Journal of Thermal Analysis and Calorimetry, Vol. 96 (2009) 1, 307–313

SYNTHESIS AND STRUCTURE OF BIODEGRADABLE HEXYLENE TEREPHTHALATE-CO-LACTIDE COPOLYESTERS

Y. Chen[1]*, *L. Tan*[1], *W. Zhou*[1], *J. Su*[1], *Y. Yang*[1] *and Y. Hu*[2]

[1]Institute of Polymers, Department of Chemistry, Nanchang University, Nanchang 330031, People's Republic of China
[2]College of Mechanical and Electronic Engineering, Jingdezhen Ceramic Institute, Jingdezhen 333001, China

To obtain a biodegradable polymer material with satisfactory thermal properties, higher elongation and modulus of elasticity, a new copolyester, poly(hexylene terephthalate-co-lactide) (PHTL), was synthesized via direct polycondensation from terephthaloyl dichloride, 1,6-hexanediol and oligo(lactic acid). The resulting copolyesters were characterized by proton nuclear magnetic resonance (^{1}H NMR), differential scanning calorimetry (DSC), thermogravimetry (TG) and wide-angle X-ray scattering (WAXS). By using the relative integral areas of the dyad peaks in ^{1}H NMR spectrum of copolyesters PHTL, the sequence lengths of the hexylene terephthalate and lactide units in the resultant copolyesters are 3.5 and 1.5, respectively. Compared to poly(hexylene terephthalate) (PHT), PHTL has lower T_m but higher T_g due to the incorporation of lactide unit into the main chains of copolyesters. The degradation test of copolyesters under a physiological condition shows that the degradability of PHTL is sped up due to incorporation of lactide segments.

Keywords: *biodegradation, copolyesters, lactide, poly(hexylene terephthalate)*

Introduction

In the world today, increasing volumes of plastics are manufactured and used for various applications because of their versatility and ability to be mass-produced. However, they usually are not naturally decomposing, and they are considered to cause some environmental problems. For this reason, many scientists have worked to develop new biodegradable polymers. Most of the synthetic biodegradable polymers are aliphatic polyesters such as poly(ε-caprolactone) (PCL), poly(*L*-lactic acid) (PLLA), poly(3-hydroxybutyrate) (PHB) and poly(butanediol succinate) (PBS) [1–4]. Unfortunately, the application field of aliphatic polyesters in industry and agriculture were greatly limited because of their high cost and poor physical and mechanical properties. Blending and copolymerization techniques have been tried to obtain biodegradable polymers with improved properties [5–9]. However, general aliphatic polyesters had relatively low mechanical properties and melting temperatures (T_m's).

On the other hand, aromatic polyesters such as poly(ethylene terephthalate) (PET) possess excellent physical and mechanical properties and low cost compared with aliphatic polyesters, but they are very resistant to bacterial or fungal attack, and hence do not biodegrade under normal environmental conditions. Some research has shown that these aromatic polyesters can be degraded when they are copolymerized with aliphatic polyesters [10]. In order to obtain lower cost biodegradable polymers with both satisfactory physical properties and biodegradability, the synthesis of copolyesters composed of aliphatic and aromatic units has been aimed [11–15]. A new type of biodegradable copolyester, poly[(butylenes succinate)-co-(butylene terephthalate)]-*b*-poly(tetramethylene glycol), has been prepared, which had the improved elongation properties and elasticity. The toughness and breaking strain of the copolymers increased with increasing poly(tetramethylene glycol) content [11]. Biodegradable poly(ether/ester)s derived from dimethyl terephthalate, 1,4-butanediol, and α-hydro-ω-hydroxypoly(oxyethylene) was synthesized using $Ti(OC_4H_9)_4$ as catalyst [12]. Poly(butylene terephthalate)/ poly(ε-caprolactone) copolyesters were prepared by blend of poly(butylene terephthalate) (PBT) and poly(ε-caprolactone) (PCL), and followed by a transesterification at 257°C [13]. A copolyester, poly(butylene succinate-co-ethylene succinate-co-ethylene terephthalate) (PBEST), was synthesized via direct polycondensation from three prepolymers of butylene succinate, ethylene succinate and ethylene terephthalate [14]. BASF has commercialized a new biodegradable polyester, Ecoflex™, which consists of several polyester units, containing 1,4-butanediol, dicarbonic acids (e.g., adipic acid), and terephthalic acid [15].

