Review

# Poly(butylene succinate) and its copolymers: Research, development and industrialization

*Jun Xu and Bao-Hua Guo*

Institute of Polymer Science & Engineering, Department of Chemical Engineering, Tsinghua University, Beijing, China

Poly(butylene succinate) (PBS) and its copolymers are a family of biodegradable polymers with excellent biodegradability, thermoplastic processability and balanced mechanical properties. In this article, production of the monomers succinic acid and butanediol, synthesis, processing and properties of PBS and its copolymers are reviewed. The physical properties and biodegradation rate of PBS materials can be varied in a wide range through copolymerization with different types and various contents of monomers. PBS has a wide temperature window for thermoplastic processing, which makes the resin suitable for extrusion, injection molding, thermoforming and film blowing. Finally, we summarized industrialization and applications of PBS.

## 1 Introduction

Due to increasing concerns on sustainable development and the impact of materials on the environment, biodegradable materials have attracted intensive interest in the past decades. Among them, poly(butylene succinate) (PBS) synthesized from succinic acid and 1,4-butanediol (BDO) exhibits balanced performance in thermal and mechanical properties as well as thermoplastic processability compared with other common plastics, as shown in Table 1 [1–3]. Via copolymerization with other dicarboxylic acids or diols, the properties of PBS can be varied in a wide range, which is a promising advantage for various applications. Ever since the pioneering work of Carothers in 1931 [4], massive efforts have been devoted to investigate the synthesis and properties of PBS and its copolymers. Crystalline structures, physical properties and

biodegradability of PBS have been reported in previous reviews [1–3]. Due to the limitation of fossil resources and the concern on the corresponding emission of $CO_2$, the feedstocks derived from renewable resources have been candidates for synthesis of PBS and its copolymers. To our knowledge, the synthesis processes of monomers and PBS starting from fossil-based or renewable feedstocks and the properties of PBS copolymers have hardly been summarized. In this review, synthesis, processability, thermal and mechanical properties, and biodegradability of PBS and its copolymers will be outlined. In addition, industrial mass production and applications will be briefly summarized.

## 2 Synthesis of PBS and its copolymers

PBS is usually synthesized via polycondensation of succinic acid (or dimethyl succinate) and BDO. The monomers can be derived from fossil-based or renewable resources. The flow chart of PBS production is schemed in Fig. 1.

### 2.1 Production of succinic acid

At present, succinic acid is commercially manufactured by the chemical process via hydrogenization of maleic anhydride (which is derived from oxida-

**Correspondence:** Dr. Jun Xu, Institute of Polymer Science & Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China
**E-mail:** jun-xu@tsinghua.edu.cn
**Fax:** +86-10-62784550

**Abbreviations: BDO**, 1,4-butanediol; **Mw**, molecular weight; **PBS**, Poly(butylene succinate); **PBSA**, poly(butylene succinate-co-butylene adipate); **PBST**, poly(butylene succinate-co-butylene terephthalate); **PLA**, poly (lactic acid)

**Table 1.** Physical properties of PBS and PBSA compared with PLA and some commodity plastics [1].

| Items | PLA (LACEA) | PBS (Bionolle) #1000 | PBSA #3000 | PP MA210 | HDPE | LDPE F082 |
|---|---|---|---|---|---|---|
| Glass transition temperature (°C) | 55 | −32 | −45 | −5 | −120 | −120 |
| Melting point (°C) | 170–180 | 114 | 96 | 163 | 129 | 110 |
| Heat distortion temperature (°C) | 55 | 97 | 69 | 110 | 82 | 49 |
| Tensile strength (Mpa) | 66 | 34 | 19 | 33 | 28 | 10 |
| Elongation at break (%) | 4 | 560 | 807 | 415 | 700 | 300 |
| Izod impact strength (J/m) | 29 | 300 | >400 | 20 | 40 | >400 |
| Degree of crystallinity (%) | | 35–45 | 20–30 | 56 | 69 | 49 |

tion of butane or benzene) to succinic anhydride, followed by hydration to succinic acid. Among the chemical routes, electrolysis can manufacture succinic acid with high purity for food and pharmaceutical applications [5].

Succinic acid can also be obtained from fermentation of microorganisms on renewable feedstocks, such as glucose, starch, xylose, etc [6]. *Actinobacillus succinogenes* [7–11], *Anaerobiospirillum succiniciproducens* [12–16], *Mannheimia succiniciproducens* [17] and recombinant *Escherichia coli* [18–20] are well-known and well-established bacterial production strains that can produce succinic acid. For batch fermentation, the highest concentration of succinic acid in the fermentation medium reported so far is 110 g/L [21, 22]. For continuous fermentation, the production rate of succinic acid reached up to 17.1 g/L/h using *Mannheimia succiniciproducens* MBEL55E [23, 24]. One ton of bio-based succinic acid can save 4.5 tons of greenhouse gas [25].

In 2004, the US Department of Energy declared bio-based succinic acid a high-potential chemical

platform for the synthesis of a multitude of chemical compounds, as well as an attractive replacement for petroleum-based maleic anhydride (MA). Recently, some companies have built pilot, demonstration or commercial scale factories to manufacture succinic acid via biofermentation (http://www.rsc.org/chemistryworld/News/2010/January/21011003.asp.). Bioamber, a joint venture between US-based DNP (Diversified Natural Products Inc.) Green Technology and France-based ARD (Agro-industrie Recherches et Développements), announced in 2008 the successful start-up and commissioning of the world's first bio-based succinic acid plant, which was integrated into an existing biorefinery located in Pomacle, France, and had an initial annual capacity of 2,000 metric tons of succinic acid. Since December 2009, the plant has been producing renewable succinic acid, using an *Escherichia coli* strain developed specifically to produce succinic acid, with wheat-derived glucose currently being used as the substrate (http://www.bio-amber.com/release/pdf/4921336d21.pdf). DSM started investing in the development of biosuccinic acid in 2008 by forming a partnership with French starch derivatives producer Roquette. The companies are already producing biosuccinic acid for commercial testing in a 300-tons/year demonstration plant in Lestrem, France, where succinic acid was produced from starch using an innovative enzyme-based fermentation technology (http://www.dsm.com/en_US/html/media/press_releases/12_09_dsm_and_roquette_commercialize_bio_based_succinic_acid.htm). They are planning to scale-up to a facility capable of producing 10 000 to 20 000 tons annually by mid to late 2011. In October 2009, BASF formed a development and production partnership with Purac for the development of the industrial fermentation and downstream processing of biosuccinic acid, using a BASF-developed bacterial strain (*Basfi succiniproducens*) and glycerine or glucose as a feedstock. They intend to start production of „commercial quality and volumes" in the second quarter of 2010 at a Purac facility in
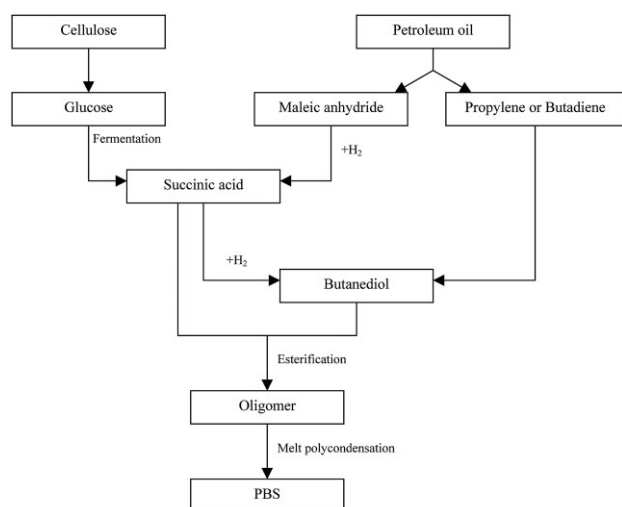


**Figure 1.** Flow chart of PBS synthesis.

Spain. Myriant Technologies in the USA has received a $50 million grant from the US Department of Energy to help build a commercial-scale biosuccinic acid facility in Louisiana. Currently, the company is producing succinic acid via fermentation of *E. coli* on unrefined sugar as a feedstock at the 20 000-L bioreactor scale.

## 2.2 Production of 1,4-butanediol

Conventional commercial processes for BDO synthesis use petrochemical feedstocks [26, 27] and PERP report 06/07-4, 1,4-Butanediol/THF (March 2008). Various industrial processes have been developed to synthesize BDO, listed as follows:

(i) The Reppe process using acetylene and formaldehyde followed by hydrogenation of the intermediate to produce BDO, which was initially developed by Walter Reppe of IG Farben in the mid-1930s [28]. This route is used mainly by BASF and BASF/Idemitsu, but also by ISP, DuPont, GAF Huls Chemicals and Novocherkassk (in the former Soviet Union). Originally, the hydration of calcium carbide was used as the source of acetylene. Now the main source is the partial oxidation of natural gas, although calcium carbide is still used. Acetylene is also produced from natural gas in the Hills electric arc reactor, and can be extracted from steam cracker streams.

(ii) Mitsubishi 1,3-butadiene acetoxylation technology, proceeding via three steps of acetoxylation, hydrogenation and hydrolysis [29–31], which was developed in the late 1970s. The Mitsubishi process is flexible and can produce both BDO and/or tetrahydrofuran (THF).

(iii) Lyondell Basell propylene oxide route, which manufactures BDO in a proprietary, multistep process based on propylene oxide. This route, developed in the late 1980s and early 1990s, has three major steps: isomerisation of propylene oxide to allyl alcohol, hydroformylation of allyl alcohol to 4-hydrobutyraldehyde, and hydrogenation of the 4-hydrobutyraldehyde to BDO [32].

