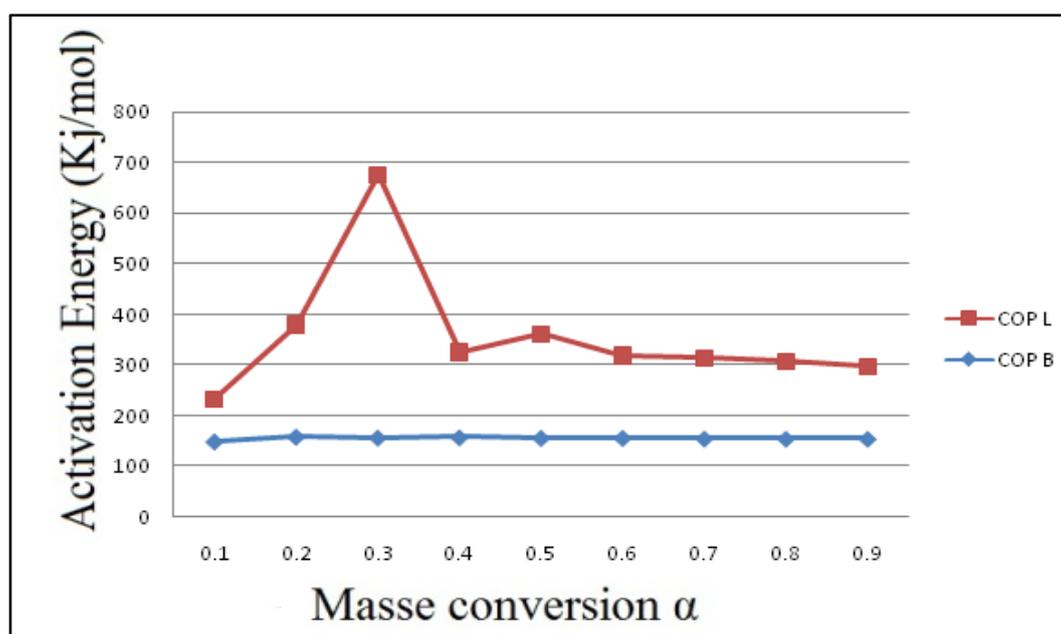


Figure 4. Dependence of the activation energy (E_a) on the mass conversion (α), as calculated with Ozawa methods for the copolyesters COPB and COP L