In this work, we prepared a new copolyester, poly(hexylene terephthalate-co-lactide) (PHTL), through the direct polycondensation and transesterification in situ of terephthaloyl chloride (TPC),

---

* Author for correspondence: ywchen@ncu.edu.cn

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

1,6-hexanediol (HDO) and α-hydroxy-ω-carboxy *DL*-oligo(lactic acid) (PLA) without catalysts. The sequence analysis of the various copolyesters was carried out and the average block length of aromatic and aliphatic units and the degree of randomness of the copolyesters were determined from ^{1}H NMR spectra. The thermal and biodegradability of copolymers were investigated with respect to the composition in the copolyesters.

Experimental

Materials

Terephthaloyl chloride (TPC, AR grade) and 1,6-hexanediol (HDO, AR grade) were purchased from Shanghai Reagent Plant (Shanghai, China) and purified by crystallization from toluene and petroleum ether, respectively. A 90% aqueous solution of racemic *DL*-lactic acid (Fluka) was heated stepwise to 200°C and kept at this temperature in a vacuum for 4 h [16]. This procedure yielded α-hydroxy-ω-carboxyoligo(lactic acid) (PLA, $\overline{M}_w$=4500, $\overline{M}_n$=1700, $\overline{M}_w/\overline{M}_n$=2.60).

Synthesis of copolyesters

In a flame dried reaction flask with magnetic stirrer 4.0606 g (20 mmol) of terephthaloyl dichloride, 2.3636 g (20 mmol) of 1,6-hexanediol, and various amounts of oligo(lactic acid) were added under nitrogen. After 30 min of evaporation, the flask was filled with nitrogen and equipped with an oil bubbler. A slow nitrogen stream was passed through the system. The reaction mixture was slowly heated to 100°C, while the formation of hydrochloric acid was observed. A homogeneous melt was formed which became more and more viscous. The reaction mixture solidified after 1–2 h and maintained for additional 12 h at 100°C. The temperature was raised to 230°C and kept for 4 h at normal pressure and for another 4 h at 10 mbar pressure. The polymer was allowed to cool to 20°C, dissolved in 50 mL of chloroform, isolated by precipitation in 800 mL of methanol, and collected on a filter. The white polymer was purified by re-precipitation from chloroform/methanol and then dried at 40°C for 8 h in vacuum.

Instrumental methods

The compositions of copolyesters were determined by proton nuclear magnetic resonance ^{1}H NMR in $CDCl_3$ solvent using a Brucker ARX 400 MHz NMR spectrometer. Gel permeation chromatography (GPC) measurements were carried out using a Waters 1515 HPLC equipped with a Styragel MIXED-C column and a Waters 2414 refractive index detector. Chloroform ($CHCl_3$) was used as the mobile phase. Monodispersed polystyrene standards (Aldrich Chemical Co.) were used to generate the calibration curve. A contact angle measurement JC2000A was used to measure static water contact angles of the polymer films at 25°C and 60% relative humidity using a sessile drop method. For each angle reported, at least five sample readings from different surface locations were averaged. The angles reported were reliable to ±1°.

Thermogravimetry (TG) was performed under nitrogen with a Perkin-Elmer TGA 7 (heating rate 20°C min^{-1}, sample size 8–10 mg). A temperature T_d (–1.5 mass%) at which 1.5 mass% of original mass of a sample was lost due to its decomposition, was tentatively applied as an index to characterize its thermal stability. Differential scanning calorimetry (DSC) measurements of copolyesters were carried out on a Perkin-Elmer DSC 7 equipped with a liquid nitrogen cooling system under a nitrogen flow at a rate 40 mL min^{-1}. The samples of about 8–10 mg were encapsulated in the DSC aluminum pans and then thermally treated. Prior to the DSC characterization heat histories of samples were removed and they were kept at ambient temperature for days to allow their crystallization to approach the equilibrium state. DSC thermal diagram was recorded at the heat speed of 10°C min^{-1} from –50 to 300°C, and glass transition temperature T_g, melting point T_m, and fusion heat ΔH_m were determined from the endothermic curves by observing the second heating run. The crystallization temperature T_c and crystallization enthalpy ΔH_c were recorded from cooling run (cooling rate 20°C min^{-1}). The surfaces of degraded samples after the hydrolytic degradation were observed with Philips 535 scanning electron microscopy (SEM) after gold vapor deposition onto the samples in an Edwards Auto 306. The X-ray diffraction (XRD) study of the samples was carried out on a Shimadzu XRD-6000 X-ray diffractometer, operating at 30 kV and 20 mA with a copper target (λ=1.54 Å) and at a scanning rate of 1° min^{-1}.