(iv) Davy Process Technology, making BDO based on maleic anhydride or maleic anhydride feedstock (butanes). This flexible process uses maleic anhydride, which can be obtained by the oxidation of butane or benzene, as the feedstock (http://www.davyprotech.com/pdfs/Butanediol%20and%20Derivatives.pdf). The original process was designed in the early 1980s by Davy in collaboration with CONSER and SISAS [33, 34]. Generally, the reaction path oxidizes butane to maleic anhydride. This is then hydrolyzed to maleic acid, followed by hydrogenation to give BDO. The Davy Process Technology butanediol process can produce in a single reaction train, varying ratios of three products: BDO, THF and $\gamma$-butyrolactone.
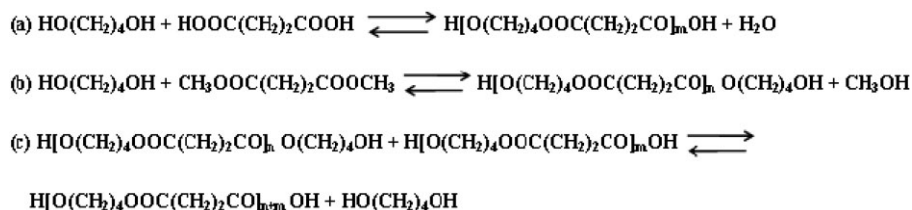
An alternative biobased process for BDO production has been described by Smith, Cooper and Vigon [35], which involves three steps: corn-derived glucose is fermented to succinic acid, which is then purified by electrodialysis, and finally the purified succinic acid is reduced catalytically to BDO [36]. In addition, the direct fermentation of BDO from sugar has been announced recently. Genomatica (a San Diego-based company) has genetically engineered *E. coli* to metabolize sugar into BDO (http://www.technologyreview.com/business/22732/).

## 2.3 Synthesis of PBS and its copolymers

Synthesis of PBS can be separated into two steps: The first step is esterification of succinic acid and BDO or transesterification of dimethyl succinate and BDO to obtain oligomers, the second step is polycondensation of the oligomers to remove BDO to form high-molecular weight (Mw) PBS (Scheme 1).

Before reaction, the reactor was equipped with a mechanical stirrer, nitrogen inlet and a condenser in a well-controlled oil bath. In the first step, the stoichiometric amounts of succinic acid (or dimethyl succinate) and BDO, or using an excess of BDO not above 15%, were added into the reactor. The temperature was increased to 160–190 °C until the acid component melted completely under $N_2$ gas atmosphere. $H_2O$ (or methanol) was distilled out. When no more water (or methanol) was distilled out under normal pressure, polycondensation under high vacuum was further carried out at high temperatures of 220–240 °C. Various catalysts, such as $SnCl_2$ [37], distannoxane [38–40], lanthanide triflates [41], p-toluenesulfonic acid [42], tetrabutyl titanate [43–48], tetraisopropyl titanate [49, 50], etc. have been used for synthesis of PBS.

The kinetics of polyesterification of succinic acid and ethylene glycol were reported by Dostal and Raf [51, 52], as well as Flory [53, 54]. Based on the data reported by Dostal, Raf and himself, Flory concluded that "the ethylene glycol-succinic acid polymerization is predominantly a trimolecular process. The rate of the reaction, which is simply an esterification, is proportional to the first power of the concentration of hydroxyl groups and to the square of the carboxyl group concentration" [53] and "polyesterification and esterification follow similar courses, from which it has been concluded that reaction rate is not affected by either increase in Mw or the concurrent increase in viscosity" [54]. Park *et al*. [55] reported the esterification kinetics

(a) $HO(CH_2)_4OH + HOOC(CH_2)_2COOH \rightleftharpoons H[O(CH_2)_4OOC(CH_2)_2CO]_mOH + H_2O$

(b) $HO(CH_2)_4OH + CH_3OOC(CH_2)_2COOCH_3 \rightleftharpoons H[O(CH_2)_4OOC(CH_2)_2CO]_n O(CH_2)_4OH + CH_3OH$

(c) $H[O(CH_2)_4OOC(CH_2)_2CO]_n O(CH_2)_4OH + H[O(CH_2)_4OOC(CH_2)_2CO]_mOH \rightleftharpoons$

$H[O(CH_2)_4OOC(CH_2)_2CO]_{n+m} OH + HO(CH_2)_4OH$

**Scheme 1.** Chemical formulations of PBS synthesis: (a) Esterification of succinic acid and 1,4-butanediol or (b) transesterification of dimethyl succinate and 1,4-butanediol to obtain oligomers. In the following stage, oligomers are polycondensed to produce the final PBS resin.

of SA and BD in the temperature range from 170 to 190°C with and without monobutyl tinoxide catalyst. It was observed that the rate of reaction increased with the increase of temperature and the catalyzed reaction showed a higher rate than the uncatalyzed one. In the absence of catalyst, SA played the role of an acid catalyst. Detailed mechanism and kinetics of polyesterification were reviewed by Fradet and Maréchal [56].

According to our experience, PBS with an Mw less than 100 000 can be extruded or injection molded; however, the material is brittle, *e.g.*, the elongation at break is only around 10% and the Izod impact strength is less than 40 J/m. In contrast, PBS with an Mw exceeding 180 000 is more ductile and can be processed via blowing. The elongation at break and the Izod impact strength of PBS can reach 270% and 73 J/m. To obtain PBS and its copolymers with high-Mw, various methods have been adopted: first, chain extension has produced PBS with hexamethylene diisocyanate [2, 57, 58] or bisoxazoline [59], adipoyl biscaprolactamate or terephthaloyl biscaprolactamate [60], which couples two PBS chains together to improve the Mw of the final product; secondly, 1:1 stoichiometry of dibasic acid and glycol must be strictly obeyed [61]. However, volatilization or side reactions occurring at high polyesterification temperature may distort the feeding stoichiometry of the feeding monomers. Consequently, an excess of BDO is generally adopted; Thirdly, removing the low molar mass byproduct of esterification from the mixture to shift the equilibrium to the side of a high molar mass polyester [61], *e.g.*, synthesis of PBS in decalin [39, 40] or dimethyl benzene [37] solvent under azeotropic conditions. Another method is direct melt polycondensation under high vacuum.

For linear PBS and its copolymers, the viscosity decreases rapidly when the processing temperature is 20 °C higher than the melting point. Due to the weak intermolecular interaction, the melt strength is low, making film blowing difficult. To solve the problem, several methods can be adopted: chain extension using chain-extending agents to couple two polymer chains to improve the Mw;

crosslinking of PBS via peroxide or irradiation; copolymerization with a small amount of trifunctional monomer (*e.g.*, triols) to introduce long-chain branches [56, 62, 63]. To avoid gel formation, the content of the branching agent must be low, *e.g.* less than 0.5–1%.

## 3 Physical properties of PBS and its copolyesters

Among the family of aliphatic poly(alkylene dicarboxylate) polyesters, poly(ethylene oxalate), poly(ethylene succinate) and poly(butylene succinate) demonstrate melting points exceeding 100 °C [64, 65], which is crucial for applications at a high temperature range. Though poly(ethylene oxalate) has an equilibrium melting point of 177 °C, it attracts less attention due to its low thermal stability. PBS is a highly crystalline polyester with its melting point at around 115 °C and heat distortion temperature at 97 °C. The tensile yield strength of unoriented specimens reaches up to 30–35 MPa, which is comparable to that of polypropylene. PBS is flexible with Young's modulus in the range of 300–500 MPa, depending on the degree of crystallinity..

To tailor design the physical properties of PBS, random copolymerization with different types of comonomer units has been examined, including adipic acid [44, 47, 57], terephthalic acid [66–70], methyl succinic acid [41, 71–73], 2,2-dimetyl succinic acid [74], benzyl succinic acid [75], ethylene glycol [43, 75–77] and 1,3-propanediol [78–80], etc.

### 3.1 Thermal and mechanical properties of PBS copolymers

Random copolymerization usually results in a decreased melting point, degree of crystallinity, heat distortion temperature and tensile strength. On the other hand, the elongation at break and impact strength usually rise with copolymerization. However, the results of poly(butylene succinate-cobutylene fumarate) are an exception, which demonstrated a constant melting point with the

**Table 2.** Thermal properties and degree of crystallinity of PBSA random polyesters (unpublished results from our lab).

| Polymer | $\Delta H_m$ (J/g) | $\Delta H^\circ_m$ (J/g) | $T_m$ (°C) | $T_g$ (°C)[a] | Crystallinity[b] (%) | Crystallinity[c] (%) |
|---|---|---|---|---|---|---|
| PBS | 67.4 | 110.3 | 112 | −18 | 61.1 | 39.66 |
| PBSA-5[d] | 96.0 | 110.3 | 108 | −21 | 87.0 | 54.47 |
| PBSA-10 | 72.5 | 110.3 | 103 | −23 | 65.7 | 45.83 |
| PBSA-15 | 79.8 | 110.3 | 99 | −27 | 72.3 | 45.27 |
| PBSA-20 | 59.5 | 110.3 | 92 | −34 | 53.9 | 46.83 |

a) The glass transition temperature (Tg) was adopted from the tanδ peak measured by dynamic thermal analysis.
b) The degree of crystallinity was the ratio of melting enthalpy determined by DSC to the melting enthalpy of completely crystalline PBS (110 J/g).
c) The degree of crystallinity was calculated from WAXD results.
d) The number indicates the molar percentage of adipic acid in the total feed acids for synthesis of PBSA copolyester.

copolymer composition up to 20 mol% [81]. The mechanism of the peculiar phenomenon is not yet clear. For the usual PBS copolymers, to ensure that the melting point of the PBS copolymers are above 100 °C, the content of comonomer units must be lower than 15 mol%. For example, the physical properties of poly(butylene succinate-co-butylene adipate) (PBSA) copolyesters can be varied with comonomer content, as presented in Table 2 and Fig. 2. It is of particular interest that PBSA with 5–15 mol% BA content possesses a higher degree of crystallinity and tensile strength than PBS, which may result from cocrystallization of BA units in the crystal lattice of PBS. The biodegradation rate of PBSA film in activated sludge enhances with increase of BA content from 0 to 20 mol% (Fig. 3).

