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Synthesis, characterization and biodegradation studies of poly(ester urethane)s

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Abstract

Bis-isocyanoto polyester was synthesized by the polymerization of PPSe with MDI and reacted with 1,3-propanediol chain extender to obtain poly(ester urethane)s. The effect of chain extender and PPSe content in polyurethane was investigated. The polymers were characterized by ^{1}H NMR, FT-IR, viscosity measurement, TGA and XRD. Their biodegradability was investigated by the hydrolytic degradation in NaOH solution (3% and 10%); enzymatic degradation by *Rhizopus delemar* lipase and soil burial degradation using garden-composted soil. Furthermore, the degraded film was characterized by molecular weight, intrinsic viscosity, DSC, XRD, FT-IR and surface morphology by SEM. The biodegradation study revealed that hydrolysis and soil burial degradation affected morphology of the PEUs. Hydrophobicity and hard segment seem to resist the hydrolytic and enzymatic degradability of PEU. Hydrolytic degradation was very rapid in 3% and 10% NaOH solutions at 37 °C, within 2 days 20% weight loss was observed. PEUs showed a much slower degradation rate under the *R. delemar* lipase at 37 °C. Experimental data showed that as soft segment increases biodegradation rate decreased. A significant rate of degradation was occurred in all PEU samples under soil burial condition. Surface morphology, which interconnected to good adhesion of bacteria on polymer surface, is considered to be a factor sensible for the biodegradation rate under soil burial condition.

Keywords: Poly(ester urethane)s; Biodegradation; *Rhizopus delemar* lipase; Soft segments

1. Introduction

Polyurethanes have been widely used in various industrial applications due to their versatile properties and some of them are biodegradable and have been used as biomaterial application [1–3] for the manufacture of medical devices such as artificial heart diaphragms, valves, vascular grafts, catheters, neurological lead insulation and connecting modules for cardiac pacemakers [4]. The use of biodegradable polyurethanes may be as an alternative to replace conventional non-degradable polymers such as polyethylene and polypropylene in the fabrication of packaging films in near future and could contribute to the solution of the environmental problem [2]. Polyurethanes made from aliphatic polyesters obtained from renewable resources are expected to be one of the most economically competitive biodegradable polymers [5]. The biodegradability of these polymers depends mainly on their chemical structure and especially on the hydrolysable ester bond in the main chain, which is susceptible to microbial attack and other factors such as molecular weight, degree of crystallinity and morphology [6].

Recently, polyurethanes were reported from poly(butylenes succinate) (PBS), polyethylene glycol (PEG), and 4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI) without any chain extender in order to obtain moderate molecular weights [1]. Darby and Kaplan [7] suggested that polyester-based polyurethanes are much more susceptible to fungal degradation than polyamine-based polyurethanes and the enzymatic attack could occur only if there were at least three adjacent methylene groups of unbranched carbon chains between the urethane linkages of the polymer, for appreciable enzymatic attack. Kim and Kim [6] synthesized polyurethanes from polyester polyols, ethylene glycol and aromatic or aliphatic diisocynate and studied the relationship between the chemical structure of polyurethanes and biodegradation under composting condition. They suggested that hydrolytic and enzymatic degradation decreases with an increase of the polyester chain length.

Of particular interest with respect to our investigation of 1,3-propanediol as an alternative to 1,4-butanediol in segmented

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poly(ester urethane) as a first step towards the understanding of the microbiological susceptibility of polyurethanes. Also, in recent years, more attractive processes have been developed for the production of commercially high quality 1,3-propanediol derived from renewable resources with low cost [8–11].

In the present article, synthesis, characterization and biodegradation study of the MDI-based polyurethanes with PPSe as soft segments were described. The chain extender 1,3-PDO was employed to synthesize the polyurethanes. The PPSe soft segments (M_n = 4700 g/mol) are explored for study; physical properties and biodegradability of PEUs with respect to PPSe were compared.

2. Materials and methods

2.1. Materials

1,3-Propanediol (1,3-PDO, 98%), sebacic acid (99%), tetra-*n*-butyl titanate $Ti(OBu)_4$ (97%), 4,4′-methylenediphenyl diisocyanate or 4,4′-methylene bis(phenyl isocyanate) (MDI), phosphate buffer (pH 7.2) and *Rhizopus delemar* lipase (Fluka, 0.73 U/mg) were purchased from the Sigma–Aldrich Chemical Co. Methanol, chloroform, acetone, 1-methyl-2-pyrrolidone (NMP), tetrahydrofurane (THF), *N*,*N*-dimethylformamide (DMF), dimethylsulphoxide (DMSO), etc., were purchased from E-Merck. All the reagents were used as received without further purification.

2.2. Synthesis of segmented poly(ester urethane)s

Segmented poly(ester urethane)s were synthesized via two-step polymerization process of PPSe with 1,3-PDO and MDI [1–3,6,12,13]. The synthesis of a segmented poly(ester urethane) with 89 wt% soft segment concentration is used here as an example. One-liter glass reaction kettle was equipped with a mechanical stirrer, thermometer, heating mantle and a gas inlet and outlet for continuous flow of nitrogen MDI (5.0052 g, 0.02 mol), PPSe (47.00 g, 0.01 mol) and DMF (100 ml). The mixture in the reactor was stirred under constant mixing and the reaction temperature was maintained at 60 °C for 2 h. In the second step, the chain extender 1,3-propanediol (0.7610 g, 0.01 mol) was added to the reactor under vigorous stirring. The mixture was then again maintained at 60 °C for another 1 h. The poly(ester urethane) formed was filtered, washed with methanol several times and dried in a vacuum oven at 65 °C for 24 h.

The synthesis of polyurethane without soft segment was carried out by reacting MDI and 1,3-propanediol in DMF (100 ml), the OH/NCO molar ratio maintained was 1:1. The other conditions are the same as described above.

2.3. Characterization of poly(ester urethane)s

2.3.1. Solubility

The solubility of the poly(ester urethane)s was performed by keeping 0.25 g of polymer in 50 ml solvent (water, chloroform, THF, DMSO, NMP, DMF, acetone, *n*-hexane, ethyl ether, ethyl acetate, ethanol, etc.) the mixture was stirred for 30 min. Then it was kept for 4 h at room temperature (30 °C). The mixture was filtered through pre-weighed sintered-glass crucible (porosity 2 μm) and then crucible was dried under vacuum to constant weight, from the weight of dissolved polymer the solubility was determined.

2.4. ^1H NMR spectra

^1H NMR spectra of poly(ester urethane)s were recorded by NMR center, IISC, Bangalore on GSX 400 NMR spectrometer operated at 400 MHz in DMSO-d_6 as solvent and tetramethylsilane as the reference standard.

2.5. FT-IR spectra

FT-IR spectra of synthesized and degraded poly(ester urethane) samples were recorded from the Department of Pharmacy, RTM Nagpur University, Nagpur on FTIR-8101A, Shimadzu spectrophotometer by KBr pellet technique.

2.6. Intrinsic viscosity

The intrinsic viscosity [η_{int}] of synthesized and degraded poly(ester urethane)s in NMP was measured at 30 °C using a Tuan-Fouss viscometer. From the time flow of solution and solvent the [η_{int}] was calculated. The M_n and M_w of polymer were found with universal calibration curve. A universal calibration curve was constructed using the polystyrene standard, whose intrinsic viscosity and molecular weight is known by GPC technique. The intrinsic viscosity of segmented polyurethane is compared with the intrinsic viscosity of polystyrene standard. The intrinsic viscosity and molecular weight from data point were plotted in accordance with the log–log representation of the Mark-Houwink equation. The molecular weight value of each polyurethane sample is matched with molecular weight.

2.7. Differential scanning calorimetry

DSC scans were recorded using a Mettler Toledo DSC-822 analyzer from SAIF, Cochin. The DSC scans were recorded under a nitrogen atmosphere in the temperature range from −50 to 450 °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 DCS scans as the midpoint of the heat capacity change.

2.8. Thermogravimetric analysis

TG thermograms of the samples were recorded on PerkinElmer Pyris Diamond TG/DTA from SAIF, Cochin, at a heating rate of 10 °C/min under nitrogen atmosphere in the temperature range of 28–600 °C.

2.9. X-ray diffraction

X-ray diffraction (XRD) pattern of original and degraded samples was recorded on a "X"Pert PRO PANalytical X-ray diffractometer using a Cu Kα radiation (λ = 1.5418 Å). Measurements were performed in the 2θ range from 5° to 80°. From the XRD data, the degree of crystallinity was calculated as the ratio of the total intensities of the crystalline reflections and the overall diffraction pattern area [14].