Hydrolytic degradation

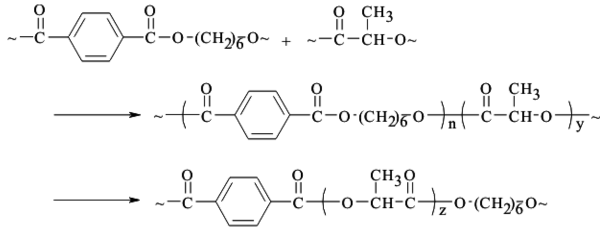
Films of polyesters were prepared by solution casting. Typically, a chloroform solution (30%) of the polymer was poured onto a glass plate and the solvent was slowly evaporated at room temperature. The formed film was separated from the glass plate. The residual solvent was evaporated under atmospheric pressure over 24 h at room temperature and then in vacuo for 48 h at 40°C. Hydrolytic degradation experiments of the polyesters were carried out at 37°C in a phosphate buffer solution (Fluka, pH 7.413 at 25°C). Square samples with dimensions of 1×4 mm^2 were cut from the various films and placed in vials containing 20 mL of buffer solution. At predetermined degradation time intervals, the specimens were removed from the medium, rinsed with distilled water, dried under vacuum at room temperature for 2 days and weighed. Before continuing the experiment, the buffer solution was renewed. Mass loss percentages of the copolyesters were obtained according to the relationship (mass loss%)=$(W_0-W_r)\cdot 100/W_0$, where W_0 is the initial mass, and W_r the dry mass of the specimens after degradation.

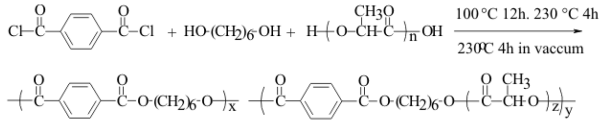
Results and discussion

Synthesis of copolyesters

The concept for achieving hydrolytical degradation is the combination of lactide moieties into aromatic segments. Copolyesters have to contain a high content of aromatic units and a certain amount of lactide moieties in order to display improved physical properties and hydrolytic degradability, respectively. However, for hydrolytic degradability, a statistical copolymer is preferred rather than a block copolymer. In view of this demand, we decided to synthesize copolyesters by melt polycondensation of terephthaloyl dichloride, 1,6-hexanediol, and oligo(lactic acid) with hydroxyl and carboxy terminal groups. The insertion of the lactide moieties by transesterification has been proved before [17–19]. As shown in Scheme 1, the synthesis process of copolyester, poly(hexylene terephthalate-co-lactide) (PHTL), is interpreted. During the synthesis of copolyesters, the transesterification between hexylene terephthalate (HT) segments and lactide (LA) units was unavoidable. The oligo(lactic acid) have two different functional groups, so the polycondensation and the transesterification between HT and LA units (or segments) may proceed as follows:

The transesterification between HT and LA segments results in the more complex structure of PHTL copolyesters in comparison with other segmented copolymers. Due to good solubility of oligo(lactic acid) in methanol, the copolyesters were re-precipitated from chloroform/methanol. Analysis of the precipitation filtrate did not show any significant amounts of extractable oligo(lactic acid).





Scheme 1 Synthesis of copolyesters

Structure characterization of copolyesters

The ^1H NMR spectra of poly(hexylene terephthalate) (PHT) and PHTL containing 30 mol% LA are shown in Figs 1 and 2. As verified by ^1H NMR spectroscopy, PHT showed the characteristic peaks at 8.12 (a), 4.37 (b), 1.82 (c) and 1.55 ppm (d), attributable to the protons of benzene ring, OCH_2, CH_2 next to the OCH_2, and CH_2 being at distance of the OCH_2, respectively. However, in the ^1H NMR spectrum of the PHTL copolyester, additional peaks at 5.18 (e) and 1.45 ppm (f) are assigned to the protons of CH and CH_3 in LA units, respectively. The integrals of the peaks at 5.18 (CH of LA units) and 4.37 pmm (OCH_2 of HT segments) provided the actual content of LA and HT units (or segments) in the PHTL copolyesters. The calculated content was approximately consistent with the feeding molar ratio (Table 1). In the ^1H NMR spectrum of the PHTL copolyester, in addition to the nuclear resonances mentioned above characteristic of HT and LA units (or segments), there are several new peaks (g and h) appearing at 4.19 and 1.64 ppm, which should be attributed to OCH_2 and next CH_2 of the hexylenedioxyl group linking a LA unit, respectively.