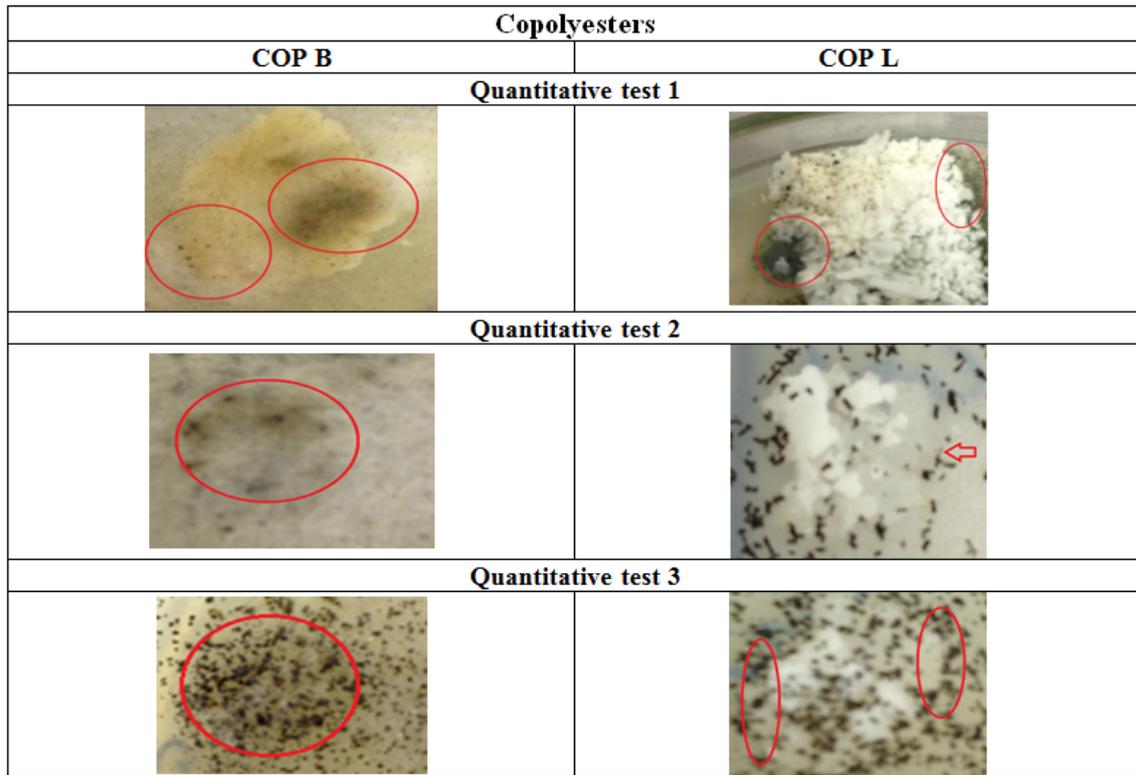


Figure 5. Quantitative tests, copolyester COP B and COPL contaminated by drops of leachate landfill Oujda north Morocco (tests repeated three times)

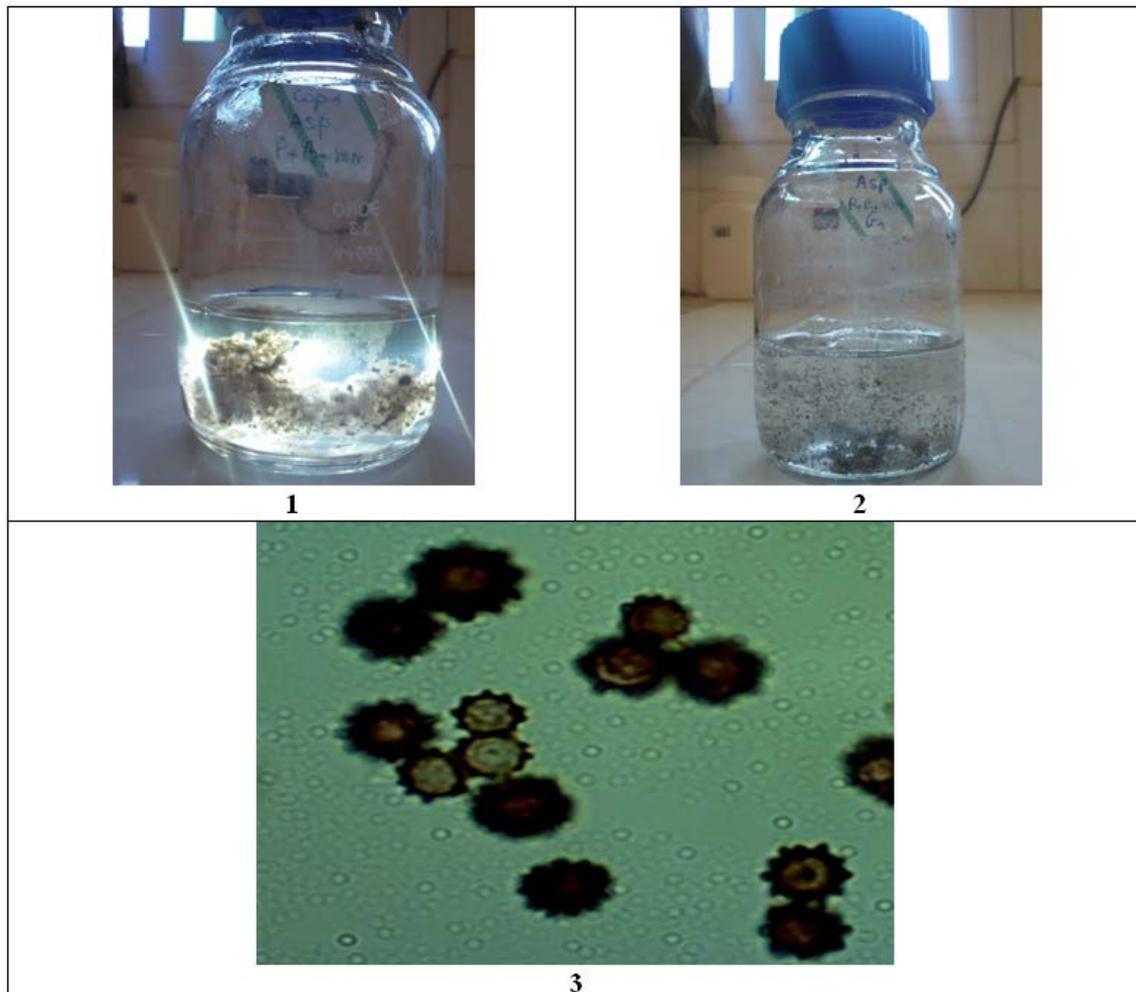


Figure 6. Culture of *Aspergillus sp S2* obtained after 28 days of incubation at 30°C on copolyesters as a sole carbon source; (1) Biomass COP L, (2) Biomass COP B, (3) spores