Terephthalic acid can be copolymerized with succinic acid and butanediol to produce aliphatic-aromatic polyester poly(butylene succinate-co-butylene terephthalate) (PBST) [66–70]. PBST reveals the lowest melting point and degree of crystallinity at 30–40 mol% butylene terephthalate (BT) units (Table 3). Figure 4 reveals that the tensile strength and elongation at break of PBST depends on the degree of crystallinity (Xc). PBST with high

Xc demonstrate high tensile strength and low elongation at break. In contrast to PBSA, PBST biodegrades more slowly with an increase of comonomer content, as shown in Fig. 5. It should be noted that although PBS copolymers with 10 mol% aromatic comonomer units demonstrate faster biodegradation rate at the beginning, they later reveal slower biodegradation rates. With an increase in aromatic comonomer content, the biodegradation rate slows down.

1,3-Propanediol (PDO) can also be copolymerized with succinic acid and butanediol, which is attractive because PDO can be produced via biofermentation from triglycerol [82]. Thermal properties of poly(butylene succinate-co-propylene succinate) (PBSPS) copolyesters are listed in Table 4 [80]. Pure poly(propylene succinate) (PPS) has a low melting point at 50 °C, which limits its applications.

Dependence of the thermal properties and the degree of crystallinity of several PBS copolymers on the comonomer content is presented in Fig. 6. Whatever the type of the comomoner, melting point and the degree of crystallinity of PBS copolymers decrease with increasing comonomer content in
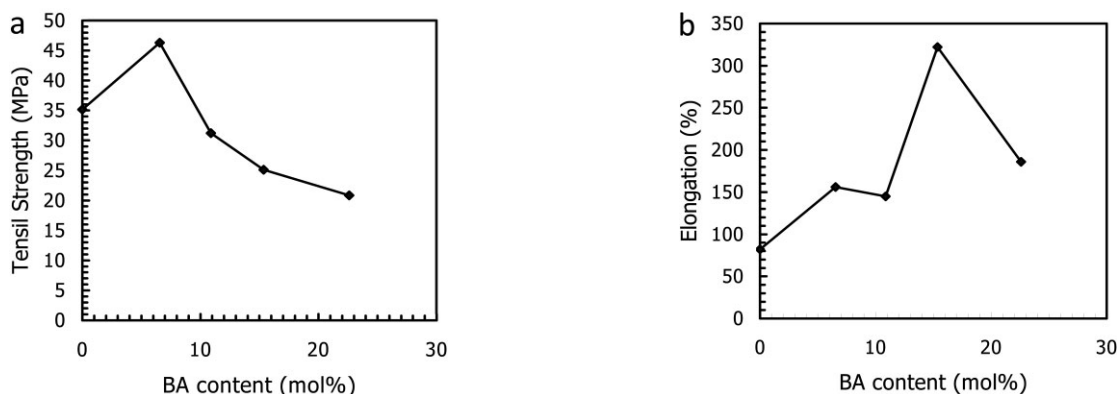


**Figure 2**. The mechanical properties of PBSA with different contents of butylene adipate (BA) content: (a) Tensile strength; (b) Elongation at break (unpublished results from our lab).
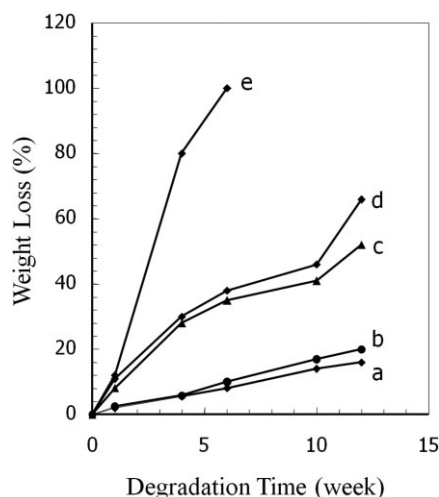
**Figure 3**. Biodegradation rate of PBS and PBSA film in activated sludge [3]: (a) PBS; (b) PBSA-5; (c) PBSA-10; (d) PBSA-15; (e) PBSA-20. The number after PBSA indicates the molar percentage of adipic acid in the total feed acids for synthesis of PBSA copolyester. The biodegradation test was carried out on films with a thickness of 0.15 mm in activated sludge maintained at 25 °C with continuously pumping air.

the studied range from 0 to 40 mol%. Introduction of benzylsuccinate units raise glass transition temperature (Tg) of PBS copolymers due to its bulky substituent. In addition, copolymerization with comonomer contents larger than 10 mol% results in a slower crystallization rate [71], which is disadvantageous for processing.

### 3.2 Biodegradability of PBS copolymers

Enzymatic degradation of PBS and its copolymers is faster than hydrolysis at neutral pH without enzyme. PBS and its copolymers are biodegradable in lipase solution, soil burial, water, activated sludge and compost [1–3].
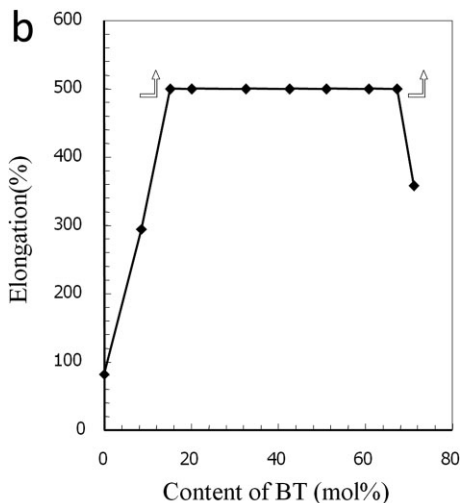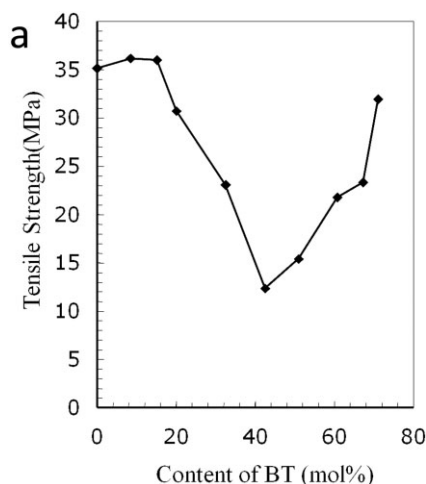


**Figure 4**. Variance of the mechanical properties of PBST copolyesters with butylene terephthalate (BT) content [68]: (a) tensile strength; (b) elongation at break. The two arrows indicate unbreaking of the specimen exceeding the measure range of the tensile-testing machine. The speed of the crosshead was 10 mm/min.

**Table 3**. Thermal properties of PBS and PBST copolyesters [68].

| Copolymer | BT mol% NMR | ΔHm (J/g) | ΔH°m (J/g) | Tm (°C) DSC | Tg (°C) DMA | Crystallinity (%) DSC | Crystallinity (%) WAXS |
|---|---|---|---|---|---|---|---|
| PBS | 0 | 67.4 | 110.3 | 112 | −18 | 61.1 | 39.66 |
| PBST-10[a] | 8.50 | 79.1 | 110.3 | 106 | −17 | 71.7 | 48.77 |
| PBST-15 | 15.16 | 61.2 | 110.3 | 99 | −12 | 55.5 | 42.82 |
| PBST-20 | 20.08 | 57.0 | 110.3 | 90 | −9 | 51.7 | 41.57 |
| PBST-30 | 32.52 | 16.4 | 121.7 | 86 | −12 | 13.5 | 32.68 |
| PBST-40 | 42.50 | 9.7 | 145.5 | 132 | −16 | 6.7 | 28.01 |
| PBST-50 | 51.05 | 8.9 | 145.5 | 138 | −7 | 6.1 | 29.63 |
| PBST-60 | 60.75 | 17.4 | 145.5 | 154 | 7 | 12.0 | 30.99 |
| PBST-65 | 67.27 | 34.3 | 145.5 | 166 | 17 | 23.6 | 32.68 |
| PBST-70 | 71.11 | 26.3 | 145.5 | 176 | 20 | 18.1 | 40.79 |
| PBT | 100 | 50.1 | 145.5 | 222 | 40 | 34.4 | |

a) The number indicates the molar percentage of terephthalic acid in the total feed acids for synthesis of PBST copolyester.
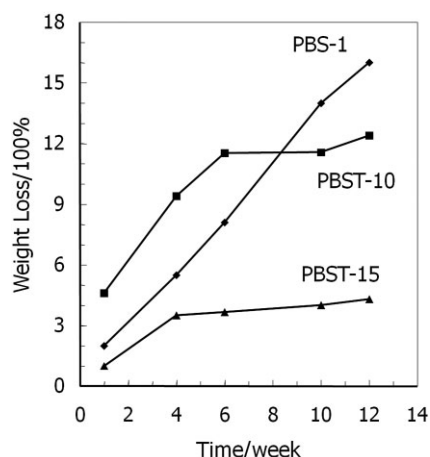
**Figure 5.** Biodegradation profile of PBST film in activated sludge (unpublished results from our lab). PBS-1: poly(butylene succinate), PBST-10: poly(butylene succinate-co-10 mol% butylene terephthalate), PBST-15: poly(butylene succinate-co-15 mol% butylene terephthalate). The biodegradation test was carried out on films with a thickness of 0.15 mm in activated sludge maintained at 25°C with continuously pumping air.