2.10. Biodegradability studies

2.10.1. Film preparation

In order to study the biodegradation of poly(ester urethane)s, the films with 3 cm × 3 cm in size and approximately 0.2 mm thickness were prepared in a hydraulic press by pressing the synthesized poly(ester urethane)s between two Teflon plates for a minute under a pressure of 2.5 tonnes/cm^2 below the samples melting temperature. The pressed films were stored at room temperature for 1 week before use in order to reach the equilibrium crystallinity. Then the films were cut into square pieces of dimensions 10 mm × 10 mm × 0.2 mm.

2.10.2. Hydrolytic degradation

Poly(ester urethane)s film samples (10 mm × 10 mm and thickness 0.2 mm) were weighed and placed in a petri dish containing 10 ml NaOH solution 3% and 10%, respectively. The films were incubated in an orbital-shaking incubator at temperature 37 °C; the films were removed from the solution at regular time interval of 2 days. The films were washed with deionized water, dried under vacuum at 50 °C and weighed to constant weight. The extent of biodegradation was quantified as the weight loss of samples as

$$\%\ \text{weight loss} = \left\{ \frac{W_0 - W_t}{W_0} \right\} \times 100$$

where W_0 is the weight of the original films and W_t is the weight of residual films after the degradation for different times.

2.10.3. Enzymatic degradation

Poly(ester urethane)s films (10 mm × 10 mm and thickness 0.2 mm) were placed in petri dishes containing 10 ml phosphate buffer solution (pH 7.2) with 1 mg *R. delemar* lipase. The petri dishes were then incubated in duplicate at 37 °C in an incubator, for 96 h, while the media were replaced after 72 h. Blank experiment without enzyme was also performed in phosphate buffer (pH 7.2) containing poly(ester urethane)s films. After a specific interval of incubation, the films were taken out from the petri dish, washed with deionized water and dried under vacuum at 30 °C to constant weight. The actual degradation by lipase was calculated by subtracting the weight loss in blank experiment from the total weight loss.

2.10.4. Soil burial degradation

The soil burial degradation test of segmented poly(ester urethane) films was conducted as per ISO: 846. Polymer films (15 mm × 15 mm and thickness 0.2 mm) were buried in soil (pH 7.5, water content capacity 45%) in which the relative humidity maintained was 50–60% (maximum water-holding capacity) by spraying water. The temperature was thermostated at 30 °C in a humidity chamber (Sonar Co.). The soil used in this study had been taken from the garden of VNIT, Deemed University, Nagpur, India. The soil was conditioned for 4 weeks before it was used for the actual test. The microbial activity of the soil was tested by using a cotton strip which loses its tensile strength within 10 days of exposure to soil. The buried poly(ester urethanes) films were removed after 30 days, then at regular interval of 10 days. Recovered film was washed with water, dried in vacuum at 30 °C and weighed to constant weight.

2.11. Scanning electron microscopy

The effect of biodegradation upon the surface morphologies of original and degraded poly(ester urethane) films were examined by scanning electron microscope (SEM), SEM model JEOL: JXA-840A equipped with an electron probe microanalyzer system. The film was coated with a gold coating in order to have a good conductivity.

3. Results and discussion

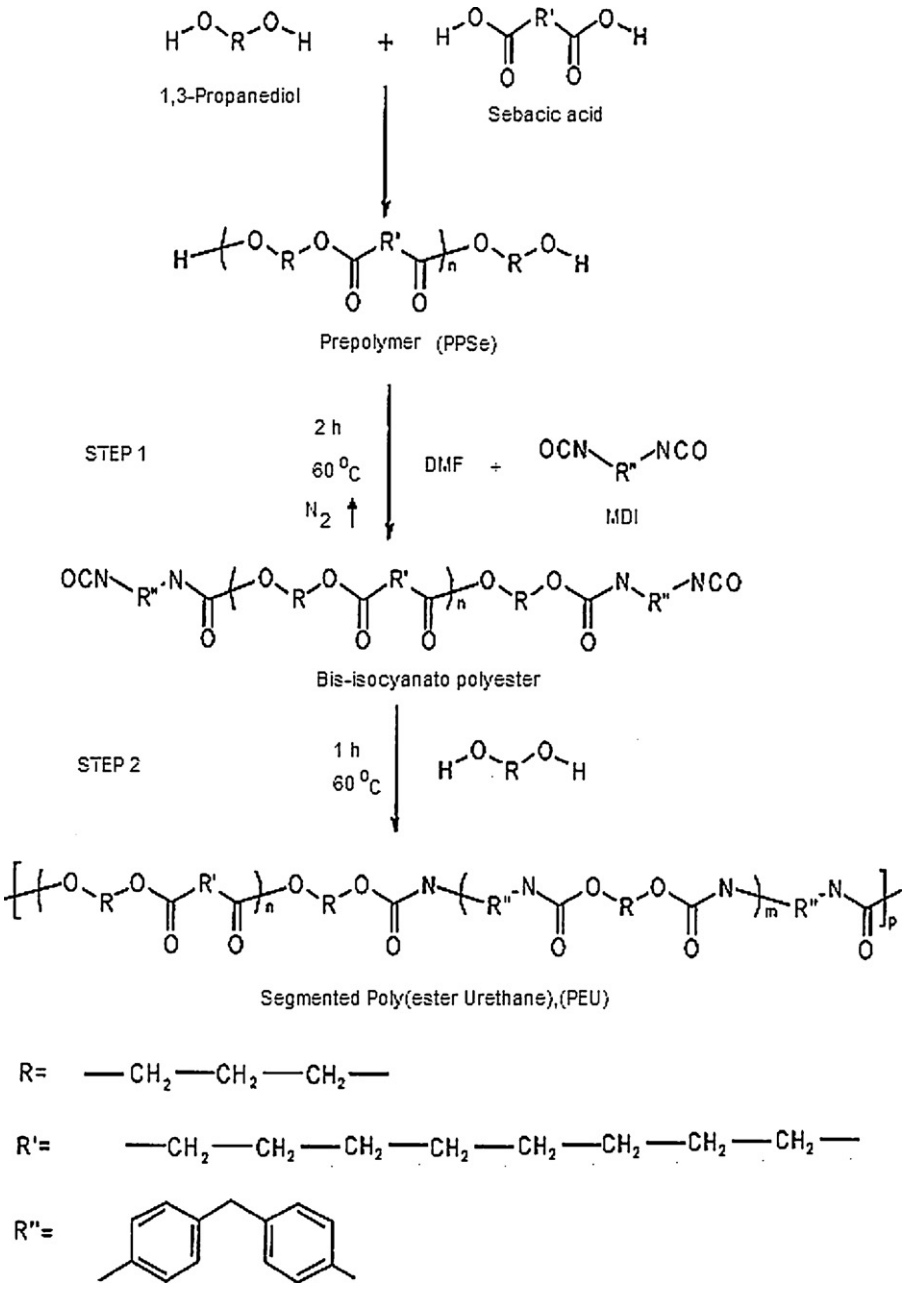
3.1. Synthesis of segmented poly(ester urethane)s

The segmented poly(ester urethane) was prepared by the "two-step" process. The steps involved in the preparation are shown in Scheme 1. The α,ω-bis-hydroxyl-terminated poly(1,3-trimethylene sebaciate) synthesized as reported earlier [8] was used for the synthesis of segmented poly(ester urethane)s using MDI and 1,3-PDO as a chain extender. The concentration of polyesters fed in the reaction mixture was varied in order to obtain polyurethanes consisting of various proportions of polyester soft segments.

Initially, bis-isocyanato-polyester was prepared from bifunctional pre-polymers, poly(1,3-propylene sebaciate) PPSe, with excess of MDI in glass reaction kettle. Then the segmented polyester-based urethanes were synthesized by a chain extension reaction between MDI and 1,3-PDO into the reactor under vigorous mixing. The polyester was first reacted with excess of MDI for 2 h in DMF at 60 °C. The bis-isocyanato-polyester was then reacted with 1,3-PDO for another hour. The final polymer was dissolved in minimum quantity of NMP and then precipitated with methanol and dried under vacuum at 65 °C for 24 h. In all reactions, the OH/NCO molar ratio maintained was 1:1. Since a linear structure of polyurethane is desired, the application of the low reaction temperature is required [6,12,15]. Therefore, a temperature of 60 °C was maintained throughout the experiment.