The relative intensives of the dyad peaks for copolyesters PHTL were used to calculate the number-average sequence lengths of the resulting copolyesters according to the following equation:

$$n_{\mathrm{HT}}=\frac{\frac{N_{\mathrm{b}}}{4}+\frac{N_{\mathrm{g}}}{2}}{\frac{N_{\mathrm{g}}}{2}},\quad \frac{M_{\mathrm{PHTL}}-M_{\mathrm{PLA}}}{n_{\mathrm{HT}}M_{\mathrm{HT}}}n_{\mathrm{LA}}=\frac{M_{\mathrm{PLA}}}{M_{\mathrm{LA}}} \qquad (1)$$

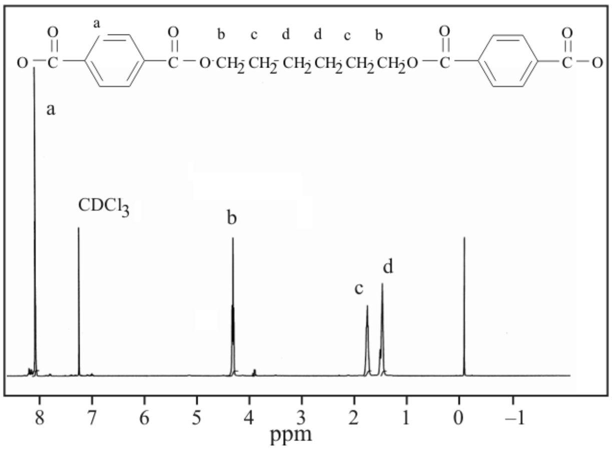


Fig. 1 400 MHz ^1H NMR spectrum of the PHT polyester

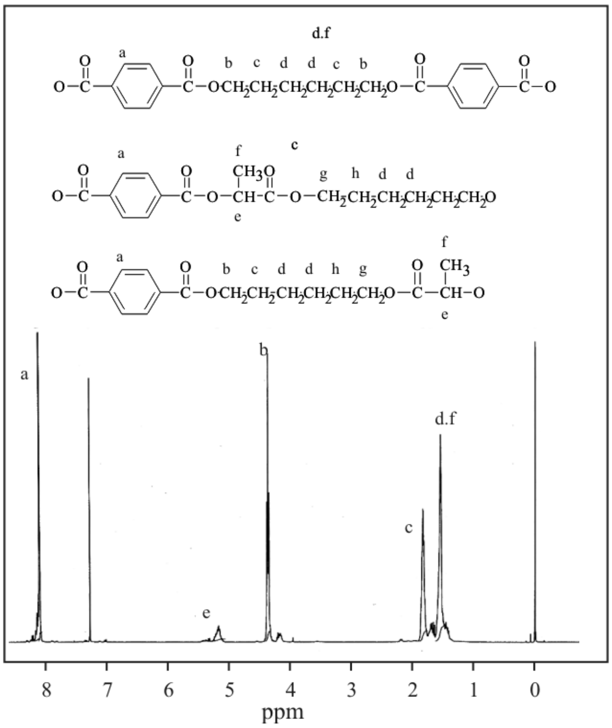


Fig. 2 400 MHz ^{1}H NMR spectrum of the copolyester PHTL30

where N_b and N_g represent the corresponding integral areas in NMR spectrum, respectively, M_{PHTL}, M_{PLA}, M_{HT} and M_{LA} are the respective molecular mass of PHTL, PLA, HT unit and LA unit. For the PHTL copolyester containing 30 mol% of LA units, the sequence lengths of the hexyleneterephthalate (n_{HT}) and lactide (n_{LA}) are 3.5 and 1.5, respectively. For the synthesis of PHTL copolyesters, the reaction temperature reached around 230°C, which was above the temperature of the ester bond cleavage in prepolymers, thus leaded to the possibility of ester exchange reaction. Meanwhile, a long reaction time was also assumed to be in favor of the ester exchange reaction.

The copolyesters are readily soluble in chloroform. With increasing content of lactide units, the copolyesters showed improved solubility in tetrahydrofuran (THF). The copolyesters were synthesized by melt polycondensation but with varying amounts of oligo(lactic acid). Yields were in the range of 93–97%. GPC traces showed unimodal molecular mass distribution. No hints for oligo(lactic acid)s were found during analysis of the methanol precipitation bath, which indicated quantitative incorporation of oligo(lactic acid) in the copolyesters. The obtained molecular mass parameters are listed in Table 1. With the increase of lactide content, to get a high molecular mass is difficult, and the molecular mass distribution becomes broader. The decrease of molecular mass of copolyesters with increasing content of lactide units is most likely due to the increasing amount of carboxyl end-groups of oligo(lactic acid). To the best of our knowledge, the reaction activity of the carboxylic group is lower than that of the carboxylic chloride group in this polymerization [17–19]. Due to good solubility of un-reacted oligo(lactic acid) in methanol, the copolyesters were not possible as mixture of the segments after re-precipitation from chloroform/methanol.

