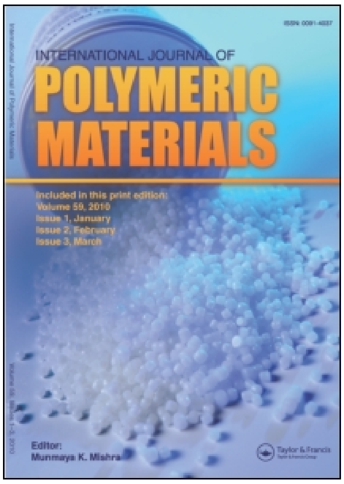

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Synthesis, Characterization and Biodegradation Study of Low Molecular Weight Polyesters

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A series of low molecular weight aliphatic biodegradable polyesters were synthesized from 1,3-propanediol and dibasic acids by thermal polycondensation, in the bulk without catalyst in N_2 atmosphere at 150°C. The synthesized aliphatic polyesters were characterized by ^{1}H-NMR, FT-IR, solubility, solution viscosity, gel permeation chromatography, and diffential scanning calorimetry. The biodegradability of the synthesized polyester films was tested by enzymatic degradation in phosphate buffer (pH = 7.2) in presence of Rhizopus delemar *lipase incubated at 37°C, and soil burial degradation at 30°C. SEM was used to study the surface morphology after incubation of the films. The result of biodegradation shows that the films become brittle on incubation and their surfaces change upon degradation. The biodegradability of the polyesters depends on the crystallinity of the polymers. The degradation was more pronounced in PPSu compared to PPAd.*

Keywords: aliphatic polyesters, enzymatic degradation, poly(propylene adipate), poly(propylene adipate-co-cyclohexanedimethylene adipate), *Rhizopus delemar* lipase

INTRODUCTION

In recent years, a conventional plastic has been widely used for packaging that generates a lot of waste. This waste is causing serious

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environmental pollution. For solving the difficult problems of fossil resources, waste management, and global environmental pollution [1], biodegradable aliphatic polyesters have been widely investigated. For packaging, sanitary and agricultural uses, manufacturing of biodegradable fibers, non-woven, films, sheets, bottles, and injection-molded products, aliphatic polyesters are the most promising materials because they are readily susceptible to biological attack and metabolize into nontoxic substances [2–5].

Over the past few years, most of the effort in making aliphatic polyesters has been focused on 1,4-butandiol and very little emphasis has been given to 1,3-propanediol. This is due to the nonavailability of sufficient quantity and quality of 1,3-propanediol. In recent years, more attractive processes have been developed for the production of commercial high-quality 1,3-propanediol derived from renewable resources at low cost [6–10]. 1,3-propanediol based polyesters are expected to be different from 1,4-butandiol because of different interaction between the diol and dibasic acid. Homopolyesters and copolyesters based on 1,3-propanediol are most promising in terms of biodegradability [11]. Thus, the authors strongly feel the need to explore the possibility of using 1,3-propanediol for synthesis of polyesters.

The present work describes the synthesis, characterization, and biodegradation of low molecular weight aliphatic homopolyesters obtained from 1,3-propanediol and dibasic acid (adipic/succinic acid) by polycondensation reaction in the bulk. Low molecular weight aliphatic copolyester is also described based on 1,3-propanediol, adipic acid and 1,4-cyclohexanedimethandiol. Their molecular and thermal properties are compared. A comparative biodegradability study of synthesized polyesters is also carried out by using enzymatic hydrolysis in phosphate buffer (pH = 7.2), in presence of *Rhizopus delemar* lipase and soil burial methods.

EXPERIMENTAL

Materials

1,3-propanediol (98%), adipic acid (99%), succinic acid (99.5%), 1,4-cyclohexanedimethandiol (Fluka, cis-trans 98%), and enzyme *Rhizopus delemar* lipase (Fluka, 0.73 U/mg) were purchased from Sigma-Aldrich Chemical Co. Toluene, methanol, chloroform, acetone, tetrahydrofurane (THF), dimethylformamide (DMF), dimethylsulphoxide (DMSO), and so on were of E-Merck Spectroscopic grade and were used without further purification.

