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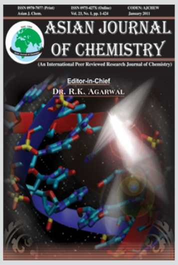

Synthesis and Characterization of Certain Biodegradable Random Aliphatic Copolyesters

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Biodegradable aliphatic random copolyesters poly(butylene succinate-co-butylene adipate) and poly(butylene succinate-co-butylene azelate) were synthesized from 1,4-butane diol, succinic acid and adipic acid/azelaic acid through direct melt polycondensation with titanium tetra isopropoxide as a catalyst. These polyesters were characterized by viscosity measurements, ^1H nuclear magnetic resonance spectroscopy, gel permeation chromatography and X-ray diffraction analysis. Thermal properties have been analysed using differential scanning calorimetry. The percentage of biodegradation of the synthesized copolyesters was investigated by enzymatic hydrolysis using the enzyme *Candida cylindracea* lipase. It appears that the key factor affecting the degradation was its crystallinity. This kind of novel biodegradable polymers are expected to have potential applications as environment friendly materials.

Key Words: Enzymatic biodegradation, Polycondensation, Crystallinity.

INTRODUCTION

The problems of environmental pollution and waste management from the bio-resistant synthetic plastics have become increasingly serious treat to environment in near several decades. Many countries put much attention and effort on the reusing and recycling of plastic waste. In the mean time, the development of biodegradable polymers offers an alternative way to solve the problems. Biodegradable polymers had been developed and applied in many fields likewise packaging, agriculture, sanitary and other biomedical applications nowadays. Among these biodegradable materials, the family of aliphatic polyesters appears to be the most attractive and promising because of their susceptibility to biological attacks[1-6].

In recent years, there is a growing interest in the synthesis of biodegradable polymers such as polycaprolactone (PCL), polyhydroxyvaleric acid, polylactic acid (PLA) and aliphatic polyesters from different lactic acid derivatives[7-9]. In addition, aliphatic polyesters synthesized from dimethyl esters and diols are expected to be of the most economically competitive biodegradable polymers[10,11].

Poly(butylene succinate) (PBS) and poly(butylene succinate-co-butylene adipate) (PBSA) have been synthesized from diacids and diols which have satisfactory mechanical properties similar to polyolefins[12]. The products obtained from these biodegradable polymers used as films for packaging and in agricultural field. In addition, they can be used as drug carriers for controlled release of drugs in biomedical industry[13-16]. The advantage of these polyesters is their biocompatibility and higher hydrolysability in the human body.

Biodegradability of polymers is controlled by several factors. The most important one is the nature of the polymer which depends on its chemical structure, especially the occurrence of specific groups along chains, as they are susceptible to hydrolysis, such as esters, ethers, amides, *etc.*[17,18]. It has been reported that an increase in the average molecular weight of the polymer upto a critical value leads to decrease in biodegradation rates. Increase in average molecular weight above this has no influence[19-21]. It is also well known that the degree of crystallinity may be a crucial factor, since enzymes mainly attack the amorphous domains of a polymer. Copolymers with low crystallinity show increased hydrolysis rates[22]. Conditions like temperature, pH and concentration of enzyme also play a particular role[23].

In the present investigation two aliphatic random copolyesters, poly(butylene succinate-co-butylene adipate) (PBSA) and poly(butylene succinate-co-butylene azelate) (PBSAz) were synthesized by melt polycondensation. Their molecular weights and thermal properties were studied. The structure of the repeating units are confirmed from spectral analysis. The biodegradation behaviour of the polyesters are studied using enzyme lipase originating from *Candida cylindracea*.

EXPERIMENTAL

Succinic acid (Merck AR grade), adipic acid (Lancaster AR grade) and azelaic acid (Lancaster AR grade) were recrystallized from deionized water and used. 1,4-Butanediol (Lancaster, AR grade) was dried with CaO overnight and then distilled under reduced pressure. Titanium tetra isopropoxide (TTiPO), used as catalyst, purchased from Lancaster was used as such. *Candida cylindracea* lipase, purchased from Sigma Aldrich was used for degradation studies. All the other materials and solvents used were of analytical grade.

Synthesis of copolyesters: The copolyesters were synthesized by two step melt polycondensation method. As an example, the synthesis of poly(butylene succinate-co-butylene azelate) (PBSAz) have been described. The polycondensation flask was a three necked one, equipped with a nitrogen inlet, a condenser and a thermometer. A magnetic stirrer is used to stir the mixture. The reaction mixture consists of 0.2 mol of 1.4-butanediol, 0.1 mol of succinic acid and 0.1 mol of azelaic acid.