Thermal behavior of copolyesters

The thermal properties were characterized by means of DSC and TG for the PHTL copolyesers. Figures 3 and 4 show the DSC cooling and second heating curves of copolyesters, and the transition temperature values are listed in Table 2. As we can see in the DSC curves, every copolyester exhibits only one glass transition temperature (T_g), and the T_gs change regularly with lactide content. By fitting the data, we find that the relationship between T_g and composition of PHTL copolyesters conforms roughly with the Gordon–Taylor equation, which reveals the random property of PHTL copolyesters,

$$T_g = \frac{T_{g,PHT} + (KT_{g,PLA} - T_{g,PHT})W_{PLA}}{1+(K-1)W_{PLA}} \tag{2}$$

where W_{PLA} is the mass fraction of the oligo(lactic acid) possibly converted from molar fraction of composition, $T_{g,PLA}$=22°C, $T_{g,PHT}$=15°C and K=14.92. The error was mainly derived from the small difference in T_g of the two polymers PLA and PHT.

Table 1 Composition and molecular mass of PHTL copolyesters

Sample	Feed molar ratio HT/LA	Composition[a] HT/LA	$\overline{M}_w \cdot 10^{-4}$	$\overline{M}_n \cdot 10^{-4}$	$\overline{M}_w/\overline{M}_n$
PHT	100/0	100/0	8.97	5.83	1.54
PHTL5	95/5	95.3/4.7	8.82	5.48	1.61
PHTL10	90/10	90.9/9.1	8.24	4.99	1.65
PHTL15	85/15	87.0/13.0	7.46	4.29	1.74
PHTL20	80/20	83.0/17.0	7.18	3.63	1.98
PHTL30	70/30	72.2/27.8	4.58	2.16	2.12

[a] The molar ratio of hexyleneterephthalate (HT) and lactide (LA) segments (or units) in resulting copolyesters

Table 2 Thermal properties of copolyesters

Sample	$T_g{}^a$/°C	$T_{m1}{}^a$/°C	$\Delta H_{m1}{}^a$/J g^{-1}	$T_{m2}{}^a$/°C	$\Delta H_{m2}{}^a$/J g^{-1}	$T_c{}^a$/°C	$\Delta H_c{}^a$/J g^{-1}	$T_d{}^b$/°C
PHT	15.0	139.6	9.87	147.6	31.55	113.9	45.72	392.4
PHTL5	15.0	133.4	9.56	143.4	29.62	105.9	42.93	390.1
PHTL10	15.4	127.8	6.61	137.9	23.36	103.2	38.86	391.7
PHTL15	17.0	122.3	3.51	133.9	19.48	86.8	32.99	388.7
PHTL20	20.0	121.4	4.93	132.4	23.70	90.1	37.73	387.4
PHTL30	22.0	114.2	1.27	128.1	21.47	80.4	33.51	386.6

[a]Melting temperature (T_m), glass-transition temperature (T_g), crystallization temperature (T_c), melting enthalpy (ΔH_m) and crystallization enthalpy (ΔH_c) were registered by DSC at a cooling rate of 20°C min^{-1} or at a second heating rate of 10°C min^{-1}
[b]T_d (1.5 mass%) was measured by TG at a heating rate of 20°C min^{-1}

In addition to T_g, PHTL copolyesters without and with lactide units also exhibit two melting endotherm and a cooling-crystallization exotherm. The melting temperature (T_m) of PHTL copolyesters shifted a little down to a low temperature as the lactide content increased. The changes in the melting behaviors were due to the lowered regularity of the copolyester backbone caused by the introduction of the lactide units into the copolyesters. As the main-chain structure of the copolyesters became more random and harder to crystallize, T_m of the copolyesters decreased. The crystallization behavior showed the same trend as the melting behavior. The crystallization peak became broad and shifted down to a lower temperature as the lactide content increased.