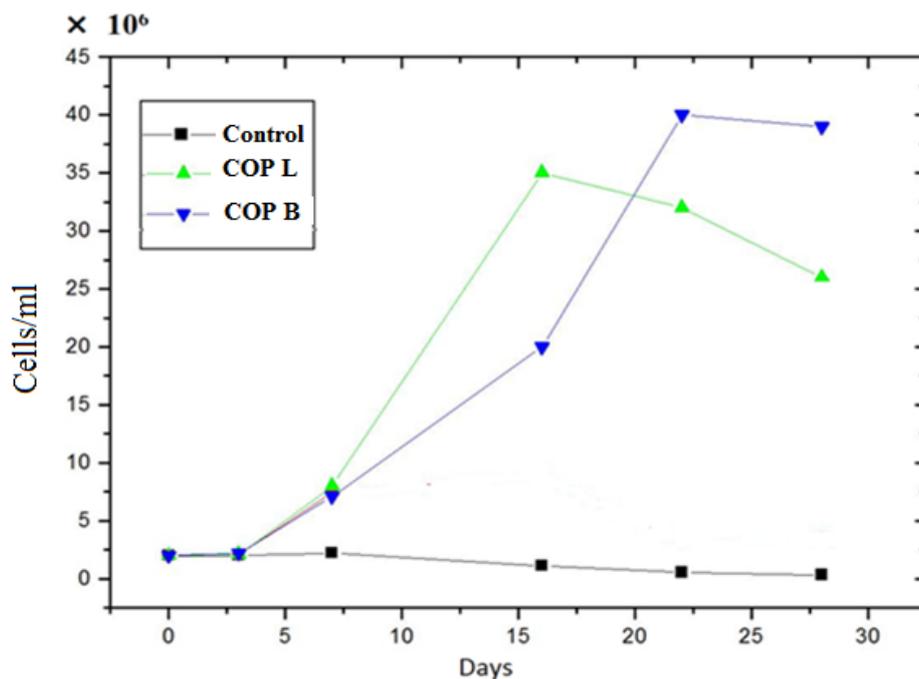


Figure 7. Variation curves of *Aspergillus sp S2* in mineral medium M1 with copolyesters COP B and COP L at 30 °C

In the presence of the copolyester COP L or COP B as carbon source, the biomass growth obtained for *Aspergillus sp S2* is reported in Figure 7, a high increase of biomass was observed to achieve, after 16 days of incubation in case of COP L and 22 days of incubation in case of COP B. A maxima of 35×10^6 and 40×10^6 cell/ml

for *Aspergillus sp S2* in case of COP L and COP B, respectively. After, a decrease of biomass was observed to achieve, after 28 days of culture, 25×10^6 cell/ml in case of COP L and 38×10^6 cell/ml in case of COP B for *Aspergillus sp S2*. While in the control no biomass growth was observed.