The reaction mixture is purged with nitrogen and heated in an oil bath. The temperature of the reaction mixture was raised to 150 ºC in 20 min. Then, the temperature was gradually raised in 10 ºC steps every minute to the final reaction temperature of 210 ºC to remove water being the esterification byproduct. When water ceased to be generated, a predetermined amount of titanium tetra isopropoxide (TTiPO) catalyst was added to the reaction mixture. Subsequently, the pressure of the reaction system was gradually decreased and condensation polymerization was continued at 210 ºC under a final reduced pressure lower than 0.5 mm Hg. Finally, the reaction was terminated when the rotation of the mechanical stirrer was stopped. The viscous slurry was cooled in the flask under nitrogen atmosphere. The crude polyester was dissolved in chloroform and then poured into excess of dry cold methanol to purify the polyesters. The precipitated polyester was dried in a desiccators to constant weight.

Gel permeation chromatography: The molecular weights of copolyesters were analyzed by gel permeation chromatography using a Shimadzu instrument equipped with a pump and a refractive index detector. Tetrahydrofuran was used as a mobile phase with a flow rate of 1.0 mL/min. Polystyrene standards from shapodex was used for calibration.

Intrinsic viscosity: The intrinsic viscosity, [η] of polymer solutions in chloroform was measured at 30 ºC in a constant temperature bath using Ubbelohde viscometer.

Nuclear magnetic resonance: ^{1}H NMR spectra were obtained with a Jeol Model GSX300 MHz NMR spectrometer using $CDCl_3$ as solvent and TMS as internal standard, respectively. The measurement were carried out at room temperature.

Differential scanning calorimetry: The differential scanning calorimetry scans were recorded at a heating rate of 10 ºC/min using a Perkin-Elmer Pyris I analyzer. Indium was used as the calibration standard.

X-Ray diffraction analysis: A siemens D 500 diffractometer with Cu K_α filtered radiations was used for assessing the crystallinity of the polymers. The samples were scanned over the range of 2θ angle, from 5º-80º.

Enzymatic degradation studies: Copolyester films were obtained by hot pressing method above the melting temperature. The hot pressed films (10 mm^2 × 10 mm^2 and about 200 µm thick) were incubated in duplicate at 30 ºC in separate petri dishes containing 7 mL of phosphate buffer (pH = 7.00 ± 0.01) in the presence of the enzyme lipase from *Candida cylindracea*. The enzyme concentration was 1 mg/mL. The films were removed from the enzymatic solution after selected time intervals, washed with distilled water and dried under vacuum at room temperature to constant weight. This procedure was repeated for every chosen time interval: 9, 24, 48, 72 and 90 h. The extent of biodegradation was quantified using the weight loss and the initial sample weight[24]. A control test without enzyme was also carried out.

Scanning electron microscope: The effect of biodegradation upon the polymer surfaces was examined using Jeol, Model JSM-840A SEM microscope. Prior to the analysis, the samples were coated with gold to avoid charging under the electron beam.

RESULTS AND DISCUSSION

Intrinsic viscosity, molecular weights and elemental analysis: The polyesters PBSA and PBSAz were synthesized by a two step melt polycondensation method. The intrinsic viscosity, the molecular weights and the polydispersity index of the copolyesters are presented in Table-1.

TABLE-1
INSTRINSIC VISCOSITY AND MOLECULAR WEIGHTS OF THE COPOLYESTERS

Polymer	Intrinsic viscosity, [η] (dl/g)	Mn	Mw	Polydispersity index
PBSA	0.72	8426	10448	1.24
PBSAz	0.86	9826	13525	1.37

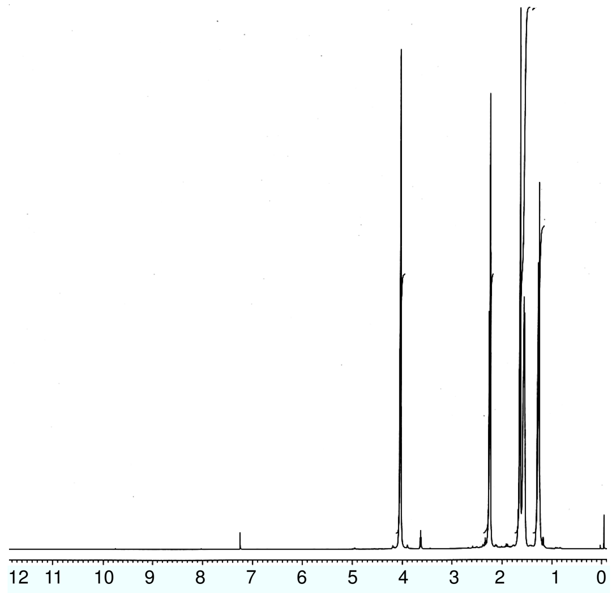
The extent of polymerization was determined by the molecular weight and the intrinsic viscosity of the polymers. The intrinsic viscosity [η] of these polyesters PBSA and PBSAz were 0.64 and 0.73 dl/g, respectively. In all GPC measurements, a single peak which differs in magnitude and elution time was received.