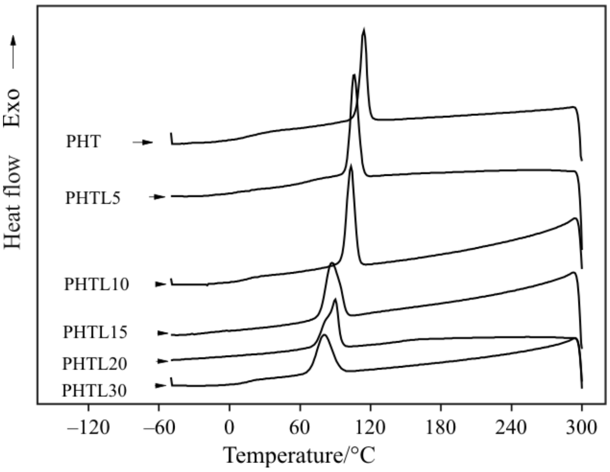


Fig. 3 DSC curves of copolyesters at the cooling scan speed of 20°C min^{-1}

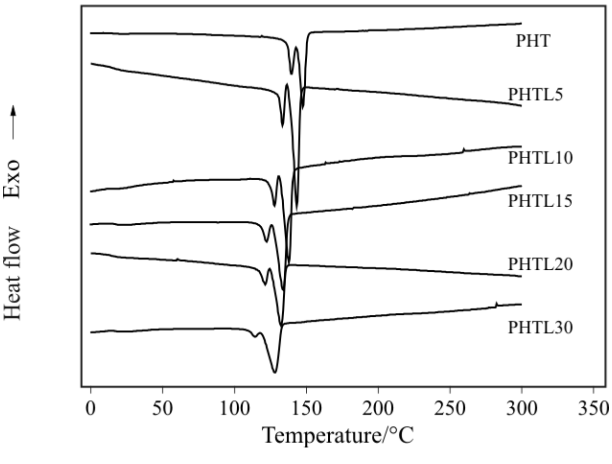


Fig. 4 DSC curves of copolyesters at the second heating scan speed of 10°C min^{-1}

The crystallization area in the copolyesters varies with the lactide content, and the change will affect not only crystalline temperature but also fusion heat. The variation of ΔH_m shows a similar tendency to that of T_m. With increase of lactide content in the copolyesters, the crystallinity of the copolyesters decrease, and thus the fusion heats of the copolyesters fall down. The variations of T_g and T_m with respect to composition, which are in agreement with the Gordon–Taylor equation and Fox–Flory equation, respectively, indicated that the copolyesters are more random.

Figure 5 presents the thermal gravimetrical traces of PHTL copolyesters, and an index of T_d (–1.5 mass%) is tentatively applied to evaluate their thermal stabilities. The values of T_d were between 392 and 386°C, and a slight decrease of T_d was observed with increasing lactide content in the copolyesters.

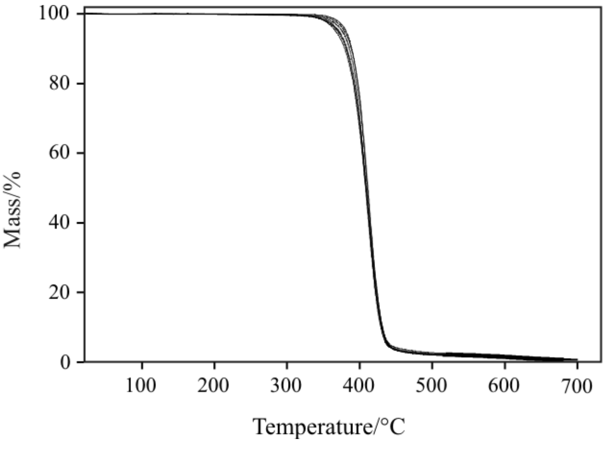


Fig. 5 TG curves of copolyesters at a scanning rate of 20°C min^{-1}

X-ray diffraction patterns and crystalline structure

Figure 6 shows the X-ray diffraction patterns of four typical copolyesters, which contain 0, 15, 20 and 30 mol% of lactide. For the copolyesters, their XRD patterns show the three strong diffraction peaks at 2θ angles of 17.6, 22.5 and 25.8°, which are similar to those of PHT homopolyester at the same 2θ angles. This suggests that copolyesters have the same crystalline structures as PHT, and indicates that although oligo(lactic acid) itself can be crystallized, it is in amorphous state due to low content of lactide comonomer which is minor component in the copolyesters. The existence of lactide units in amorphous states results in a decrease of the crystallinity of copolyesters compared with that of PHT. As the content of lactide increases, the crystalline structures of PHT in copolyesters are gradually destroyed and amorphous regions increase, which is in accordance with the fact that the T_m of copolyesters shows a tendency to decline. The XRD diffractograms proved that the crystallinity of the copolyesters was not high and the size of the crystallites was small.