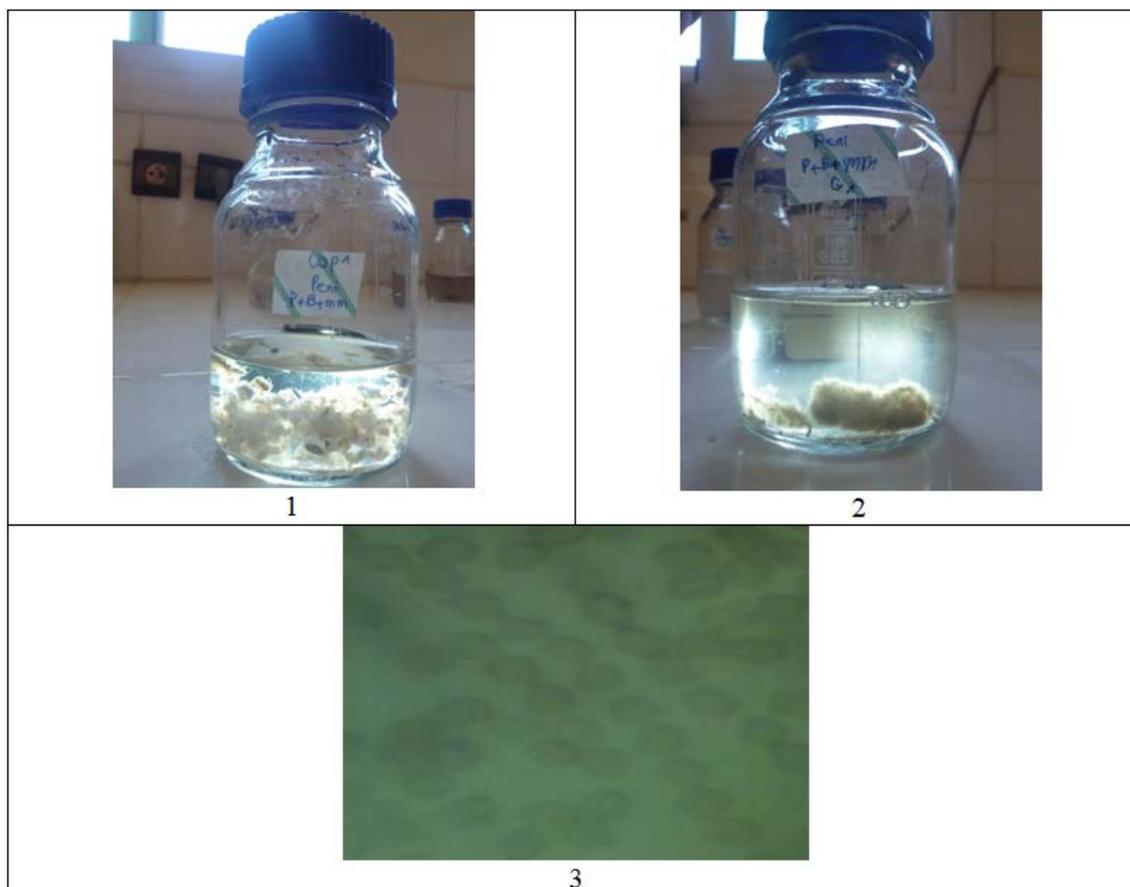


Figure 8. Culture of *Penicillium sp S1* obtained after 28 days of incubation at 30°C on copolyesters as a sole carbon source; (1) Biomass COP L, (2) Biomass COP B, (3) spores

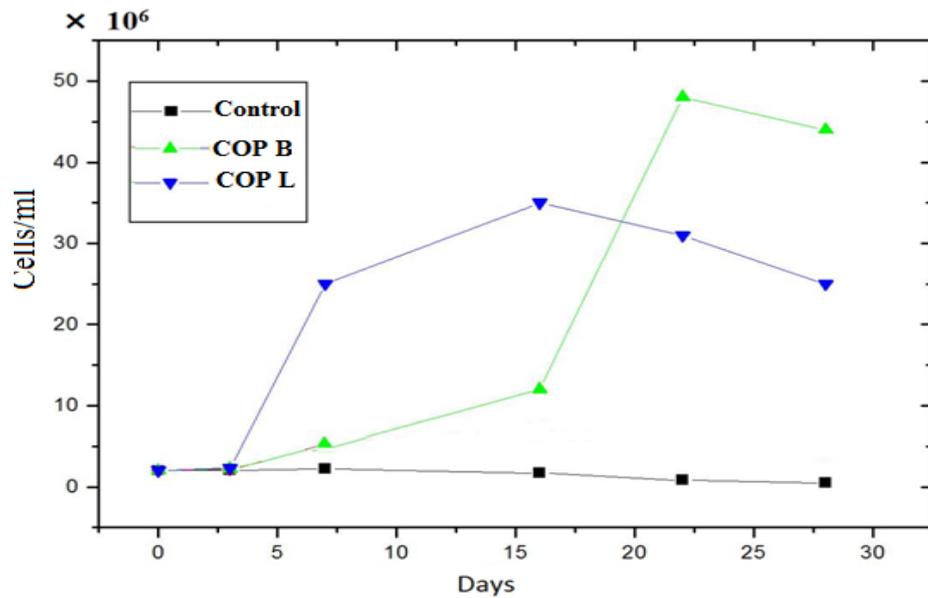


Figure 9. Variation curves of *Penicillium sp S1* in mineral medium M1 with copolyesters COP B and COP L at 30 °C

In the presence of copolyesters COP L or COP B as carbon source, the biomass growth obtained for *Penicillium sp S1* is reported on (Figure 9). a high increase of biomass was observed to achieve, a maximum of 33×10^6 cells/ml after 16 days of incubation in case of COP L, and a maximum of

48×10^6 cells/ml after 22 days of incubation in case of COP B. After, a decrease of biomass was observed to achieve, after 28 days of culture, 22×10^6 cells/ml showed in case of COP L and 44×10^6 cell number/ml in case of COP B. While in the control “blank” no biomass growth was observed.