^{1}H NMR: The structure of the repeating units of the polymers are confirmed by elemental analysis and NMR spectroscopy. The elemental analysis values of the resulting polymers were in good agreement with the calculated values for the proposed structures Table-2.

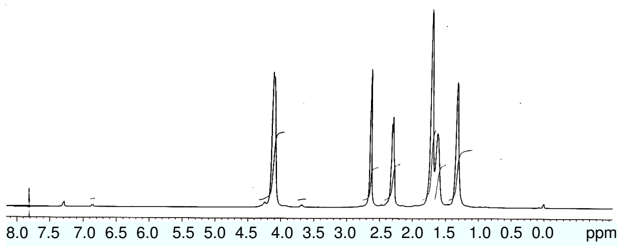
TABLE-2

Polymer	Formula	Elemental analysis (%): calcd. (found)	
		C	H
PBSA	$(C_{18}H_{28}O_8)n$	58.06 (58.00)	7.50 (7.21)
PBSAz	$(C_{21}H_{34}O_8)n$	60.86 (60.21)	8.93 (8.61)

A ^{1}H NMR spectrum of the polyesters are shown in Fig. 1. The peak at $\delta = 2.63$ ppm was attributed to methylene protons of dicarboxylic acid at $\delta = 1.63$-1.71 ppm due to ester moieties, respectively. In addition the peak at $\delta = 1.7$ ppm was attributed to central methylene protons of 1,4-butane diol while $\delta = 4.1$ ppm is due to terminal methylene groups of 1,4-butanediol moiety.



PBSA



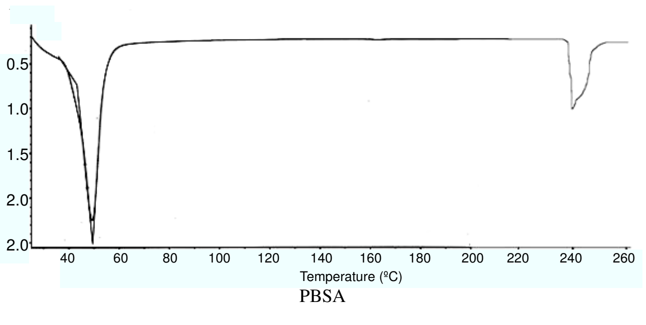
PBSAz

Fig. 1. ^{1}H NMR spectrum of PBSA, PBSAz

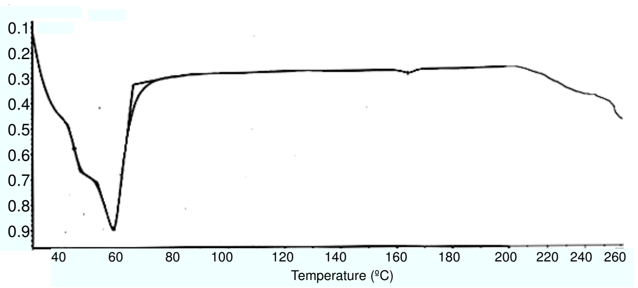
Thermal properties: The thermal property data of the synthesized polyesters are summarized in Table-3 and the corresponding thermograms are shown in Fig. 2.

