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Synthesis and Characterization of Branched Polyester: Thermal and Microbial Degradation Studies

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Abstract A branched polyesters was synthesized using ethylene glycol, adipic acid and glycerol. It was characterized by FTIR, ^{1}H and ^{13}C-NMR, GPC, TGA/DTA. According to TGA analysis it was found that the mass loss is accomplished in two stages, the lower one was slightly distinguished in TGA. The Flynn-Ozawa-Wall method was applied for the principal reaction and the activation energies for all values of α were determined. The biodegradation process was also investigated in liquid culture media using two strains of *Penicillium sp* S1 and *Aspergillus sp* S2 which were isolated from the discharge of Oujda city (Morocco). According to the growth curves, it was found that the *Penicillium sp* S1 and *Aspergillus sp* S2 used the polyester as source of carbon. We have noted using FTIR spectra a decrease of the band intensity at $\delta = 1170\ \text{cm}^{-1}$ characteristic of the stretching vibration of C–O–C and also a decrease of the ester band group. The results obtained were compared with those of polyesters biodegradation reported in our previous work [27,28,29]. We have also proposed an enzyme degradation mechanism and hypothesis for an empirical mathematical formula giving the relationship between the thermal degradation and the biodegradation rate constant of the polyester.

Keywords: *branched polyester, thermal degradation, biodegradation*

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1. Introduction

Branched polyesters are synthesized generally from various monomers, such as pentaerythritol, xylitol, erythritol, and polyfunctional acids such as sebacic acid, succinic acid, adipic acid and glutaric [1,2,3,4,5], and particularly from glycerol and bifunctional acids [6-14]. Glycerol or glycerin is a viscous compound, obtained from natural resources. The glycerol presents three alcohols groups which are not equivalent, responsible for its solubility in water and has hygroscopic nature, also can create three ethereal bonds. Furthermore the glycerol is used in many drugs’ compositions, because of its low toxicity. Recently, polyester was synthesized by associating adipic acid and glycerol in the presence of dibutyltin oxide as catalyst [15]. Branched polyester synthesized by associating glycerol, sebacic acid and ethylene glycol was also reported [16]. 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 [17-26].

In this work, we prepare biodegradable branched polyester (**P2**) by combining ethylene glycol, adipic acid and glycerol. The quantitative and qualitative biodegradation phenomenon of the prepared polyester was studied by using two selected strains of *Aspergillus sp* S1 and *Penicillium sp* S2. The obtained results were compared with those of already polyesters reported [27,28,29]. On the other hand, we propose a mechanism illustrating this process and hypothesis for an empirical mathematical formula giving the relationship between the thermal degradation and the biodegradation rate constant of the branched polyester.

2. Materials and Methods

2.1. Reagents

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 the Branched Polyester

The synthesis of the branched polyester, based on adipic acid, ethylene glycol and glycerol, was carried out in two steps. In the first one some oligomers were obtained. In a flask of 500 ml we introduced of 0.123 mol of adipic acid, 0.099 mol of ethylene glycol, 20 ml of toluene and a catalytic amount of paratoluene sulphonic acid. The mixture was maintained at refluxed for 5 hours with continuous stirring. The second step was conducted after removal of toluene. The titanium butoxide was added under vacuum and the reaction proceeds at 230 °C. The reaction mixture was dissolved in dichloromethane and precipitated in an excess of diethyl ether. The product with yellow color was isolated by filtration, dried and stored under vacuum until a stable mass was achieved.

2.3. Measurements

2.3.1. IR Spectroscopy

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

2.3.2. Nuclear Magnetic Resonance (^1H NMR, ^{13}C-NMR)

The spectra of the synthesized polyester was recorded using spectrometer BRUKER (300 HZ), the solvent used is $CDCl_3$ added with one drop of trifluoroacetic acid and the TMS as reference.

2.3.3. TGA/DTA Investigation

Thermogravimetric analysis was carried out with SHIMADZU TGA/DTG. Samples were placed in alumina crucible. An empty alumina crucible was used as reference. The Samples were heated from room temperature to 600 °C in a 50 ml/min flow of N_2. 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 method 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) [30].

$$\alpha = \frac{\mathrm{w0} - \mathrm{wt}}{\mathrm{w0} - \mathrm{wf}} \qquad (1)$$

Where: W_t, W_0, and W_f are time, initial and final weights of the sample respectively.

We have

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

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

$$K(T) = Ae^{-Ea/RT} \qquad (3)$$

The isoconversional method of Ozawa, Flynn and Wall (OFW) is in fact, a (model free) method which assumes that the conversion function does not change with the alteration of the heating rate for all value of α. It involves the measure of the temperature corresponding to a fixed value of α at different heating rates β. Therefore, plotting Ln (β) against $\frac{1}{T}$ in the form of

$$Ln(\beta) = -\frac{E_a}{RT} + const \qquad (4)$$

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

If the determined activation energy is the same for various values of α, the existence of a single step reaction can be concluded certainly. 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. These complications are significant, especially in the case that the total reaction involves competitive mechanisms [31].

2.3.4. GPC Investigation

Gel Permeation Chromatography was carried out with Model: Malvern Viscotek TDA 305, Apparatus Tetra detection Gel Permeation Chromatography, using tetrahydrofuran as the mobile phase, flow rate 1ml.min^{-1} at 25°C. Poly(methymethacrylate) standards were used to calibrate the GPC.

2.3.5. Crystallinity Investigation

The crystallinity investigation was carried out with shimadzu XRD 6000 using Cu k_α radiation (λ=15) at 40KV and 30 mA with scan of 4°/min.

2.4. Biodegradability Testing Method

The 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 [32]. For each test, blanks with microbial inoculum and without polyester samples were also performed for checking the micro-organisms activity.

2.4.1. 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 ($MgSO_4/7H_2O$: 0.7 g); ammonium nitrate (NH_4NO_3: 1 g); sodium chloride (NaCl: 0.005 g/l); ferrous sulfate heptahydrate ($FeSO_4/7H_2O$: 0.002 g); zinc sulfate heptahydrate ($ZnSO_4/7H_2O$: 0.002 g); manganese Sulfate heptahydrate ($MnSO_4/7H_2O$: 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 between 6.0 and 6.5.

2.4.2. 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 [27]. The microorganisms were previously purified and stored in YEG medium (yeast extract + Glucose).