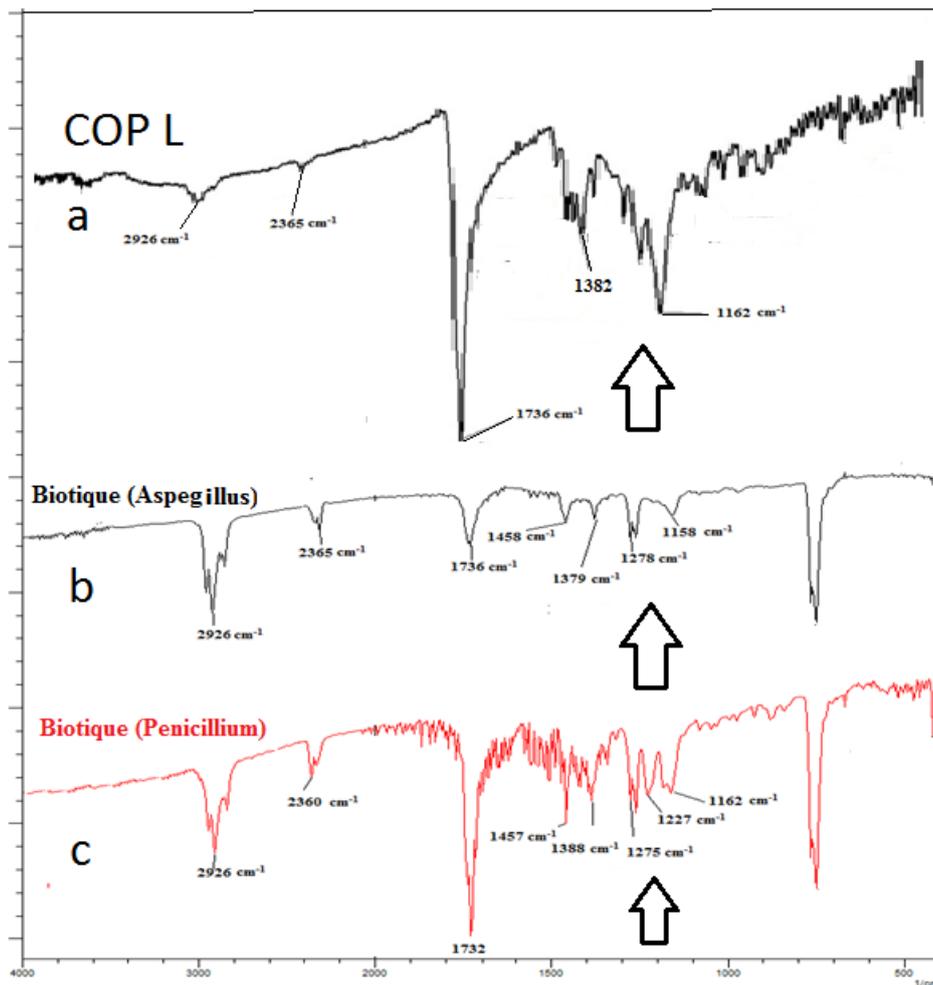


Figure 10. FTIR Spectra of the polyester COP L: before incubation (a), and after incubation during 28 days with *Aspergillus sp S2* (b) and *Penicillium sp S1* microorganisms (c)

Figure 10 shows the changes in FTIR spectrum of the pure COP L. In comparison with the reference (spectrum a), a decrease in the intensities of some bands was observed in polyesters inoculated with *Aspergillus* sp S2 (spectrum b) and *Penicillium* sp S1 (spectrum c) particularly the absorption band at $\delta = 1161.31 \text{ cm}^{-1}$ characteristic the stretching vibration of the repeated $-\text{OCH}_2\text{CH}_2-$ and also a decrease of the $\text{C}=\text{O}$ stretching vibrations of the ester carbonyl group. This phenomenon has been elucidated in the literature. The microorganisms secrete enzymes (mainly esterase) hydrolyzing the ester group, so that the large molecules become small and easily used as nutrients. The esterase enzymes produced are generally lipase [35].