(butylene succinate), as shown in Fig. 7. Compared to aliphatic copolyesters with the same comonomer content, PBS copolymerized with aromatic comonomers revealed slower biodegradation rates. However, PBS copolyesters with 20 mol% aromatic comonomers still showed higher biodegradation rates in the activated sludge during the first 3 weeks. For aliphatic copolyesters, the biodegradation rate enhances with an increase of the comonomer content below 40 mol%, resulting from the decreased degree of crystallinity [44]. For aliphatic-aromatic copolyesters, the biodegradation rate slows down with an increase in the aromatic content in the range of 10–70 mol% [83]. Consequently, the biodegradation rate of PBS can be tailored via copolymerization with different types and contents of comonomer units to meet various requirements. Biodegradation behavior of PBS and its copolymers under various conditions has been summarized in a recent book chapter [3].

The biodegradation rate of PBS copolymers varies with the chemical structure, the condensed state structures (such as the degree of crystallinity and specimen size) and the biodegradation environment. The biodegradation profile of PBS copolymer films with a similar degree of crystallinity in the activated sludge was investigated in our lab, as presented in Table 5. For PBS copolymers with substituted succinic acid as the comonomer, at the same comonomer content of 20 mol%, the biodegradation rate at the first stage follows the order: poly(butylene succinate-co-butylene methylsuccinate) ≈ poly(butylene succinate-co-butylene dimethylsuccinate)> poly(butylene succinate-co-butylene adipate)> poly(butylene succinate-co-butylene phenylsuccinate)> poly

## 4　Processability of PBS and its copolymers

Thermoprocessability of semicrystalline polymers depends on thermal stability, viscosity, melt strength and crystallization rate, etc. The thermal stability of PBS materials is sensitive to water content, the content of residual carboxylic acid terminals and the molecular structure of polymer chains, etc. Before thermal processing, PBS pellets can be dried with hot air to decrease the water content to less than 0.1% to avoid hydrolysis, which will happen with traces of water at high temperatures. When the processing temperature of PBS exceeds 200 °C a considerable decrease of shear viscosity is observed. For instance, after being kept at 210 °C for 30 min, the viscosity will decrease to half the

**Table 4.** Thermal properties of of poly(butylene succinate-co-propylene succinate) polyesters [80].

| Polymer | $T_m$/°C | $\Delta H_m$/Jg$^{-1}$ | $T_c$/°C | $T_g$/°C | $T^0_m$/°C | $X_{C\text{-}DSC}$ (%)[a] | $X_{C\text{-}WAXD}$ (%)[b] | $T_d$/°C (50wt%) |
|---|---|---|---|---|---|---|---|---|
| PBS | 113 | 69.8 | 76 | −30.0 | 132 | 63.2 | 52.8 | 404 |
| PBSPS-5[d] | 111 | 57.2 | 69 | −31.3 | 124 | 51.8 | 49.9 | 385 |
| PBSPS-10 | 105 | 56.0 | 60 | −32.9 | 118 | 50.7 | 49.3 | 377 |
| PBSPS-15 | 100 | 49.7 | 56 | −33.5 | 114 | 45.0 | 47.7 | 368 |
| PBSPS-20 | 96 | 43.4 | 52 | −33.9 | 108 | 39.3 | 46.0 | 374 |
| PBSPS-30 | 84 | 39.8 | 40 | −34.8 | 103 | 36.0 | 43.9 | 371 |
| PBSPS-40 | 76 | 37.3 | 39 | −35.1 | 99 | 33.8 | 40.2 | 362 |
| PBSPS-50 | 63 | 20.9 | ----[c] | −35.5 | 89 | 18.9 | 37.3 | 361 |
| PPS | 50 | 36.4 | ---- | 36.0 | ---- | ---- | 44.6 | 378 |

a) $X_{C\text{-}DSC}$ was calculated from DSC method for a 100% crystalline PBS (110.5 J/g).
b) $X_{C\text{-}WAXD}$ was calculated from the X-ray method.
c) "----" indicated no crystallization peak was observed by DSC at the cooling rate of 10°C/min.
d) The number indicates the molar percentage of 1,3-propanediol in the total feed diols for synthesis of PBSPS copolyester.
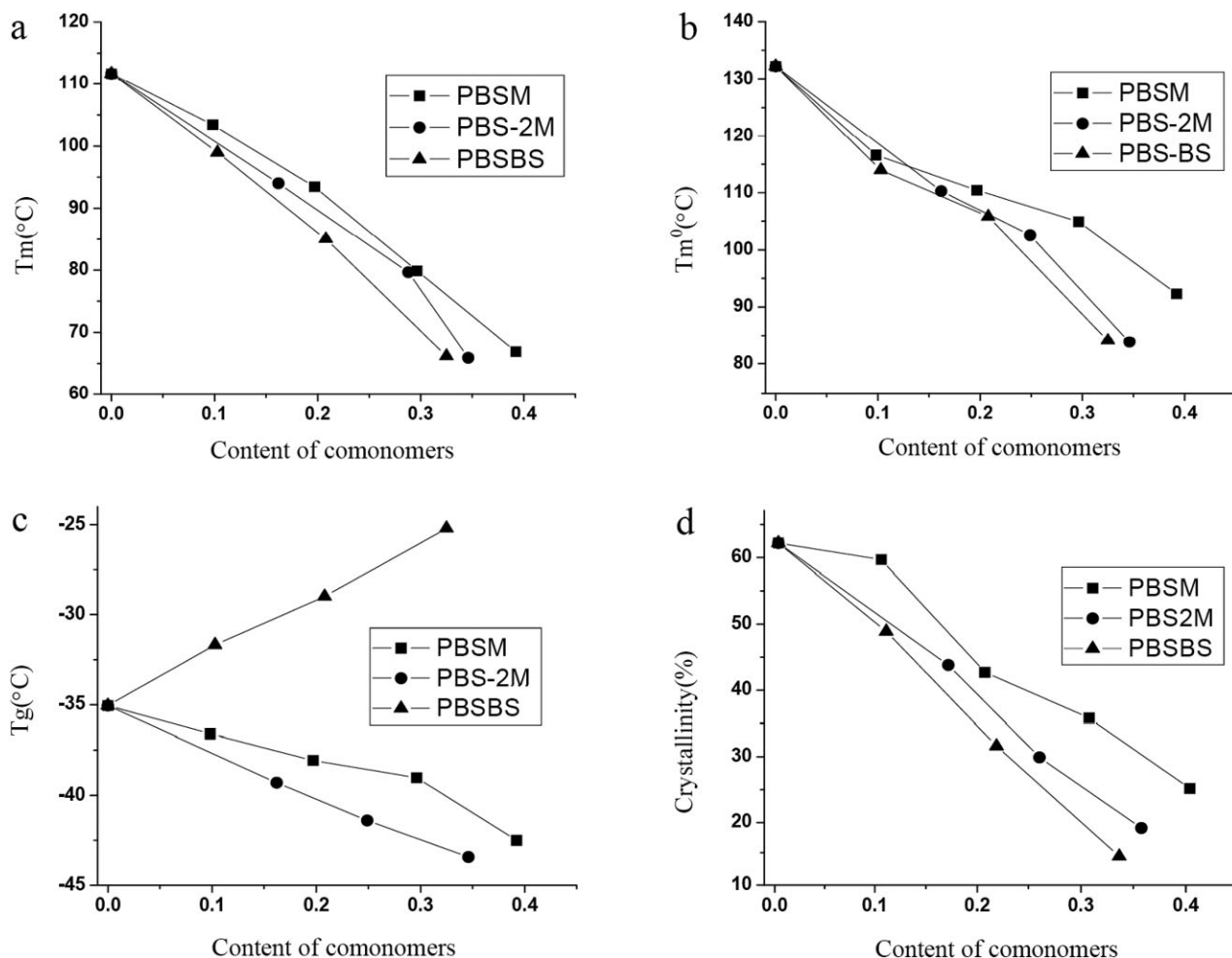
Figure 6. Dependence of the physical properties of PBS copolymers on the content of comonomer units (unpublished results from our lab). (a) Melting point; (b) equilibrium melting point; (c) glass transition temperature; (d) degree of crystallinity. PBSM: poly(butylene succinate-co-butylene methylsuccinate); PBS-2M: poly(butylene succinate-co-butylene dimethylsuccinate); PBSBS: poly(butylene succinate-co-butylene phenylsuccinate).

original value. Copolymerization with other comonomers, such as terephthalic acid may improve the thermal stability according to the thermogravimetric analysis (TGA) results [69].