Synthesis of Polyesters

Low molecular weight aliphatic polyester α, ω-bis-hydroxy-terminated poly(1,3-propylene adipate) PPAd-1, was synthesized by thermal polycondensation in the bulk [12–13]. The polycondensation reactor was a three necked flask equipped with a magnetic stirrer, nitrogen inlet, a condenser, and thermometer. Adipic acid (14.61 g; 0.1 mole) and 1,3-propanediol (7.99 g; 0.105 mole) were charged into the reactor. The reaction mixture was purged with nitrogen and refluxed on oil bath at 130°C for 2 h with constant stirring. It was then cooled down to 50°C and toluene (50 ml) was added under agitation. Then it was gradually heated at 85°C, to distill off the water/toluene azeotrope, and then, excess toluene at 110°C. Finally the reaction mixture was heated at 150°C under continuous stirring for 2 h so that the remaining traces of water could be distilled off. The process of cooling the reaction mixture to 50°C, addition of toluene (50 ml), removal of water/toluene azeotrope (85°C), removal of excess toluene (110°C), and final removal of traces of water and toluene (150°C) was repeated seven times until only traces of water were detectable in the azeotrope distillate. Finally, a viscous liquid/white solid polyester product was obtained. The polyester was dissolved in minimum amount of chloroform and re-precipitated with methanol. It was then dried under vacuum at room temperature (30°C) for 48 h. The yield was ~90%. PPAd-2 was synthesized by varying the monomer composition of adipic acid and 1,3-propanediol (1:1.1). In a similar manner in α,ω-bis-hydroxy-terminated poly(1,3-propylene succinate) PPSu, was also synthesized from succinic acid and 1,3-propanediol.

The copolyester α,ω-bis-hydroxy-terminated poly(1,3-propylene adipate-co-1,4 cyclohexanedimethylene adipate) (PAd-co-CA) was synthesized from the comonomers adipic acid (146.14 g; 1 mole), 1, 3-propanediol (38.8 g; 0.51 mole) and 1,4-cyclohexanedimethandiol (73.54 g; 0.51 mole). The comonomers were introduced into the reactor and the process was carried out as described for the synthesis of homopolyesters. The copolyester product obtained was a white solid and the yield was 95%.

Characterization of Polyesters

The solubility of polyesters were tested by keeping 100 mg of polyester sample in 20 ml appropriate solvent (water, chloroform, acetone, DMF, DMSO, THF, hexane, and ethyl ether), the mixture was kept for 4 h at room temperature (30°C). The observations were then recorded. The mixture was then warmed upto the boiling point of the solvent and the observations were once again recorded.

^{1}H-NMR spectra of polyesters were recorded by SAIF, IIT Madras on JEOL GSX 400 NMR spectrometer operated at a frequency of 400 MHz. The polyester samples were dissolved in deuterated chloroform ($CDCl_3$), and tetramethylsilane was used as the reference standard. FT-IR spectra of the polymers were recorded at JNARDDC, Nagpur on AVTAR-320 Nicolet instruments, by KBr pellet technique. The intrinsic viscosity $[\eta_{int}]$ was measured using a Tuan-fouss viscometer, by preparing the solution of polyesters in chloroform at 30°C. From the time flow of solution and solvent the $[\eta_{int}]$ was calculated.

Average molecular weights and molecular weight distributions were determined by gel permeation chromatographic (GPC) analysis using a Varian Vista 5500 instrument. The number average (M_n) and weight average molecular weights (M_w) were calculated from a calibration curve, obtained from polystyrene standards with low polydispersity indices.

M_n of oligomers was also determined by carboxyl end-group analysis. Polyester solution was prepared in benzyl alcohol. It was then titrated with standard aqueous sodium hydroxide (0.01 N) using phenolphthalein as an indicator [13–14]. From the volume of sodium hydroxide consumed in the titration the number average molecular weight was determined.

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC-822 analyzer. The DSC scans were recorded under a nitrogen atmosphere in the temperature range of 60 to 250°C at a heating rate of 10°C/min. The melting temperature (T_m) was determined from the first scan as the temperature of the main peak in the DSC curves. The glass transition temperatures (T_g) were calculated from the DSC scans as the mid point of transition of the heat capacity [3].

Biodegradation Studies

Film Preparation

In order to study the biodegradation of the synthesized polyesters, polyester films of approximately 0.2 mm thickness were prepared in a hydraulic press [15] by pressing the synthesized polyesters between two Teflon sheets for one minute under a pressure of 1.5 ton/cm^2 below the melting temperature. The pressed films were stored at 30°C for one week before use in order to reach the equilibrium crystallinity.

