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Synthesis and Characterization of Biodegradable Poly(ethylene succinate)

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ABSTRACT

The Biodegradable poly(ethylene succinate) (PESu) was synthesized by melt polycondensation of ethylene glycol and succinic acid. The synthesized polymer was analyzed by 1H nuclear magnetic resonance (NMR) and Fourier transform-infrared (FT-IR) spectroscopy, diffraction X-rays (DRX) and were confirmed the chemical structure with weight-average molecular weight higher than 60,000 $g.mol^{-1}$. We also investigated the Biodegradation of PES by incubating the polymer with micro-organisms such as fungi (*Aspergilus Niger*) and bacteria (basilus subtili). The decomposition of polymer was confirmed by observed weight loss of the polymer and microbial growth around it and the changing of structure of the polymers were confirmed by IR spectral analyses after biodegradation test.

Introduction

Due to the associated problems result from a remarkable use of the petroleum-based plastics; People are looking for ways to replace these materials by biodegradable polymers. The idea of Biodegradable polymers appeared to be as a promising solution because they are environmentally-friendly. The biodegradable polymers in this connection are defined as those which are degraded in biological environments, where living cells or microorganisms are present, such as soils, composts, seas, rivers, lakes, bodies of human beings and animals through enzymatic or non-enzymatic hydrolysis (Kenawy, 2002). Biodegradation is a complex process including chemical and biological (i.e. enzymatic) reactions, which can occur at the same time (IKADA, 2000). The variety of chemical, physical and biological processes and thus different degradation mechanisms is dependent the chemical and physical characteristics of the polymer. These include diffusivity, porosity, morphology, crosslinking, purity, chemical reactivity, mechanical strength, thermal tolerance, and resistance to electromagnetic radiation (Kenawy, 2002; Lenz, 1993; Amass, 1998; Scott, 1999). In addition, it is dependent to the environmental conditions such as pH, phase, temperature, exposure, mechanical stress, and biological activity.

In recent decades, a great advancement has been made in the development of several type of biodegradable polymers from different origin of the raw material, including a biodegradable polymers from renewable resources as polymers of microbiological origin as well as synthetic polymers from renewable monomers; and a biodegradable polymers from fossil (non-renewable) resources (Avérous, 2008). The poly(ethylene succinate)s (PESu) are a synthetic poly(aliphatic esters) with a wide variety of physical properties, mechanical properties, and biodegradability (Carothers, 1929).

In this paper, we was synthesized the polyesters by melt polycondensation of succinic acid, and ethylene glycol, toluene was used as solvent and as water-removing agent. The chemical structure of a synthesized polymer was identified by 1H-NMR spectrometer and FT-IR spectrophotometer. We also investigated the biodegradation of poly(ethylene succinate) PESu by different microorganisms, which can meet in the environment We also investigated the biodegradation of poly(ethylene succinate) PESu by different microorganisms, which can meet in the environment such as marine, active

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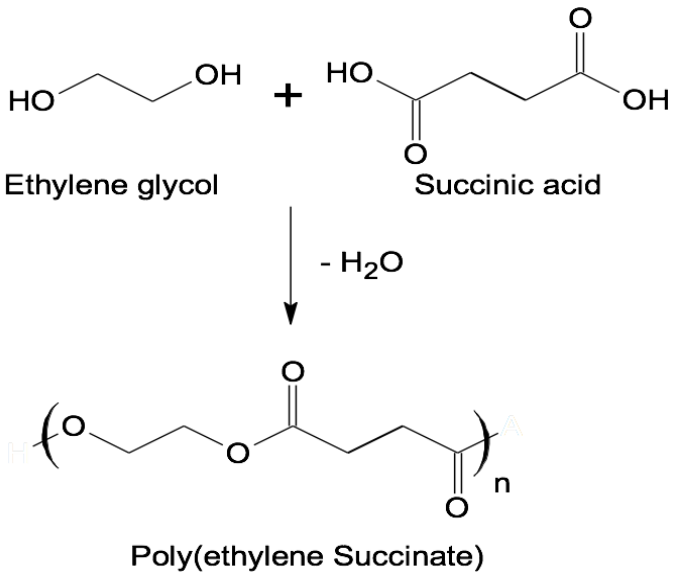
sludge, soil, river and lake water etc..
In particular, the bacteria and/or fungi are involved in the degradation of both natural and synthetic polymers. Their development and growth require a variety of inorganic and organic nutrients in the medium. The carbon is one of the most important elements for microbial growth, as carbon compounds provide energy for cell growth and serve as the basic units to build the cell materials. The nitrogen is also essential to the organisms, as well as others elements (hydrogen, oxygen and phosphorus) (Moore, 1998). Hence, the use of polymers as a source of nutrition for growth and in particular the poly(ethylene succinate), since it has carbon, oxygen and azote in its structure. In this study, we are used a standard test methods to test the microbial biodegradation PESu by using a bacterial strain (*Basillus subtilus*) and fungi (*Aspergillus Niger*) in solid and liquid media. TThe polymer was characterized before and after biodegradation by FTIR for improved the biodegradation.