PBS with an Mw of less than 100 000 can be used for extrusion and injection molding. However, for film blowing and casting, where high melt strength is necessary, PBS with higher Mw or long-chain branches is preferred to ensure smooth processing [2]. Figure 8 shows the rheological behavior of linear PBS and long-chain-branched PBS. It is demonstrated that a small amount of long branch-

Table 5. Parameters of PBS and its copolymers used for biodegradation study [3].

| Item[a] | $M_w$ ($\times 10^4$ g/mol) | Content of copolymer (mol%) | Crystallinity (%) | Film thickness (μm) |
|---|---|---|---|---|
| PBS | 6.44 | 0 | 62.2 | 150 |
| PBSA-20 | 4.42 | 22.6 | 53.9 | 150 |
| PBSM-20 | 3.58 | 19.7 | 42.7 | 150 |
| PBS-2M-20 | 4.32 | 16.2 | 43.8 | 150 |
| PBSBS-20 | 5.48 | 20.8 | 34.9 | 150 |

a) PBSA-20: poly(butylene succinate-co-20 mol% butylene adipate); PBSM-20: poly(butylene succinate-co-20 mol% butylene methylsuccinate); PBS-2M-20: poly(butylene succinate-co-20 mol% butylene dimethylsuccinate); PBSBS-20: poly(butylene succinate-co-20 mol% butylene phenylsuccinate).
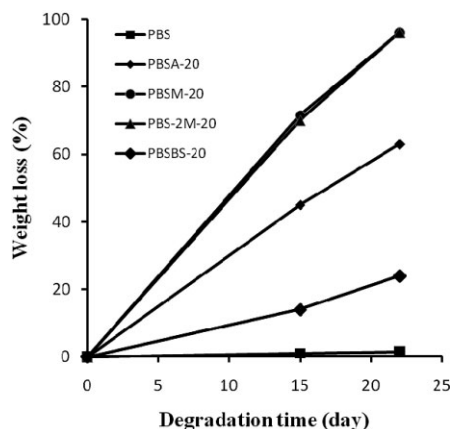
**Figure 7.** Biodegradation of the films of PBS and its copolymers in activated sludge. Properties of the specimens are listed in Table 5. The activated sludge was maintained at 25°C with continuously pumping air (unpublished results from our lab).

es (less than 1%) can considerably increase the zero viscosity, the storage and loss modulus at the terminal region (low frequency range) due to more chain entanglements. In addition, entanglements of long-chain branches result in high melt tension, enabling easier production of stretched blown bottles and highly expanded foams [2].

A high crystallization rate is required for fast processing of semicrystalline polymer products. To achieve this goal, nucleating agents can be incorporated, which is also beneficial for improving the transparency of the product. Talc and α-cyclodextrin can greatly accelerate the nucleation and crystallization of PBS [84].

PBS is soluble in various solvents, such as dichloromethane, chloroform, 1,1,1,3,3,3-hexafluo-

ro-2-propanol, o-chlorobenzene, etc [85, 86]. PBS solution has been electrospinned to produce nonwoven mats with ultrafine fibers with the average diameter in the range of 100–300 nm [87–90]. Electrospinning of PBSA solution in methylene chloride/N, N-dimethylformamide mixtures can obtain microbeads, beads in thread and ultrafine fibers, depending on the ratio of the two solvents [91].

## 5　Blends of PBS and other biodegradable polymers

Blending two different polymers is a promising method to improve the material performance. PBS can be blended with other biodegradable polymers, such as starch [92], polylactide [93–98], polyhydroxybutyrate [99] and its copolymers [100], etc.

The morphology, thermal behavior and mechanical properties of poly (lactic acid) (PLA)/PBS blends have been investigated in detail in our lab. Optical micrographs show that PLA and PBS are immiscible in melt in the studied composition range, which agrees with the report of Liu *et al.* [93]. However, when the blending ratio is 80/20 and 20/80, the dispersed phase is finely distributed in the matrix, with the size around several microns, as demonstrated in Fig. 9. As a result, PBS/PLA and PBSA/PLA blends with blending ratios of 80/20 and 20/80 demonstrate good mechanical properties, as listed in Tables 6 and 7. Blending PBS with PLA improves the tensile strength and elastic modulus without much loss of ductility. Only a small amount of PBS or PBSA (20 wt%) can turn PLA from brittle to ductile, increasing the elongation break from 24% to more than 200%. These results

**Table 6.** Mechanical properties of injection molded bars of PLA/PBS blends (unpublished results from our lab).

| PLA/PBS | Elongation at break (%) | Tensile strength at yield (Mpa) | Tensile strength at break (Mpa) | Izod impact strength (J/m) |
|---------|-------------------------|----------------------------------|----------------------------------|-----------------------------|
| 100/0   | 24±17                   | 62±1                             | 33±23                            | 11±2                        |
| 80/20   | 277±47                  | 45±4                             | 22±9                             | 28±2                        |
| 60/40   | 112±82                  | 39±3                             | 12±5                             | 29±4                        |
| 0/100   | 275±35                  | 35±1                             | 29±2                             | 73±28                       |

**Table 7.** Mechanical properties of injection molded bars of PLA/PBSA blends. PBSA indicates poly(butylene succinate-co-10 mol% butylene adipate) (unpublished results from our lab).

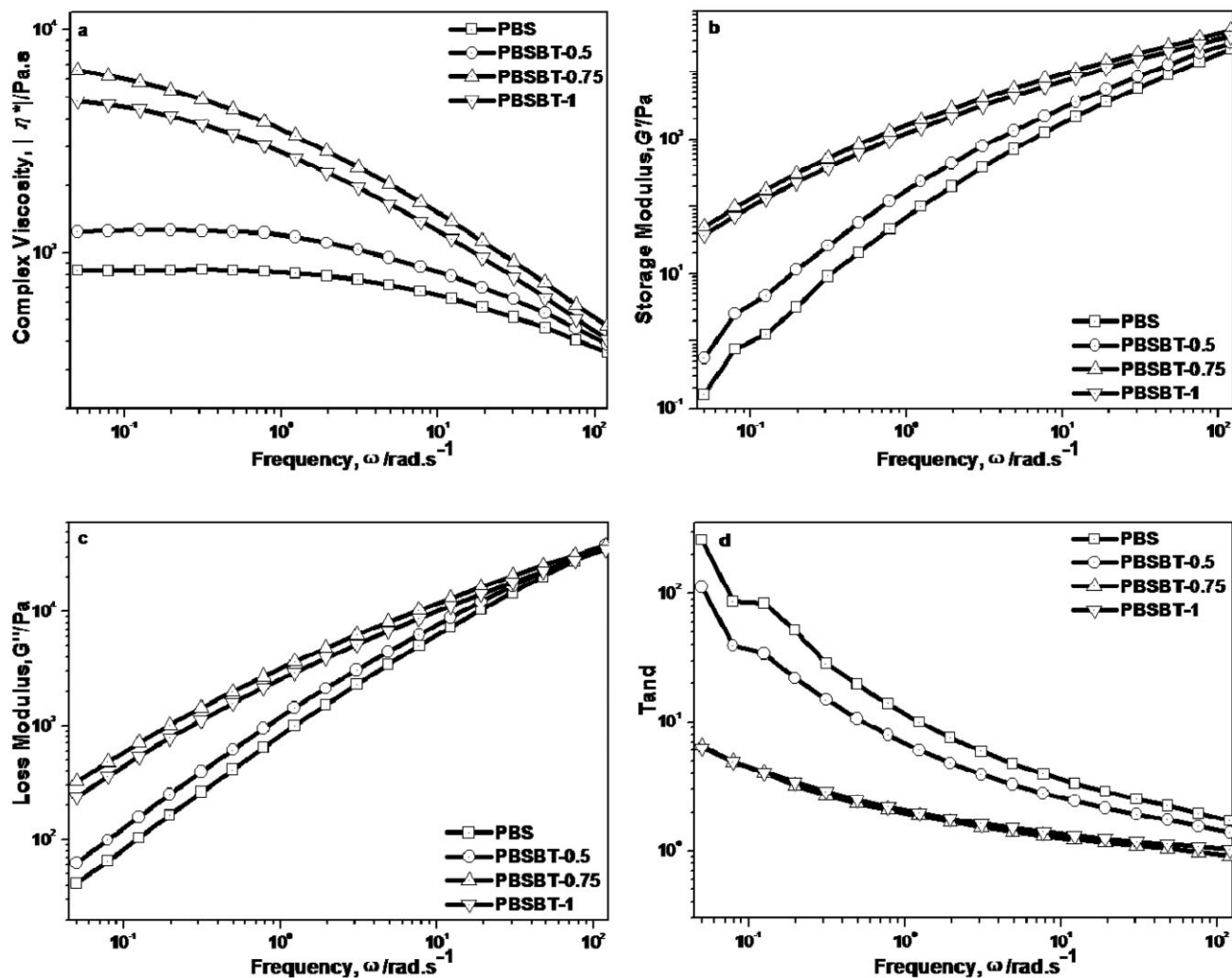| PLA/PBS | Elongation at break (%) | Tensile strength at yield (Mpa) | Tensile strength at break (Mpa) | Izod impact strength (J/m) |
|---------|-------------------------|----------------------------------|----------------------------------|-----------------------------|
| 100/0   | 24±17                   | 62±1                             | 32±23                            | 11±2                        |
| 80/20   | 319±17                  | 49±1                             | 23±8                             | 24±2                        |
| 60/40   | 225±64                  | 37±1                             | 17±11                            | 39±4                        |
| 0/100   | 476±124                 | 30±1                             | 28±3                             | 132±32                      |

**Figure 8**. Dynamic complex viscosity ($|\eta^*|$) (a), storage modulus (G′) (b), loss modulus (G″) (c), and damping factor (tanδ) (d) as a function of frequency of linear PBS and long-chain-branched PBS (unpublished results from our lab).

reveal that PBS and PLA are compatible during melt processing although they are not miscible at a molecular level. Reactive agents, lysine triisocyanate [96] and dicumyl peroxide [101] can enhance the compatibility of PLA and PBS and improve the impact strength of the blends considerably.