The molar ratio of PPSe, 1,3-PDO and MDI were altered to obtain the poly(ester urethane)s with varied hard segment. The hard segment in the polyurethane was derived from the 1,3-PDO and MDI [13,16]:

$$\%\ \text{hard segment content} = \frac{\text{weight of MDI} + \text{weight of 1, 3-PDO}}{\text{weight of MDI} + \text{weight of 1, 3-PDO} + \text{weight of polyester}}$$



Scheme 1. Synthetic route and structure of the segmented poly(ester-urethane) from 1,3-propanediol and sebacic acid.

The theoretical hard segment content is equivalent to the weight percentage of charged 1,3-PDO and MDI. The synthesized polyurethanes with different % of hard segment and different molecular weights are listed in Table 1. It has been observed that an excess of the isocyanate group in the polymerization reaction can cause the formation of allophanate, which results in branching/crosslinking.

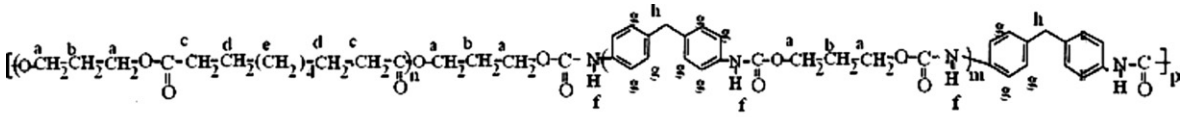
Table 1
Segmented poly(ester urethane)s with different hard segment contents and their molecular properties

Polymer	PPSe:1,3-PDO:MDI	$[\eta_{int}]$ (dl/g)	M_n (g/mol)	M_w (g/mol)	PD
PEU-1	0:1:1	0.73	63,390	83,700	1.4
PEU-2	1:3:4	0.74	53,700	83,950	1.6
PEU-3	2:2:4	0.75	64,120	84,200	1.6
PEU-4	3:1:4	0.76	64,400	84,450	1.6

$[\eta_{int}]$ carried out in NMP using Tuan-Fouss viscometer at 30 °C.

3.2. Solubility

The segmented poly(ester urethane)s are insoluble in chloroform, THF, acetone, methanol and toluene. It is partially soluble in DMF, DMSO and soluble in NMP at room temperature and completely soluble at boiling temperature of DMF and DMSO. The insolubility of poly(ester urethane) samples in most of the solvents may be due to the existence of urethane linkages and high molecular weight of polymer.



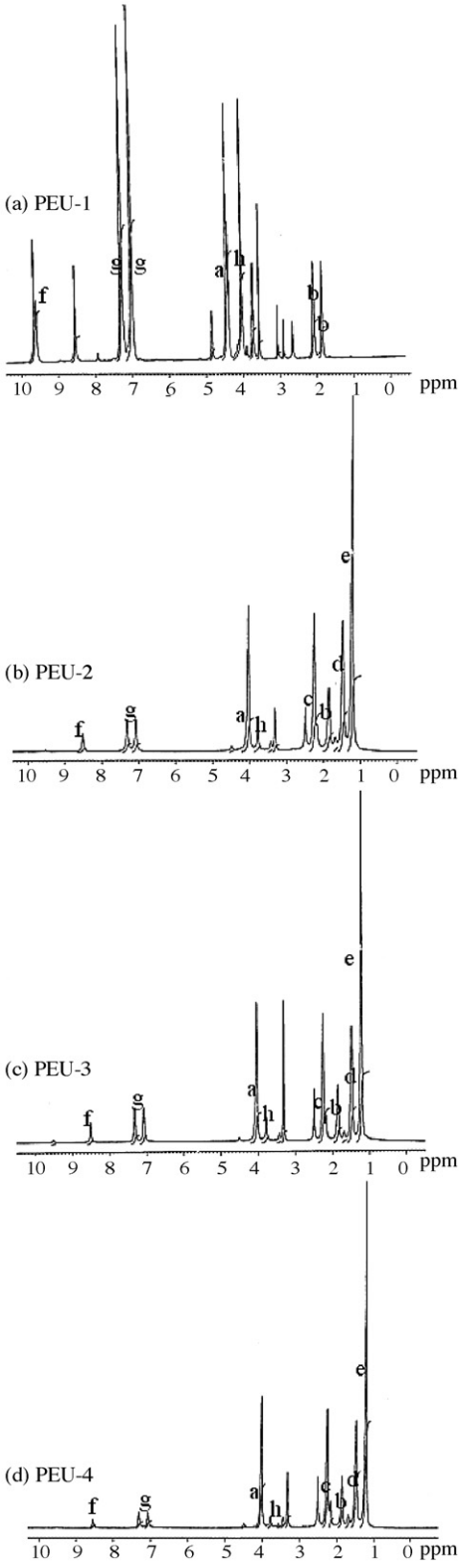


Fig. 1. ^{1}H NMR spectrums of poly(ester urethane)s in DMSO-d_6.

3.3. Structural characterization

3.3.1. ^1H NMR spectra

Since segmented PEUs are insoluble in chloroform and THF, we chose DMSO-d_6 as solvent for ^{1}H NMR measurement. Fig. 1 shows ^{1}H NMR spectrums of segmented polyurethanes. The urethane protons are observed at $\delta = 9.54$ ppm (s, –N*H* in urethane). The aromatic protons from the MDI appeared at $\delta = 7.32$ and 7.09 ppm (m, –C_6H_4– in MDI), respectively. The methylene proton from MDI was assigned to the peak at $\delta = 3.77$ ppm (s, –C_6H_4–CH_2–C_6H_4–). The methylene protons from 1,3-PDO residue assigned at $\delta = 4.13$–4.17 ppm (t, –CH_2–CH_2–CH_2–) and $\delta = 1.83$–1.96 ppm (m, –C_2–CH_2–CH_2–), respectively. The methylene protons from PPSe soft segments observed at $\delta = 1.22$ ppm (m, –CH_2–CH_2–$(CH_2)_4$–CH_2–CH_2–), 1.60 ppm (m, CH_2–CH_2–$(CH_2)_4$–CH_2–CH_2) and 2.29 ppm (t, –CH_2–COO), respectively.

The assignment of the chemical shifts in ^{1}H NMR verifies the molecular structure and confirms copolymer formation. The soft segment contents are usually estimated with the weight percentage of pre-polyester in feedings. More accurate information on the ratio of soft segment to hard segment can be obtained from ^{1}H NMR and molecular weight measurement. When small co-monomer units are assembled randomly into a polyurethane molecule: ~~~~~~~ABAABABBBAAABBAB~~~~~~~~ the resulting random copolymer has an overall average structure that is fairly uniform and forms a single homogeneous phase containing this average composition and structure. When the growth of a copolymer molecule produces fairly large area (blocks) of one monomer unit alternating with fairly large area (blocks) of another monomer unit: ~~~~~~~AAAABBBB~~~~~~~~ these blocks will tend to separate into microphase or domains and each type of domain will contribute independently to the properties of the block copolymer [12]. In one-step synthesis of polyurethane, the polyol generally forms fairly large blocks even before they are reacted with the polyisocyanate [16]. Furthermore, in two-step synthesis of polyurethane, the first stage pre-polymer forms one type of block (often called the soft block), while the reaction of chain extender with isocyanate forms another type of block (often called the hard block). Thus, polyurethane is block copolymer, which is presented with general formula $(A_nB_m)_p$ [12,15,16]. The values of n, m and p are average values. In many cases, the separation of these blocks into domains has a major synergistic effect on the properties of the resultant polymer.

