Synthesis and thermal characterization of poly(ester-ether urethane)s based on PHB and PCL-PEG-PCL blocks

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Received: 15 July 2010 / Accepted: 26 October 2010 / Published online: 16 November 2010
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Abstract A series of block poly(ester-ether urethane)s, poly(PHB/PCL-PEG-PCL), based on poly(3-hydroxybutyrate) (PHB-diol), as hard segments, and poly(ε-caprolactone)-b-poly(ethylene glycol)-b-poly(ε-caprolactone), (PCL-PEG-PCL) triblock copolydiol, as soft segments, were prepared using 1,6-hexamethylene diisocyanate (HDI), as non-toxic connecting agent. Polyurethanes block copolymer was synthesized from bacterial PHB and PCL-PEG-PCL blocks. The chemical structure and molecular weights of polymers prepared were characterized by FTIR, 1H NMR and GPC. The effect of chemical structure on the thermal and mechanical properties was studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and tensile testing. The DSC results revealed that poly(PHB/PCL-PEG-PCL) urethanes are semi-crystalline with two crystallizable PHB and PCL-PEG-PCL blocks. The thermal stability of the urethanes is less than neat PHB. The results of tensile testing showed that the extensibility of PHB is largely enhanced by the incorporation of PCL-PEG-PCL soft segments. Activation energy $E_a$, as a kinetic parameter of thermal decomposition, was estimated by each of the Ozawa and Kissinger methods. Close values of activation energy were obtained by both methods. The swelling behaviour of the copolymers was also investigated.

Keywords Poly(3-hydroxybutyrate) · Poly(ester-ether urethane) · Thermal properties · Thermal degradation · Kinetics · Swelling behaviour

Introduction

Biodegradable polymers have been studied extensively in recent years due to their use in new applications and to their contribution towards diminishing the environmental problems caused by non-biodegradable materials, through the replacement of the latter by environmentally friendly materials. Poly[(R)-3-hydroxybutyrate], PHB, is perhaps the most members appearing to nearly meet all criteria; it is produced biologically from renewable resources [1–4]. It is stable under normal usage conditions, and biodegraded under different environmental conditions. Unfortunately, PHB, due to its high crystallinity, has several inherent deficiencies that limit its application as technical material, since it is brittle, lacks transparency, and has a high melting temperature and a small temperature window for thermoplastic processing [5–7]. Several methods have been applied to overcome these difficulties and to obtain useful materials based on bacterial PHB. The development of biodegradable polymers based on PHB, having an optimum balance of physical properties and susceptibility to microbial attack, undergoes biodegradation which is very important to relieve environmental plastics and medical applications. The preparation of biodegradable segmented poly(ester urethane)s from telechelic blocks of PHB “as hard segments” and blocks of more flexible biodegradable synthetic blocks as “soft segments”, such as poly(ε-caprolactone) [8–10], poly(butylenes glycol adipate) [11, 12], poly(ethylene glycol adipate) [11, 12], and poly (ethylene glycol) [13–18] allows man to overcome the difficulties connected with the use of bacterial PHB as a thermoplastic material. These copolymers possess much better physical properties such as lower melting points and higher extensibility compared to PHB homopolymer. In addition, the extent of biodegradation is controlled by
composition. Physicochemical and degradation characteristics of these copolymers are directly related to the length of the respective blocks, the chemical composition, molecular weight and ratio of hard to soft segments [9–12].

Poly(ε-caprolactone) (PCL) is one of the most frequently used building blocks for soft segments of degradable polyurethanes [19–24]. The labile aliphatic ester linkages of the PCL can be hydrolyzed and its degradation product, 6-hydroxyhexanoic acid, is a non-toxic metabolic product [21]. However, the rate of degradation of PCL is rather slow due to its hydrophobicity and semi-crystalline structure [25, 26]. To obtain a better degradability and physical properties balance, a study using mixed ester and ether segment polyol soft segments for the preparation of copolymers may be appropriate route. Hence, poly(ethylene glycol) (PEG) is introduced as co-monomer for soft segment of polyurethane backbone. PEG presents many attractive properties, such as hydrophilicity, solubility in water and non-toxicity [27]. The synthesis of biodegradable polyurethanes based on PCL and PEG diblock or triblock copolymers has been reported by many researchers [28–30], where they studied the relationship between the chemical structure of these polyurethanes and their biodegradation rates. They suggested that PCL usually enhances crystallinity and elastomeric mechanical properties of the polyurethanes, while PEG increases hydrophilicity and aqueous absorption. Consequently, copolymerization of PHB-diol, as hard segments, and PCL-PEG-PCL triblock copolydiol, as soft segments, can offer the possibility to combine the advantages of these polymers in one copolymer. By balancing the hydrophobic/hydrophilic ratio and soft/hard portions in the block copolymers, the properties of the materials can be adjusted to meet different demands. The purpose of the present study is to synthesize a series of poly(ester urethane)s based on PHB-diol blocks, as hard segments, and PCL-PEG-PCL copolydiol blocks, as soft segments, using 1,6-hexamethylene disiocyanate as non-toxic connecting agent. The thermal and mechanical properties will be investigated according to the composition of the synthesized poly(PHB/PCL-PEG-PCL) urethanes. One of the main goals of this article focuses on the kinetic study of the thermal degradation of poly(PHB/PCL-PEG-PCL) urethanes.

