Int. J. Chem. Sci.: 10(4), 2012, 1859-1868
ISSN 0972-768X
www.sadgurupublications.com

SYNTHESES AND CHARACTERIZATION OF BIODEGRADABLE MATERIALS BASED ON POLY-ε CAPROLACTONE AND ETHYL CELLULOSE

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ABSTRACT

The block polymers PCLgEC was preparing with extender chain 1,4 phenylene bis (2-oxazoline (PBO) by reacting of the prepolymers poly (e-caprolactone) produced by the ring opening polymersation of ε-caprolactone by adipic acidic with ethyl cellulosein the presence of a catalytic amount of titanium isopropoxide [Ti-$(OCH_2(CH_3)_2)_4$]. The reaction was conducted at 170°C for 40 min the inert atmosphere.

The expected structures of the polymers were confirmed by FTIR. Enzymatic degradations in solid media using *Aspergilus Niger* of the materials were performed the biodegradation of block polymers were also carried in liquid medium and the source of microorganisms is an inoculum based on activated sludge, by measuring the net biochemical oxygen demand (BOD) under the aerobic conditions. The biodegradation of polymers was observed by changing of BOD a long of 30 days.

Key words: Degradation, Poly (ε-caprolactone), Chain extender, BOD.

INTRODUCTION

An effective way to achieve high molecular weight polyester is to treat condensation polymers with chain extenders. These chain extension reactions are economically advantageous because they can be carried out in the melt, with only low concentrations of chain extending agents, and because separate purification steps are not required. Improved mechanical properties and flexibility to manufacture copolymers with different functional groups are other benefits of the use of chain extending agents[1]. Typical chain extenders for

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polyesters, which contain –OH and –COOH groups, are diisocyanates, diepoxides, bisoxazolines, dianhydrides and bisketeneacetals. The very high reactivity of the isocyanates has encouraged their use for coupling and chain extension of oligomers[2,3]. 2-oxazolines, which react with carboxylic acids through ring-opening, provide a route to novel families of polyesteramides[4,5]. Moreover, because 2-oxazolines are inert towards aliphatic alcohols, selective modification is possible through the carboxyl end-group of polyester[6].

In recent years, there has been an increasing interest in biodegradable polymers. However, the high cost of producing such polymers compared to conventional plastics is still one of the major problems to be solved. Most high molecular weight biodegradable polymers are polyesters that contain functional ester groups in their structures, which makes them more susceptible to attack and hydrolysis by fungi. At present, standard test methods to study the microbial biodegradation of plastic materials are available, mainly based on respirometric techniques[7,8]. The test material is exposed to microorganisms under optimised conditions and analytical techniques are applied to measure either the oxygen consumed or the gaseous inorganic carbon evolved (i.e. CO_2 under aerobic conditions or biogas, CO_2 and CH_4, under anaerobic conditions) during the metabolic respiration of the test material. The source of microorganisms is an inoculum based on activated sludge, soil or compost according to the different respirometric test methods.

The international standard test method ISO 14851 is used to determine the biodegradation of plastic materials under aerobic conditions by measuring the oxygen consumption[9,10]. The test method ISO 14852 is similar to the previous one but the biodegradation is detected by measuring the evolved CO_2 ethyl cellulose (EC) is a kind of cellulose derivative that possesses good biocompatibility, high mechanical intensity, and stability[11-13]. Therefore, the work present here demonstrates the preparation block copolymers based on the EC backbone. These unique copolymers could be used as biomaterials for their excellent biocompatible components. Moreover, block structure of copolymers and the degradation rates of PCL produce controllable stepwise biodegradation of block polymers the enzymatic degradation study by fungi and sludge showed this result

EXPERIMENTAL

Materials

Ethyl cellulose was obtained from (Sigma Aldrich), heptane and dioxane, were purchased from FLUKA Chemical, 1,3 phenylene bis (2-oxazoline) (PBO) was purchased from Mikuni Chemical, tetrahydrofurane (THF) and methanol and all solvents were purchased from Biochem. (Chemopharma) and Techanal, respectively.