Figure 11 shows the changes in FTIR spectrum of the pure COP B. In comparison with the reference (spectrum a), a decrease in the intensities of some bands was observed in polyesters inoculated with *Aspergillus* sp S2 (spectrum b) and *Penicillium* sp S1 (spectrum c) particularly at 1736 cm^{-1} (stretching vibration of $-\text{C}=\text{O}$ ester), 1284 cm^{-1} (stretching vibration $\text{O}=\text{C}-\text{O}$), 1262 , 1170 , 1145 , 1080 and 1069 cm^{-1} (stretching vibration CO). The intensities of these bands dramatically decreased in the traces of *Penicillium* sp S1. This result indicates that probably the *Penicillium* sp S1 is more active than *Aspergillus* sp S2 in these experimental conditions. The apparition of a new band at 750 cm^{-1} is probably due to the metabolites of *Aspergillus* sp S2 them self. This

phenomenon as previously noted has been elucidated in the literature. The microorganism secretes enzymes (mainly esterase) hydrolyzing the ester, so that the large molecules become small and easily used as nutrients, the esterase enzymes produced are generally lipase [35].

Biodegradation of copolyesters is a complex and heterogeneous process. Microorganisms cannot assimilate insoluble molecules in water or having large sizes. The microorganisms produce extracellular enzymes that depolymerize the copolyester outside their cells, these enzymes belong to the family of hydrolases namely esterases, lipases, proteases, amidases, epoxide hydrolases, nitrolases and glycosidases, which catalyze the hydrolysis of the ester group [35]. When the molecular weight of the polyester is sufficiently reduced, the micro-organisms intervene to generate the intermediates which are soluble in water and assimilate them. The assimilation process generates the production of water, carbon dioxide and biomass. Lipases are produced by a wide variety of microorganisms such as *Aspergillus* and *Penicillium*. The team of Soni et al. [31] studied the mechanism of enzymatic degradation of the copolyester, taking into account its results we have proposed a mechanism for the enzymatic degradation of copolyester based on lactic acid, ethylene glycol and succinic acid (cop L) (Scheme 3). This mechanism can be generalized for all synthesized copolyesters and branched copolyesters.