Scheme1. Synthesis of Poly(Ethylene Succinate).

Materials and methods

Materials

Succinic acid (AA) (99%) and ethylene glycol (EG) (99%) were purchased from Sigma–Aldrich. Toluene, tetrahydrofurane (THF) and methanol and all solvents were obtained from Biochem. All reagents were used without further purification. All culture media and supplements were from chemopharma and Techanal, respectively.

Preparation of Poly(Ethylene succinate) (PESu)

PES was synthesized as described previously using a solution polymerization technique (Scheme 1) (Carothers, 1929). Briefly, equimolar quantities of succinic acid and ethylene glycol were dissolved in toluene and placed in a three-necked flask fitted with a magnetic stirring bar, a thermometer and a reflux condenser connected to a Dean-Stark tube. The reaction mixture is placed in an oil bath and then the mixture was gradually heated up again to distill the water/toluene azeotrope (85°C), and toluene (110°C). Continuous stirring was carried out at a temperature of 110°C for collection of almost the theoretical amount of H_2O. After the reaction was completed, products were cooled and filtered, then the viscous liquid was purified by dissolution in methanol to remove oligomers and unreacted monomers and recrystallized with THF after that the product was dried in vacuum at room temperature to furnish pure polyester as a white solid in quantitative yields (Lin, 1977).

Polymer characterization

Fourier transformed-infrared spectroscopy spectra were obtained at room temperature using a Perkin-Elmer FTIR spectrometer, model Spectrum 1000 in the range 4000 to 800 cm^{-1}. The solid was placed directly onto a KBr pellet. Nuclear magnetic resonance 1H-NMR spectra of polymer were recorded with a Bruker spectrometer operating at a frequency of 200 MHz and performed with 5% (w/v) polymer solution in $CDCl_3$. Tetramethylsilane was used as the internal reference. The Crystallinity of the PESu was acquired by WAXD experiments using a XRD: Philips; PW1800, which has a X-ray generator of 3 kW, CuK_α radiation (wavelength, λ = 0.15418 nm) and operated at 40 kV/15 mA. The samples were scanned at °/min under the diffraction angle 2θ in the range of 2-79°.

Study of the biodegradation of the poly(ethylene succinate)

The microorganisms used for the determination of biodegradation of synthesized polymer include the Gram-positive bacteria Bacillus Subtilis and the filamentous fungi Aspergillus niger. The bacterium was isolated from soil sample on nutrient agar, and the champignon was kept on potato dextrose agar from mold jam.

A. Growth media.

For champignon: (Per litre of distilled water): $NaNO_3$: 2 g, KH_2PO_4: 0.7 g, K_2HPO_4: 0.3 g, $MgSO_4.7H_2O$: 0.5 g, KCl: 0.5 g, $FeSO_4.7$ H2O: 0.01 g (06 <pH ≤ 6.5). The medium was supplemented with 14 g/L agar to generate solid medium.
For bacteria (Per liter of distilled water) 1 g/l yeast extract, NH_4NO_3: 1.0 g ; KH_2PO_4 0.7 g ; K_2HPO_4: 0.7 g ; $MgSO_4$, 7 H_2O: 0,7 g ; NaCl 0,005 g ; $FeSO_4$, $7H_2O$: 0.002 g ; Mg_2SO_4, 7 H_2O: 0.02 g ; $MnSO_4$, 7 H_2O: 0.001 g (pH=6.4).
The same components were used for the preparation of the liquid media only the medium was supplemented with14g/l agar to generate solid medium. The solid and liquid medium was inoculated in the oven for 20 min (120°C, 2 bars). The mixture was then autoclaved in a 250 ml conical flask at 121°C for 20 min. The stock cultures of the microorganisms were stored on solid culture medium (25 ml), in Petri dishes, maintained at 4°C in the refrigerator.

