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PJBS

ISSN 1028-8880

Pakistan Journal of Biological Sciences

ANSInet
Asian Network for Scientific Information
308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

Pakistan Journal of Biological Sciences 8 (7): 1041-1044, 2005
ISSN 1028-8880

Biodegradable Polymeric Films of PHB from *Burkholderia saccharia* in Presence of Polyethyleneglycol

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Abstract: The poly-3-hydroxibutirate (PHB), a natural polymer produced in the *Burkholderia saccharia bacteria,* has been investigated as an intelligent and biodegradable alternative for plastic film. The objective of this research was to study the thermal and mechanical properties, water vapor permeability and water solubility of PHB polymeric blends with low molecular weight polyetilenoglicol in different plasticizer concentrations. Casting process produced the biofilms. The mechanical and thermal properties, puncture resistance, water vapor permeability and solubility were highly influenced by the presence of plasticizer polyethyleneglycol (PEG) in the biofilms. The plasticizer effect exercised by the PEG, which ascribes good flexibility to the films allow to the production of smaller thickness than those performed so far. The PHB/PEG biofilms are totally biodegradable, with the increase of PEG levels is observed a light decrease of the water vapor barrier and solubility properties. It has thermal properties of resistance compatible with domestic and industrial plastic packing.

Key words: Biofilm, poly-3-hydroxibutirate, biodegradable, polyethyleneglycol

INTRODUCTION

In the contemporary world, plastics are indispensable to due day-by-day products. American statistics estimates that about 160 millions of tons of solid residues are left off in the environment, where 11 millions of tons are plastic residues. The utilization of this material generates proportionally an environmental problem. The accumulating waste, owing to the degradation time of plastic of 100 years and more.

In this context, many studies have been developed for new materials. As an alternative, this research study the poly-3-hydroxibutirate (PHB) in blends with PEG. Recently some kind of PHB blends were produced using other types of polymers, some examples are poly (ethylene oxide)[1], poly (butylene succinate)[2], starch[3], poly-ε-caprolactone[4], glycerol and glycerol triacetate[5], poly(vinyl butyral)[6].

The PHB is produced in the *Burkholderia saccharia bacteria* (identified by Instituto de Pesquisas Tecnológicas-IPT/Brasil). This bacterium transforms its metabolism exceeding in intercells grains, which are the polyester: PHB. Using a solvent the cellular wall of the microorganisms is broken and consequently, the release of grains occurs. PHB is thermoplastic polyester. Polyethyleneglycol, a plasticizer, has the function to improve the flow in process, reducing the weakness[7] and providing flexibility to the PHB films.

Study on the influence on the mechanical and thermal properties; water vapor permeability and water solubility of the biofilms with different plasticizer concentration were evaluated. Commercial synthetic plastics film of polyvinyl chloride (PVC) was compared.

MATERIALS AND METHODS

Materials:

- Poly-3-hydroxibutirate (PHB) provided by Usina da Pedra-SP (Brazil)
- Polyethyleneglycol (PEG-300) provided by Oxiteno (Brazil)
- Chloroform provided by Labsynth
- Polyvinyl chloride film from domestic use, the brand Easy PacK, Theoto S.A.

Methods: The polymeric PHB films were produced through the casting process. The polyester is dissolved in chloroform, adding the plasticizer in the desired concentrations. The solution is heated, with content mixing and than dropped into a mold to evaporate the solvent and to obtain the film.

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The PHB/PEG 300 films were obtained in different concentrations of PEG: 2, 5, 10, 20 and 40 (% on PHB weigh).

The average thickness of these films is $0{,}04.10^{-3}$ m. Samples of the films were storage sealed on polyethylene bags and kept on moisture and temperature controlled conditions.

Mechanical properties

Tension test: The tests were performed in a Universal Machine of Mechanical Tests-INSTRON 4400R. Equipped with pneumatic claws and speed of $1{,}0.10^{-3}$ m/s. Five samples of each type of the film, prepared according to the ASTM D 412-80, with dimensions of $4{,}0.10^{-2}$m of length and $2{,}7.10^{-2}$m of width were analyzed.

Puncture tests were performed in a texturemeter TA.XT2i (SMS, Surrey UK), with a probe of diameter of 3.10^{-3} m. The film samples was fixed in a mold with 3, 3.10^{-2}m of diameter. Figure 1 shows the puncture test scheme.