Enzymatic Degradation

Hydraulic pressed polyester films (10×10 mm and thickness 0.2 mm) were placed in petri dishes containing 10 ml phosphate buffer solution (pH 7.2) with 1 mg *Rhizopus delemar* lipase. The petri dishes were then incubated in duplicate at 37°C, in an incubator for 96 h where the media were replaced after 72 h. Blank experiments without enzyme were also carried out on phosphate buffer (pH 7.2) solutions containing only polyester films. After a specific period of incubation, the films were removed from the petri dishes, washed with distilled water, and weighed until constant weight. The degradation by lipase was obtained by measuring the mass loss per unit area of the film. Therefore, actual degradation by lipase was calculated by subtracting the weight loss by blank test from the total weight loss.

The Soil Burial Degradation Test

The soil burial degradation test of polyesters films was conducted [16] as per ISO 846:1997. Hydraulic pressed polyester films (15 × 15 mm and thickness 0.2 mm) were buried in soil (pH 7.5, water content capacity 45%). The soil used in this study had been taken from the garden of VNIT, DEEMED University (Nagpur, India). The soil was taken in a tray, in which the relative humidity was adjusted to 50–60% and temperature was thermostated at 30°C with the help of a humidity chamber (Sonar Make). The buried polyester films were removed at regular intervals of 7 days up to a span of 28 days. Recovered films were washed with deionized water and dried in vacuum at 30°C to constant weight.

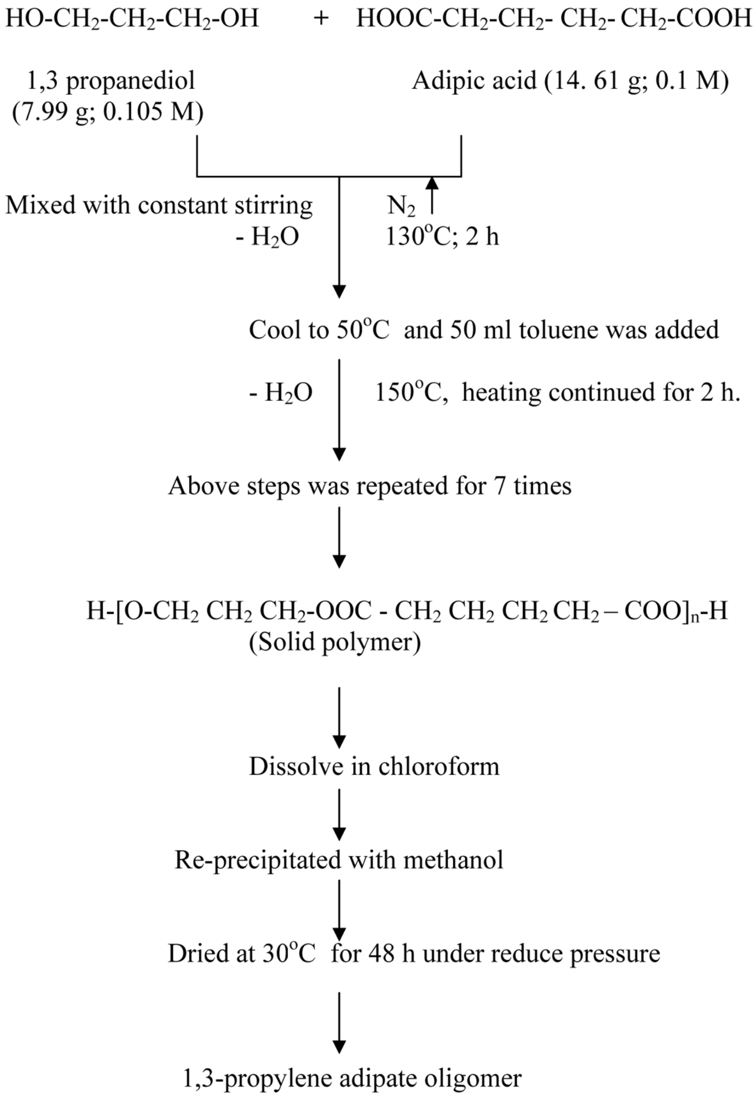
Scanning Electron Microscopy

The surface morphology of original and degraded polyester films was examined by Scanning Electron Microscope (SEM) Model JEOL: JXA-840A equipped with an electron probe micro-analyzer system. The films were coated with a gold coating in order to have good conductivity.