3.3.2. FT-IR spectra

FT-IR spectrums of segmented polyurethanes are shown in Fig. 2. The absorption bands around 3314 cm^{-1} (urethane N–H stretch), $\upsilon_s(CH_2)$ at 2853 cm^{-1} and the very strong bands around 1726–1735 cm^{-1} (free urethane C=O) were assigned in the urethane linkage. The strong band at 1363 cm^{-1} was assigned to δ(NH) + υ(C–N). The band at 1310 cm^{-1} corresponds to $\omega(CH_2)$. The very strong bands 1254 cm^{-1} assigned to υ(–C–O–C) in hard and soft segments. The linkage at 1176 cm^{-1} corresponds to υ(–C–O–C) ester grouping soft segment. The $\upsilon(CH_2)_n$ band observed at 1145 cm^{-1}. The linkage at 1057 cm^{-1}

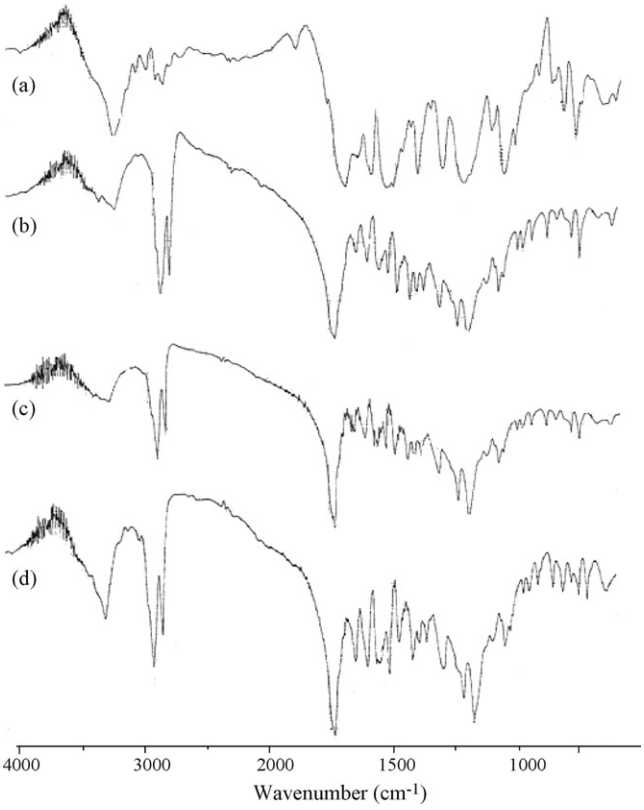


Fig. 2. FT-IR spectra of poly(ester urethane)s: (a) PEU-1, (b) PEU-2, (c) PEU-3 and (d) PEU-4.

(C–O–C) in hard segment stretch showed the formation of the urethane linkage [17]. The existence of bands for N–H and C=O of the urethane bonds indicates that the polymerization takes place.

3.4. Intrinsic viscosity and molecular weight

The results of intrinsic viscosity [η_{int}] of poly(ester urethane)s are presented in Table 1. It is found that the [η_{int}] of poly(ester urethane)s lies between 0.75 and 0.76 dl/g. The higher [η_{int}] value of poly(ester urethane)s may be due to the existence of soft and hard segments in copolymer chain. Table 1 shows the molecular weight data of polyurethanes estimated from intrinsic viscosity. The number of average molecular weight (M_n) of poly(ester urethane)s is 53,000–64,400 g/mol. The M_n and the polydispersity index (M_w/M_n) of all the poly(ester urethane)s were uniform.

3.5. Thermal properties

DSC is a commonly used tool for determining molecular organization changes, such as phase separation, glass transition and melting. The phase separation between the soft and hard segments is the main reason for the polyurethanes properties. The interaction between the soft and hard segments can increase the glass transition temperature of the soft segment and decrease the T_g of the hard segments. The DSC thermograms data of the poly(ester urethane)s are summarized in Table 2. The melting

Table 2
Thermal analysis data of the synthesized segmented poly(ester urethane)s

Polymers	T_g (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)	Weight loss (%) temperature (°C)		
					5	50	90
PEU-1	–	210	144.5	79.8	260	390	600
PEU-2	−40.5	57.9	118.8	44.1	297	430	475
PEU-3	−34.6	57.2	88.2	43.9	300	410	490
PEU-4	−27.7	57.8	69.1	39.3	287	415	430

temperature of hard segment microcrystalline declines with an increase in soft segment content meanwhile, the crystallinity of hard segment microcrystalline decreases with increasing soft segment contents [2–3]. The T_m of the poly(ester urethane)s containing soft segment are very close to PPSe [8]. Whereas PEU-1 has very high T_m which only contains hard segment. On comparing the T_g of the segmented poly(ester urethane) as a function of polyester concentration in feeding, T_g of the soft segments decreases with increasing soft segment content due to the increase of molecular aggregation of soft segments [2,13].

Heat of fusion of the segmented poly(ester urethane) decreased on increase of polyester concentration in feeding indicates that an increase of soft segment contents can reduce the crystallinity as well as the melting temperature of the polymer. Thereafter, it results in a weaker interaction of microcrystalline between polymer chains. Thus, a higher value of heat of fusion could be obtained at lower soft segment contents. It also hinders the crystallization.

In order to compare the relative thermal stability of poly(ester urethane)s, the temperatures for weight losses of 5%, 50% and 90% from TG thermograms is presented in Table 2. The 5% weight losses are considered to represent the beginning of mass loss. It can be observed that 5% weight losses in nitrogen atmosphere is in between 270 and 300 °C for all samples. This indicates that the thermal stability of the segmented polyurethanes does not significantly depend on molecular

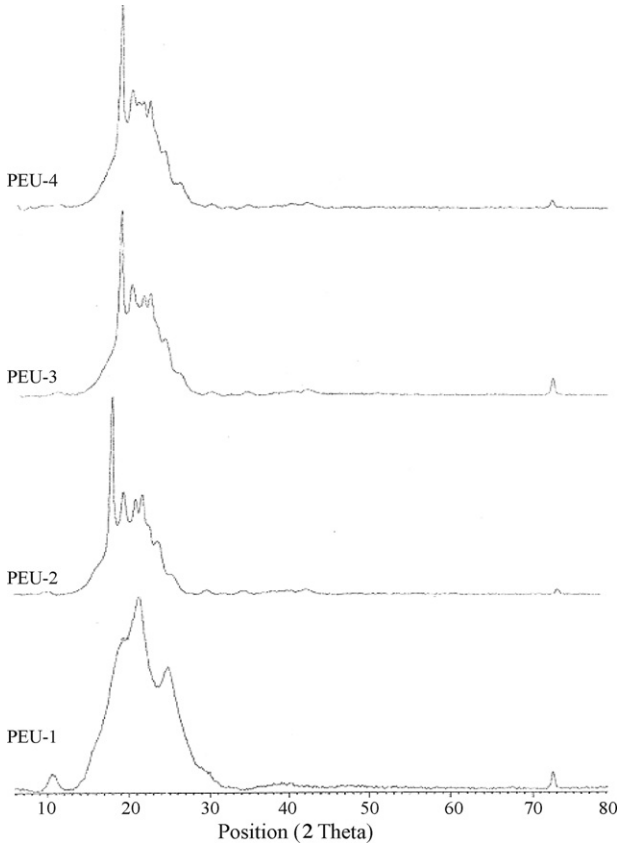


Fig. 3. XRD pattern of poly(ester urethane)s.

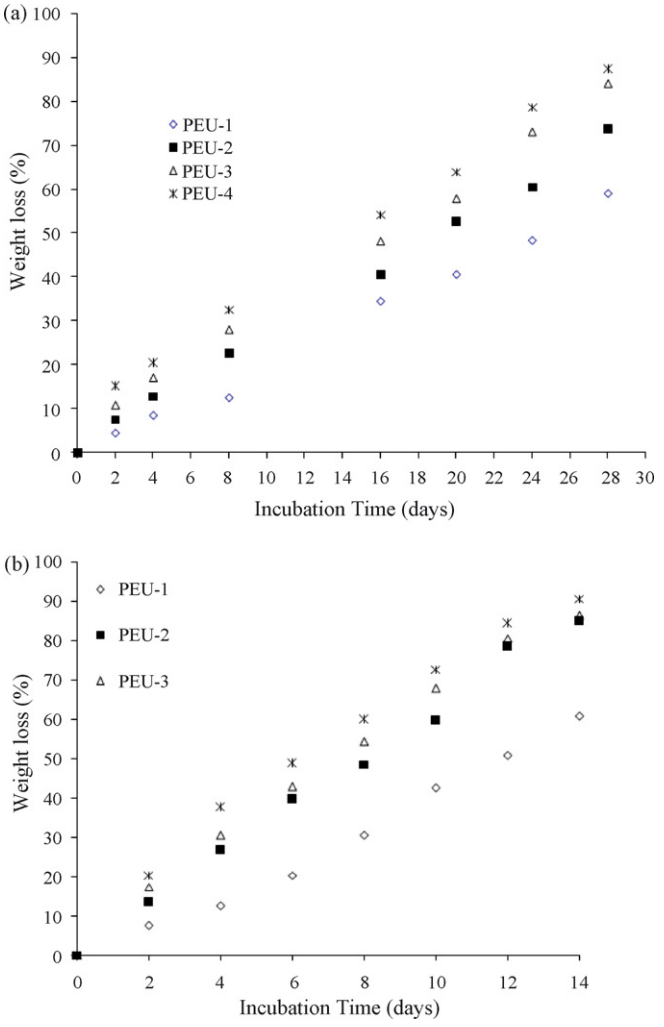


Fig. 4. Weight loss during hydrolytic degradation of poly(ester urethane)s in (a) 3% NaOH and (b) 10% NaOH.

weight and type of soft/hard segment concentration. Instead, thermal stability is more dependent on the stability of the urethane bond, which is the weakest linkage in the polyurethane structure [13]. The degradation of polyurethane in nitrogen atmosphere is a two-step process, in which the first major weight loss occurs at 380 °C and the second at 450 °C. From the value of the temperature of 90% weight loss, it is observed that the PEU-1, is most stable among the poly(ester urethane)s that does not contain the polyester soft segment [18–20]. The highest thermal stability of PEU-1 may be due to its crystalline nature and absence of soft segment. This result is also supported by the heat of fusion data of DSC. Thus, the thermal stability of the PEU-1, which had 100% hard segment, is very different from the rest of the samples that contained the polyester soft segment.