The deformation at puncture was calculated in accordance with the expression (1):

$$\frac{\Delta l}{l_0} = \frac{\left(\sqrt{D^2 + l_0^2} - l_0\right) x100}{l_0} \qquad (1)$$

Where:

D: Displacement of the probe leads until at the rupture taken directly on the curves of force versus displacement, with the use of the program Texture Expert 1,15 (Stable Systems Micron).

l_0:Initial length of the film (measured cell ratio=$16{,}5.10^{-3}$ m)

Thermal properties: DSC tests analyses were performed on a DSC-821 from Mettler–Toledo, with the samples (10±0.1 mg) under N_2 atmosphere, with temperature program of heating 223 to 473 K at 283 K/min, cooling 473 to 223 K at 283 K/min; reheating 223 to 473 K at 283 K/min. The DSC apparatus was calibrated with indium metal (m.p. 429.61 K; ΔH =28,54 J g^{-1}).

TGA curves were recorded in TGA/SDTA-851^e thermo balance from Metter-Toledo. The mass loss was recorded by the TGA test with the samples (10 mg) in alumina crucible under dynamic nitrogen atmosphere (50 mL/min) at heating rate of 283 K/min from 298 to 773 K.

Water vapor permeability: This property is determined by the desiccant method based on standard method E96-80. The influence of the plasticizer in the permeability of the PHB films was determined according to the increase of mass due to water vapor absorption of the PHB films. Samples in duplicate, had been placed in cells with silica gel in its interior. After that they had been conditioned in desiccators containing distilled water at constant temperature of 298 K during seven days. The films had been weighed at each 24 h. Figure 2 shows the cell scheme of the test.

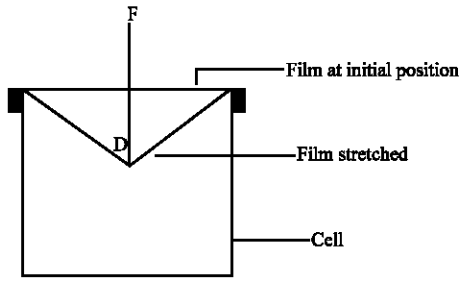

Fig. 1: Assay to the puncture test

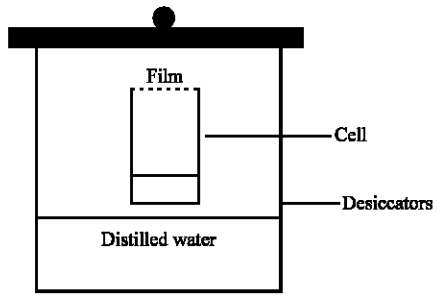

Fig. 2: The cell to the water vapor permeability test

Solubility in water: This test is applied to evaluate the integrity of materials under hydrophilic condition. Losses of mass during a period show the influence of the plasticizer concentration on the solubility of the films. The test occurred in duplicate and the samples were weighted, in an analytical balance (+ 0.1 mg) from Quimis. Samples with the diameter of 4.10^{-2} m had been placed in a container with 0.1 L of distilled water and covered to prevent possible losses of water. The essay was left under constant agitation for 24 h at room temperature. The samples were collected and dried for 24 h At 363 K in a stove from Diatom.

The solubility of each film can be determined according to the expression (2):

$$\%MS = \frac{Mi - Mf}{Mi} \times 100 \qquad (2)$$

where:

%MS = Percentage of soluble mass
Mi = Initial mass of the sample (kg)
Mf = Final mass of the sample (kg)

RESULTS AND DISCUSSION

The aspect of the PHB/PEG films varies in accordance to the amount of plasticizer in its composition. The transparency of biofilms decreases with the increase on the concentration of polyethyleneglycol. Films with 2 and 5% of the plasticizer are the most transparent in the group. Opacity was observed at concentration of 10% and upper. Moreover, the increase on the concentration of plasticizer results in films with more adherent surface. This occurs due to the excess of polyethyleneglycol that migrates to the surface of those films. Figure 3 presents the film at 5% of plasticizer concentration. Figure 4 shows a contrast of commercial PVC film and the PHB 2% film.

The puncture force decreases until PHB/PEG at 10%, due to the decrease in the intermolecular interactions as the plasticizer effect (Fig. 5). The puncture force is restored at higher plasticizer levels. This is justified by the migration of the plasticizer to the surface and loses of it from the film. The puncture deformation is not effected until at the level of 10%. It is showed an increase of puncture deformation when comparing the levels of 10, 20 and 40% of plasticizer in the film. If we consider