Experimental

Materials

Poly(ethylene glycol) (PEG-400, M_w 400 g mol⁻¹) was obtained from Aldrich and dried at 50 °C under vacuum for 48 h to remove any residual water before use. ε-Caprolactone (ε-CL) was supplied from Aldrich and distilled under vacuum over calcium hydride (CaH₂) and dried by 4Å molecular sieves before use. Poly[(R)-3-hydroxybutyrate], PHB, (M_n=58,000, M_w/M_n=2.3) was supplied from Copersucar, Piracicaba, Brazil. The sample was purified by dissolution in CHCl₃, filtered to remove any insoluble matter, and precipitated in diethyl ether. Stannous octoate, dibutyltin dilaurate, 1,6-hexamethylene disiocyanate and p-toluensulfonic acid were supplied from Fluka. 1,4-Butanediol and 1,2-dichloroethane were purchased from Aldrich and purified before use.

Synthesis of poly(PHB/PCL-PEG-PCL) urethanes

Preparation of PHB-diol prepolymer

Dihydroxyl terminated prepolymer PHB-diol was prepared by transesterification between the purified high molecular weight PHB and 1,4-butanediol using p-toluensulfonic acid as catalyst [10, 12]. Typically, PHB (60 g) was heated in 300 ml dry chloroform at 60 °C under nitrogen, to which 90 ml of 1,4-butanediol and 15 g of anhydrous p-toluensulfonic acid were added, successively. The temperature of the reaction was kept constant at 60 °C, aliquots were taken periodically from the reaction vessel to follow the progress of the reaction. The aliquots were precipitated from chloroform by cold methanol. The solid formed was filtered and washed several times with cold methanol, acetone and diethyl ether, respectively and then dried under vacuum at 60 °C for 48 h. The properties of PHB-diol are collected in Table 1.

Preparation of PCL-PEG-PCL diol

Poly(ether-ester) triblock copolydiols (PCL-PEG-PCL-diol) were synthesized according to the method described previously [27]. Polymers were prepared by using PEG-400 to initiate the polymerization of ε-caprolactone (molCL/molPEG=15) in presence of stannous octanoate (0.5 wt.% of the total reactants). Polymerization was carried out at 130 °C for 12 h under a nitrogen atmosphere. The copolymer obtained was dissolved in dichloromethane, and reprecipitated from the filtrate using excess cold petroleum ether. The mixture was then filtered and dried under vacuum to constant weight at room temperature. PCL contents were determined from ¹H NMR spectrum by means of the analysis of intensity corresponding to methylene group of PCL moiety (−COCH₂CH₂CH₂CH₂CH₂O−) at δ=4.06 and that corresponding to ethylene group from PEG, (−CH₂CH₂O−) at δ=3.6. The molecular weight of the copolymer was estimated from its composition and the known molecular weight of the central PEG block. The composition, the number-average molecular weight M_n determined from ¹H NMR, GPC and the thermal properties of PCL-PEG-PCL copolydiol are included in Table 1.
A series of poly(PHB/PCL-PEG-PCL) copolymers were synthesized from the corresponding diols in dry 1,2-dichloroethane using stoichiometric amount of 1,6-hexamethylene diisocyanate (HDI), as non-toxic coupling agent, and dibutyltin dilaurate (0.5% w/w) as a catalyst by one step solution polymerization as reported elsewhere [10, 12]. Briefly, telechelic PHB and PEG-PCL-PEG diols were dissolved in dry 1,2-dichloroethane at 60 °C and the corresponding amount of 1,6-hexamethylene diisocyanate HDI (NCO/OH=1) was added gradually in the presence of dibutyltin dilaurate. Then the mixture was refluxed at 80 °C for 24 h. All the copolymers were separated in high yields (≥ 95%) from the reaction mixture by precipitation from low boiling petroleum ether. The isolated copolymers were redissolved in 1,4-dioxane, filtered, reprecipitated in distilled water and dried under vacuum at 70 °C for 24 h. The PHB content in the obtained poly(ester urethane)s varied from ~30 to 70 wt.%.