B. Testing in solid media.

The bacterial strains (basilus subtilis) and the fungi (Aspergillus niger) were screened by culturing on Petri dishes containing 25 mL of solid culture medium with the addition of poly(ethylene succinate) and without (control culture). After the medium sterilization in the autoclave, the agar was cooled to 40-45°C and the microorganisms from recent cultures were transferred to the surfaces of the agar plates and the poly(ethylene succinate) was deposited on the surface. Plates were incubated for 48H at 35°C (Moore, 1998).

C. Testing in liquid media.

Two small slices of the solid medium (1.2 cm x 1.2 cm) were born bearing the microorganisms were transferred to a test-tube containing 20 ml of the liquid mineral medium, previous-

ly sterilized in the autoclave for 20 minutes at 121°C. Next, the poly(ethylene succinate) was added to the medium, and then incubated for 48H at 35°C (Cletus, 2011).

Results and discussions

The FT-IR spectrum is showing in Fig.1 confirms the formation of the PBSu. IR vibrational band characteristic of ester bond is observed at 1733.71 cm^{-1}. The peak at 1385.41 cm^{-1} confirm the existence of the final acid function carried by the chains of polymers, and the functions OH of carbonyl group of poly(ethylene succinate) appeared around 2900.33 and 3001.60 cm^{-1}.

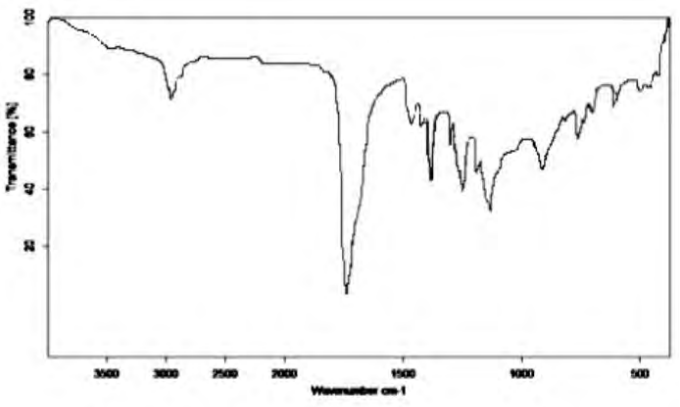


Fig 1. FT-IR spectrum of poly(ethylene succinate).

The chemical structure of PES was characterized by 1H-NMR spectra between 0 and 15 ppm. The spectroscopic study of PES (Fig. 2) shows the existence of the signals occurring at 1.3 (d_{Hd}), 1.8 (d_{Hc}), and 2.4 (d_{Hb}) ppm could be reasonably assigned to methylene protons of SA. The peaks of ethylene glycol shifted to the PES ester bond –CH_2COO- at 4.2 ppm.

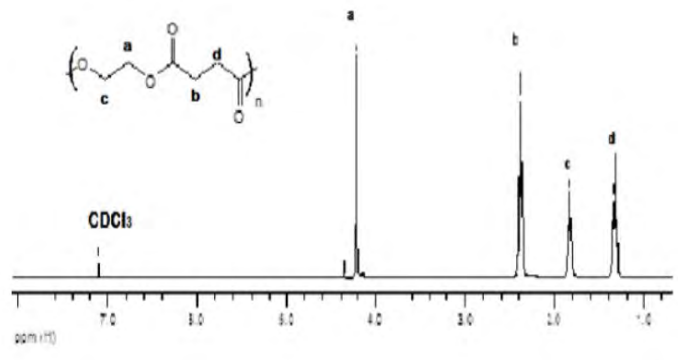


Fig. 2. Nuclear magnetic resonance (1H NMR) spectra of poly(ethylene succinate).