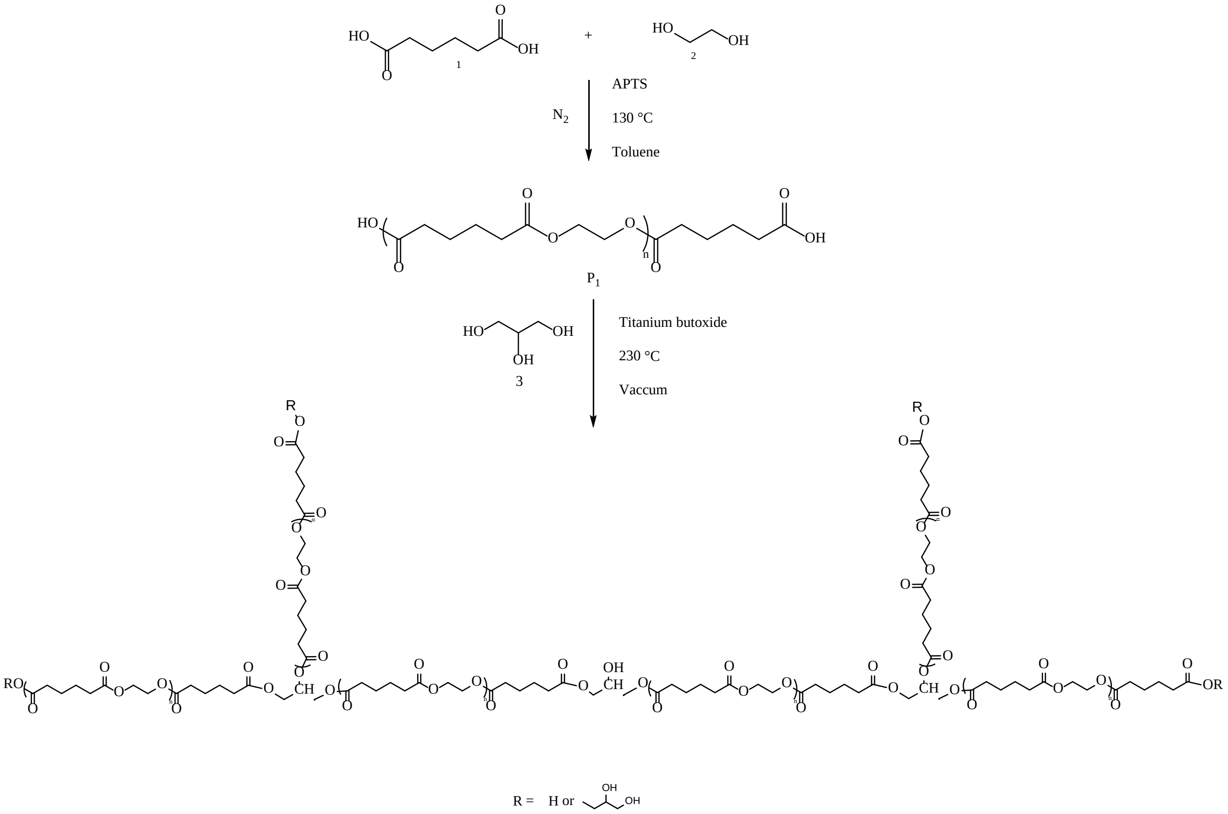
2.4.3. Biodegradability Investigation by Invasion Method

The biodegradation of polyesters was studied in 200mL bottles containing tested material (powder 1.5g/L) as a sole carbon source. The strain (*Penicillium sp S1* or *Aspergillus sp S2*) at 2 10^6 cells/ml as initial inoculum in 150 ml of mineral medium M. The polyester was 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 (hematimetre). The tests are repeated three times to check the reproducibility. The results of these studies were presented as cell growth curves.

3. Results and Discussion

3.1. Synthesis of Branched Polyester

The synthesis of branched polyester based on adipic acid, ethylene glycol and glycerol is carried out in two steps as shown in the scheme 1. The first one leads to oligomers (**P1**). Then in the second step the **P1** is reacted with glycerol in the presence of titanium butoxide under vacuum to offer the branched polyester named **P2**.



Scheme 1. Synthesis of the branched polyester **P2**, reagent and conditions

The FTIR spectroscopy was performed to characterize the function group change in the main chain of the polyester. As shown in Figure 1, the characteristic bands in the main chain of the polyesters can be assigned at: 3450-3500 cm^{-1} (-OH stretching bond), at 2960-2900 cm^{-1} (-CH stretching of $–CH_2$ and C-H groups), at 1757 cm^{-1} (-C=O stretching vibration) and around 1169-1030 cm^{-1} appears the C-O-C stretching peak. FTIR spectroscopy showed that the ester group is formed during the polycondensation reaction.

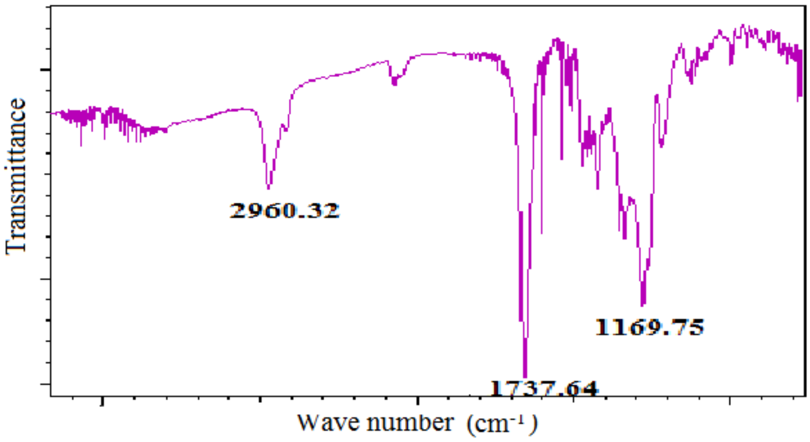


Figure 1. FTIR spectrum of the branched polyester **P2**

The ^{1}H-NMR spectrum recorded for the branched polyester is shown in Figure 2. Resonance signals show its microstructure. The polycondensation reaction generates new chemical bonds. It is clear that the peaks at 1.6 ppm and 2.4 ppm are assigned to the protons of two centered methylene of adipic acid and it’s methylene in α position of ($\underline{CH_2}$–C=O) the ester group respectively.