Fig. 3: PHB/PEG 5% films

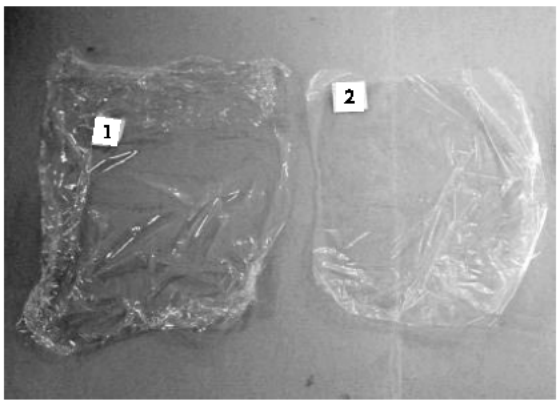

Fig. 4: PVC commercial film (left) and PHB/PEG 2% film (right)

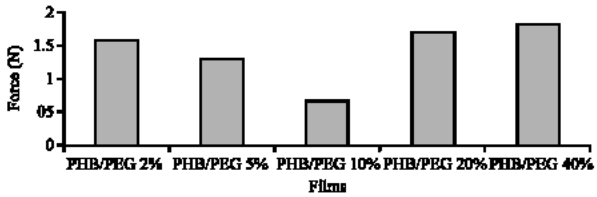

Fig. 5: Puncture force of the films

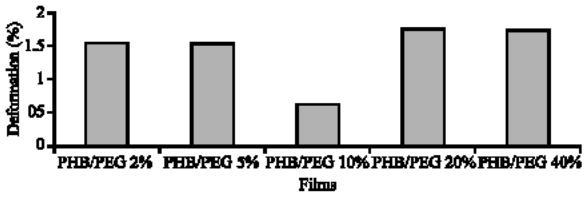

Fig. 6: Puncture deformation of the films

the migration phenomenon of the PEG (20-40%) one possible plasticizer effect to justify this fact is the water content (2-4,8%) (Table 1). Increase of the puncture deformation as effect of higher mobility intermacromolecular chains.

The T_{onset} of decomposition showed at Table 1 indicated the thermal resistance of the films practically not affected by the plasticizer content. On the other hand the crystallization temperature is affected and the T_c is displaced at around 20°C.

Table 2 shows the results of permeability and solubility tests. The presence of the plasticizer, due to the hydrophilic character of PEG, increases the absorption of the water content in the polymer matrix of PHB. On the other hand the free volume of the polymeric system is increased and consequently the water diffusion through it. Solubility is also increased by the plasticizer concentration.

Mechanical properties of tensile strength were evaluated and the results (Table 3) show values as typically affected by the plasticizer presence. The deformation at break increases with the increase of PEG concentration.

PHB films plasticized with Polyethyleneglycol produce flexible transparent biofilms by casting process. The mechanical and thermal properties, puncture resistance, water vapor permeability and solubility were highly influenced by the presence of the plasticizer polyethyleneglycol (PEG) in the biofilms. The plasticizer effect of the PEG component promotes good flexibility and allows achieving smaller thickness than those performed so far. The PHB/PEG biofilms, decrease in efficiency of the water vapor barrier property with the increase of PEG levels due to the hydrophilic PEG character. The films have thermal resistance compatible with

Table 1: Thermal properties of the films

PEG (%) on PHB Film (1.10^{-1} kg)	T_{onset} of decomposition (K)	Residue (%)	Water (%)	First melting temperature (K)	Second melting temperature (K)	Crystallization temperature T_c (K)
0	530	1.00	1.15	447	443	364
2	530	0.00	0.57	442	441	346
5	529	2.52	0.15	431	430	343
10	532	4.03	0.14	439	423	347
20	529	1.26	2.65	440	425	337
40	527	3.30	4.80	446	432	345
PVC	552	11.42	0.94	335	-	-

Table 2: Water vapor permeability and water solubility of the films

Film (1.10^{-1} kg)	PEG (%)	Water vapor permeability (10^{-9} g mm h^{-1} cm^{-2} Pa^{-1})	Solubility in water (%)
PHB	0	0.347	1.5
PHB	2	0.628	2.0
PHB	5	1.0577	1.6
PHB	10	1.1895	7.3
PHB	20	1.5491	22.0
PHB	40	1.5849	26.0
PVC	-	0.192	0.72

Table 3: Mechanical properties of deformation at break of the PHB/PEG films

Film (1.10^{-1} kg)	PEG (%)	Deformation at break (%)
PHB	0	8.90±3.03
PHB	2	25.05±6.26
PHB	5	22.48±10.62
PHB	10	25.35±8.45
PHB	20	31.89±7.97
PHB	40	31.24±10.41
PVC	-	75.02±9.08

domestic and industrial plastic packing. Increase of the puncture deformation is effect of higher mobility intermacromolecular chains that depends of the plasticizer content including water acting as plasticizer. The obtained biofilms are potential alternative as biodegradable products.

ACKNOWLEDGMENTS

The authors thank to FAPESP and CNPQ for financial support.

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