RESULTS AND DISCUSSION

Polyester Synthesis

The synthesis of PPAd, PPSu, and copolyester PAd-co-CA was performed by a direct thermal polycondensation. The reaction was carried out in the bulk in the absence of catalyst and heat stabilizer. The water was eliminated as by-product by azeotropic distillation with toluene. The various steps involved in the synthesis of aliphatic low molecular weight polyesters are presented in Scheme 1. The



SCHEME 1 Synthesis of low molecular weight polyester.

synthesized PPAd was purified by dissolution in chloroform and re-precipitated in methanol in order to remove the unreacted monomers. In order to differentiate the properties of PPAd, the ratio of their monomers 1,3-propanediol and adipic acid was varied to get PPAd-1 (1.05:1) and PPAd-2 (1.1:1).

Solubility

The solubility of various polyesters is compared in Table 1. It is observed that the solubility of polyesters in organic solvent is strongly dependent on the chemical nature of the solvents. As can be seen from Table 1, the listed solvents are quite different in nature, they include species that are acidic such as DMSO with strong hydrogen bonding group or close to neutral such as chloroform. All solvents that dissolve polyesters are organic substances that enable effective interaction of these solvents with the polyester chains through the formation of hydrogen bonds with oxygen. The solvents are of relatively low dielectric constant and relatively large size. It may be noted that all the samples exhibit on the whole similar solubility pattern despite of their different composition. In particular, they have good solubility in acetone, THF, DMF, and DMSO, which is an important quality in view of application because it avoids the use of chlorinated solvent in processing such as casting or microsphere preparations.

Structural Characterization

The structures of the polyesters were examined by ^{1}H-NMR and FT-IR analysis. In the ^{1}H-NMR spectra of the polyesters the methylene (CH_2) protons of the succinic ester moiety appear at 2.63 ppm. The middle methylene protons of adipic ester moiety appear at 2.33 ppm. The terminal and central methylene protons of the 1,3-propanediol residue appear at 1.65–1.9 ppm and 4.15– 4.2 ppm, respectively. There is a difference in the intensity of peak at 2.18 ppm due to the middle methylene proton in PPAd-1, PPAd-2 that may be due to the difference

TABLE 1 Solubility Behavior of Low Molecular Weight Polyesters in Different Solvents

	PPAd-1		PPAd-2		PPSu		PAd-co-CA	
Solvents	RT	BP	RT	BP	RT	BP	RT	BP
Water	i	i	i	i	i	i	i	I
Chloroform	s	s	s	s	s	s	s	s
Acetone	s	s	s	s	s	s	s	s
DMF	s	s	s	s	s	s	s	s
DMiO	s	s	s	s	s	s	s	s
THF	s	s	s	s	s	s	s	s
Hexane	i	i	i	i	i	i	i	i
Ethyl ether	i	—	i	—	i	—	i	—

s—soluble; i—insoluble; BP—at boiling point; RT—at room temperature (30°C).

in concentration of the monomers. The composition of the polyesters was determined from the relative intensities of the peaks due to the methylene group of the succinic ester moiety, adipic ester moiety, and to the terminal methylene group of the 1,3-propanediol residue. It can be concluded that the composition of the copolyesters is in good agreement with those expected from the composition of the feed.

In the FT-IR spectra of polyesters, the common characteristic bands observed are: strong band in the region at 1734–1735 cm^{-1} $-C{=}O$ (Stretch) indicate aliphatic ester groups. $O-H$ (Stretch) at 3433–3439 cm^{-1}, $-CH_2-C$ ($C-H$ Stretch) at 2927–2969 cm^{-1}, $-CH_2-C$ ($C-H$ bend) at 1454–1474 cm^{-1}, $C-C{=}O-O$ (Stretch) at 1260–1267 cm^{-1}, $C-C-O$ (Stretch) at 1035–1056 cm^{-1} and $C-O-C$ (Stretch) at 1163–1167 cm^{-1}, respectively [17].