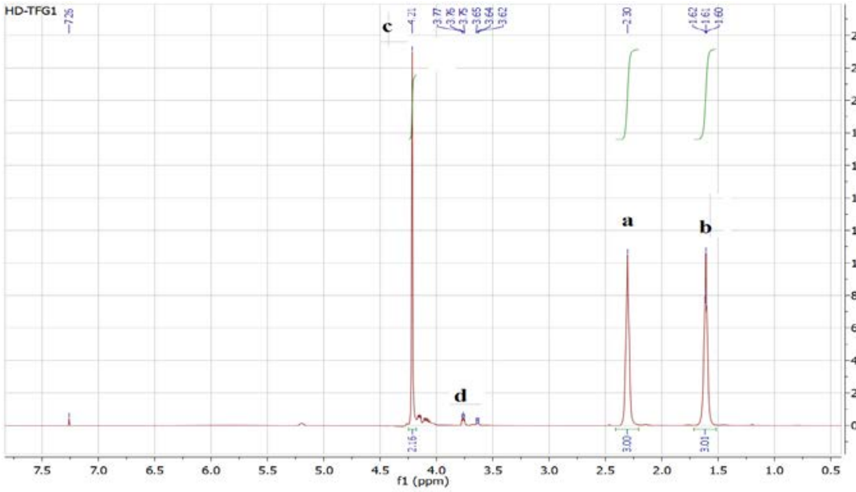


Figure 2. ^{1}H-NMR spectrum of the polyester **P2** in CDCl$_3$

The new peak assigned at 4.20 ppm is attributed to the protons of the methylenes of ethylene glycol and glycerol moieties situated on α-position of the ester group ($\underline{CH_2}$-O-C=O), indicating that the reaction between alcohol and acid groups is performed. We noted also the disappearance of the signal at 3.7 ppm assigned to the methylenes (ethylene glycol, glycerol) in α-position of the alcohol groups -CH$_2$-OH.

The ^{13}C NMR spectrum recorded for the branched polyester is presented in Figure 3. Some chemical shifts are shown at 177, 173, 76, 60, 33 and 24 ppm. The chemical shift at 177 ppm was due to the carbonyl –COOH and is a very weak peak. In addition the chemical shift at 173ppm was attributed to the carbon of the ester group. The chemical shift at 60ppm, 33ppm and 24ppm were assigned respectively to the carbon of ethylene glycol methylene (-O-$\underline{C}$H$_2$-$\underline{C}$H$_2$-O), methylene of adipic acid in α position of carbonyl –C (=O)-$\underline{C}$H$_2$- and finally to centered methylene –$\underline{C}$H$_2$-$\underline{C}$H$_2$- of adipic acid.

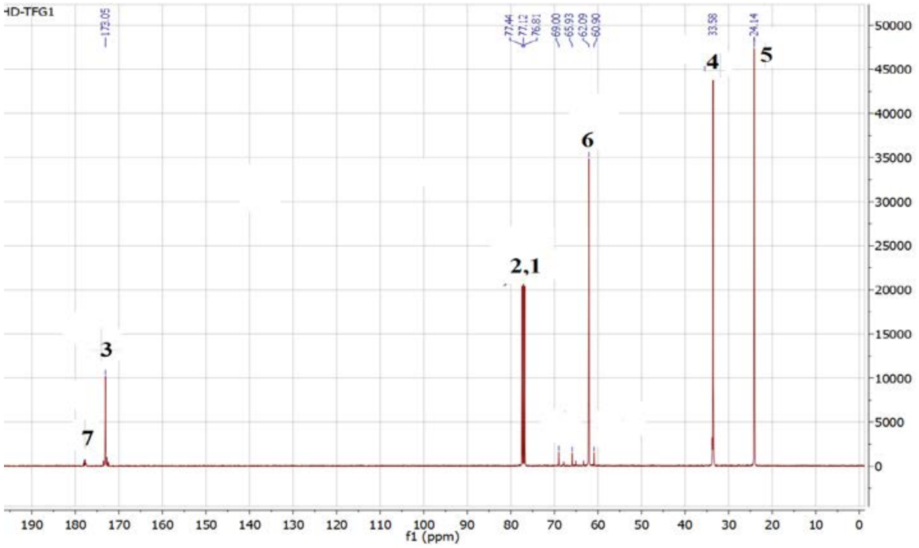


Figure 3. ^{13}C-NMR spectrum of the polyester **P2** in CDCl$_3$

The branched polyester was occurred in the second step of the polycondensation, by the esterification reaction of the carboxylic acid or their derivatives hydroxyl functionalities of glycerol. The most common method for synthesizing branched polyesters is via the addition of small amounts trifunctional comonomers to the polymerization. To prevent gelation, only small amounts (< 2 wt% relative to the polyester prepolymer) of the trifunctional branching agent were used. Some reaction parameters such as catalyst concentration, reaction time, temperature and concentration of branching agent influence the average molecular weight and the probability of formation of 3D polymer network. Glycerol has two primary and one secondary alcohol group with different reactivity; therefore, the degree of branching was expected to be lower. The final product was easily soluble in some of organic solvents (THF, CDCl3...), this indicates a low degree of chain-chain crosslinked polyester. In fact, a high level of multifunctional comonomer results in insoluble crosslinked systems. The gelation phenomenon occurs at high levels of multifunctional agent and at high conversion.

4. GPC Analysis of the Polyester P2

The average molecular weight and molecular weight distribution of the branched polyester were monitored by GPC technique. The chromatogram obtained is shown on Figure 4. The results are summarized in Table 1.

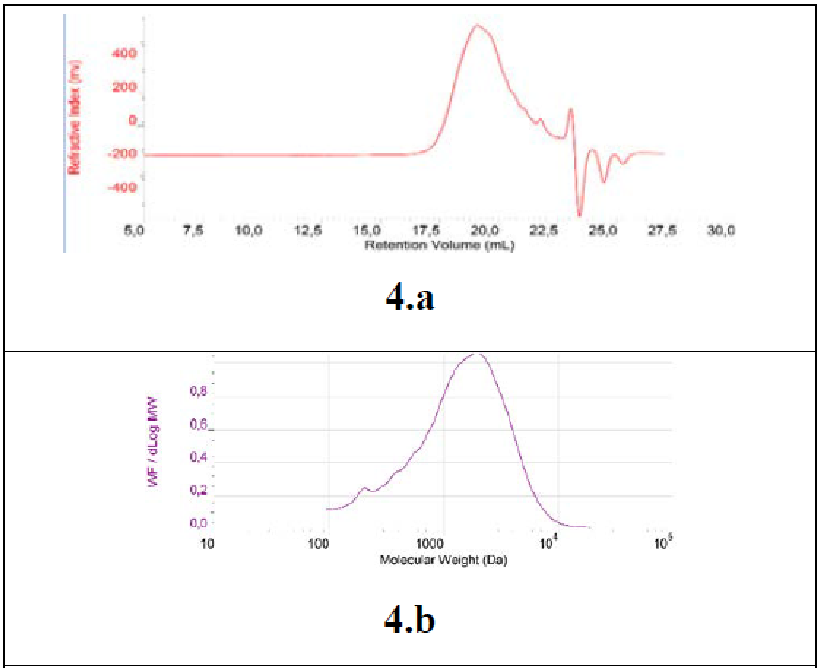


Figure 4. GPC analysis of the polyester **P2**

Table 1. GPC analysis of the polyester P2

Copolymer	M_n (g/mol)*	M_w (g/mol)*	M_z (g/mol)*	M_p*	M_w/M_n*
P2	1400	3300	5800	3300	2.4

M_n: The number average molecular weight, M_w: The weight average molecular weight, M_z: Z-average molecular weight, M_p: Molecular weight of the high peak, Mw/Mn: Polydispersity index.