## 6 Industrialization and applications of PBS and its copolymers

In 1994, Showa High Polymers commercialized PBS under the tradename "Bionolle", which is the first commercialized PBS resin. The Mitsubishi Chemical built a 3000-ton/year PBS production line and began its practical market introduction of PBS named "GS Pla" in April 2003. In 2006, we collaborated with Hexing Chemical Anhui, China

and launched a project to establish a 3000-ton/year PBS manufacture line by direct melt polycondensation. In October 2007, Xinfu Pharmaceutical in Hangzhou, China built a PBS-production line by one-step polymerization technology, which was supported by the Technical Institute of Physics and Chemistry of the Chinese Academy of Sciences. In 2009, a facility capable of manufacturing 10 000 tons/year of PBS and its copolymers was constructed by Hexing Chemical. The facility can manufacture PBS and its copolymer resins for extrusion, injection molding, thermoforming and blowing grade. The average Mw of the products can reach up to 200 000. Biodegradability of the products was tested at the China National Center for Quality Supervision & Test of Plastics Products according to the standard of ISO 14855:1999. After biodegradation in compost for 95 days, 64.4% of the
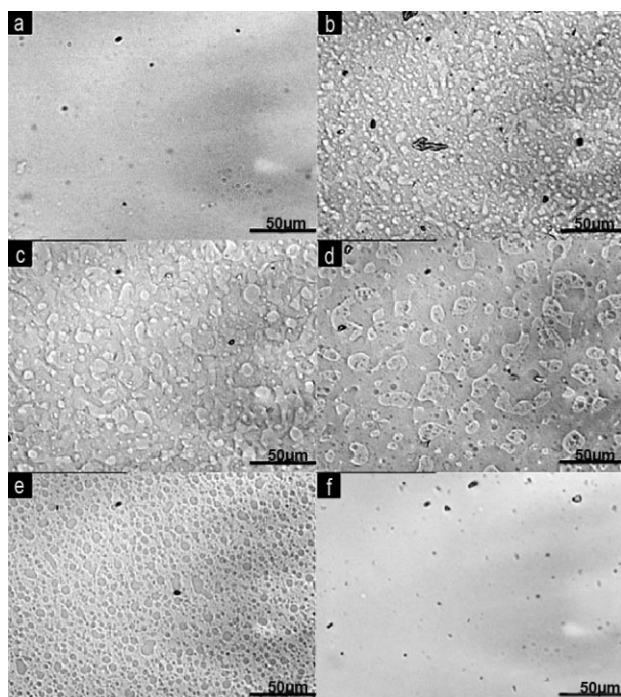
**Figure 9**. Optical micrographs of PLA/PBS blends in the melt state at 180 °C. PLA/PBS blend ratio: (a)100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80 and (f) 0/100 (unpublished results from our lab).

PBS pellets were biodegraded. The major manufacturers of biodegradable poly(alkylene dicarboxylate) (including PBS and its copolymers) are listed in Table 8.

PBS and its copolymer resins have been utilized to produce fast food packages, bottles, supermarket bags, flushable hygiene products, mulch film and compost bags, etc [1–3]. PBS oligomers can also be used as building blocks of polyurethane elastomers as well [102].

## 7 Conclusions and future perspectives

Via copolymerization with different types and contents of comonomer units, thermal behavior, mechanical properties and biodegradation rate of PBS can be varied in a wide range. In general, copolymerization leads to a decrease in melting point, degree of crystallinity, tensile strength and modulus; at the same time, elongation at break and impact strength improves with copolymerization when the content of comonomer units is less than 30 mol%. Effect of copolymerization on biodegradation rate depends on the type of comonomer: copolymerization with aliphatic comonomers results in a faster biodegradation rate in activated sludge, while that with aromatic comonomers leads to a slower biodegradation rate. The melt strength of PBS is considerably enhanced by long-chain branching, meeting the demands posed by film blowing processes. Industrialization of PBS and its copolymers has been successfully pursued in several countries, such as Japan, China, Germany and Korea, etc. PBS resins for extrusion, injection molding, thermoforming, fiber spinning and film blowing have been commercialized.

**Table 8**. Manufacturers of biodegradable poly(alkylene dicarboxylate) [3].

| Manufacturer | Product | Monomers | Production capacity (tons/year) |
|---|---|---|---|
| Hexing Chemical, China | Hexing PBS | Succinic acid, butanediol, branched alkanedicarboxylic acid | 10 000 |
| Xinfu Pharmaceutical, China | PBS, PBSA | Succinic acid, adipic acid, butanediol | 3000 |
| Jinfa Tech, China | PBSA | Succinic acid, adipic acid, butanediol | 300 |
| BASF, Germany | Ecoflex | Adipic acid, terephthalic acid, butanediol | 14 000 |
| Eastmann, USA | East Bio | Adipic acid, terephthalic acid, butanediol | 15 000 |
| Showa, Japan | Bionolle | Succinic acid, adipic acid, butanediol | 5000 |
| Mitsubishi Chemical, Japan | GS Pla | Succinic acid, lactic acid, butanediol | 3000 |
| Mitsubishi Gas Chemical, Japan | Iupec | Succinate, carbonate, butanediol | |
| Nippon Shokubai, Japan | Lunare | Succinic acid, adipic acid, ethylene glycol | |
| Ube, Japan | ETERNACOLL 3050 | Decanedicarboxylic acid, ethylene glycol | |
| Ire Chemical, Korea | Enpol | Succinic acid, adipic acid, terephthalic acid, butanediol | |
| SK Chemical, Korea | Skygreen | Succinic acid, adipic acid, butanediol, ethylene glycol | |

In the future, attempts will be devoted to improving the tear resistance, impact strength and transparency of the films of PBS and its copolymers, which will greatly expand the market for these biodegradable plastics. Additives compatible with biodegradable materials, such as nucleating agents and impact modifiers are being developed to manufacture PBS articles meeting the requirements of various applications. In addition, monomers derived from renewable feedstocks have been considered to decrease the carbon footprint of these materials. Throughout the whole world there is a large demand for biodegradable plastics. Several companies are planning to expand their manufacturing capabilities of PBS to meet the rapid increase in demand for biodegradable plastics, especially in the packaging field.

# 8 References

[1] Ishioka, R., Kitakuni, E., Ichikawa, Y., Aliphatic polyesters: "Bionolle". In: Doi, Y., Steinbüchel, A. (Eds.), *Biopolymers, Vol 4, Polyesters III Applications and Commercial Products*. Wiley-VCH, New York 2002, pp. 275–297.

[2] Fujimaki, T., Processability and properties of aliphatic polyesters, 'BIONOLLE', synthesized by polycondensation reaction. *Polym. Degrad. Stab.* 1998, *59*, 209–214.

[3] Xu, J., Guo, B. H., Microbial succinic acid, its polymer poly(butylene succinate), and applications. In: Chen, G. Q. (Ed.), *Plastics from Bacteria: Natural Functions and Applications*, Microbiology Monographs, Vol. 14, Springer-Verlag, Berlin, Heidelberg 2010, pp. 347–388.

[4] Carothers, W. H., Polymerization. *Chem. Rev.* 1931, *8*, 353–426

[5] Kanakam, R., Pathy, M. S. V., Udupa, H. V. K., Electroreduction of Maleic acid and Fumaric acid at a Rotation Cathod. *Electrochim. Acta* 1967, *12*, 329–332.

[6] Song, H., Lee, S. Y., Production of succinic acid by bacterial fermentation. *Enzym. Microb. Technol.* 2006, *39*, 352–361.

[7] Guettler, M. V., Rumler, D., Jain, M. K., *Actinobacillus succinogenes* sp. nov., a novel succinic-acid-producing strain from the bovine rumen. *Int. J. Syst. Bacteriol.* 1999, *49*, 207–216.

[8] Park, D. H., Zeikus, J. G., Utilization of electrically reduced neutral red by *Actinobacillus succinogenes*: physiological function of neutral red in membrane-driven fumarate reduction and energy conservation. *J. Bacteriol.* 1999, *181*, 2403–2410.

[9] Kim, P., Laivenieks, M., McKinlay, J., Vieille, C. *et al.*, Construction of a shuttle vector for the overexpression of recombinant proteins in *Actinobacillus succinogenes*. *Plasmid* 2004, *51*, 108–115.

[10] Urbance, S. E., Pometto, A. L., DiSpirito, A. A., Denli, Y., Evaluation of succinic acid continuous and repeat-batch biofilm fermentation by *Actinobacillus succinogenes* using plastic composite support bioreactors. *Appl. Microbiol. Biotechnol.* 2004, *65*, 664–670.

[11] Liu, Y. P., Zheng, P., Sun, Z. H. Ni, Y. *et al.*, Economical succinic acid production from cane molasses by *Actinobacillus succinogenes*. *Bioresource Technology* 2008, *99*, 1736–1742.

[12] Podkovyrov, S. M., Zeikus, J. G., Purification and characterization of phosphoenolpyruvate carboxykinase, a catabolic $CO_2$-fixing enzyme, from *Anaerobiospirillum succiniciproducens*. *J. Gen. Microbiol.* 1993, *139*, 223–228.

[13] Nghiem, N. P., Davison, B. H., Suttle, B. E., Richardson, G. R., Production of succinic acid by *Anaerobiospirillum succiniciproducens*. *Appl. Biochem. Biotechnol.* 1997, *63/65*, 565–576.

[14] Lee, P. C., Lee, S. Y., Hong, S. H., Chang, H. N. *et al.*, Biological conversion of wood hydrolysate to succinic acid by *Anaerobiospirillum succiniciproducens*. *Biotechnol. Lett.* 2003, *25*, 111–114.

[15] Jabalquinto, A. M., González-Nilo, F. D., Laivenieks, M., Cabezas, M. *et al.*, A*naerobiospirillum succiniciproducens* phosphoenolpyruvate carboxykinase, mutagenesis at metal site 1. *Biochimie* 2004, 86, 47–51.