3.6. X-ray diffraction

An X-ray diffractogram for the poly(ester urethane)s is shown in Fig. 3. Characteristic peaks for PEU-1 appear at $2\theta = 21.1°$ and 24.7°. The characteristic peaks for the PEUs with the content of sebacic residues are at $2\theta = 18.9°$, 20.4° and 22.7°. The degree of crystallinity of PEU is calculated from the X-ray patterns and the results are specified in Table 2. The thermal and crystallinity data show that the PEU-2, PEU-3 and PEU-4 exhibit the lower degree of crystallinity than PEU-1 which is having total hard segment, due to the shortening of the crystallizable block and the enhanced number of connection between soft and hard segments [13,18]. Hence, the highest degree of crystallinity of PEU-1 may be due to the absence of soft segment. This result is also supported by the heat of fusion data of DSC. Whereas

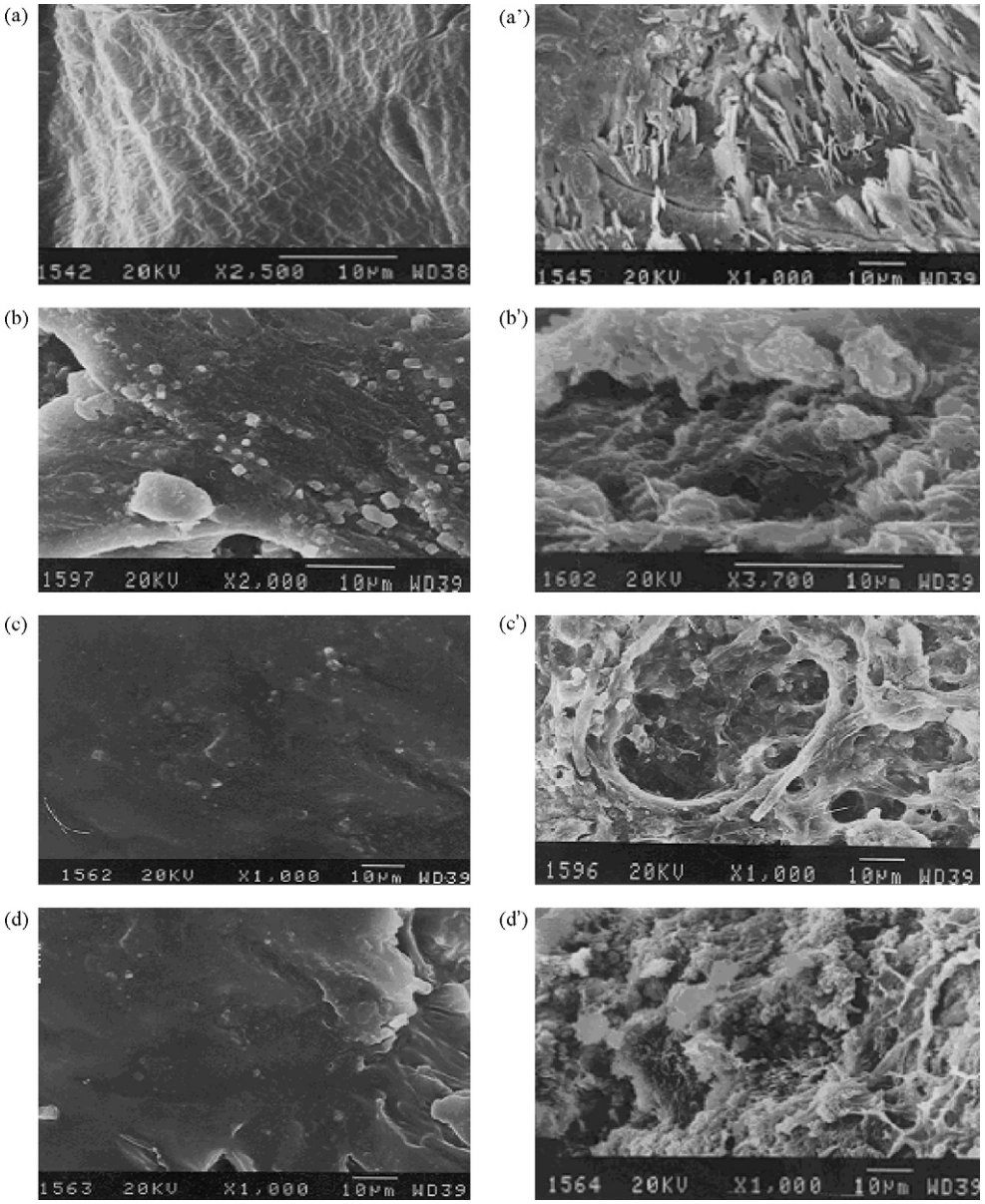


Fig. 5. SEM micrographs of hydrolytic degraded poly(ester urethane)s in 3% NaOH. Original films: (a) PEU-1, (b) PEU-2, (c) PEU-3 and (d) PEU-4; after 16 days of degradation: (a′) PEU-1, (b′) PEU-2, (c′) PEU-3 and (d′) PEU-4.

PEU-4 film has a minimum value as compared to other poly(ester urethane)s due to the highest % of soft segment. The difference in the degree of crystallinity between soft segments containing poly(ester urethane)s is not pronounced, which favors biodegradation; in this series of PEUs a lower degree of crystallinity indicates more biodegradability.

3.7. Biodegradation studies

3.7.1. Hydrolytic degradation

The hydrolytic degradation results of the polyurethanes in aqueous 3% and 10% NaOH at 37 °C were shown in Fig. 4. It was observed that weight loss increases linearly with incubation time. This phenomenon indicates that chain scission by hydrolysis occurs in a random fashion through the entire amorphous region [2]. PEU-l undergoes the alkaline hydrolysis more slowly than other PEUs indicating that the hard segments in the polyurethanes inhibit the degradation [6]. The hydrolysis rate of the polyurethanes containing the PPSe segments is greater than that of PEU-l, and the rate of hydrolysis increases with increase in the PPSe content. Non-enzymatic hydrolysis of polymers in aqueous solutions is reported to be usually facilitated by the hydrophilicity of the polymer structure because water can more efficiently penetrate into the polymers and hydrolyze the esters bond [18]. The greater the hydrophilicity of the polymer, the faster the degradation. This order of the hydrolytic degradation of polyurethanes is corresponding to the order of the PPSe content and the lesser concentration of the hard segment in the polymers, indicating that the degradation of the polyurethanes is affected by their hydrophilicity and hard segment content. Since the degradation of polymer was influenced by the polymer composition, polyester properties such as molecular weight, melting temperature, crystallinity and glass transition temperature. Kim and Kim [6] reported that the number of diol carbon chain in the polyol plays an important role in hydrolytic degradation. 1,4-Butanediol, 1,6-hexanediol and 10-decanediol impart a stronger hydrophobicity to the polyester segment than does ethylene glycol making hydrolytic attack more difficult. The slower degradation rate of PEU-1 is presumably due to the absence of the hydrophilic segments (PPSe) as well as the high crystallinity. The hard segments are hydrophobic and difficult to degrade, thus inhibiting the penetration of water into the material. Whereas the fast degradation of segmented poly(ester urethane) may come from the fact that these have less crystallinity so that water permeation into each polymer is easier. In addition to that, the lower glass transition temperature of the samples than experimental temperature maintains the chain mobility [21]. In hydrolytic degradation experiment, the weight loss of all the poly(ester urethane) samples was faster under alkaline conditions because base promotes hydrolysis of esters by providing the strongly nucleophilic reagent OH^- [21].