Measurements

FTIR Infrared analysis was carried out between 400 and 4,000 cm\(^{-1}\) using a Perkin–Elmer B25 spectrophotometer. All measurements were carried out with 64 scans at a resolution of 2 cm\(^{-1}\) at room temperature.

\(^{1}\)H-NMR analyses of samples were carried out at room temperature in CDCl\(_3\) (20 mg/ml) using a Bruker AC-400 NMR spectrometer with tetramethylsilane (TMS) as an internal standard.

Average molecular weights were determined by gel permeation chromatography (GPC) at 30 °C using a water model 510 GPC system and a model 410 refractive index detector with 10\(^{3}\)–10\(^{5}\) ultrastyragel column connected in series. Chloroform was used as eluent with a flow rate of 1.5 cm\(^{3}\)/min, and sample concentrations of 20 mg/cm\(^{3}\). The number-average (M\(_n\)) and weight-average (M\(_w\)) molecular weight were calculated by using a calibration curve which was constructed using polystyrene with low dispersity as standard (polystandard series, Mainz, Germany).

Differential Scanning Calorimetry (DSC) was performed on a PL–DSC (Polymer Laboratories, England). The calorimeter was calibrated with ultra-pure indium. Samples (10–12 mg) were first heated from −40 to 190 °C with a heating rate of 20 °C/min (Run I). After keeping them at 190 °C for 2 min, samples were rapidly cooled to −100 °C at a rate of 60 °C/min to obtain specimen with low crystallinity, and then heated again with a heating rate of 20 °C/min to 190 °C (Run II). The melting temperature (T\(_m\)) and the cold crystallization temperature (T\(_{cc}\)) were taken as the peak values of the respective endothermal and exothermal processes in DSC thermograms. The apparent melting enthalpy (ΔH\(_m\)) was determined from the area of the

<table>
<thead>
<tr>
<th>Prepolymer</th>
<th>M(_n)(^a) (gmol(^{-1}))</th>
<th>M(_w)(^b) (gmol(^{-1}))</th>
<th>M(_w)/M(_n)(^b)</th>
<th>% PCL weight(^a)</th>
<th>T(_m)^((c) (°C))</th>
<th>T(_g)^((c) (°C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB-diol</td>
<td>–</td>
<td>3,000</td>
<td>1.62</td>
<td>–</td>
<td>141</td>
<td>−14</td>
</tr>
<tr>
<td>PCL-PEG-PCL-diol</td>
<td>2,145</td>
<td>2,100</td>
<td>1.41</td>
<td>81.5</td>
<td>52</td>
<td>−61</td>
</tr>
</tbody>
</table>

\(^a\) Determined from \(^1\)H NMR
\(^b\) Determined from GPC in CHCl\(_3\)
\(^c\) Determined from DSC of quenched samples
endothermic peaks. The glass transition temperature (Tg) was taken as the midpoint of the specific heat capacity. The cooling curve run (III) was scanned over the temperature range from 190 °C to −40 °C at a constant rate of 20 °C/min. The melt crystallization temperature (Tmc) was determined from the exothermic peaks in this run. To minimize the risk of degradation of the copolymers and the consequent molecular weight decrease, a new sample was used for each measurement, and all measurements were carried out under flow of nitrogen gas (20 ml/min).

Thermal degradation studies were conducted in air under dynamic heating rate of 5, 10 and 20 °C/min using a Shimadzu TGA-50 H Thermal Analyzer. All experiments were conducted from room temperature to 600 °C and the reference material was α–alumina. The sample weights in all experiments were taken in the range of 7–10 mg.