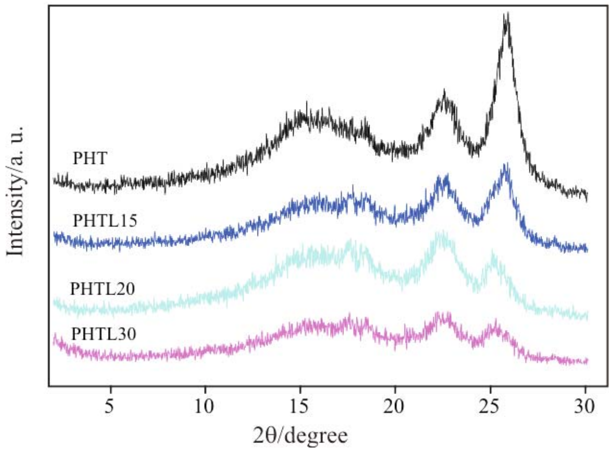


Fig. 6 Wide-angle X-ray diffraction patterns of copolyesters

Contact angle and hydrolytic biodegradability of copolyesters

The surface properties of solution cast films of copolyesters were analyzed by contact angle measurements (Fig. 7). The contact angles of copolyesters is significantly smaller than the contact angle observed for PHT homopolyester. Further decrease of contact angle was observed by increasing the content of lactide in copolyesters. From the contact angle analysis, thermodynamic parameters such as surface tension could be obtained as a function of the content of lactide in copolyesters. Thus, smaller contact angles usually result in better hydrophilicity.

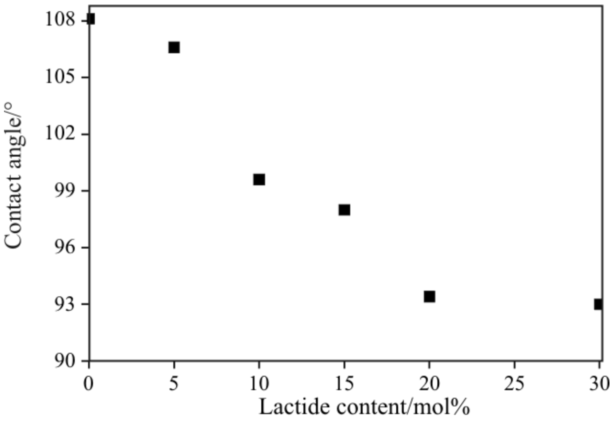


Fig. 7 Static water contact angles of copolyester films

For preliminary test of hydrolytic degradability, films of the copolyesters were placed in 20 mL of a phosphate buffer solution at 37°C. The samples were removed at various times, rinsed with distilled water, drie, and weighed. Before continuing the experiment, the buffer solution was renewed. Mass loss data of the copolyesters are shown in Fig. 8. PHT homopolyesters slightly displayed degradation under physiological conditions. In contrast, all copolyesters were distinctly degraded in phosphate buffer solution at 37°C, and a mass loss of 5% was observed for PHTL copolyester containing 30 mol% of lactide, after immersion in phosphate buffer solution at 37°C for 35 days. With increase of lactide, the copolyesters show enhanced hydrolytic degradation. Surface morphology changes were investigated by scanning electron microscopy (SEM). Photographs of PHTL copolyester containing 30 mol% of lactide content before and after immersion tests are shown in Fig. 9. Dark areas and dents on the surfaces of the samples represented biodegraded parts. The surface of the films before degradation was smooth with small holes due to the evaporation of the solvent (part a). After degradation for 10 days, the smooth surface of the

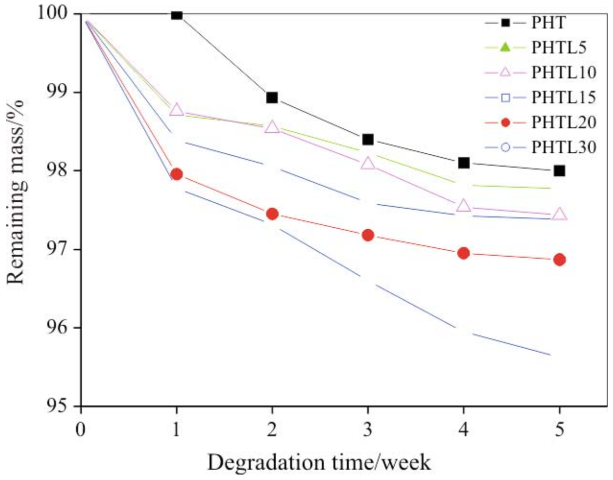


Fig. 8 Mass loss *vs*. time during hydrolytic degradation of copolyesters

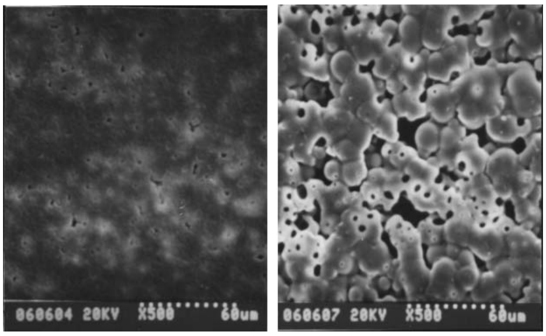


Fig. 9 Scanning electron micrographs of the surface of the PHTL30 film before and after hydrolytic degradation for 10 days

copolyester films became cracked or porous (part b). The copolyesters produced by transesterification showed good biodegradability. The degradation of copolyesters occurred on the film surfaces.