Synthesis of polyester (PCL) and block polymers PCL and ECgPCL with PBO

Two different polymers were prepared. The synthesis of PCL is reported in literature[14]. The block polymers ECgPCL (PBO) was prepared by reating extender chain 1,3 phenyle bis (2-oxazoline), and PCL with ethyl cellulose in the presence of a catalytic amount of titanium isopropoxide (0,3% wt.). The reaction was conducted at 170°C for 40 min the inert atmosphere, the block polymer was prepared in one-pot synthesis by mixing the 1,3 phenylene bis (2-oxazoline (1.56 g), PCL (2.5 g) and) and EC (2.5 g) to obtain poly (ester-amide) (PEA). The study of degradation was conducted in liquid media inoculated with sludge and in solid media inolucted by *Aspergillus Niger*. The polymers were characterized before and after biodegradation by FTIR and by measuring BOD for 40 days.

Study of enzymatic degradation

Solid media

The polymers were purified by dry sterilisation in an oven at 170°C.

Growth media

The composition of the degradation medium was the following: (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, $FeSO_4.7\ H_2O$: 0.01 g.

The medium was supplemented with 14 g/L agar to generate solid medium. The PCL and PCLgECgPBO were inoculated with *Aspergillus Niger* and the solid media were incubated at 30°C for 72 H and 30 days. The polymers PCL and PCLgECgPBO were deposed to solid media.

- Liquide media:

Liquid medium biochemical oxygen demand

The compostion of the growth media is -

- Biodegradation tests

The assessment of biodegradability has been performe following the standard test method ISO 14851[7]. Glass flasks with a 300 mL capacity were used as test vessels. The

flasks were filled till a final 200 mL volume and kept closed with glass caps. The test liquid medium was the ‘‘standard test medium’’ described in the ISO 4851, based on the following solutions.

Solution A : KH_2PO_4 (8.5 g/L), K_2HPO_4 (21.75 g/L),

$Na_2HPO_4.2H_2O$ (33.4 g/L), NH_4Cl (0.5 g/L)

Solution B : $MgSO_4.7H_2O$ (22.5 g/L)

Solution C : $CaCl_2.2H_2O$ (36.4 g/L)

Solution D : $FeCl_3.6H_2O$ (0.25 g/L)

The test medium was prepared by adding solution A (10 mL), solutions B, C, and D (1 mL each) to about 500 mL of water and bringing the volume to 1000 mL with water. The inoculum solution was prepared as follows. A sample was drawn from the municipal waste water, Each vessel was filled with 97 mL of test medium and inoculated with 0.15 g of inoculum activated solide sludge. Test or reference material was added to each vessel (14 mg), with the exception of the blanks. Two replicates were used for each material and for blanks. The tests were stopped when O_2 consumption was no longer detectable. The vessels were kept at 23^oC in a rotary shaker REFE at 110 rpm. At intervals, BOD of each simples was releved. Afterwards, each vessel was kept under aeration for 15 min to restore the original oxygen concentration of the liquid medium. The vessels were then closed and put back in incubation. The net biochemical oxygen demand (BOD) of the test material was calculated as the difference between oxygen consumption in the test and in the blank flasks using the Equation:

$$\text{Net BOD} = BOD_{tm} - BOD_b$$

Where BOD_{tm} is the total biochemical oxygen demand of the test material from one flask; BOD_b is the biochemical oxygen demand of the blanks (average of two flasks).

RESULTS AND DISCUSSION

Enzymatic degradation of PCLgECgPBO namely PEA

Solid media: The *Aspergilus Niger* was isolated from tomatoes. The solidmedia

namely TGEA was inoculated by bacterial suspension prepared and the solid media was incubated 48 h at 30° in the oven. The result was illustrated in Fig. 1.

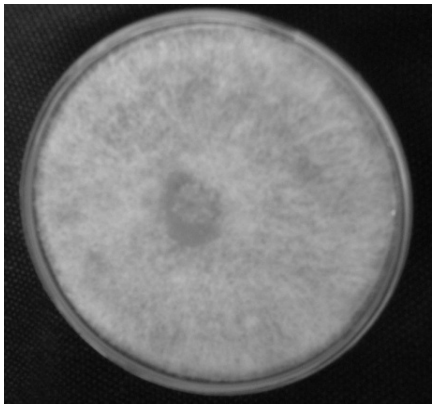


Fig. 1: *Aspergilus Niger* isolated in TGEA medium

The PCL and block polymer ECgPCL (PBO) were inoculated with *Aspergilus Niger* isolated from tomatoes and the solid media was incubated at 30°C for 45 days. Polymers were deposited on the surface of the solid media.