The SEM micrographs of hydrolytic degraded poly(ester urethane) films are shown in Fig. 5. The morphology of the original poly(ester urethane) film changes upon degradation. After hydrolytic degradation films surface irregularities and large numbers of small holes, cracks were appeared. The number of cracks and small holes became deeper with increasing the exposure time. Especially, after increasing the exposure time, the cracks were more pronounced and fragmentation of film occurred.

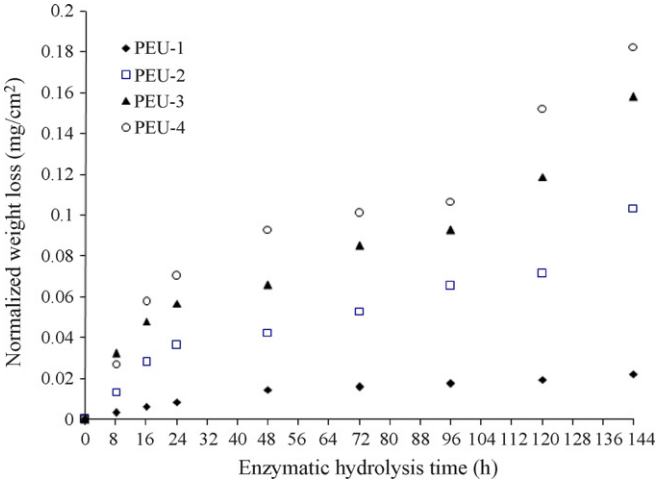


Fig. 6. Normalized weight loss per unit area of poly(ester urethane)s film with incubation time during enzymatic degradation.

3.7.2. Enzymatic degradation

Fig. 6 shows the normalized weight loss of the poly(ester urethane)s film as a function of time. The rate of enzymatic attack is very less during the initial few hours of biodegradation in poly(ester urethane)s, while afterwards the weight loss continues, but it is at a slower rate. On comparing the enzymatic hydrolysis of PPSe [8], it is observed that in poly(ester urethane)s the rate of enzymatic attack drops drastically. Such low enzymatic degradability may be due to the introduction of the polyurethane segments significantly reduces the enzymatic degradability of the polymer.

Enzymatic hydrolysis is a heterogeneous process. Enzymes can attack on the surface of polyester segments of polyurethane, degrading them to smaller molecular units via hydrolytic attack and hydrolysis takes place via surface erosion, and hydroly-

Table 3
Thermal analysis and crystallinity data of segmented poly(ester urethane)s after enzymatic hydrolysis

PEU	Incubation time (h)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
PEU-2	0	−40.5	57.9	118.8	44.1
	48	−40.5	57.9	118.8	45.3
	96	−40.2	58.1	119.9	45.9
	144	−40.1	58.3	121.0	46.0
PEU-3	0	−34.6	57.2	88.2	43.9
	48	−34.6	57.6	89.8	44.3
	96	−33.8	57.9	90.9	44.8
	144	−33.5	58.2	93.1	45.4
PEU-4	0	−27.7	57.8	69.1	39.3
	48	−27.4	57.9	70.3	40.5
	96	−26.5	58.1	72.7	41.1
	144	−26.0	58.5	74.6	42.6

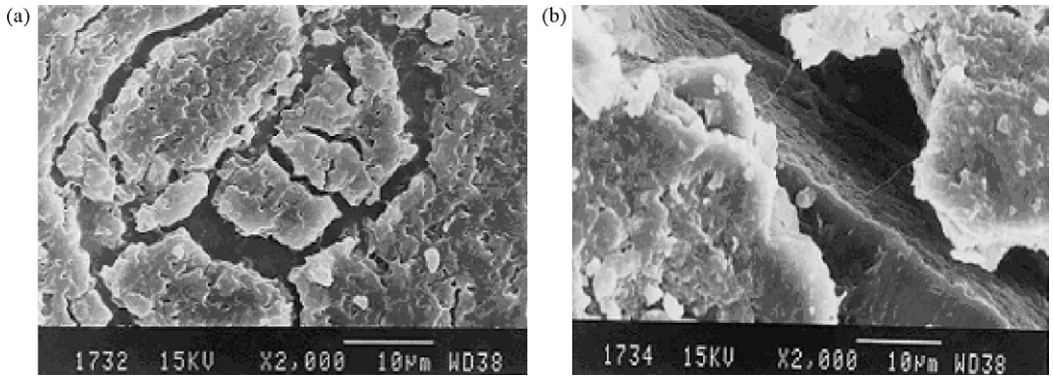


Fig. 7. SEM micrograph of PEU-4 film after enzymatic degradation of (a) 72 h and (b) 96 h.

sis rate is decreased after the consumption of the amorphous material of the surface.

The rate of weight loss during enzymatic degradation of poly(ester urethane)s samples is as follows: PEU-4 > PEU-3 > PEU-2 > PEU-1. PEU-1 does not show much significant weight loss in the presence of enzyme which may be due to the presence of larger amount of hard segment concentration and its higher degree of crystallinity.

Table 3 shows the thermal data of enzymatically hydrolyzed poly(ester urethane)s. Slight increase in melting temperature, also corresponding increase in the heat of fusion was observed on increase of the time of hydrolysis. This increase in melting temperature of degraded sample may be due to the increase in crystalline mass and decrease of polyester segments of polyurethane. Furthermore, the polymer glass transition temperature was slightly shifted to higher temperatures. This is reasonable, since mainly the free amorphous material of aliphatic polyester segments of polyurethane was consumed and in principle the remaining amorphous fraction is rather constraint between crystallites.

The SEM micrograph of poly(ester urethane) PEU-4 films after enzymatic hydrolysis is presented in Fig. 7. Small holes, cracks and surface irregularities were initiated on the surface after 96 h of enzymatic hydrolysis (Fig. 7a). Whereas, after 144 h, the film surface (Fig. 7b) irregularities and cracks became deeper. This indicates that the action of *R. delemar* lipase led to the formation of surface irregularities, cracks and holes, which

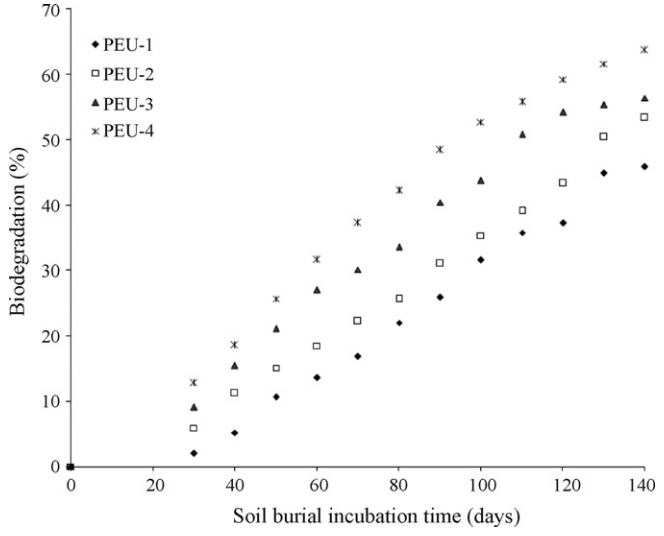


Fig. 8. Weight loss % of poly(ester urethane)s film against incubation time during soil burial degradation.

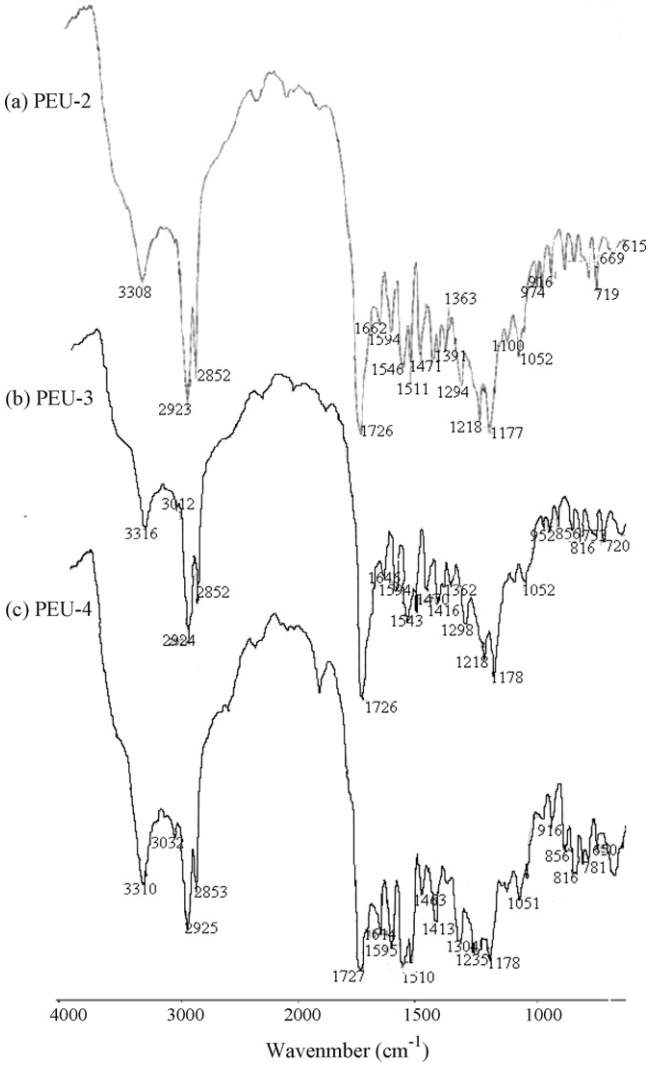


Fig. 9. FT-IR spectra of soil degraded poly(ester urethane)s: (a) PEU-2, (b) PEU-3, and (c) PEU-4.