The results showed that the average molecular weights of the obtained polyester were slightly lower than those reported in the literature. This effect can be ascribed to a number of different phenomena, probably due to the different experimental conditions chosen in this study making a comparison with literature data difficult. It's possible also that higher temperature led to catalyst deactivation, partially preventing the tranesterification step. Moreover, the tranesterification process doesn't reach a higher level conversion.

5. Crystallinity of the Polyester P2

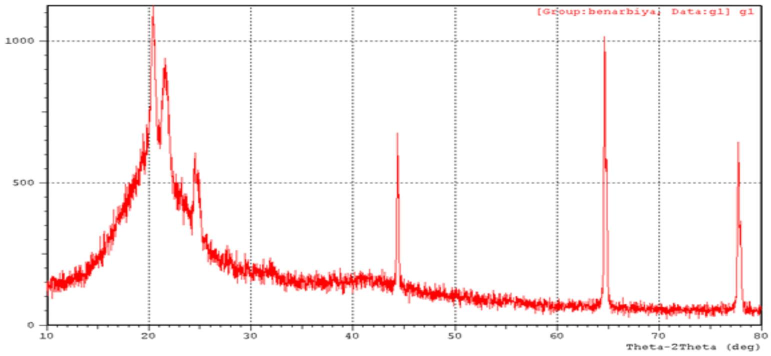


Figure 5. X-ray diffraction patterns of the polyester **P2**

As reported in Figure 5, the branched polyester, exhibited some diffraction peaks which appeared around 2θ = 21°, 22° and 24.5° indicating different size of crystallines and attributed to the order arrangement of the polyester chains. Moreover, we noted the presence of others peaks at 44.65°, 64.60° and 78° which are assignable to (010), (110) and (100) plans. The polyester P2 presents simultaneous amorphous and crystalline areas, it's a semicristalline material.

6. Thermal Analysis of the Polyester P2

Thermal stability and thermal degradation traces of the prepared sample were also measured, Figure 6 illustrates the noted thermogravimetric traces TGA/DTG of the polyester at the heating rate of β= 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 β=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.

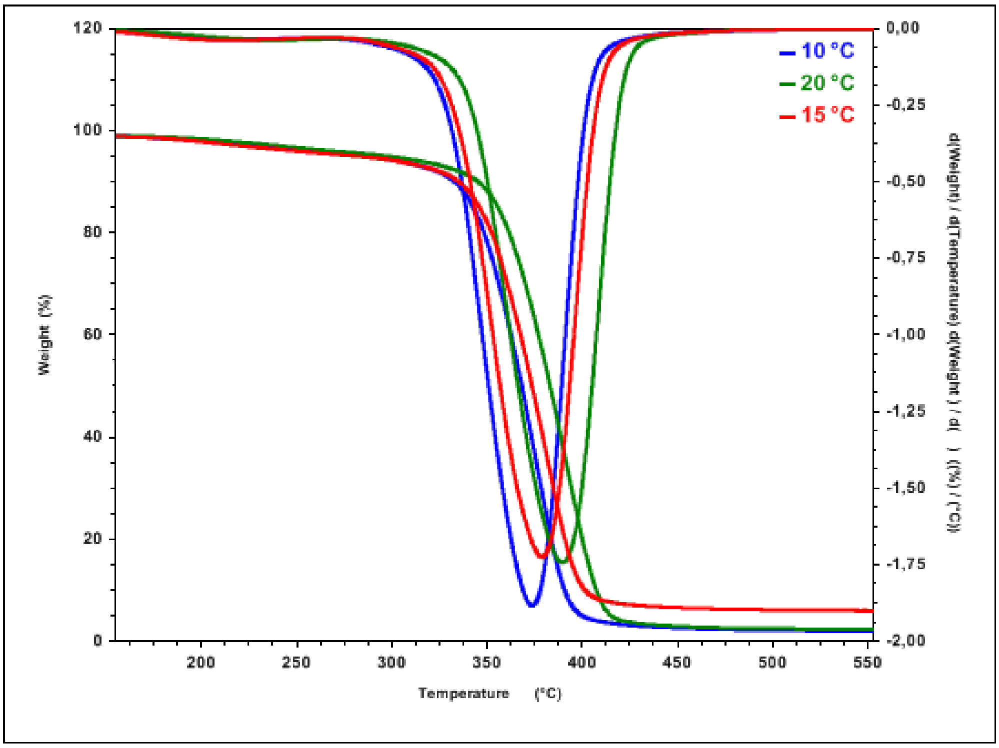


Figure 6. TGA/DTG of the polyester P2, at heating rate β: 10, 15 and 20 °C/min

We study the reaction principle following the Ozawa method [30], and the traces (Figure 7) are obtained by using the equation (4) and the calculation results are summarized in Table 2.

$$Ln(\beta) = -\frac{E_a}{RT} + const \qquad (4)$$

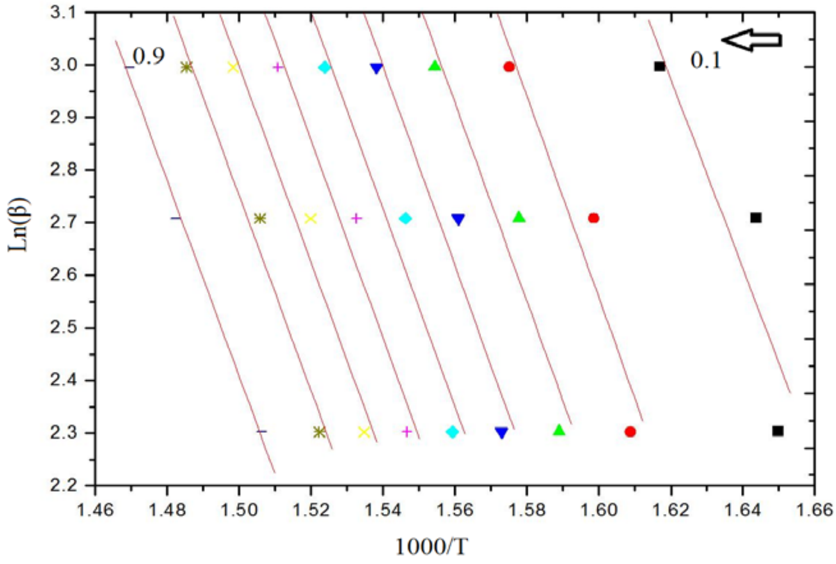


Figure 7. Ozawa plots of the polyester P2 at fractional extent of reaction: α = 0.1; 0.2; 0.3; 0.4; 0.5;0.6 ; 0.7 ; 0.8 et 0.9

The apparent activation energy (E_a) previously determined (Table 2) were evaluated using the classical Ozawa method. It can be seen that there is three important steps (Figure 8), in the first one E_a increases when α appeared between 0.1 ≤ α ≤ 0.2; in the second one E_a is relatively stable and α was between 0.2 ≤ α ≤ 0.6 and finally, in the third step Ea decreases when α is situated between 0.6 < α < 0.9.