Tensile strength and elongation at break of the copolymers were measured using the zwick 1445 testing machine (zwick Gmbh, Germany). Dumbbell-shaped samples of copolymer cast films (thickness 0.15±0.02 mm, base width 5±0.2 mm, base length 10±0.2 mm) were used for measurements. The elongation at break and tensile strength were determined at room temperature at extension rate of 10 mm/min.

Water uptake

The extent of swelling of the copolymers was determined gravimetrically. In order to determine the swelling behaviour of the copolymers investigated, the copolymers films (width = 2 cm, length = 4 cm and thickness = 0.15–0.17 mm) were soaked in deionised water at 37 °C for different time intervals. Then, they were taken out and the excess surface water was removed by filter paper, and weighed. The swelling ratio percent (W%) is defined as:

\[ W = \left( \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \right) \times 100. \]

Results and discussion

Characterization of poly(PHB/PCL-PEG-PCL) urethanes

The poly(PHB/PCL-PEG-PCL) was synthesized from PHB-diol and PCL-PEG-PCL triblock macrodiol using 1,6-hexamethylene diisocyanate (HDI) in one step solution polymerization process in the presence of dibutyltin dilaurate as a catalyst according to Scheme 1. The feed reaction mixture is varied to control the content of PHB in the copolymer between 30 and 70 wt.%. Purified products were investigated by FTIR and 1HNMR to confirm their chemical structure. FTIR spectra of the investigated polyurethanes and their corresponding prepolymers are shown in Fig. 1, and sample labels are shown in Table 2. All the characteristic absorptions of PHB, PCL and PEG segments were clearly recognized of the segmented poly(PHB/PCL-PEG-PCL) urethane. The absorption band appearing at 1,728 cm\(^{-1}\) is attributed to free carbonyl groups stretching of PHB and PCL whereas the peak at 1,686 cm\(^{-1}\) is assigned to hydrogen bonded carbonyl groups [31, 32]. The intensity of C=O of PHB blocks obviously increases with the increase in the content of PHB block in the urethane. C–H stretching

![Fig. 1 FTIR spectra of poly(PHB/PCL-PEG-PCL) urethanes, their PHB-diol and PCL-PEG-PCL copolydiol](image_url)

Table 2 Chemical composition and molecular weights of poly(PHB/PCL-PEG-PCL) urethanes

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Compositions a</th>
<th>Yield%</th>
<th>Mn b (g/mol)</th>
<th>Mw/Mn b</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL-PEG-PCL-HB30 (A1)</td>
<td>29.1 52.3 11.8 6.8</td>
<td>98.3 41,500</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>PCL-PEG-PCL-HB50 (A2)</td>
<td>49.5 36.4 7.8 6.3</td>
<td>96.6 37,200</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>PCL-PEG-PCL-HB70 (A3)</td>
<td>68.9 20.7 4.6 5.8</td>
<td>94.5 31,000</td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

a Determined from 1 HNMR spectra, expected error 3%

b Determined from GPC in CHCl\(_3\) at 30 °C
vibration band and ether stretch assigned to the –OCH2CH2– repeating unit of PEG appear at 2,883 and 1,116 cm⁻¹, respectively. When compared with the absorption bands of PHB-diol and PCL-PEG-PCL diols prepolymer, it was noticed that the hydroxyl O–H absorption at 3,500 cm⁻¹ in the product was disappeared, whereas two new characteristic absorptions at 3,346 cm⁻¹ and 1,530 cm⁻¹ belonging to N–H unit in urethane linkage, were observed. These results confirm the formation of the polyurethane and the coupling reaction between the prepolymer occurred. The absorption bands at 3,939 and 2,866 cm⁻¹ are associated with asymmetric and symmetric –CH2 groups, while other modes of –CH2 vibrations are manifested by the bands at 1,462, 1,373 and 1,238 cm⁻¹.