After 48 H of incubation a hydrolysis zone ref 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. We observed than the fungi was deposed in surface of ECgPCL (PBO) (Fig. 2) and the hydrolysis zone was noted after 48 h and the specific color of *Aspergilus Niger* (dark) was observed after 45 days in PCL (Fig. 3).

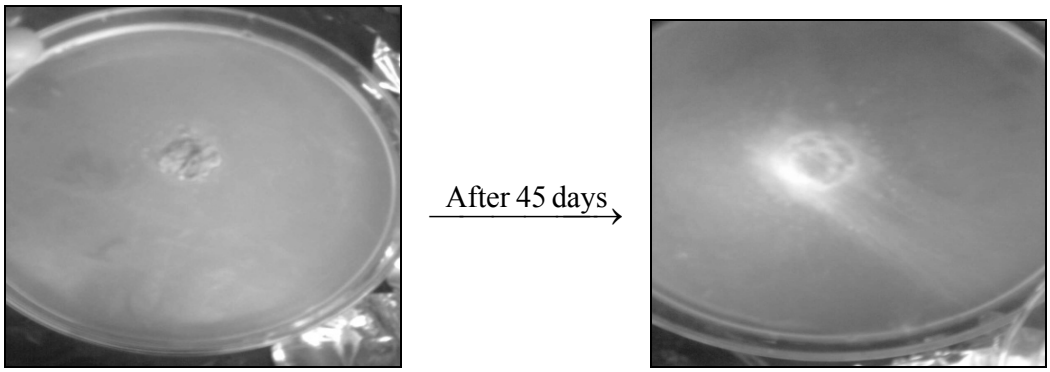


Fig. 2: PEA /ECgPCL (PBO) deposed on solid medium of growth of fungi

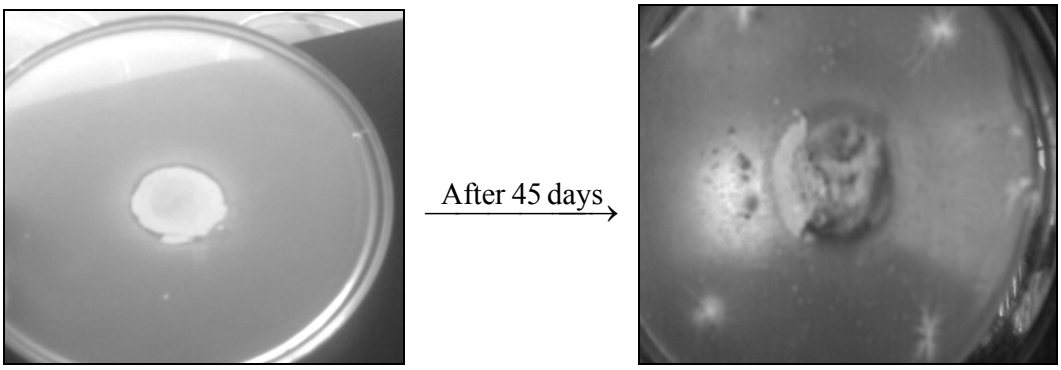
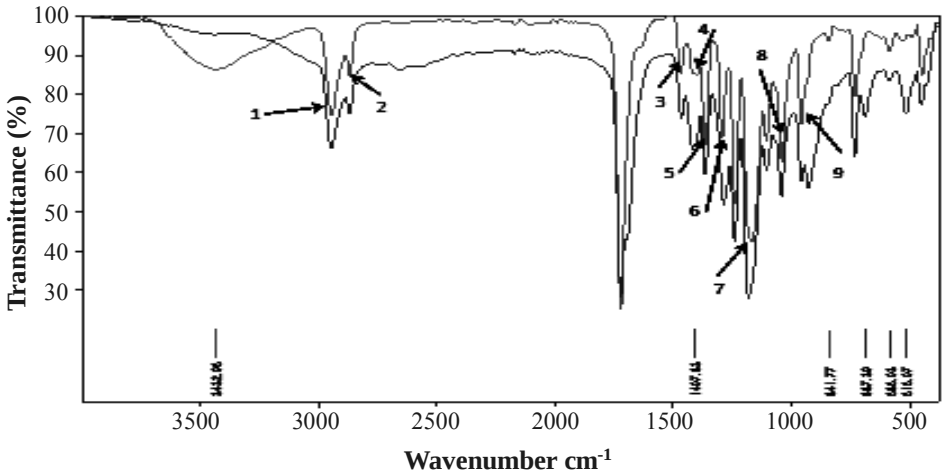


Fig. 3: PCL deposed on solid medium of growth of *Aspergilus Niger*

FTIR

The biodegradation in solid media of PCL was invigested by infra red spectra before and after 45 days. The Fig. 4 shows that the intensity infrared bands were changed and specially the characteristic bands of alkanes (C-H) with degradation time (Fig. 4). We noted, the intensity of stretch C-H band frequency (3000-2850 cm^{-1}) of stretch was decreased at the end of biodegradation test, the result shows that the *Aspergilus Niger* has great affinity to the CH group compared to the CO function, the Fig. 5 showed this result.