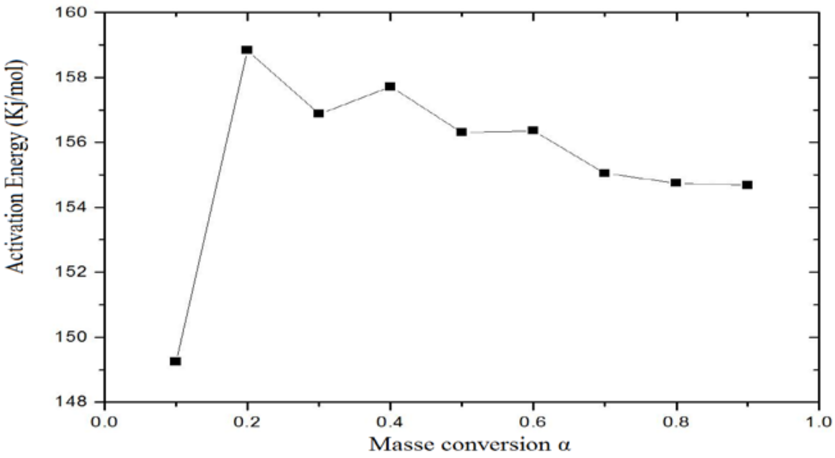


Figure 8. Dependence of the polyester P2 activation energy (E_a) on the mass conversion (α), as calculated using Ozawa methods

Table 2. Summary of the Ozawa method data of the polyester P2 at fractional extent of the reaction α = 0.1; 0.2; 0.3; 0.4; 0.5;0.6 ; 0.7 ; 0.8 et 0.9

Conversion α	E_a (KJ /mol)	R^2
0.1	149.24	0.815
0.2	158.84	0.902
0.3	156.88	0.912
0.4	157.71	0.926
0.5	156.31	0.939
0.6	156.36	0.951
0.7	155.04	0.960
0.8	154.75	0.975
0.9	154.67	0.994
Mean	155.53	

7. Biodegradation Study

The evolution of biomasses of *Penicillium sp* S1 and *Aspergillus sp* S2 in mineral medium M1 (without polyester) is reported in Figure 9. The growth curves showed a very slight increase, from 6.3 to 6.35 log units during the first 7 days of culture. From the 7th day to the 28th day, a drastic decrease of the biomass is observed from 6.35 log units to 5.5 log units and 5.7 log unit, for *Penicillium sp* S1 and *Aspergillus sp* S2, respectively. These results indicate the impossible growth of *Aspergillus sp* S1 and *Penicillium sp* S2 in mineral medium (M1) without the presence of carbon source. The strain *Penicillium* sp S1 was more sensitive to the absence of carbon source than *Aspergillus sp* S2.

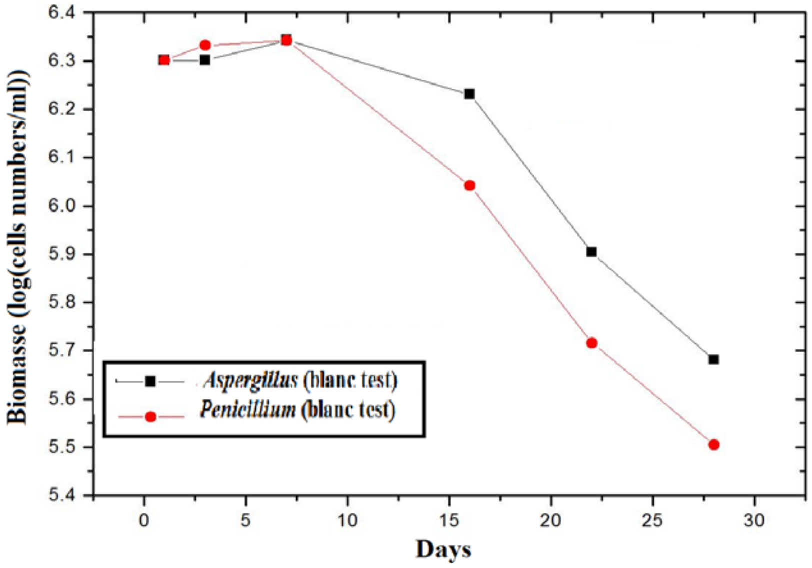


Figure 9. Variation curves of *Penicillium sp* S1 and *Aspergillus sp* S2 in mineral medium M1 without polyester P2 at 30 °C

In the presence of the polyester as carbon source, the biomasses obtained are reported on Figure 10. After inoculation, a short lag phase was observed indicated by a slight increase from 6.3 to 6.35 log units during the first 3 days. Then the biomasses showed high increases and achieve their maxima values at the 15th days 7 and 7.3 log units respectively for *Aspergillus sp* S2 and *Penicillium sp* S1. After 15 days of incubation, a decrease was observed until 28 days of incubation and reached 6.6 and 6.65 log units for *Aspergillus sp* S2 and *Penicillium sp* S1 respectively.