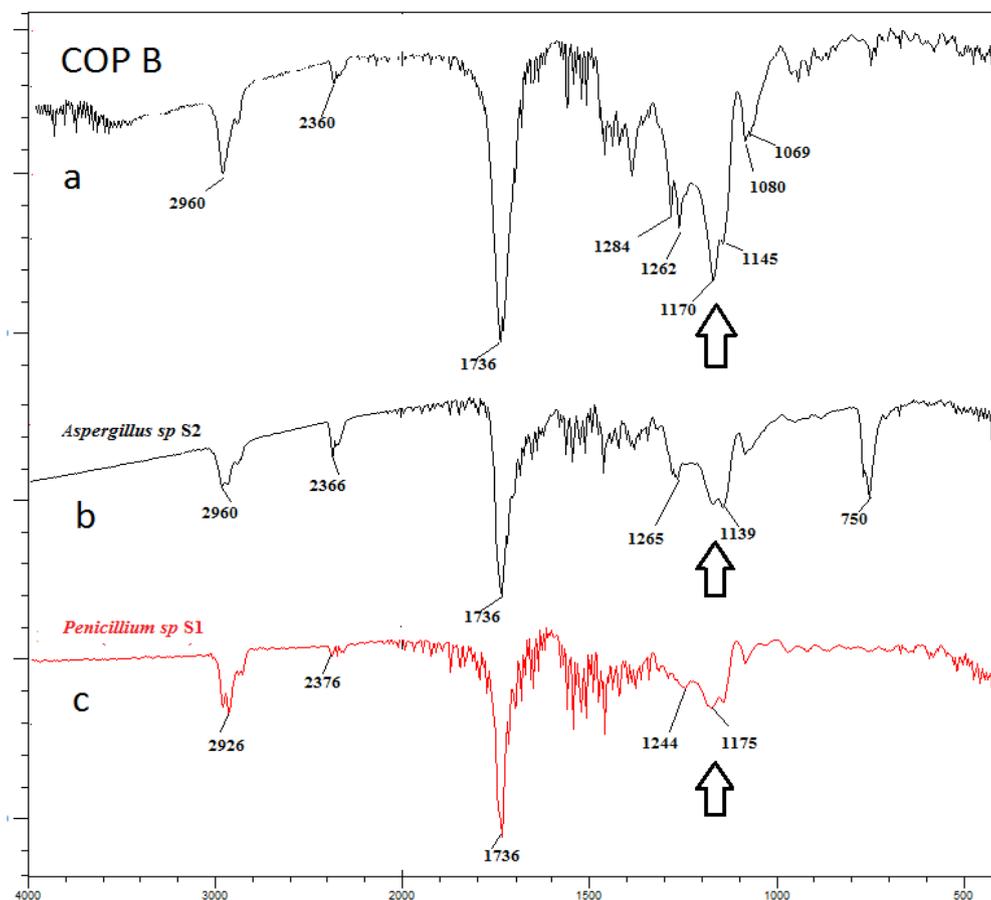


Figure 11. FTIR Spectra of the polyester COP B: before incubation (a), and after incubation during 28 days with *Aspergillus* sp S2 (b) and *Penicillium* sp S1 microorganisms (c)