TABLE-3
THERMAL PROPERTIES OF THE SYNTHESIZED CO-POLYESTERS

Polymer	T_g (ºC)	T_m (ºC)	T_d (ºC)	ΔHm (J/g)
PBSA	43.2	44.1	190.2	16.42
PBSAz	42.7	44.9	212.5	18.67



PBSA



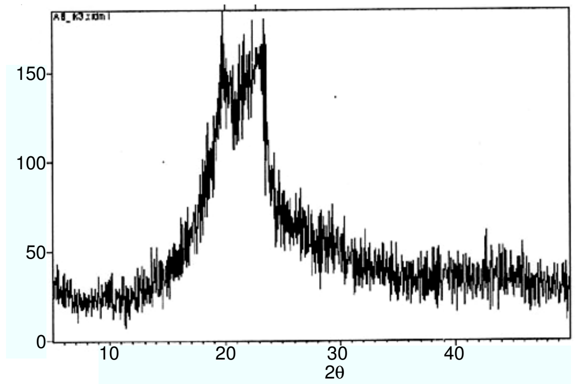
PBSAz

Fig. 2. DSC thermogram of PBSA and PBSAz

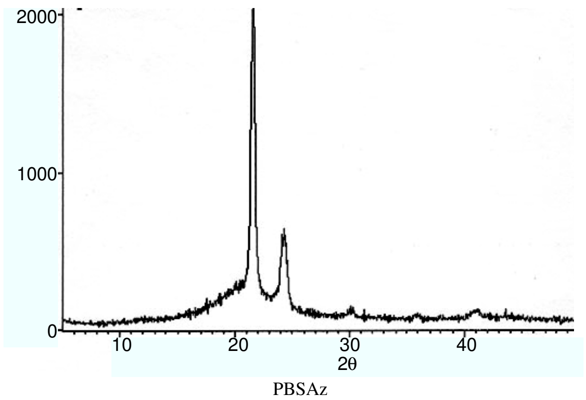
Poly(butylene succinate-co-butylene azelate) is a highly crystalline polymer exhibiting a melting point (T_m) of 44.9 ºC and a heat of fusion of 18.69 J/g. It is worth noting than an increase of methylene units in the chain increases the crystalline nature of the resulting copolyester.

The glass transition temperature (T_g) values of the PBSA and PBSAz are 43.2 and 42.7 ºC, respectively. The glass transition temperature (T_g) of polymers is closely related to the flexibility of the chains because a high T_g is generally assumed to be connected with relatively high barriers of bond rotations. The results show that the T_g values decreases with increase in methylene units. This indicates that the increase in the length of flexible spacers reduced the proportion of mesogens and decreased the rigidity of polymers. Hence, the T_g values decrease from PBSA to PBSAz.

X-Ray diffraction analysis: X-Ray diffractogram of the synthesized polymers are shown in Fig. 3. The crystalline nature of polyesters was determined from X-ray diffractogram. Gaussian curves are used to describe the amorphous phase



PBSA



PBSAz

Fig. 3. X-Ray diffractogram of PBSA and PBSAz

and all crystal reflections of a diffractogram[25]. In the X-ray diffractogram, the intensity of diffraction peaks increases with the increase in the length of the flexible spacer group. This is in accordance with the study of Chen *et al.*[26]. This indicates that the crystallinity of the polymer increases with the length of flexible segments. From the X-ray diffratogram, it is observed that PBSAz is highly amorphous in nature than PBSA.

Enzymatic degradation: The biodegradability of the copolyesters was determined by monitoring the weight loss or erosion of films with time. The time course of the enzymatic degradation of the polyesters during 90 h is shown in Fig. 4. The weight loss due to hydrolytic degradation could be neglected for the same incubation period. From the enzymatic degradation, it was observed that PBSA exhibit the highest weight loss while PBSAz shows least weight loss.

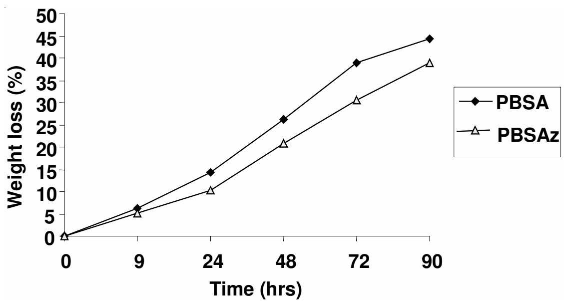


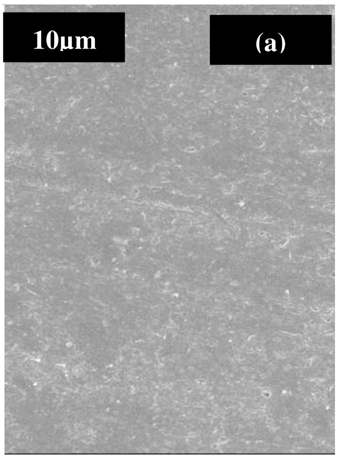
Fig. 4. Enzymatic biodegradation of PBSA and PBSAz

It is well known that aliphatic polyesters are biodegradable in a wide variety of ecosystems. In order to examine the biodegradability of the synthesized polyesters, enzymatic hydrolysis was carried out. The enzymatic degradation of aliphatic copolyesters is usually related to their crystallinity and chemical structure of polyesters of the same series. Tokiwa and Suzuki reported that the enzymatic hydrolysis by the enzyme rhiozopus delemar lipase was greatly affected by the melting temperature of the polyesters[27]. From the reports it is concluded that the polymer degradation usually proceeds in a selective manner, with the amorphous region being preferentially degraded as compared to crystalline ones. From the investigation of biodegradation using *Candida cylindracea* lipase enzyme, it is clear that the PBSA undergoes more degradation which indicates the less crystalline nature of PBSA[28].