The molecular weights of the polymers have been measured by GPC using THF as solvent and polystyrene as standard. All the polyesters gave similar type of molecular weight distribution. On the basis of the monodispersed polystyrene calibration, the GPC peak molecular weight was estimated. The number average molecular weights (M_n), weight average molecular weight (M_w) and polydispersity measured by GPC are listed in Table 2. The number average molecular weights of the polyesters ranged from 1979 to 2650 g/mol, while the polydispersity index was in the range 2.37–2.94. It can be observed from Table 2 that the diols content has an effect on the molecular weight. The molecular weight is higher in case of PPAd-2 and lower in PPAd-1, PPSu, and copolymer.

The intrinsic viscosity $[\eta_{int}]$ was determined by Huggins equation for dilute polyester solution. The intrinsic viscosities of polyesters are presented in Table 2. From Table 2, it is found that the intrinsic viscosity of PPAd-2 is more than the other homopolyesters and

TABLE 2 Intrinsic Viscosity and Molecular Weight Data of Polyesters

Polyesters	$[\eta_{int}]$ (dL/g)	M_n^a (g/mol)	M_n^b (g/mol)	M_w^b (g/mol)	PD^b
PPAd-1	0.302	2400	2559	6107	2.38
PPAd-2	0.438	2540	2675	6340	2.37
PPSu	0.334	2200	2257	5633	2.49
PAd-co-CA	0.369	2000	1979	5828	2.94

$[\eta_{int}]$: Intrinsic viscosity carried out in chloroform using Tuan-fouss viscometer at 30°C.

M_n^a: Number average molecular weight determined by end-group titration.

M_n^b: Number average molecular weight determined by GPC.

M_w^b: Weight average molecular weight determined by GPC.

PD^b: Polydispersity index (M_w/M_n) determined by GPC.

copolyester. The intrinsic viscosity results of polyesters are consistent with molecular weight results.

Thermal Analysis

DSC thermograms of the synthesized aliphatic polyesters with melting endotherms are shown in Figure 1. Table 3 shows the melting temperature and heat of fusion of the homopolymers and copolymer. From Table 3, it is observed that the heat of fusion is more in case of PPAd-2 and it is less in other homopolyesters and copolyester. The low heat of fusion in PPAd-1, PPSu, and copolyester may be due to low molecular weight and asymmetry in polyesters structure. Also, there was no appreciable weight loss up to 240°C. This indicates that no thermal degradation takes place during synthesis. Hence, there is no need to use a heat stabilizer during the synthesis of these polyesters.

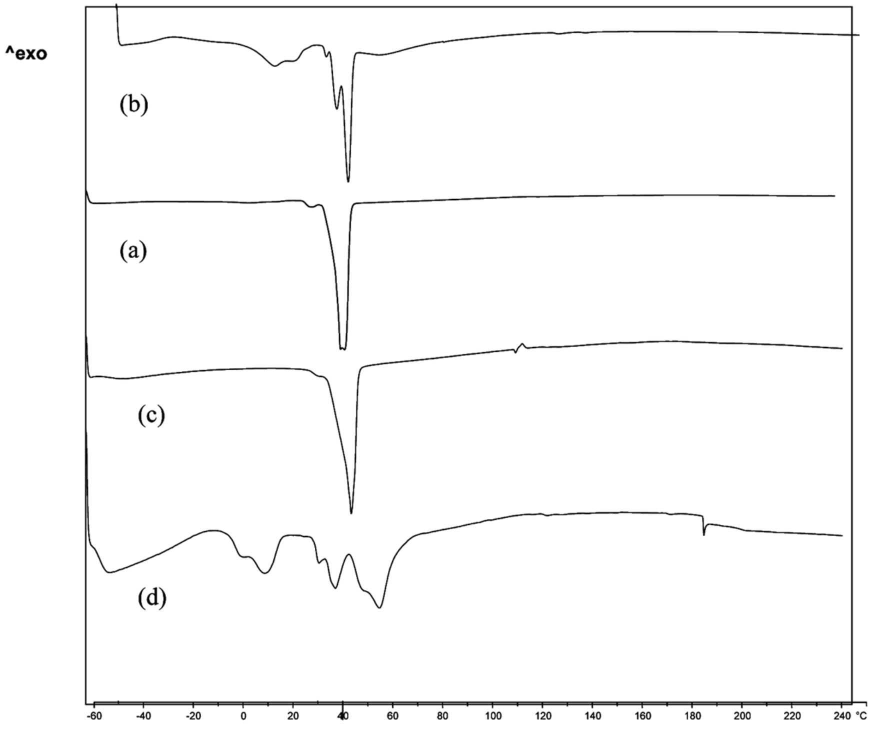


FIGURE 1 DSC curves of (a) PPAd-1, (b) PPAd-2, (c) PPSu, and (d) PAd-co-CA.