- [5] Mickaël, A., Stéphanie, D., Sinisa, M., Boris, E. and Véronique, N.R., "Characterization, stability and ecotoxic properties of readily biodegradable branched oligoesters based on bio-sourced succinic acid and glycerol", *Polymer Degradation and Stability*. 97(10). 1956-1963. March 2012.
- [6] Bruggeman, J.P., Bettinger, C.J., Nijst, C.L.E., Kohane, D.S. and Langer, R., "Biodegradable Xylitol Based Polymers", *Advanced Materials*. 20(7). 1922-1927. 2008.
- [7] Barret, D.G., Luo, W. and Yousaf, M.N., "Aliphatic polyester elastomers derived from erythritol and alpha, omega-diacids", *Polymer Chemistry*. 1(3). 296-302. January 2010.
- [8] Cao, H., Zheng, Y., Zhou, J., Wang, W. and Pandit, A., "A novel hyperbranched polyester made from aconitic acid (B3) and di(ethylene glycol) (A2)". *Polymer International*. 60(4). 630-634. April 2011.
- [9] Yang, Y., Lu, W., Cai, J., Hou, Y., Ouyang, S., Xie, W. and Gross, R., "Poly (oleic diacid-co-glycerol): Comparison of Polymer Structure Resulting from Chemical and Lipase Catalysis". *Macromolecules*. 44(7). 1977-1985. March 2011.
- [10] Yang, Y., Lu, W., Cai, J., Hou, Y., Ouyang, S., Xie, W. and Gross, R., "Poly (oleic diacid-co-glycerol): Comparison of Polymer Structure Resulting from Chemical and Lipase Catalysis". *Macromolecules*. 44(7). 1977-1985. March 2011.
- [11] Kulshrestha, S., Bishwabhusan, S., Wei, G., Hongyong, F. and Gross, A., "Lipase Catalysis. A Direct Route to Linear Aliphatic Copolyesters of Bis(hydroxymethyl)butyric Acid with Pendant Carboxylic Acid Groups". *Macromolecules*. 38(8). 3205-3213. March 2005.
- [12] Carnahan, M.A. and Grinstaff, M.W., "Synthesis and characterization of poly(glycerol-succinic acid) dendrimers". *Macromolecules*. 34(22). 7648-7655. September 2001.
- [13] Stumbe, J.F. and Bruchmann, B., "Hyperbranched Polyesters Based on Adipic Acid and Glycerol". *Macromolecular Rapid Communications*. 25(9). 921-924. March 2004.
- [14] Wyatt, V.T. and Strahan G.D., "Degree of Branching in Hyperbranched Poly(glycerol-co-diacid)s Synthesized in Toluene". *Polymers*. 4(1). 396-407. February 2012.
- [15] Carnahan, M.A. and Grinstaff, M.W., "Synthesis and characterization of polyether-ester dendrimers from glycerol and lactic acid". *Journal of American Chemical Society*. 123 (12). 2905-2906. March 2001.
- [16] Li, Y., Cook, W.D., Moorhoff, C., Huang, W.C. and Chen, Q.Z., "Synthesis, characterization and properties of biocompatible poly(glycerol sebacate)". *Polymer International*. 62(4). 534-547. April 2013
- [17] Tracy, Z., Bob, A., Adina, D., Steven, J. and Patrick, B., "Synthesis and Characterization of Glycerol-Adipic Acid Hyperbranched Polyesters". *Polymer*. 55(20). 5065-5072. September 2014.
- [18] Coneski, P.N., Rao, K.S. and Schoenfisch, M.H., "Degradable nitric oxide-releasing biomaterials via post-polymerization functionalization of cross-linked polyesters". *Biomacromolecules*. 11 (11). 3208-3215. October 2010.
- [19] Cao, W., Zhou, J., Mann, A., Wang, Y., Zhu, L., "Folatefunctionalized unimolecular micelles based on a degradable amphiphilic dendrimer-like star polymer for cancer cell-targeted drug delivery". *Biomacromolecules*. 12(7). 2697-26707. Jun 2011.
- [20] Ifran, M. and Seiler, M., "Encapsulation using hyperbranched polymers: from research and technologies to emerging applications". *Ind. Eng. Chem. Res.* 49(3). 1169-1196. January 2010.
- [21] Lin, C. and Gitsov I "Synthesis and Physical Properties of Reactive Amphiphilic Hydrogels Based on Poly(pchloromethylstyrene) and Poly(ethylene glycol): Effects of Composition and Molecular". *Macromolecules*. 43 (7). 32563267. March 2010.
- [22] Shi, X., Wang, S.H., Lee, I., Shen, M. and Baker, J.R., "Comparison of the internalization of targeted dendrimers and dendrimer-entrapped gold nanoparticles into cancer cells". *Biopolymers*. 91(11). 936-942. November 2009.
- [23] Ye, L., Letchford, K., Heller, M., Liggins, R., Guan, D. and Kizhakkedathu, J.N., "Synthesis and characterization of carboxylic acid conjugated, hydrophobically derivatized, hyperbranched polyglycerols as nanoparticulate drug carriers for cisplatin". *Biomacromolecules*. 12(1). 145-55. January (2011).
- [24] Chatterjee, S. and Ramakrishnan, S., "Understanding SelfSegregation of Immiscible Peripheral Segments in Pseudodendritic Hyperbranched Polydithioacetals: Formation of Improved Janus Structures". *Macro Letter*. 3(9). 953-957. September 2014.
- [25] Gao, C. and Yan, D., "Hyperbranched polymers: from synthesis to applications". *Progress in Polymer Science*. 29(3). 183-275. March 2004.
- [26] Lea, A., Matthias, W. and Thomas, K., "The role of branched polyesters and their modifications in the development of modern drug delivery vehicles. role of branched polyesters and their modifications in the development of modern drug delivery
- [27] Benarbia Abderrahim, Elidrissi Abderrahman, Aqil Mohamed1, Amyay Aicha, Bellaouchi Reda, Asehraou Abdeslam, Jalal Isaad, Tahani abdeslam4 *Journal of Polymer and Biopolymer Physics Chemistry*, 2016, Vol. 4, No. 1, 16-27
- [28] Benarbia, A., Elidrissi, A., Aqil, M., Tabaght, F., Tahani, A. and Ouassini, K., "Kinetic Thermal Degradation of Cellulose, Polybutylene Succinate and a Green Composite: Comparative Study". *World Journal of Environmental Engineering*. 3(4). 95110. September 2015.
- [29] Zoubida SAADI. Université du Maine - U.F.R. Sciences et Techniques. 154.2008
- [30] Benarbia, A., Elidrissi, A., Bellaouchi, R. and Asehraou, A., "Polybutylene succinate preparation and Biodegradation study of cellulose and cellulose blends". *International Journal Engineering Technical Research*. 3(3), 348-354. March (2015).
- [31] Soni R.K., Soam S., Dutt K. *Polymer Degradation and Stability*. 94 (2009) 432.
- [32] Chrissafis K., Paraskevopoulos K.M., Bikiaris D.N. *Thermochimica Acta*. 435 (2005) 142.
- [33] Persenaire O., Alexandre M., Dubois P. *Biomacromolecules* 2 (2001) 288.
- [34] Buxbaum L.H., *Angew. Chem. Int. Ed.* 7 (1968) 182.
- [35] Ueno T., Nakashima E., Takeda K. *Polymer Degradation and Stability*. 95 (2010) 1862.
- [36] Bikiaris D.N., Chrissafis K., Paraskevopoulos K.M., Triantafyllidis K.S., Antonakou E.V. *Polymer Degradation and Stability*. 92 (2007) 525.
- [37] Draye A.-C., Persenaire O., Brožek J., Roda J., Košek T., Dubois Ph. *Polymer*. 42 (2001) 8325.
- [38] Angeles M., Corres., Zubitur M., Cortazar M., Múgica A. *Journal of Analytical and Applied Pyrolysis*. 92 (2011) 407.