[16] Samuelov, N. S., Datta, R., Jain, M. K., Zeikus, J. G.., Whey fermentation by *Anaerobiospirillum succiniciproducens* for production of a succinate-based animal feed additive. *Appl. Environ. Microbiol.* 1999, *65*, 2260–2263.

[17] Lee, P. C., Lee, S. Y., Hong, S. H., Chang, H. N., Isolation and characterization of new succinic acid producing bacterium, *Mannheimia succiniciproducens* MBEL 55E, from bovine rumen. *Appl. Microbiol. Biotechnol.* 2002, *58*, 663–668.

[18] Millard, C. S., Chao, Y. P., Liao, J. C., Donnelly, M. I., Enhanced production of succinic acid by overexpression of phosphoenolpyruvate carboxylase in *Escherichia coli*. *Appl. Environ. Microbiol.* 1996, 62, 1808–1810.

[19] Vemuri, G. N., Eiteman, M. A., Altman, E., Succinate production in dualphase *Escherichia coli* fermentations depends on the time of transition from aerobic to anaerobic conditions. *J. Ind. Microbiol. Biotechnol.* 2002, *28*, 325–332.

[20] Lin, H., Bennett, G. N., San, K. Y., Fed-batch culture of a metabolically engineered *Escherichia coli* strain designed for high-level succinate production and yield under aerobic conditions. *Biotechnol. Bioeng.* 2005, *90*, 775–779.

[21] Guettler, M. V., Jain M. K., Rumler, D., Method for making succinic acid, bacterial variants for use in the process, and methods for obtaining variants. 1996, US patent 5,573,931.

[22] Van der Werf, M. J., Guettler, M. V., Jain, M. K. *et al.*, Environmental and physiological factors affecting th1e succinate product ratio during carbohydrate fermentation by *Actinobacillus* sp. 130Z. *Arch. Microbiol.* 1997, *167*, 332–342.

[23] Kang, K. H., Ryu, H. W., Enhancement of succinate production by organic solvents, detergents, and vegetable oils. *J. Microbiol. Biotechnol.* 1999, *9*, 191–195.

[24] Wee, Y. J., Yun, J. S., Kang, K. H., Ryu, H. W., Continuous production of succinic acid by a fumarate-reducing bacterium immobilized in a hollow-fiber bioreactor. *Appl. Biochem. Biotechnol.* 2002, *98*, 1093–1104.

**Dr. XU Jun** received his B.Sc. and Ph.D. at the Department of Chemical Engineering, Tsinghua University, China in 1997 and 2002, respectively. He has worked in the department since 2002, and has been promoted to Associate Professor of Polymer Science and Engineering in 2006. His research specializes in the field of polymer physics and processing of biodegradable polymers, including crystallization, characterization and tuning of the condensed state structures, applications of biodegradable polymers, such as polybutylene succinate, microbial polyhydroxyalkanoates and polylactide, etc.

**Professor GUO Baohua** received his B.Sc. and M.Sc. in chemical engineering at the Department of Chemical Engineering, Tsinghua University. He has worked in the department since 1992, and then became a Professor in 2004. His current research interests include environmentally friendly polymers, biomedical polymers, polymer physics, reactive extrusion, polymer blends and nanocomposites. He was awarded Beijing City Awards for Science and Technology Progress (Second Class) in 2000 and 2003, respectively.

[25] Hermann, B. G., Blok, K., Patel, M. K., Producing bio-based bulk chemicals using industrial biotechnology saves energy and combats climate change. *Environ. Scil. Technol.* 2007, *41*, 7915–7921.

[26] de Munck, N. A., Gas phase hydroformylation of propylene and allyl alcohol with immobilized rhodium complexes. Delft University Press, Delft 1980.

[27] Cukalovic, A., Stevens, C. V., Feasibility of production methods for succinic acid derivatives: a marriage of renewable resources and chemical technology. *Biofuels Bioprod. Bioref.* 2008, *2*, 505–529.

[28] Kirk-Othmer, R. E., *Encyclopedia of chemical technology*. 3rd ed., Vol. 1, John Wiley and Sons, New York 1978, pp. 245–264.

[29] Onoda, T., Yamura, A., Ohno, A., Haji, J. *et al.*, Process for preparing an unsaturated ester. US patent number 3,922,300, to Mitsubishi Chemical, 1974.

[30] Toriya, J., Shiraga, K., Onoda, T., Ohno, A. Process for hydrogenation of diacetoxybutene. US patent number 4,225,729, to Mitsubishi Chemical, 1980.

[31] Matar, S., Hatch, L. F. *Chemistry of Petrochemical Processes* (2nd edn.), Gulf. Publishing Company, Houston, Texas 2000, pp. 258.

[32] Haas, T., Jaeger, B., Weber, R., Mitchell, S. F., *et al.*, New diol processes: 1,3-propanediol and 1,4-butanediol. *Appl. Catal. A* 2005, *280*, 83–88.

[33] Production of butane-1,4-diol. European patent application number 18163, to Davy-McKee, 1980.

[34] Production of tetrahydrofuran. European patent application number 18164, to Davy-McKee, 1980.

[35] Cooper, J. S., Vigon, B., Life Cycle Engineering Guidelines. Chapter 5: New Design. National Risk Management Research Laboratory. Office of Research and Development, U.S. EPA, Cincinnati, OH. EPA/600/R-01/101. 2001, pp 51–52.

[36] Wolf, O, (Ed.), Techno-economic Feasibility of Large-scale Production of Bio-based Polymers in Europe. Technical Report EUR 22103 EN, 2005.

[37] Zhu, C. Y., Zhang, Z. Q., Liu, Q. P., Wang, Z. P. *et al.*, Synthesis and biodegradation of aliphatic polyesters from dicarboxylic acids and diols. *J. Appl. Polym. Sci.* 2003, *90*, 982–990.

[38] Velmathi, S., Nagahata, R., Sugiyama, J. I., Takeuchi, K., A rapid eco-friendly synthesis of poly(butylene succinate) by a direct polyesterification under microwave irradiation. *Macromol. Rapid Commun.* 2005, *26*, 1163–1167.

[39] Takahashi, H., Hayakawa, T., Ueda, M. Convenient synthesis of poly(butylene succinate) catalyzed by distannoxane. *Chem. Lett.* 2000, *29*, 684–685.

[40] Ishii, M., Okazaki, M., Shibasaki, Y., Ueda, M. *et al.*, Convenient synthesis of aliphatic polyesters by distannoxane-catalyzed polycondensation. *Biomacrol.* 2001, *2*, 1267–1270.

[41] Takasu, A., Oishi, Y., Iio, Y., Inai, Y. *et al.*, Synthesis of aliphatic polyesters by direct polyesterification of dicarboxylic acids with diols under mild conditions catalyzed by reusable rare-earth triflate. *Macromolecules* 2003, *36*, 1772–1774.

[42] Song, D. K., Sung, Y. K., Synthesis and characterization of biodegradable poly(1,4-butanediol succinate). *J. Appl. Polym. Sci.* 1995, *56*, 1381–1395.

[43] Mochizuki, M., Mukai, K., Yamada, K., Ichise N. *et al.*, Structural effects upon enzymatic hydrolysis of poly(butylene succinate-co-ethylene succinate)s. *Macromolecules* 1997, *30*, 7403–7407.

[44] Nikolic, M. S., Djonlagic, J., Synthesis and characterization of biodegradable poly(butylene succinate-co-butylene adipate)s. *Polym. Degrad. . Stab.* 2001, *74*, 263–270.

[45] Jin, H. J., Kim, D. S., Kim, M. N., Lee, I. M. *et al.*, Synthesis and properties of poly(butylene succinate) with N-hexenyl side branches. *J. Appl. Polym. Sci.* 2001, *81*, 2219–2226.

[46] Nikolic, M. S., Poleti, D., Djonlagic, J., Synthesis and characterization of biodegradable poly(butylene succinate-co-butylene fumarate)s. *Europ. Polym. J.* 2003, *39*, 2183–2192.

[47] Tserki, V., Matzinos, P., Pavlidou, E., Vachliotis, D. *et al.*, Biodegradable aliphatic polyesters. Part I. Properties and biodegradation of poly(butylene succinate-co-butylene adipate). *Polym. Degrad. Stab.* 2006, *91*, 367–376.

[48] Bikiaris, D. N., Papageorgiou, G. Z., Achilias, D. S., Synthesis and comparative biodegradability studies of three poly(alkylene succinate)s. *Polym. Degrad. Stab.* 2006, *91*, 31–43.

[49] Yang, J., Zhang, S. P., Liu, X. Y., Cao, A. M., A study on biodegradable aliphatic poly(tetramethylene succinate): the catalyst dependences of polyester syntheses and their thermal stabilities. *Polym. Degrad. Stab.* 2003, *81*, 1–7.

[50] Chen, C. H., Peng, J. S., Chen, M., Lu, H. Y. *et al.*, Synthesis and characterization of poly(butylene succinate) and its copolyesters containing minor amounts of propylene succinate. *Colloid. Polym. Sci.* 2010, *288*, 731–738.

[51] Dostal, H., Raff, R., On the mechanism of thermal polycondensation. *Monatsh. Chem.* 1936, *68*, 188–201.

[52] Dostal, H., Mark, H., Raft, R., Mechanism of thermal polymerization and polycondensation. *Ind. Eng. Chem.* 1937, *29*, 595–599.

[53] Flory, P. J., Kinetics of condensation polymerization: the reaction of ethylene glycol with succinic acid. *J. Am. Chem. Soc.* 1937, *59*, 466–469.

[54] Flory, P. J., Kinetics of polyesterification: A study of the effects of molecular weight and viscosity on reaction rate. *J. Am. Chem. Soc.* 1939, *61*, 3334–3340.