TABLE 3 Thermal Characterization of Polyesters

Polyesters	T_g (°C)	T_m (°C)	ΔH (J/g)
PPAd-1	–23.7	45.5	47.4
PPAd-2	–38.7	46.4	77.4
PPSu	–28.3	47.2	56.7
PAd-co-CA	–8.9	56.9	17.9

Biodegradation Studies

Enzymatic Degradation

Aliphatic polyesters are more susceptible to enzymatic degradation in comparison with aromatic ones, and therefore they are currently proposed as biodegradable commercial materials. The enzymatic degradation of aliphatic polyesters is related to the chemical structure as well as to the hydrophilic/hydrophobic balance within the main chain, and the degree of crystallinity of the material [2,18–19]. It is also affected by the degradation temperature, as well as by the species of enzyme used. For aliphatic polyesters, as the temperature increases, approximating the melting temperature, enzymatic hydrolysis is accelerated [20]. Thus, quite satisfactory hydrolysis rates are obtained when the temperature is 10–20°C lower than the polymers melting point. For poly(butylene succinate) enzymatic degradation by *Pseudomonas* species at pH 7.0, could not be detected after 20 h at 50°C and as a consequence it was assumed not to be biodegradable. Furthermore, with increasing temperature, chemical hydrolytic cleavage of ester bonds begins, without any need of enzyme. In the present study, enzymatic hydrolysis was carried out at 37°C.

Figure 2 shows the normalized weight loss per unit area of the polyester films as a function of time. As can be seen, a rather abrupt weight loss occurs during the first few hours of biodegradation (12–24 h), whereas afterward the weight loss continues, but at a slower rate. This might be due to the easier degradation of amorphous mass during the first few hours.

As it is well known,, enzymatic hydrolysis is a heterogeneous process. Enzymes are attached on the surface of an insoluble substrate and hydrolysis takes place via surface erosion. Thus, the hydrolysis rate decreased after consumption of the amorphous material of the surface. Afterward, a layer of crystalline domains remains, where only slow degradation may occur. They inhibit penetration of water into the body of the film, resulting in decreased rates of hydrolysis. On addition of fresh lipase after 72 h incubation of film, the rate of hydrolysis

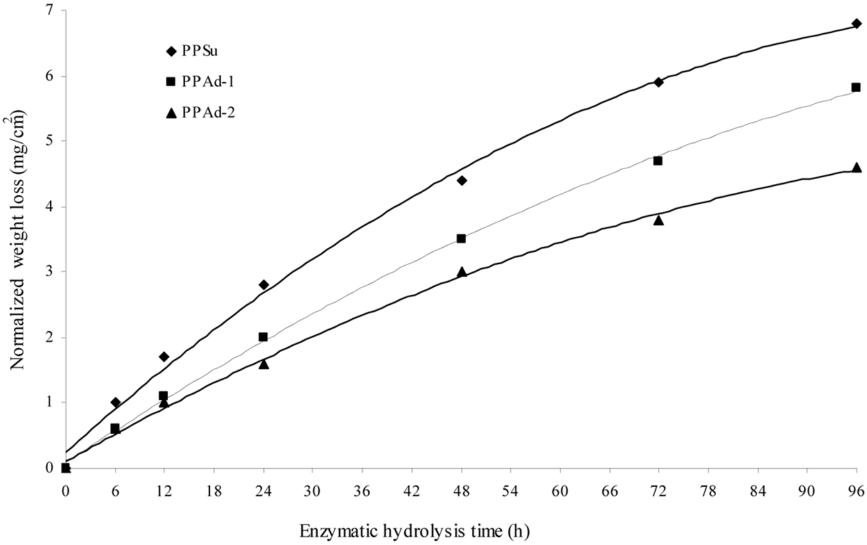


FIGURE 2 Normalized weight loss per unit area of polyesters with incubation time in enzymatic degradation.