Figure 2 shows the ¹H NMR spectrum of copolymer sample A1, in which the signal protons of PHB, PCL-PEG-PCL blocks and urethane junction unit are assigned. The signals attributed to PHB component were observed at δ = 1.27 (-OCH(CH₃)-CH2CO-), δ = 2.35–2.71 (-OCHCH₃(CH₂)CO-) and δ = 5.21–5.30 (-O(CH)CH₂CH₂CO-). The signal assigned
at $\delta = 4.06$ is due to the ethylene group of the caprolactone units ($-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$) and at $\delta = 3.60$ is due to the ethylene group of the ethylene glycol units ($-\text{CH}_2\text{CH}_2\text{O}$) in the PCL-PEG-PCL triblock. The signal appears at $\delta = 4.8$ is due to NH- of urethane linkage. The integrations of proton intensity of the peaks at $\delta = 5.21–5.30$, 4.06, 3.6 and 4.8 ppm of HB, CL, EG and urethane linkage units, respectively, were used to calculate the copolymers compositions. The results, summarized in Table 2, demonstrate that the calculated compositional data are equivalent, within the limits of experimental error, which is reasonable on the basis of the near quantitative yield of the materials product. Hence, the composition of the copolymer reflects the input of the components. The molecular weight and the distribution were characterized by GPC and included in Table 2. In all cases, GPC chromatograms of the synthesized urethanes copolymers show peaks that are unimodal and of higher molecular weight than the starting PHB-diol and PCL-PEG-PCL copolydiol prepolymers. As can be seen from Table 2, the molecular weights decrease with increasing PHB content.

**Thermal properties**

**Differential Scanning Calorimetry (DSC)**

The thermal parameters of the synthesized segmented polyurethanes, determined by DSC with typical thermograms, are displayed in Figs. 3, 4 and 5. In the first heating scan (run I) (Fig. 3), it is seen that all the copolymers investigated exhibited two distinct melting temperatures. The lower melting endotherm corresponds to the crystalline phase of PCL-PEG-PCL soft segments and the higher one to the crystalline PHB hard segments. These melting temperatures appear as double peaks and are comparable with the $T_m$ of the prepolymers (Table 1). In the second heating scan (run II) (Fig. 4), all the investigated samples exhibit a glass transition temperature ($T_g$) of soft segments from $-46$ to $-38$ °C. However, the shift of $T_g$ of the soft segments to higher temperature with increasing PHB content, suggests some mixing of the hard into the soft segment phase. This increase can be explained on the basis of a decreased mobility of the soft segments because of their attachment to stiffer urethane groups and/or the penetration of rigid PHB hard segment units into the soft segments. (As expected, increasing the PHB hard segment content has leaded to an increase in the glass transition temperature of the copolymer due to the restriction imposed on the soft segment motion by the hard segments). Further heating, beyond $T_g$, results in complex phase behavior, especially for sample containing $\sim 50\%$ PHB (sample A2). The DSC thermograms showed exo-and endothermic peaks around $-16$ °C and $50$ °C, which are due to crystallization, then melting of PCL-PEG-PCL soft segments followed by the endothermic peak around $141$ °C, corresponding to the PHB segments. No cold crystallization was detected for PHB segments in polyurethanes. Therefore, the PHB hard segments in these materials, compared with that of PHB-diol which exhibits cold crystallization peak at $\sim 60.5$ °C.

![Fig. 5 DSC thermograms of poly(PHB/PCL-PEG-PCL) urethanes, their PHB-diol and PCL-PEG-PCL copolydiol obtained from cooling scans (Run III)](image)

### Table 3  Thermal properties of poly(HB/PCL-PEG-PCL) urethanes

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$T_g$ (°C)</th>
<th>PEG-PCL-PEG block</th>
<th>PHB block</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H_m$ (J/g)</td>
<td>$T_{cc}$ (°C)</td>
<td>$T_m$ (°C)</td>
</tr>
<tr>
<td>A1</td>
<td>-46</td>
<td>38,51</td>
<td>6.1</td>
</tr>
<tr>
<td>A2</td>
<td>-41</td>
<td>36,50</td>
<td>2.25</td>
</tr>
<tr>
<td>A3</td>
<td>-38</td>
<td>48</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ $T_m$ was determined by DSC from first heating scan (Run I)

$^b$ Enthalpy of melting was calculated from intensities of the endothermic peaks in the DSC first heating scan (Run I)