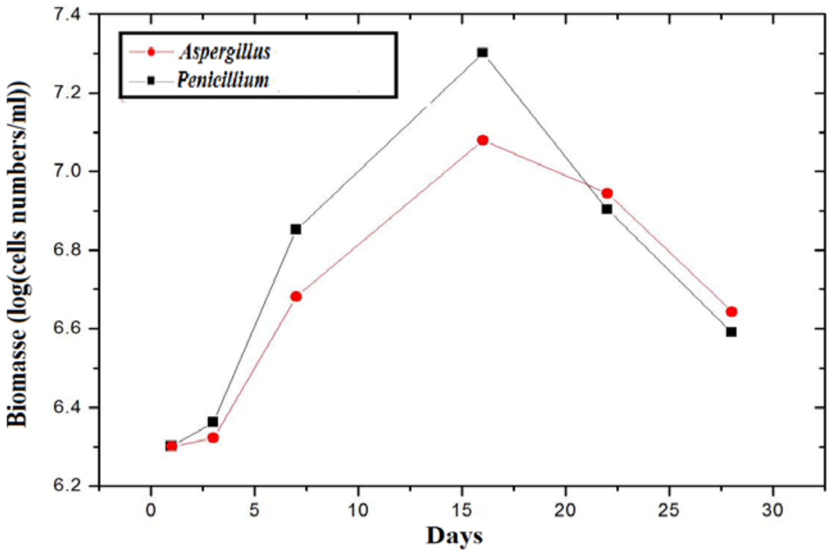
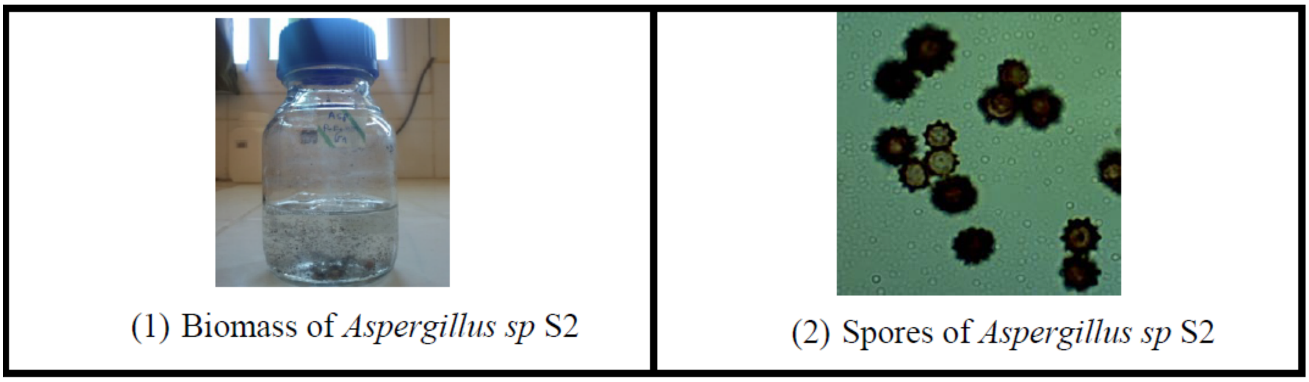


Figure 10. Variation curves of *Penicillium sp* S1 and *Aspergillus sp* S2 in mineral medium M1 with polyester P2 at 30 °C

The increase of biomass of the studied strains (*Penicillium sp* S1 and *Aspergillus sp* S2) in the presence of the polyester as a sole carbon source indicates their capacity to degrade this compound and use it in their growth metabolism. The strain of *Penicillium* sp S1 showed higher production capacity of biomass than *Aspergillus* sp S2 (Figure 10-Figure 12).

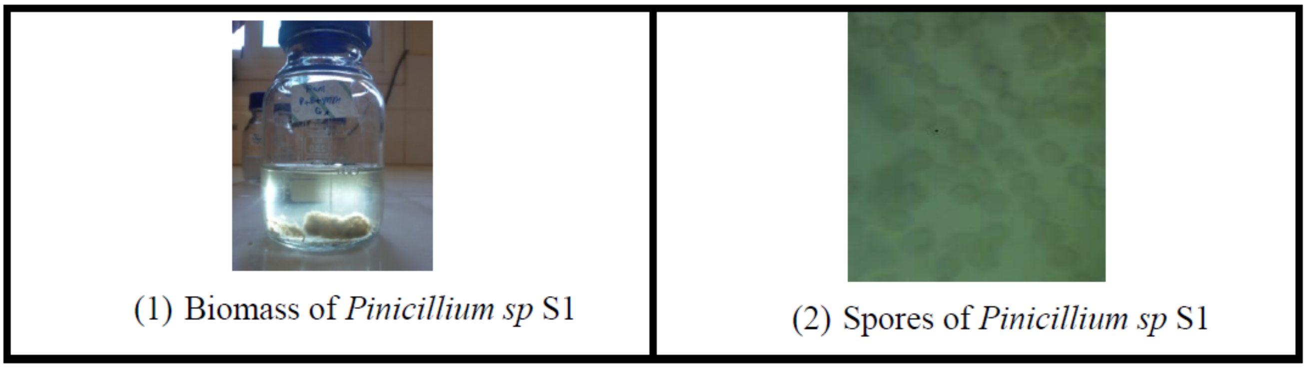
The polyesters allow entry of water into their structure via the amorphous areas only (swelling), and initiate their hydrolysis, leading to the formation of oligomers and monomers used as nutrients by microorganisms. The progressive degradation changes the microstructure of the matrix due to the formation of pores then oligomers and monomers are released. It was found that adipic acid is released by abiotic and/or biotic hydrolysis [33]. Organic acids are considered as one of the main causes of biodegradation [34]. Also, bacteria and fungi are able to use organic acids as carbon sources [35]. The crystalline zones of the polyester prevent the diffusion of water so their biodegradation will be limited in bulk and surface erosion [36].



(1) Biomass of *Aspergillus sp* S2

(2) Spores of *Aspergillus sp* S2

Figure 11. Culture of *Aspergillus sp* S2 obtained after 28 days of incubation at 30°C on polyester P2 as a sole carbon source; (1) Biomass, (2) spores



(1) Biomass of *Pinicillium sp* S1

(2) Spores of *Pinicillium sp* S1

Figure 12. Culture of *Penicillium sp* S1 obtained after 28 days of incubation at 30°C on polyester as a sole carbon source; (1) Biomass, (2) spores

Figure 13 shows the changes in FTIR spectra of the pure polyester P2. 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 -C=O ester), 1284 cm^{-1} (stretching vibration O=C-O), 1262, 1170, 1145, 1080 and 1069 cm^{-1} (stretching vibration C-O). 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. The microorganism secretes enzymes hydrolyzing the ester, so that the large molecules become smaller and easily to be used as nutrients. The esterase enzymes produced in similar conditions are generally lipases [37], which are water-soluble and capable to attack the polyester in its amorphous zones. On the other hand, quantitative tests showed an effective and a simple biodegradation of the polyester by simple contamination with drops of leachate landfill of Oujda City (Figure 14)**.**