also extend to a large depth within the film mass with increase in incubation time. The formation of the holes and cracks inside the surface of poly(ester urethane)s film may be due to the penetration of water into the amorphous regions of aliphatic polyester (soft) segments of polyurethane, causing further hydrolysis and enhancing the fragmentation. The effect of the enzymes is more pronounced in PEU-4 compared to other poly(ester urethane)s. This indicates that biodegradation is strongly dependent on the content of PPSe soft segment, molecular weight, polymer structure and crystallinity of the polymers.

Table 4
Molecular weights, thermal analysis and degree of crystallinity data of poly(ester urethane)s after soil burial degradation

PEU	After soil burial degradation of 140 days					
	$[\eta_{int}]$ (dl/g)	M_n (g/mol)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
PEU-1	0.58	23,700	–	110	137	65.1
PEU-2	0.54	17,500	−29.4	65.5	138	58.8
PEU-3	0.52	15,600	−25.3	64.5	115	57.4
PEU-4	0.52	15,100	−20.3	67.5	97	50.3

3.7.3. Soil burial degradation

Fig. 8 shows the weight loss of poly(ester urethane)s film against incubation time during soil burial degradation. It shows that the weight decreased linearly with incubation time. It may be due to the degradation of amorphous and crystalline matter by bacteria and fungi in the soil. In PEU-4 the effect of biodegradation is more compared to other poly(ester urethane)s indicating that attack of microorganism is more accelerated.

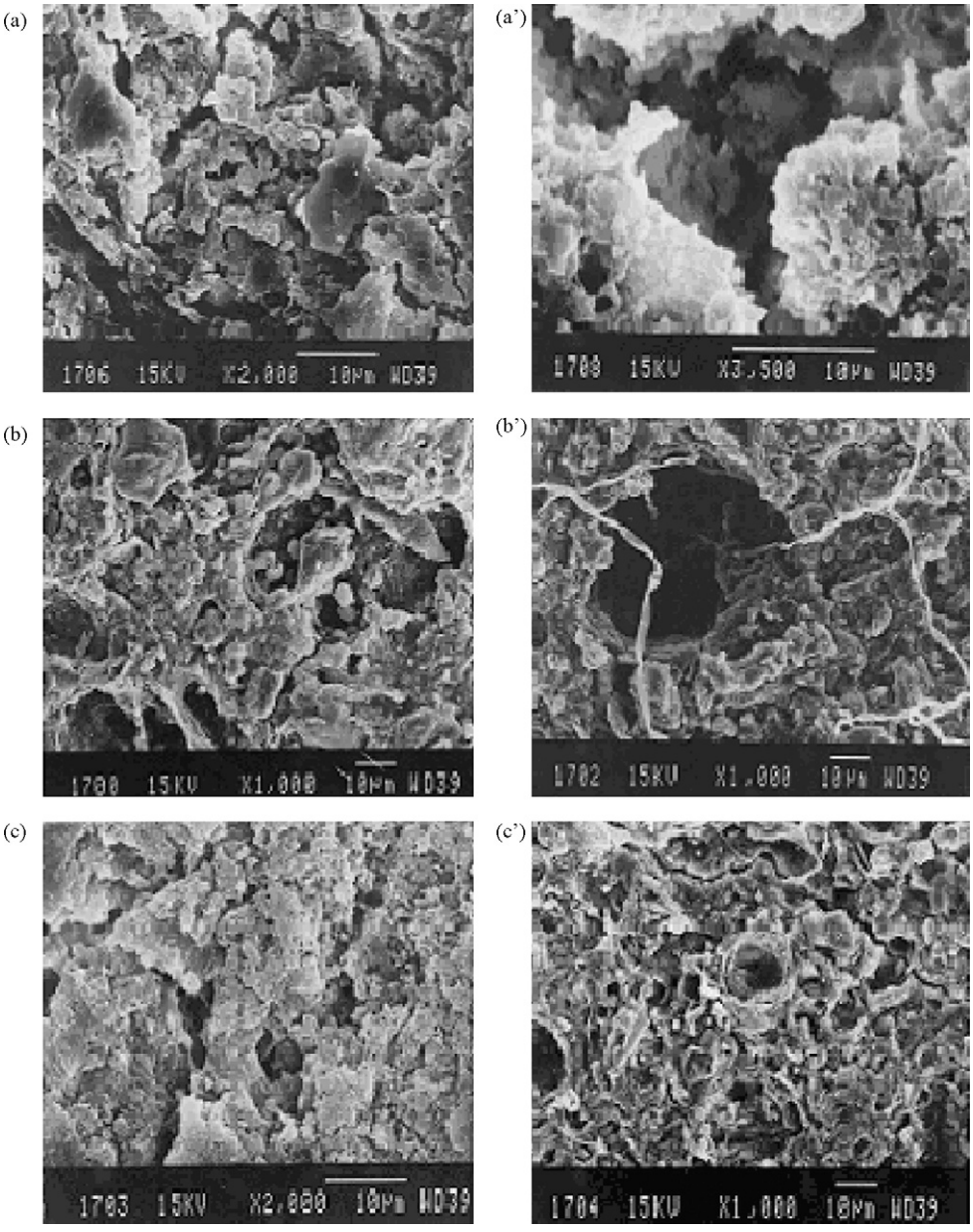


Fig. 10. SEM micrographs of poly(ester urethane)s during soil burial degradation. After 70 days: (a) PEU-2, (b) PEU-3, and (c) PEU-4; after 90 days: (a′) PEU-2, (b′) PEU-3, and (c′) PEU-4.

Fig. 9 shows the FT-IR spectra of poly(ester urethane)s after soil burial degradation and the spectrums show a significantly reduced absorption intensity of C–C–O bands, compared to the original sample (Fig. 2). It was observed that after soil burial degradation C=O stretching vibration shifted to lower absorption intensity and C=O band is weakened which appears at lower wavenumber with the poor intensity and some new peaks were appeared after the degradation. This indicates that the chemical structure of polymer changed after the soil burial test, mainly due to the hydrolysis of the ester bonds, C–C–O and urethane bond in the main chain by the action of microorganism [22–24].

Table 4 shows M_n of soil burial degraded poly(ester urethane)s film. With increasing biodegradation time, M_n of all poly(ester urethane)s decreased. It can be seen that the biodegradability of all poly(ester urethane)s initially commences with surface erosion, followed by the random chain scission of the esters bond and urethane bond main chain by the soil microbes attack [23]. The decreased molecular weight of degraded poly(ester urethane)s may be attributed to the hydrolysis of the ester linkage of soft segment polyesters, as well as the formation of low molecular weight materials such as oligomer and monomer. On degradation increase in melting temperature, degree of crystallinity as well as heat of fusion (Table 4) was observed may be due to the consumption of amorphous soft mass of poly(ester urethane)s. Thus, for PEU-4 the heat of fusion after 140 days of incubation was highest among the other poly(ester urethane)s. PEU-1 shows the lower value of weight loss during biodegradation, the increase in the heat of fusion was lower than the other polymer. Similar type of results were reported by Tuominen and co-workers [25,26] and showed in their study that the hydrolysis rate of the polymer is affected by the polymer properties such as molecular weight, glass transition temperature, crystallinity and hydrolysis conditions such as pH, temperature, presence of enzymes and microorganisms, etc. The above results are also in agreement with other studies of biodegradable polyesters [8]. For PCL-based polymers the crystallinity, glass transition point and melting temperature were increased during composting. This is reasonable, since mainly the free amorphous material was consumed and in principle the remaining amorphous fraction is rather constraint between crystallites.