$^b$ Glass transition temperature from DSC second heating scan (Run II)
are so easily crystallized that they even crystallize almost completely during rapid cooling. This behavior suggests that the flexibility of the PCL-PEG-PCL soft segments may promote the crystallization of the PHB hard segments. Figure 5 shows the DSC cooling thermograms (third scan) from the free crystal melt. Two melt-crystallization temperatures were observed in each of the copolymer samples A1 and A2 containing ~30 and 50 wt.% PHB. The higher temperature peak is attributed to the crystallization of PHB hard segments, while the lower one corresponds to the crystallization of PCL-PEG-PCL soft segments. However, since both components are chemically linked, crystallization cannot occur freely. Therefore, with increasing the content of PHB, the PCL-PEG-PCL segments are most constrained in their tendency to crystallize, which results in a lowering of the $T_{mc}$ and the enthalpy of melt crystallization ($\Delta H_{mc}$). Both of melt crystallization temperature ($T_{mc}$) and enthalpy of melt crystallization ($\Delta H_{mc}$) of the melt crystallization of PCL-PEG-PCL segments were found to decrease with increasing PHB content, reflecting a decrease in the rate of melt crystallization of PCL-PEG-PCL segments. Similarly, the $T_{mc}$ and $\Delta H_{mc}$ of the PHB segments decrease with increasing PCL-PEG-PCL content. This indicates that the soft segments retard the crystallization of PHB hard segments. Comparing the $T_{mc}$ of the PHB and PCL-PEG-PCL diols prepolymer with the corresponding polyurethanes, it can be observed that the $T_{mc}$s of the prepolymer are higher than those components in the copolymer. This confirms that the crystallization of PHB and PCL-PEG-PCL segments is retarded by each other and its own content. So, for A3 copolymer containing high content of PHB, the crystallization of PCL-PEG-PCL becomes difficult to detect. This result is ascribed to the fact that the higher the PHB content, the ease is the crystallization of the PHB hard segment, which crystallizes first upon cooling and acts as physical cross-links, and consequently the higher is the restriction imposed on the crystallization of the PCL-PEG-PCL soft segments.

The relative percent crystallinity ($X_c%$) of PHB segments in poly(PHB/PCL-PEG-PCL) urethanes was determined from the melting enthalpy using the following equation:

$$X_c% = \frac{\Delta H_m}{\Delta H_{m,w}} \times 100$$

Where $\Delta H_m$ is melting enthalpy of the PHB component, $\Delta H_{m,w}$ is the heat enthalpy of melting of 100% crystalline PHB; the literature values being 146 J/g [33] and $w$ is the weight fraction of PHB in the copolymer. Computed results are included in Table 3, which reveal that the degree of crystallinity of PHB increases with increasing its content.

### Thermogravimetric analysis

The thermal stability of the prepared copolymers was determined from thermogravimetric results. Figure 6 represents the weight loss curves (TGA) and the corresponding derivatives (DTGA) of the copolymers at heating rate 10 K/min. The thermogram of PHB homopolymer is

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{5%}$ (°C)</th>
<th>$T_{1%}$ (°C)</th>
<th>$T_{2%}$ (°C)</th>
<th>$T_r$ (°C)</th>
<th>$\Delta T$ (°C)</th>
<th>Char yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB</td>
<td>257</td>
<td>284</td>
<td>–</td>
<td>–</td>
<td>27</td>
<td>1.7</td>
</tr>
<tr>
<td>A1</td>
<td>228</td>
<td>260</td>
<td>299</td>
<td>386</td>
<td>158</td>
<td>2.9</td>
</tr>
<tr>
<td>A2</td>
<td>225</td>
<td>263</td>
<td>298</td>
<td>388</td>
<td>163</td>
<td>2.3</td>
</tr>
<tr>
<td>A3</td>
<td>203</td>
<td>256</td>
<td>–</td>
<td>391</td>
<td>188</td>
<td>2.7</td>
</tr>
</tbody>
</table>
included in the figure for the sake of comparison. For a quantitative comparison of different investigated polymers, values of the following parameters were determined: the decomposition temperature at 5% weight loss (T_{5\%}), which represents the lowest temperature at which the onset of a weight change can be detected, the temperature of maximum rate of degradation (T_p), the end decomposition temperature (T_f), the temperature interval between T_f and T_{5\%}, (\Delta T=T_f-T_{5\%}), and the char yield. The characteristic data obtained from dynamic TGA data are listed in Table 4. In contrast to PHB homopolymer whose thermal degradation takes place as a single weight loss step [6] with the temperature of maximum weight loss rate centered around 257 °C, the decomposition of copolymers is more complex. It is obvious that the degradation of the copolymers takes place mainly via two steps. In comparison with the TGA curves of pure PHB and PCL-PEG-PCL prepolymers and the chemical composition of the copolymers, the first one is assigned to the thermal decomposition of PHB segments, while the other to the thermal degradation of PCL-PEG-PCL blocks. As shown from the thermograms (Fig. 6) the extent of each individual weight loss closely reflects the amount of the corresponding PHB and PCL-PEG-PCL components in the copolymer. This result is consistent with pervious findings [12, 34]. Additionally, the corresponding onset and main decomposition temperature of the PHB segments in the copolymers become lower compared to neat PHB and are decreased with increasing PHB content. This is because the molecular weight of the copolymer is less than that of neat PHB. Although the copolymers become less thermally stable, they degrade over a wide range of temperature compared to neat PHB. At the same time the T_m of the PHB segments in the copolymers is around 140 °C which is below the onset of the thermal degradation of PHB [5–7], while that of PHB homopolymer of high molecular weight is around 180 °C [34] according to DSC measurements; thus the difference between T_{1p} and T_m becomes larger in the copolymers, except for sample A1, indicating that the range of the processing temperature of copolymers is enlarged compared to PHB homopolymer. Hence, the processing property of the copolymer is better than PHB homopolymer.
Kinetic analysis