slightly increases. PPSu exhibits the highest weight loss values, whereas PPAd-2 showed the lowest ones. For PPAd-1, weight loss rate seemed to be slightly more than that of PPAd-2. Because in the present study the prepared polyesters have almost identical molecular weights, crystallinity seems to be the predominant factor that controls the biodegradation rates. Therefore, the higher degree of crystallinity of the PPAd-2 may be responsible for a lower degree of biodegradation compared to that of PPAd-1 and PPSu. On comparing the degradability between the adipates, PPAd-1 is less crystalline and shows more degradability compared to PPAd-2. This result is also supported by heat of fusion data of DSC. Similar type results were also reported by Kang and Park [19] in their biodegradability study of poly(butylene adipate-co-succinate)/poly(butylene terephthalate). In the studied polyesters the molecular structure has much less effect on biodegradation rather than physical structure. This may be the case because the distance between ester groups differs only by two methylene groups as in PPAd.

The scanning electron micrographs of PPSu, PPAd-1, and PPAd-2 films before and after enzymatic degradation are presented in Figure 3. One can observe that the surface of original film changes upon degradation. The original film (Figures 3a–c) was smooth and homogeneous, degradation occurs randomly at the film surface (Figures 3a′–c′) making it rough by forming surface cracks and surface irregularities. It is clear that the action of *Rhizopus delemar* lipase led

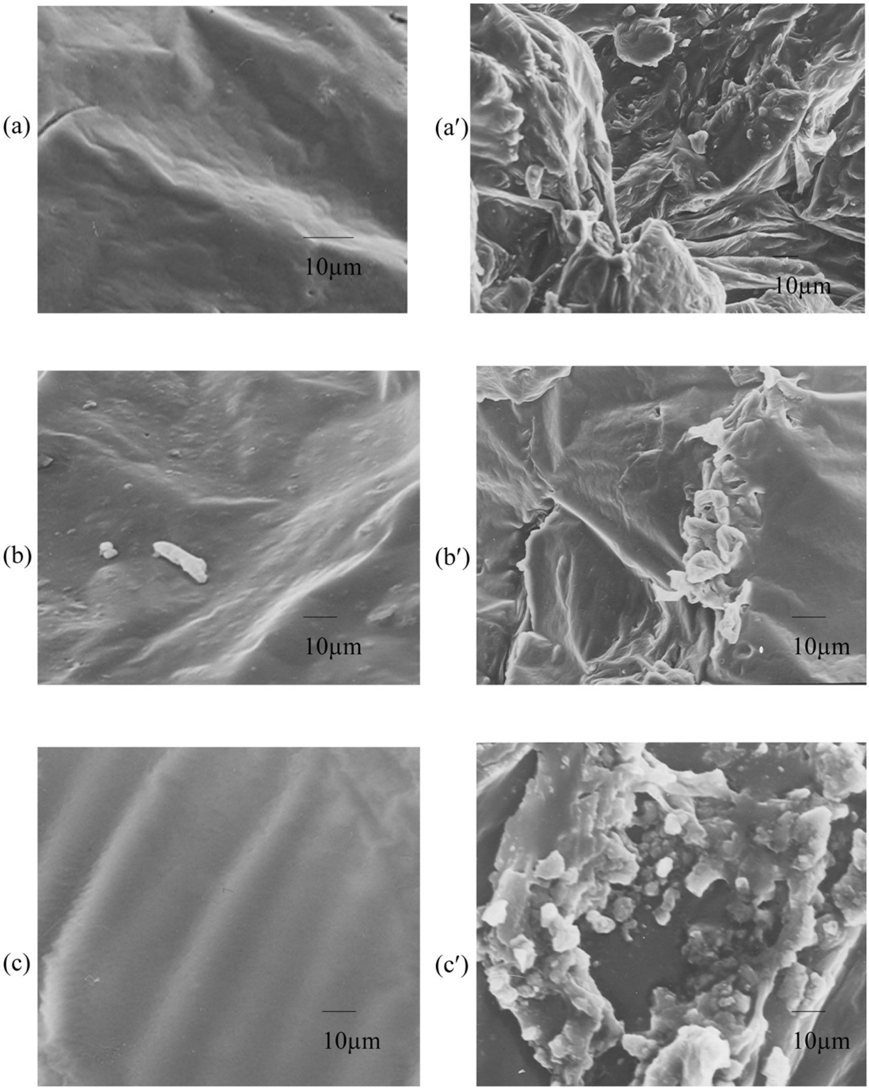


FIGURE 3 SEM image of enzymatic degraded polyester films (a) PPSu original, (a′) after 12 h, (b) PPAd-1 original, (b′) after 12 h, (c) PPAd-2 original, and (c′) after 96 h.