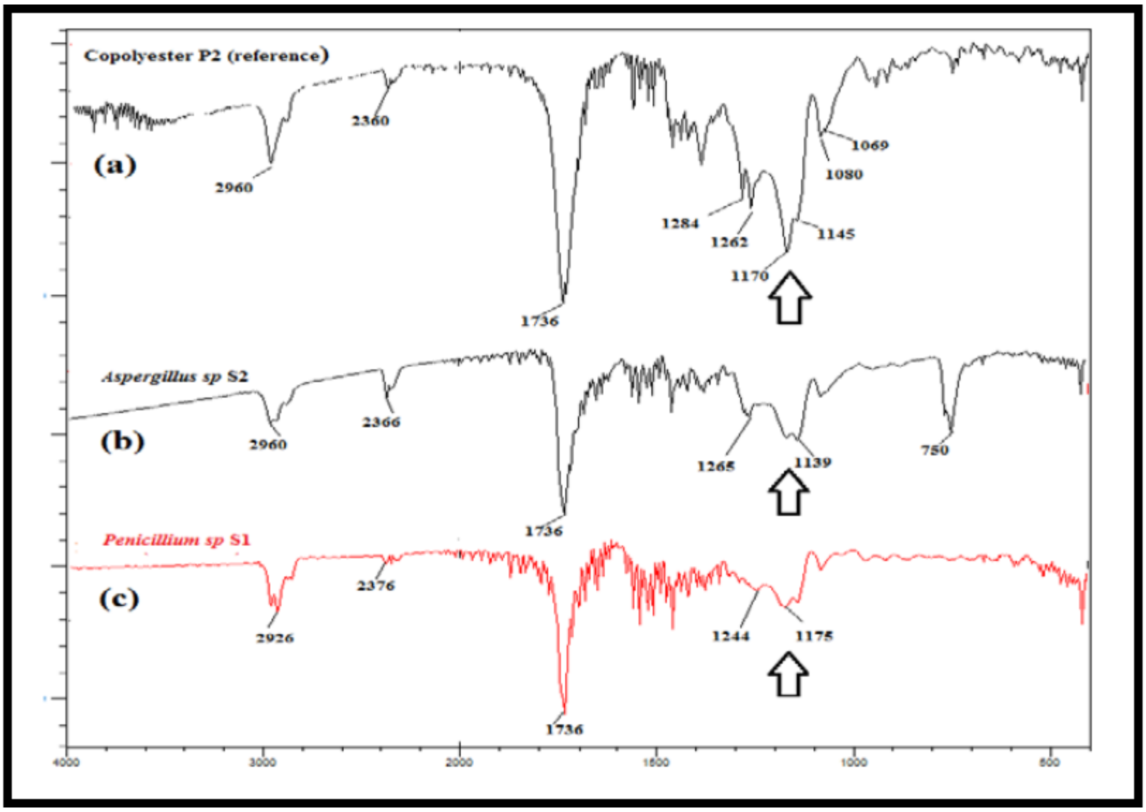


Figure 13. FTIR Spectra of the polyester P2: before incubation (a), and after incubation during 28 days in *Aspergillus sp* S2 (b) and *Penicillium sp* S1microorganisms (c)

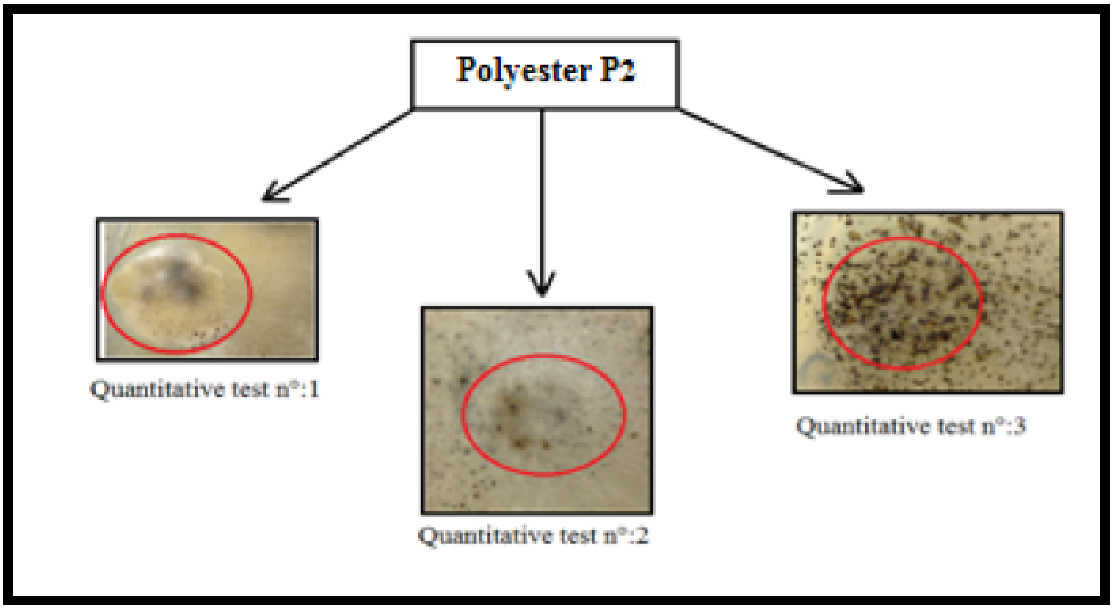
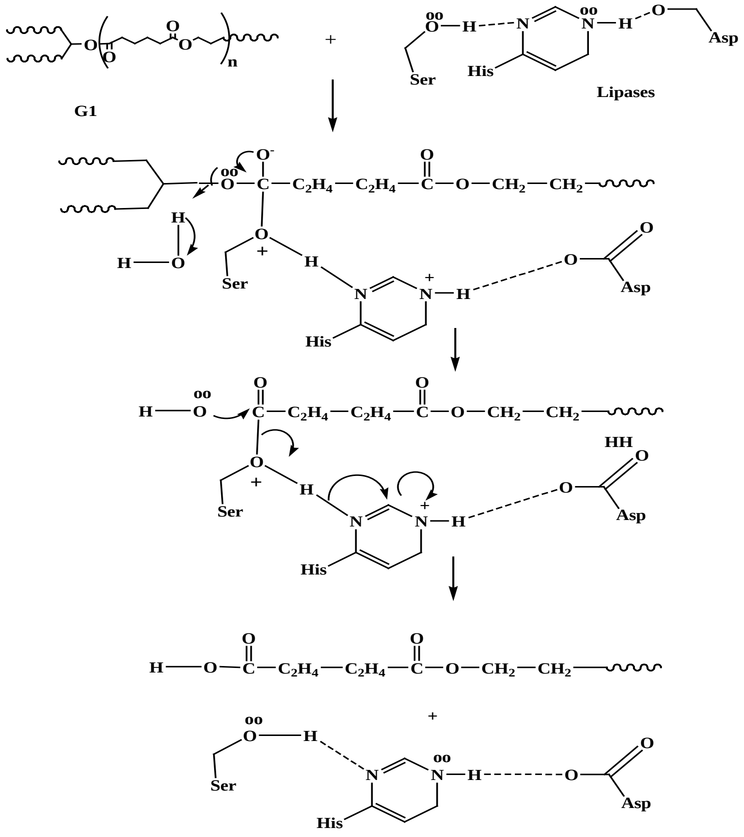


Figure 14. Tests of the polyester P2 contaminated by drops of leachate landfill- Oujda-Morocco

The scheme 2 reports our proposed mechanism in order to explain the degradation of the copolyester P2 by the lipase enzyme secreted by *Aspergillus sp* S2 or *Penicillium sp* S1.