The thermal degradation of the prepared copolymers was evaluated using non-isothermal thermogravimetric analysis. Figure 7 shows the TGA and DTGA thermograms of sample A1, as a representative example, corresponding to dynamic experiments carried out at different heating rates ($\beta$) (5, 10, 20 K/min). It was noticed from the TGA curves that $T_p$ shifts to higher values at higher heating rates.

Ozawa and Kissinger methods [35–37] were individually applied to calculate activation energy of the thermal degradation reaction ($E_a$) and frequency factor ($A$) because they were both simple ways to deal with the thermal degradation process without the need of any assumption about conversion-dependent function. Ozawa’s equation is expressed as:

$$\ln \beta = A' - 1.052 \left( \frac{E_o}{RT_p} \right)$$

(2)

Where $A'=\ln(AE_og(\alpha)R)-5.3305$, $E_o$ is the activation energy calculated from Ozawa method, $g(\alpha)$ is the integral form of the kinetic model, $\beta$ is the heating rate. $R$ is the universal gas constant. The activation energy $E_o$ and $A'$ are obtained from the slope and ordinate intercept respectively, of the linear plot between $\ln \beta$ versus $1/T_p$ (Fig. 8a).

Kissinger’s equation is given by:

$$\ln \left( \frac{\beta}{T_p^2} \right) = - \frac{E_K}{RT_p} + \ln \frac{4R}{E_K}$$

(3)

Where $E_k$ is the activation energy calculated from Kissinger method. Therefore, $E_k$ could be obtained from the slope of plotting $\ln(\beta/T_p^2)$ against $1/T_p$ (Fig. 8b). $A'$ can be calculated with the following equation:

$$A' = \frac{\beta E_o \exp\left(E_o/RT_p\right)}{RT_p^2}$$

(4)

Here, $\beta$ is the heating rate (K/min), $T_p$ is the maximum degradation rate temperature (K), $R$ is the gas constant and $A'$ is a pre-exponential factor.

On the basis of the experimental results from the dynamic TGA study, $E_a$ and $A'$ were obtained using the above equations and results are listed in Table 5. The results indicate that the apparent activation energies of the PHB component in the poly(PHB/PCL-PEG-PCL) urethanes obtained by each of Kissinger and Ozawa methods are nearly close and decrease with increasing the content of PHB in the copolymer. The pre-exponential factor, $A'$, followed a similar trend to that of $E_a$. The activation energy of $E_a$ of the non-isothermal degradation of neat PHB was determined by various methods: Flynn-Wall-Ozawa and Kissinger [38–40], Horowitz–Metzger [41] and Coats-Redfern [42] methods. The reported values are inconsistent and they vary from 80 to 137 kJmol$^{-1}$ [38–40] to around 300 kJmol$^{-1}$ [41, 42]. The obtained $E_a$ are close to the value reported by Yeo et. al [40].