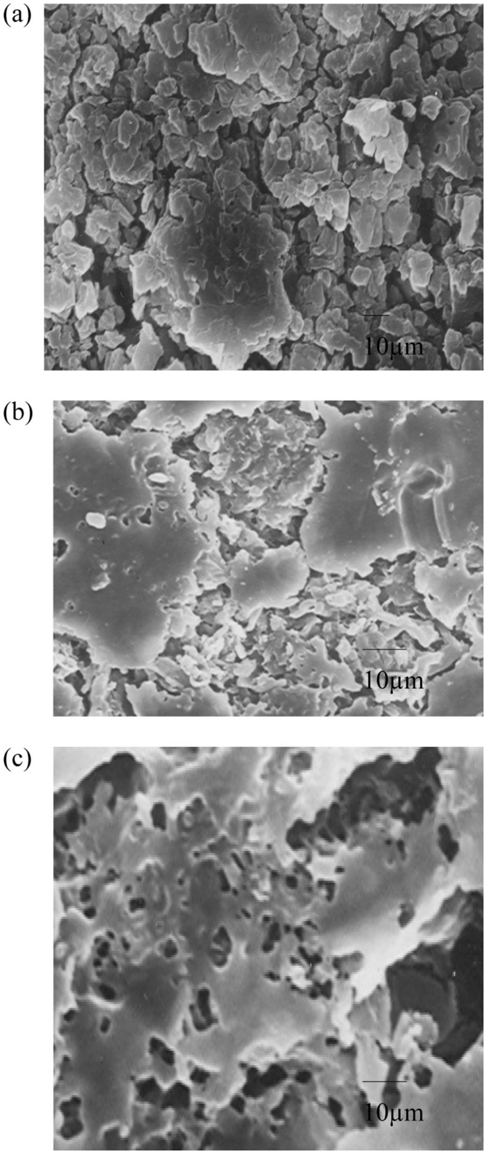


FIGURE 4 SEM image of soil burial degraded film after 35 days (a) PPSu, (b) PPAd-1, and (c) PPAd-2.

to the formation of a rough surface with large holes, which also extend to a large depth within the film mass. The effect of the enzymes is more pronounced in the case of PPSu compared to PPAd polyesters.

This indicates that the biodegradation depends strongly on the crystallinity of the polymers.

Soil Burial Degradation Test

Figure 4 shows the SEM micrographs of PPSu, PPAd-1, and PPAd-2 films after 35 days soil burial degradation; it shows the formation of holes in the polymeric film surface as a result of degradation. In soil burial degradation, the effect of microorganisms arises on the surface of the polymer [21–23]. The calculation of the biodegradation rate from films weight loss in soil burial test constitutes a practical problem because the soil sticks on the film surface, and weight measurements are not accurate.

CONCLUSIONS

A series of low molecular weight aliphatic polyesters were synthesized from 1,3-propanediol and adipic acid and succinic acid and 1,4-cyclohexanedimethandiol by thermal polycondensation without catalyst and heat stabilizer. The solubility results of polyesters indicated that all the polymers are soluble in acetone, THF, DMF, DMSO, and so on GPC results revealed that the number average molecular weight of polyesters is in the range of 2 to 3 thousands and the molecular weight is less in the copolyester. The thermal properties characterized by DSC indicated that the homopolyesters have low glass transition and melting temperature. Therefore, their dimentional stability may be lost at temperatures not much higher than room temperature. This may narrow the field of their practical applications. However, in copolyester PAd-co-CA has a low T_g but its melting point is high. Hence, the dimensional stability may not be lost in temperature slightly higher than room temperature: Also, there is no degradation of polymers during synthesis. On exposure of polyester films to *Rhizopus delemar* lipase in phosphate buffer, films become brittle and the brittleness increases with incubation time. The morphology of the original polyester films changes upon degradation. The molecular structure has much less effect on biodegradation rather than physical structure. Hence, the crystallinity is responsible for the biodegradation rate in the polyesters.

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