Sheme 2. Mechanism proposed for the degradation of the polyester P2 by lipase enzyme secreted by *Aspergillus sp* S2 and *Penicillium sp* S1

8. Relationship between the Thermal Degradation and the Biodegradation Rate Constant:

The biodegradation kinetics of polyesters has been investigated extensively, but no correlation has been reported between thermal degradation and biodegradation phenomena. In this study, we try to address the relationship between both processes. The change of biomass weight with time is a linear growth phase and can be described as a linear relationship [38]:

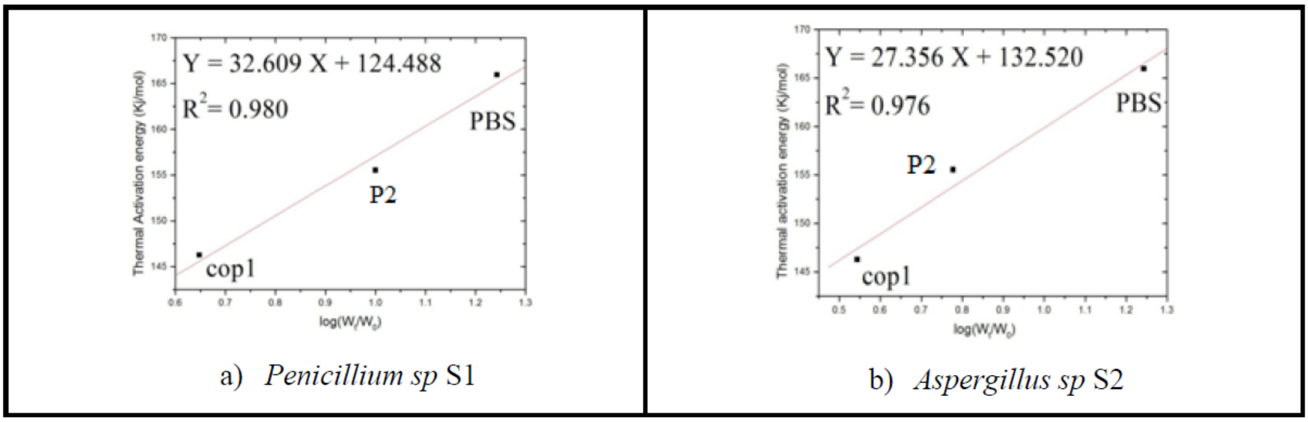
$$X = K_{Bd}.t$$

(where: X= biomass (mg), K_{Bd} = microbial growth rate (mg/day), t = time (day))

The microbial growth rate can be calculated from the change of biomass during biodegradation, so the biodegradation constant can be determined. The temperature dependence of K_b can also be correlated by Arrhenius equation

$$K_{Bd}(T) = Ae^{-Ea/RT}$$

It was also evaluated that K_b increased linearly with speed in culture solution. This indicates that the whole biodegradation process was enhanced by the agitation then the activation energy E_a was enhanced too [38].



a) *Penicillium sp* S1

b) *Aspergillus sp* S2

Figure 15. The fitting curves of the activation energy from thermal degradation data versus the maximal biomass amount produced by *Penicillium* sp S1 and *Aspergillus sp* S2, for polybutylene succinate, poly (acide lactique-co-éthylène glycol-co-acide succinique), and poly (glycerol-co-éthylène -acide adipique)

Marten et al. [39] proved that the concept of chain mobility seems to be a quite universal way to describe and predict the biodegradation rate of synthetic polymers, independent on their composition or microstructure. Some results demonstrate that the hydrolytic degradation of polyesters catalyzed by enzymes is predominantly controlled by the overall thermal properties. From this concept, we have already studied the kinetic thermal degradation of polybutylene succinate (**PBS**) [27,28], poly (acide lactique-co-éthylène glycol-co-acide succinique) (**cop**1) [29] and poly (glycerol-co-éthylène - adipic acid) (**P2)**. We draw the activation energy values that govern the thermal reaction against the biomasses amount produced during the phase growth (particularly the 9th day of culture) of *Aspergillus* and *Penicillium* on the polymers cop1, P2 and PBS (Figure 15)).

The plot of activation energy (E_a) values already calculated from thermal degradation versus the maximal amount of biomass produced by biodegradation of polyesters at time equal to 9 days gives a linear relationship:

$$f\left(E_a\right) = a \times \log\left(\frac{w(t)}{w_0}\right) + b\left(\text{constante}\right);$$

where E_a is the thermal biodegradation activation energy, w_t is the biomass produced at t = 9 days, and W_0 is the biomass at t = 0.

This linear relationship between the activation energy obtained from thermal degradation and the amount of biomass can be used to predict the rate of biomass production consequently to the polymer biodegradation rate constant as follow:

$$E_A = E_0 + k_{Bd}.\log\frac{w_{B,t}}{w_{B,0}}\ ,\ \text{or}\ E_A = E_0 + k_{Bd}.\log\alpha$$

($\alpha = \frac{w_{B,t}}{w_{B,0}}$), if the hydrolysis process can be neglected we can write: $\alpha = \frac{w_{B,t}}{w_{B,0}} = k\frac{Mt}{Mo}$ (k = 1 as a first approximation) and can be verified if the E_0 of different polymers is identical $E_A = E_0 + k_{Bd}.\log.k\frac{Mt}{M0}$, which can be made in the form of $E_A = E_0 + \log k + k_{Bd}.\log.\frac{M_t}{M0}$. If k = 1 log (k) =0 and we can write:

$E_A = E_0 + k_{Bd}.\log\frac{Mt}{M_{0,}}$ and k_{Bd} can be assimilated to the biodegradation rate constant. In case of *Penicillium sp* S1 k_{Bd} = 32.609 Kj/mol, and in case of *Aspergillus sp* S2 k_{Bd} = 27.356 Kj/mol.

9. Conclusion

In this work we have synthesized branched polyester based on ethylene glycol, adipic acid and glycerol. The prepared polyester was characterized by FTIR, ^{1}H and ^{13}C-NMR, GPC and TGA/DTG. According to TGA analysis it was found that mass loss is accomplished in two stages, the small one is barely designable. The Flynn-Ozawa-Wall methods were developed for the principal reaction and the activation energies for all values of α, were determined. The biodegradation of branched polyester was also investigated; the tests were performed in a liquid culture medium under aerobic conditions during a period of 28 days. These tests were carried out according to Microbial invasion method. The strains of *Penicillium sp* S1 and *Aspergillus sp* S2 were isolated from landfill lixivia of Oujda city (Morocco). The growth curves showed that the tested polyester is a biodegradable material in the environment. The results were compared with those reported in our previous work [27,28,29]. We have proposed an enzyme degradation mechanism and an empirical mathematical formula giving the relationship between the thermal degradation and the biodegradation rate constant in case of polyesters.

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