Tensile mechanical properties

The results of the tensile properties for the investigated samples (taken as cast films) are listed in Table 6. All the copolymers investigated are tough materials and retain high elasticity conveyed by PCL-PEG-PCL component. Expectedly, increasing PHB hard segment content leads to higher tensile strength with a concurrent decrease in the elongation at break values (Table 6). Discussing this finding on the basis of a segregation phenomenon, it appears from DSC study that the tendency towards segregation of PHB and

![Swelling behaviour of polyurethanes films in deionized water at 37 °C](image)

Table 5 Activation energy of poly(PHB/PCL-PEG-PCL) urethanes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ozawa method</th>
<th></th>
<th>Kissinger method</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$ (kJ/mol)</td>
<td>$R^2$</td>
<td>$A$</td>
<td>$E_a$ (kJ/mol)</td>
</tr>
<tr>
<td>A1</td>
<td>154.8</td>
<td>0.989</td>
<td>5.46 × 10$^{17}$</td>
<td>154.0</td>
</tr>
<tr>
<td>A2</td>
<td>159.9</td>
<td>0.999</td>
<td>1.36 × 10$^{18}$</td>
<td>159.3</td>
</tr>
<tr>
<td>A3</td>
<td>139.1</td>
<td>0.984</td>
<td>1.12 × 10$^{16}$</td>
<td>137.5</td>
</tr>
</tbody>
</table>

Table 6 Tensile properties of poly(PHB/PCL-PEG-PCL) urethanes

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Elongation at break (%)</th>
<th>Ultimate tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>448±15</td>
<td>9.2±0.2</td>
</tr>
<tr>
<td>A2</td>
<td>348±10</td>
<td>9.6±0.4</td>
</tr>
<tr>
<td>A3</td>
<td>280±6</td>
<td>10.5±0.3</td>
</tr>
</tbody>
</table>

Fig. 9 Swelling behaviour of polyurethanes films in deionized water at 37 °C
PCL-PEG-PCL domains decreases with increasing PHB content in the copolymer. However, the extent of phase mixing between PHB and PCL-PEG-PCL increases with increasing PHB content, as mirrored with increasing Tg, which might lead to a rigidification of the soft segments, thus explaining the increase of tensile strength and decrease of elongation. In addition to these factors, there are many intrinsic properties, which may affect their properties, such as the crystallinity, crystallite sizes and distribution of crystallites that control the mechanical properties of the end-product.

Water uptake

Figure 9 shows the water uptake percentage of the investigated copolymers as a function of time. This parameter is taken as an indirect measurement of the bulk hydrophilicity of the materials. It can be seen that the swelling ratio of the copolymers based on PHB and PCL-PEG-PCL increases with time and reaches a maximum after 20 min. The highest water uptake is demonstrated by sample A1, the copolymer with high content of PEG (see Table 2). As a comparison, water uptake of poly(ester urethane) sample, sample B, based on PHB (Mn=3,000 g/mol) having 30 wt.% PHB was also investigated, confirming that in absence of PEG moieties, no significant swelling took place.

Conclusions

Poly(ester ether urethane)s based on poly(3-hydroxybutyrate) and poly(ε-caprolactone)-b-poly(ethylene glycol)-b-poly(ε-caprolactone) triblock were synthesized from the corresponding prepolymer diols via coupling reaction of HDI. The obtained urethanes were confirmed by FTIR and 1H NMR.GPC results showed that the molecular weight decreases with the increase of PHB content. The DSC analysis showed that the prepared urethanes are semi-crystalline thermoplastics whose crystalline domains stem from PHB and PCL-PEG-PCL segments. The Tm of PHB segments in the urethanes is decreased to ~141 °C, about 40 °C less than that of neat PHB, hence the urethanes are considered to be more processable than neat PHB. The crystallization of PCL-PEG-PCL was physically constrained with increasing PHB content in the urethanes. All the investigated samples were found to exhibit one Tg corresponding to PCL-PEG-PCL soft segments components. The TGA analysis showed that the urethanes were less stable and the decomposition range became wider than neat PHB. For comparison, the activation energy is calculated using Kissinger and Ozawa methods from non-isothermal degradation mode. Mechanical tensile testing proved that the elongation at the break point is much higher than that in the neat PHB. The tensile strength increased while the elongation at the breakpoint is decreased with increasing PHB content. The effect of the length of PEG, PCL and PHB blocks and compositions, on the physical and biodegradation properties is planned to be investigated in the future to optimize the structure material properties. The swelling ratio of the investigated copolymers based on PHB and PCL-PEG-PCL increases with time and the highest water uptake is demonstrated by the copolymer with high content of PEG.

Acknowledgment Special thanks to Cairo University for supporting this research through Graduate Research Challenge Fund (GRCF) for distinguished young researchers.

References

Synthesis and thermal characterization of biodegradable poly(ester-urethane-urea)s based on poly[(R)-3-hydroxybutyrate] and poly(ethylene glycol) as soft segment. Eur Polym J 43:1838–1846