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C:\Program Files\OPUS_65%MEAS\A2.1	A2	ATR platinum Diamond 1 Refl	02/11/2011

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Fig. 4: Infrared spectra of PCL before and after 45 days of biodegradation

The rate of biodegradation were calculated from the peak of CO (100%) since the function CO has not been attacked by *Aspergilus Niger*. We noted that the surface of the peak of the OH function has increased due to presence of water molecule observed during breathing of fungi for PCL and PEA. We noted for PEA the *Aspergilus Niger* attacked the majority of functions : the carbonyl (ester) and amide function and alkanes (CH) the fungi has shown great infinity for PEA compared at the biodegradable polyester (PCL).

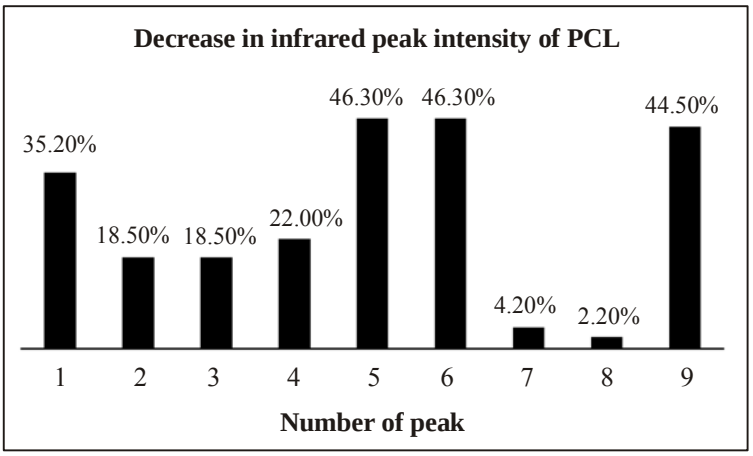


Fig. 5: The rate of biodegradation of PCL for 45 days

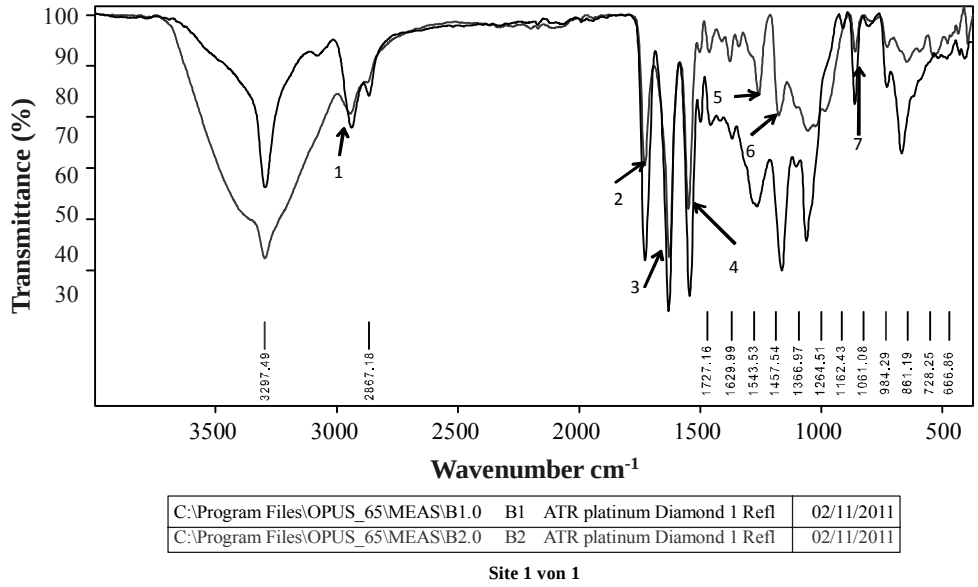
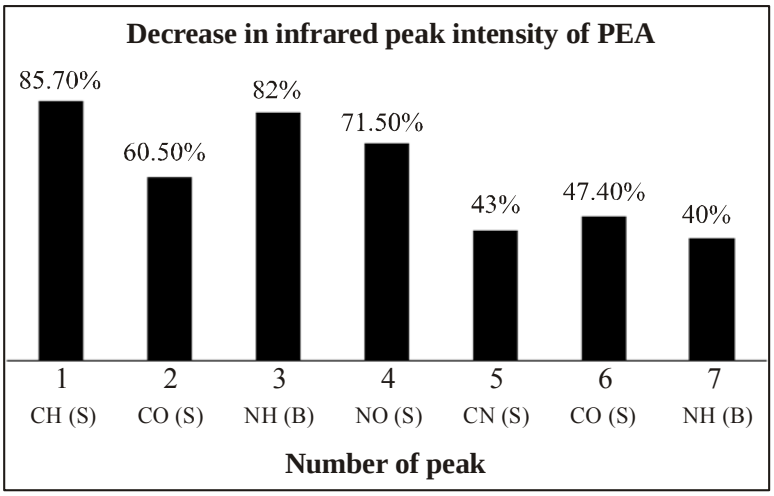