The X-ray diffraction pattern of PESu is is given in Fig. 3. The characteristic of the crystalline peaks of PESu were observed at 2θ value of 20.38 - 26.42°.
Degradation rates of polymer vary with chemical structures, physical morphologies, and crosslinking densities (Ray, 2005) The experiments were made by using PES and different microorganisms. Thus, we could observe different properties concerning the degradation of a polymer. Complementing the biodegradation studies, an experiment was conducted in mineral medium that demonstrated, through the percentage of degradation of PESu, that the fungi and the bacterial could be using the polymers as a source of carbon, since this was the sole carbon source present in the reaction medium.

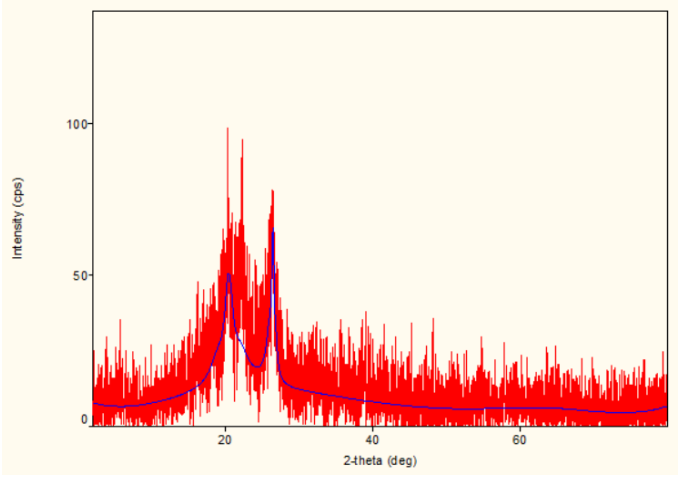


Fig. 3. X-ray diffraction pattern of the PESu.

The results for both microorganisms (*A. Niger*, *B. Subtilis*) showed a difference percentage of biodegradation of the two PES at 3 days of reaction. The data for biodegradation of PES pure in solid medium and liquid medium at 37°C is presented in Fig. 4. After 48 H of incubation, in the screening of microorganisms strains on solid medium, in the presence of PESu, a hydrolysis zone and water was observed at surface of polymers and in petri dishes this proves that there is an affinity between the fungi and the polymers. By comparing the growth of fungal colonies on Petri dishes, the A. niger showed excellent growth in the presence of the PES, compared to the B.s subtilis. We observed than the fungi was deposed in surface of PES (Fig. 4a) and the hydrolysis zone was noted after 48 h.

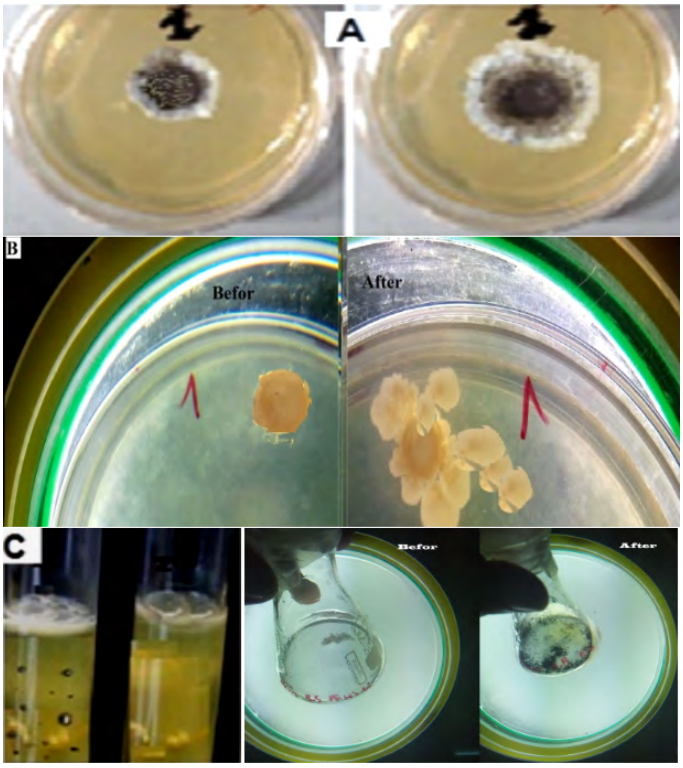


Fig. 4. (a) PESu disintegrated at the end of 3 days with A.Niger, (b) solid media swirled to show growth of bacterial et (c) Evolution the mediums of biodegradation of the PESu after 3 days with BS and *A.niger*.