Conclusions

In this work, new biodegradable copolyesters were prepared through melt polycondensation and transesterification in situ of terephthaloyl chloride, 1,6-hexanediol and oligo(lactic acid). The existence of new heterolinkages inside the backbones of the copolyesters, resulting from the transesterification reaction, was confirmed. The block lengths decreased with the transesterification at 230°C and the copolymers finally attained an almost random microstructure. The T_m and T_c values of the copolyesters varied with the lactide content used for the transesterification reaction. Wide-angle X-ray diffraction revealed that the crystalline structure of PHT is preserved for the semicrystalline copolyesters. The PHTL copolymers underwent significant hydrolytic degradation at 37°C, which increased with the content of lactide units. Hydrolysis occurs mainly on the aliphatic ester groups. A stress-stain curve of solution-cast/re-molten film of copolyester was recorded at room temperature. The Young's modulus of the solution-cast and re-molten film is around 55 MPa. The further research is being performed on improvement of mechanical properties by orientation and thermal treatment of the samples. The results will be reported in the following paper.

Acknowledgements

Financial support for this work was provided by the Program for New Century Excellent Talents in University (NCET-06-0574), the National Natural Science Foundation of China (50773029), the Natural Science Foundation of Jiangxi Province (520044), the fund from the Jiangxi Provincial Department of Education and the Program for Innovative Research Team of Nanchang University.

References

1 E. Takiyama and T. Fujimaki, Biodegradable Plastics and Polymers, Elsevier, Amsterdam 1994, p. 584.
2 N. Lotti, V. Siracusa, L. Finelli, A. Munari and P. Manaresi, J. Therm. Anal. Cal., 66 (2001) 827.
3 W. S. Drumond, C. G. Mothe and S. H. Wang, J. Therm. Anal. Cal., 85 (2006) 173.
4 J. A. F. R. Rodrigues, D. F. Parra and A. B. Lugao, J. Therm. Anal. Cal., 79 (2005) 379.
5 H. Fukuzaki, Y. Aiba, M. Yoshida, M. Asano and M. Kumakura, Makromol. Chem., 190 (1989) 1553.
6 K. Imasaka, T. Nagai, M. Yoshida, H. Fukuzaki, M. Asano and M. Kumakura, Makromol. Chem., 191 (1990) 2077.
7 H. Fukuzaki, M. Yoshida, M. Asano, M. Kumakura, K. Imasaka, T. Nagai, T. Mashimo, H. Yuasa, K. Imasi and H. Yamanaka, Eur. Polym. J., 26 (1990) 1273.
8 R. K. Pannu, S. Tanodekaew, W. Li, J. H. Collett, D. Attwood and C. Booth, Biomaterials, 20 (1999) 1381.
9 K. Bechtold, M. A. Hillmyer and W. B. Tolman, Macromolecules, 34 (2001) 8641.
10 Y. Tokiwa and T. Suzoki, J. Appl. Polym. Sci., 26 (1981) 441.
11 Y. H. Park and C. G. Cho, J. Appl. Polym. Sci., 79 (2001) 2065.
12 S. Fakirov and T. Gogeva, Makromol. Chem., 191 (1990) 603.
13 D. Ma, X. Xu, X. Luo and T. Nishi, Polymer, 38 (1997) 1131.
14 L. M. Deng, Y. Z. Wang, K. K. Yang, X. L. Wang, Q. Zhou and S. D. Ding, Acta Mater., 52 (2004) 5871.
15 S. Dirk and S. Gabriel, Kunststoffe, 91 (2001) 100.
16 M. Asano, M. Yoshida and I. Kaetsu, Makromol. Chem. Rapid Commun., 6 (1985) 509.
17 Y. Chen, R. Wombacher, J. H. Wendorff, J. Visjager, P. Smith and A. Greiner, Biomacromolcules, 4 (2003) 974.
18 Y. Chen, R. Wombacher, J. H. Wendorff and A. Greiner, Chem. Mater., 15 (2003) 694.
19 Y. Chen, R. Wombacher and J. H. Wendorff and A. Greiner, Polymer, 44 (2003) 5513.

Received: January 23, 2008
Accepted: August 26, 2008

DOI: 10.1007/s10973-008-9031-1