Fig. 6: Infrared spectra of biodegradation before and after of PEA



(s) Stretching (B) Bending

Fig. 7: The rate of biodegradation of PEA for 45 days

Biochemical oxygen demand (BOD)

Evolution of the BOD shows that the inoculum of activated sludge has an affinity to degrade our materials. We noted a slight adaptation phase of the control of activated sludge followed by an increase of BOD showing the beginning of the biodegradation of materials

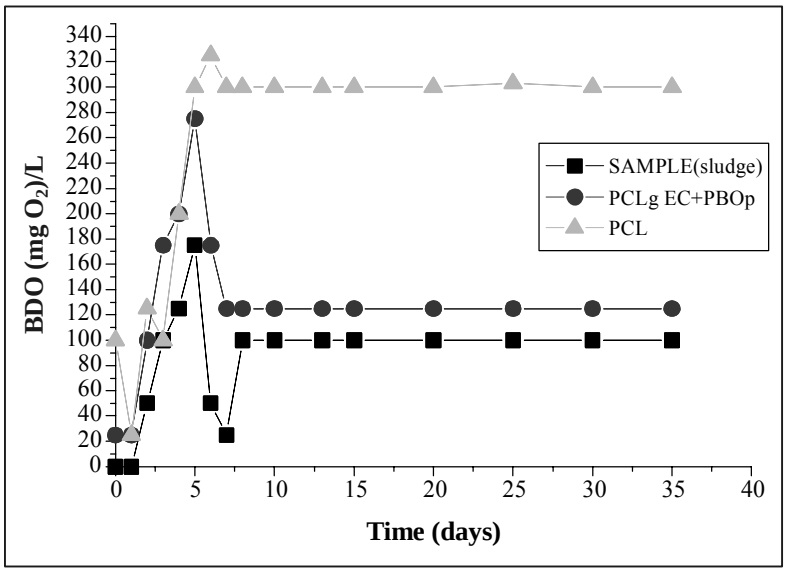


Fig. 8: Evolution of BOD of PCL, PEA and sample of sludge at 23°C

the biodegradation of PCL was the fastest compared with PEA. The variation of BOD was due to the high mass of PEA. Beyond 10 days of the BOD is almost constant. The bacterial stains have used the PCL and PEA as the only source of source for the survival and the rate of biodegradation is more important for PCL since is a biodegradable polymer. Ethyl cellulose is a biocompatible polymer by reacting with the PCL gave a biodegradable block polymer with a high mass which explains the slow biodegradation of PEA.

CONCLUSION

In this work, the effect of *Aspergilus Niger* on biodegradable (PCL) and biocompatible (EC) was investigated, the result of study of biodegradation on solid media showed that the PCL and ECgPCLgPBO have great affinity for the fungi, and this block polymers and the polyester can be degraded by activated sludge. The standardized test procedures are well defined can verify the biodegradability a given polymer. The test procedures ISO 14851 and ISO 14852 in order to measure the biodegradation (BOD) of some materials (PCL and block polymers based on PCL and EC) but the obtained results were disappointing. The reproducibility was very low, even if tests had been carried out in the same conditions, with the same test procedure.

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Revised : 02.10.2012 *Accepted : 05.10.2012*