The results were also satisfactory, with degradation of PES. This test proved that in liquid medium, as well as on solid media, we observed turbidity in the broth in both tubes (*Aspergillus niger* and *B. Subtilis*) with a partial disintegration of PES and a swelling of polymer without disintegration with the stump *Bacillus Subtilis* in the first day. After 3 days, PES been disintegrated as the other middle.

The biodegradation of PBSu was confirmed by repeat the analyzed FT-IR spectrophotometer on polymer from a solid media after 14 days. The FT-IR spectrum (Fig. 5) has shown a change in the intensity infrared bands, especially the characteristic bands of alkanes (C-H) between 2886-2861 cm^{-1}. the stetch wa decreased after time of incubation of PESu with *B. Subtilis* and *A. Niger*, then the two microrganisms have great affinity to the CH group and we noted in increased in the surface of the pick between 3091.33 and 3380.60 cm^{-1} of the OH function because the presence of water molecule during the biodegradation and the growth of microorganisms. the result showed that the function CO has not been attacked by *A. Niger* compared to the *B. Subtilis*. We indicates that the bacteria strain was attacked the majority of functions : alkanes (CH) and the carbonyl (ester); the intensity of the band at 1733.71 cm^{-1} attributed to the C=O wa decreased and The peak at 1385.41 cm-1 confirm the existence of the final acid function carried by the chains of polymers was disappeared and a new absorption band of the formation of carboxylate ions (COO-) was appeared at 1610.23 cm^{-1} of corresponds a carboxylic acid in the ends of chains of PESu generated by enzymatic hydrolysis then the bacteria consuming the oligomers of surface.

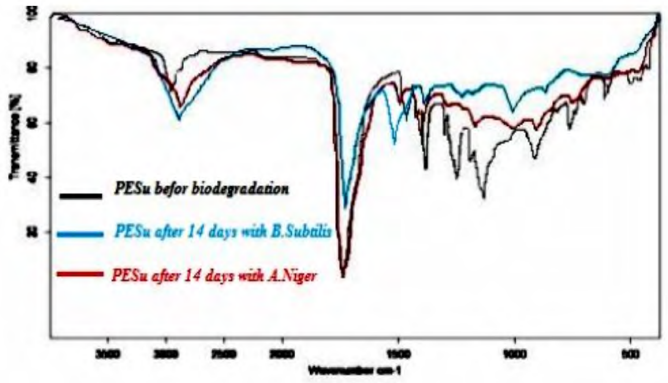


Fig. 5. Infrared spectra of PESu before and after 14 days of biodegradation.

Conclusion

The polyThe poly(ethylene succinate)(PESu) was synthesized by transesterfication direct of ethylene glycol and succinic acid. The molecular structure was confirmed by IR and 1HNMR spectroscopy and X-Ray Analysis, the compositions very similar to the initial feed compositions.

We further explored the biodegradation behaviors of poly(ethylene succinate) with different strain., biodegradation of PES pure in solid medium and liquid medium at 37°C showed that polymer was fully biodegradable with the fungi and the bacterial but there are a difference between the size of the colony formed on the surface of the plates and the growth of strain in the tube relative to the control culture. the biodegradation can be confirmed by the differences in the structure of PESu befor and after contact with the microorganisms, the functional ester groups contain in the structure of polyesters, makes these polymer more susceptible to attack and hydrolysis by fungi and bacteria. The degradability can change mainly due to the various crosslinking degrees, and rigidity of different polymer chains, and the different microorganisms.

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Conflicts of interest

Authors declare no conflict of interests.

Notes

The authors declare no competing financial interest.

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