The SEM micrographs of soil burial degraded poly(ester urethane)s films showed large number of small holes, cracks, cavities and surface irregularities (Fig. 10), indicated that the surface of polymer was attacked by the microorganism under soil environment [27,28]. The number of cracks, small holes became deeper with increasing the exposure time and fragments had been removed from surface with increase in the size of cracks and appearances of cavities due to the enhanced attack of microorganism.

The higher soft segment contents resulted in higher degradability. According to the degradation study of semi-crystalline polymer materials, an assumption is usually accepted that the degradation occurs first or/and faster in the amorphous phase than in crystalline phase [29]. Our results also indicated that lower hard segment content and lower crystallinity are favorable for degradation. The biodegradability of poly(ester urethane)s in the soil test was enhanced relative to that of the enzymatic test due to the slow rate of hydrolysis at low temperature in soil.

4. Conclusions

Poly(ester urethane)s were synthesized having PPSe as soft segment by reacting with MDI and 1,3-propanediol as the chain extender in DMF. Hydrophilicity and low crystallinity seem to accelerate the biodegradation of poly(ester urethane)s. Presence of hard segment in poly(ester urethane)s was found to have more dominant effect on biodegradation rate under hydrolytic, enzymatic and soil burial degradation. The percentage weight loss was significant in the hydrolytic degradation (3% and 10% NaOH) and soil burial test. The reduction in the physical properties and percentage weight loss of poly(ester urethane)s in soil burial test was significant because of the favorable conditions in humidity chamber.

FT-IR, DSC, XRD and molecular weight data proved that the chemical structure of poly(ester urethane)s changed after the soil burial test due to the hydrolysis of the ester and urethane bonds in the main chain and formation of low molecular weight materials by activated microorganisms, bacteria and fungi.

On comparing the biodegradability, it was observed that the rate of degradation of poly(ester urethane)s was more accelerated in the soil test. The soil conditions are suitable for the growth of microorganism due to the high humidity, proper temperature of 30 °C, pH 7.5 and microorganisms present in soil are more numerous because of the additional nourishment provided in a soil environment. As biodegradability test progressed, T_g, T_m and degree of crystallinity of poly(ester urethane)s as well as the ΔH_m shifted to higher value.

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References

[1] S.-I. Lee, S.-C. Yu, Y.-S. Lee, Degradable polyurethanes containing poly(butylene succinate) and poly(ethylene glycol), Polym. Degrad. Stab. 72 (2001) 81–87.
[2] S.-Y. Moon, Y.-D. Park, C.-J. Kim, C. Won, Y.-S. Lee, Effect of chain extenders on polyurethanes containing both poly(butylene succinate) and poly(ethylene glycol) as soft segments, Bull. Korean Chem. Soc. 24 (9) (2003) 1361–1364.
[3] S.-I. Lee, Y.-S. Lee, K. Nahm, Y. Hahn, S.-B. Ko, Degradable polyurethanes synthesized from poly(butylene succinate) polyol, poly(ethylene glycol), and 4,4′-methylene bis (cyclohexyl isocyanate), Bull. Korean Chem. Soc. 21 (11) (2000) 1145–1148.
[4] R.S. Labow, E. Meek, J.P. Santerre, Hydrolytic degradation of poly(carbonate)-urethanes by monocyte-derived macrophages, Biomaterials 22 (2001) 3025–3033.
[5] U. Edlund, A.-C. Albertsson, Polyesters based on diacid monomers, Adv. Drug Del. Rev. 55 (2003) 585–609.
[6] Y. Kim, S. Kim, Effect of chemical structure on the biodegradation of polyurethanes under composting conditions, Polym. Degrad. Stab. 62 (1998) 343–352.

[7] R.T. Darby, A.M. Kaplan, Fungal susceptibility of polyurethanes, Appl. Microbiol. 16 (1968) 900–905.
[8] S.S. Umare, A.S. Chandure, R.A. Pandey, Synthesis, characterization and biodegradable studies of 1,3-propanediol based polyesters, Polym. Degrad. Stab. 92 (3) (2007) 46–479.
[9] http://www.dupont.com/sorona/apps.html.
[10] http://www.shell.com.
[11] D.R. Kelsey, US Patent 6,093,786 (2000).
[12] Y. Liu, M. Söderqvist Lindblad, E. Ranucci, A.-C. Albertsson, New segmented poly(ester-urethane)s from renewable resources, J. Polym. Sci. Part A: Polym. Chem. 39 (2001) 630–639.
[13] B. Bogdanov, V. Toncheva, E. Schacht, L. Finelli, B. Sarti, M. Scandola, Physical properties of poly(ester-urethanes) prepared from different molar mass polycaprolactone-diols, Polymer 40 (1999) 3171–3182.
[14] S.M. Nikolic, D. Poleti, J. Djonlagic, Synthesis and characterization of biodegradable poly(butylene succinate-co-butylene fumarate)s, Eur. Polym. J. 39 (2003) 2183–2192.
[15] M. Söderqvist Lindblad, Y. Liu, A.-C. Albertsson, E. Ranucci, S. Karlsson, Polymers from renewable resources, Adv. Polym. Sci. 157 (2002) 139–161.
[16] G. Odian, Principles of Polymerization, John Wiley & Sons, New York, 1991, p. 146.
[17] M. Kischel, D. Kisters, G. Strohe, W.S. Veeman, Dynamic infrared spectroscopy, a tool to detect hydrogen bonds in polymers? Eur. Polym. J. 34 (11) (1998) 1571–1577.
[18] X. Loh, K. Tan, X. Li, J. Li, The in vitro hydrolysis of poly(ester urethane)s consisting of poly[(*R*)-3-hydroxybutyrate] and poly(ethylene glycol), Biomaterials 27 (2006) 1841–1850.
[19] X. Li, X. Loh, K. Wang, C. He, J. Li, Poly(ester urethane)s consisting of poly[(*R*)-3-hydroxybutyrate] and poly(ethylene glycol) as candidate biomaterials: characterization and mechanical property study, Biomacromolecules 6 (2005) 2740–2747.
[20] X. Loh, S. Goh, J. Li, New biodegradable thermogelling copolymers having very low gelation concentrations, Biomacromolecules 8 (2) (2007) 585–593.
[21] H.C. Ki, O.O. Park, Synthesis, characterization and biodegradability of the biodegradable aliphatic–aromatic random copolyesters, Polymer 42 (2001) 1849–1861.
[22] D.Y. Kim, Y.H. Rhee, Biodegradation of microbial and synthetic polyesters by fungi, Appl. Microbiol. Biotechnol. 61 (2003) 300–308.
[23] T. Nakajima-Kambe, Y. Shigeno-Akutsu, N. Nomura, F. Onuma, T. Nakahara, Microbial degradation of polyurethane, polyester polyurethanes and polyether polyurethanes, Appl. Microbiol. Biotechnol. 51 (1999) 134–140.
[24] Schoonovera, D. Thompson, J.C. Osborn, E.B. Orler, D.A. Wrobleski, A.L. Marsh, H. Wang, A. Richard, Palmer infrared linear dichroism study of a hydrolytically degraded poly(ester urethane), Polym. Degrad. Stab. 74 (2001) 87–96.
[25] K. Hiltunen, J. Tuominen, J. Seppälä, Hydrolysis of lactic acid based poly(ester urethane)s, Polym. Int. 47 (1998) 186–192.
[26] J. Tuominen, J. Kylmä, A. Kapanen, O. Venelampi, M. Itävaara, J. Seppälä, Biodegradation of lactic acid based polymers under controlled composting conditions and evaluation of the eco-toxicological impact, Biomacromolecules 3 (2002) 445–455.
[27] H.-S. Kim, H.-J. Kim, J.-W. Lee, I.-G. Choi, Biodegradability of bio-flour filled biodegradable poly(butylene succinate) bio-composites in natural and compost soil, Polym. Degrad. Stab. 91 (2006) 1117–1127.
[28] M. Kimura, K. Toyota, M. Iwatsuki, H. Sawada, Effects of soil conditions on biodegradation of plastics and responsible microorganisms, in: Y. Doi, K. Fukuda (Eds.), Proceedings of the Third International Scientific Workshop on Biodegradable Plastics and Polymers, Osaka, Japan, November 9–11, 1994, pp. 92–109.
[29] G.W. Hastings, P. Ducheyue, Macromolecular Biomaterials, CRC Press, Boca Raton, 1984, p. 120.