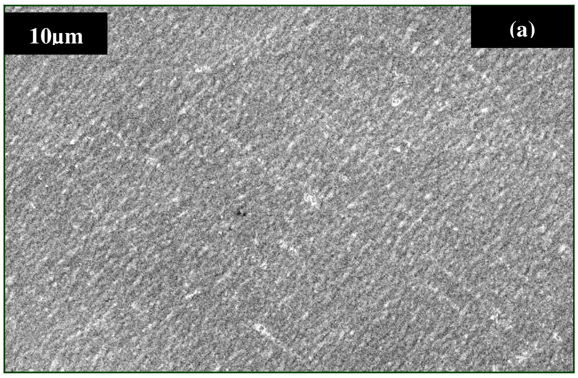
SEM Observations: SEM micrographs are used to study the morphology of the aliphatic polyester films during enzymatic degradation. Further, the biodegradation of the polyesters was confirmed by SEM. As seen in the micrographs of Fig. 5, the hydrolytic action of the enzyme *Candida cylindracea* lipase led to the formation of a rough surface with large cavities on the film surface of the polyesters.

Conclusion

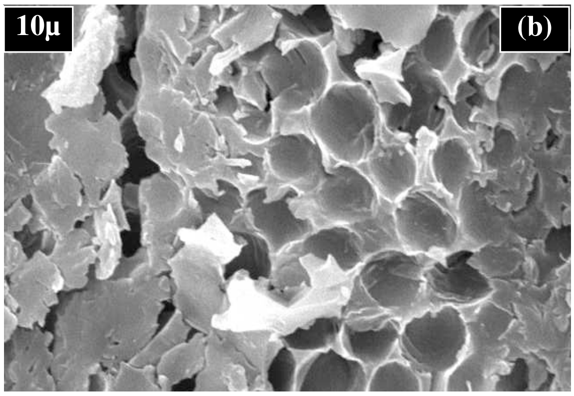
The high molecular weight aliphatic random copolyesters derived from succinic acid, adipic acid, azelaic acid and 1,4-butanediol were synthesized by the two step melt polycondensation method in the presence of a highly effective catalyst TTiPO at 215 ºC. The synthesized polyesters were characterized by thermal and spectral methods of analysis. The enzymatic biodegradation of these polyesters was investigated using the enzyme lipase from *Candida cylindracea*.



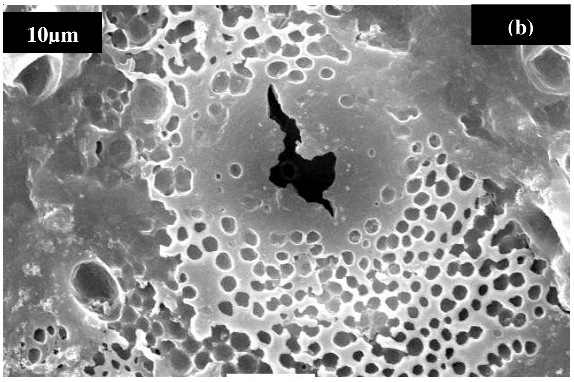
PBSA



PBSAz



PBSA



PBSAz

Fig. 5. SEM micrographs of PBSA, PBSAz polyester during enzymatic hydrolysis. (a) Before degradation (b) After degradation using *Candida cylindracea* lipase

The results indicate that the highest degradation was observed for the PBSA polyester as it was expected due to lower crystallinity and flexibility of chain backbone. The major factor which controls the biodegradation rate to observe tightly the polymer chains are fixed in the crystalline regions of the polymer material. This is characterized by the melting point of the material. The order of enzymatic biodegradation of the copolyesters was PBSA > PBSAz. This investigation clearly demonstrates that the hydrolytic degradation of polyesters catalyzed by *Candida cylindracea* lipase enzyme is predominantly controlled by the degree of crystallinity of the material and structural differences in the polymer chain.

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