[55] Park, S. S., Jun, H. W., Im, S. S., Kinetics of forming poly(butylene succinate) (PBS) oligomer in the presence of MBTO catalyst. *Polym. Eng. Sci.* 1998, *38*, 905–913.

[56] Fradet, A., Maréchal, E., Kinetics and mechanisms of polyesterifications I. Reactions of diols with diacids. *Adv. Polym. Sci.* 1982, *43*, 51–142.

[57] Han, Y. K., Kim, S. R., Kim, J., Preparation and characterization of high molecular weight poly(butylene succinate). *Macromol. Res.* 2002, *10*, 108–114.

[58] Tserki, V., Matzinos, P., Pavlidou, E., Panayiotou, C., Biodegradable aliphatic polyesters. Part II. Synthesis and characterization of chain extended poly(butylene succinate-co-butylene adipate). *Polym. Degrad. Stab.* 2006, *91*, 377–384.

[59] Huang, C. Q., Luo, S. Y., Xu, S. Y., Zhao, J. B. *et al.,* Catalyzed chain extension of poly(butylene adipate) and poly(butylene succinate) with 2,20-(1,4-phenylene)-bis(2-oxazoline). *J. Appl. Polym. Sci.* 2010, *115*, 1555–1565.

[60] Zhao, J. B., Li, K. Y., Yang, W. T., Chain extension of polybutylene adipate and polybutylene succinate with adipoyl- and terephthaloyl-biscaprolactamate. *J. Appl. Polym. Sci.* 2007, *106*, 590–598.

[61] Duda, A., Penczek, S., Mechanisms of aliphatic polyester formation. In: Steinbuchel, A., Doi, Y. (Eds.), *Polyesters II—properties and chemical synthesis, Polyesters II—properties and chemical synthesis* vol. 3b, Wiley-VCH, Weinheim 2002, p. 371.

[62] Hudson, N., MacDonald, W. A., Neilson, A., Richards, R. W. *et al.*, Synthesis and characterization of nonlinear PETs produced via a balance of branching and end-capping. *Macromolecules* 2000, *33*, 9255–9261.

[63] Kim, E. K., Bae, J. S., Im, S. S., Kim, B. C. *et al.*, Preparation and properties of branched polybutylenesuccinate. *J. Appl. Polym. Sci.* 2001, *80*, 1388–1394.

[64] Papageorgiou, G. Z., Bikiaris, D. N., Crystallization and melting behavior of three biodegradable poly(alkylene succinates). A comparative study. *Polymer* 2005, *46*, 12081–12092.

[65] Wunderlich, B., *Thermal Analysis*, Chap. 5, and ATHAS Appendix, Academic Press, New York 1990, pp. 417–431.

[66] Nagata, M., Goto, H., Sakai, W., Tsutsumi, N., Synthesis and enzymatic degradation of poly(tetramethylene succinate) copolymers with terephthalic acid. *Polymer* 2000, *41*, 4373–4376.

[67] Honda, N., Taniguchi, I., Miyamoto, M., Kimura, Y., Reaction mechanism of enzymatic degradation of poly(butylene succinate-co-terephthalate) (PBST) with a lipase originated from *Pseudomonas cepacia*. *Macromol. Biosci.* 2003, *3*, 189–197.

[68] Guo, B. H., Ding, H. G., Xu, X. L., Xu, J. *et al.*, Studies on the sequence structure and crystallinity of poly(butylene succinate) copolymers with terephthalic acid. *Journal of Chinese Universities-Chinese* 2003, *24*, 2312–2316.

[69] Li, F. X., Xu, X. J., Li, Q. B., Li, Y. *et al.*, Thermal degradation and their kinetics of biodegradable poly(butylene succinate-co-butylene terephthate)s under nitrogen and air atmospheres. *Polym. Degrad. Stab.* 2006, *91*, 1685–1693.

[70] Luo, S. L., Li, F. X., Yu, J. Y., Cao, A. M., Synthesis of poly(butylene succinate-co-butylene terephthalate) (PBST) copolyesters with high molecular weights via direct esterification and polycondensation. *J. Appl. Polym. Sci.* 2010, *115*, 2203–2211.

[71] Park, J. W., Kim, D. K., Im, S. S., Crystallization behaviour of poly(butylene succinate) copolymers. *Polym. Inter.* 2002, *51*, 239–244.

[72] Chae, H. G, Park, SH, Kim, B. C, Kim, D. K., Effect of methyl substitution of the ethylene unit on the physical properties of poly(butylene succinate). *J. Polym. Sci. Part B: Polym. Phys.* 2004, *42*, 1759–1766.

[73] Sun, Y. B., Xu, J., Xu, Y. X., Yan, L. T. *et al.*, Synthesis and characterization of biodegradable poly(butylene succinate-co-butylene methyl succinate). *Chemical Journal of Chinese Universities-Chinese* 2006, *27*, 360–364.

[74] Sun, Y. B., Synthesis and characterization of biodegradable poly(butylenes succinate) copolymers. Master thesis, Tsinghua University, 2005.

[75] Sun, Y. B., Xu, J., Xu, Y. X., Guo, B. H., Synthesis and crystallization behavior of biodegradable poly(butylene succinate-co-butylene phenylsuccinate). *Acta Polymerica Sinica-Chinese* 2006, *6*, 745–749.

[76] Cao, A. M., Okamura, T., Nakayama, K., Inoue, Y. *et al.*, Studies on syntheses and physical properties of biodegradable aliphatic poly(butylene succinate-co-ethylene succinate)s and poly(butylene succinate-co-diethylene glycol succinate)s. *Polym. Degrad. Stab.*,2002, *78*, 107–117.

[77] Deng, L. M., Wang, Y. Z., Yang, K. K., Wang, X. L. *et al.*, A new biodegradable copolyester poly(butylene succinate-co-ethylene succinate-co-ethylene terephthalate). *Acta Materialia* 2004, *52*, 5871–5878.

[78] Papageorgiou, G. Z., Bikiaris, D. N., Synthesis, Cocrystallization, and enzymatic degradation of novel poly(butylene- co-propylene succinate) copolymers. *Biomacromolecules* 2007, *8*, 2437–2449.

[79] Xu, Y. X., Xu, J., Guo, B. H., Xie, X. M., Crystallization kinetics and morphology of biodegradable poly(butylene succinate-co-propylene succinate)s. *J. Polym. Sci. Part B: Polym. Phys.* 2007, *45*, 420–428.

[80] Xu, Y. X., Xu, J., Liu, D. H., Guo, B. H. *et al.*, Synthesis and characterization of biodegradable poly(butylene succinate-co-propylene succinate)s. *J. Appl. Polym. Sci.* 2008, *109*, 1881–1889.

[81] Nikolic, M. S., Poleti D., Djonlagic, J., Synthesis and characterization of biodegradable poly(butylene succinate-co-butylene fumarate)s. *Europ. Polym. J.* 2003, *39*, 2183–2192.

[82] Homann, T., Tag, C., Biebl, H., Deckwer, W. D. *et al.*, Fermentation of glycerol to 1,3-propanediol by *Klebsiella* and *Citrobacter* strains. *Appl. Microbiol. Biotechnol.* 1990, *33*, 121–126.

[83] Li, F. X., Xu, X. J., Yu, J. Y., Cao, A., The morphological effects upon enzymatic degradation of poly(butylene succinate-co-butylene terephthalate)s (PBST). *Polym. Degrad. Stab,* 2007, *92*, 1053–1060.

[84] Dong, T., He, Y., Zhu, B., Shin, K. M. *et al.*, Nucleation mechanism of alpha-cyclodextrin-enhanced crystallization of some semicrystalline aliphatic polymers. *Macromolecules* 2005, *38*, 7736–7744.

[85] Yoo, E. S., Im, S. S., Melting behavior of poly(butylenes succinate) during heating scan by DSC. *J. Polym. Sci. Part B: Polym. Phys.* 1999, *37*, 1357–1366.

[86] Gan, Z., Abe, H., Kurokawa, H., Doi, Y., Solid-state microstructures, thermal properties and crystallization of biodegradable poly(butylene succinate) (PBS) and its copolyesters. *Biomacromolecules* 2001, *2*, 605–613.

[87] Jeong, E. H., Im, S. S., Youk, J. H., Electrospinning and structural characterization of ultrafine poly(butylene succinate) fibers. *Polymer* 2005, *46*, 9538–9543.

[88] Liu, Y., He, J. H., Yu, J. Y., Preparation and morphology of poly(butylene succinate) nanofibers via electrospinning. *Fibres & Textiles in Eastern Europe* 2007, *15(4)*, 30–33.

[89] Zhang, D., Chang, J., Zeng, Y., Fabrication of fibrous poly(butylene succinate)/wollastonite/apatite composite scaffolds by electrospinning and biomimetic process. *J. Mater. Sc.–Mater. Med.* 2008, *19*, 443–449.

[90] Sutthiphong, S., Pavasant, P., Supaphol, P., Electrospun 1,6-diisocyanatohexane-extended poly(1,4-butylene succinate) fiber mats and their potential for use as bone scaffolds. *Polymer* 2009, *50*, 1548–1558.

[91] Tserki, V., Philippou, J., Panayiotou, C., Preparation and characterization of electrospun poly(butylene succinate-co-butylene adipate) nanofibrous nonwoven mats. *Proc. I Mech. E. Part N: J. Nanoengineering and Nanosystems* 2007, *220*, 71–79.

[92] Lai, S. M., Huang, C. K., Shen, H. F. Preparation and properties of biodegradable poly(butylene succinate)/starch blends. *J. Appl. Polym. Sci.* 2005, *97*, 257–264.

[93] Liu, X., Dever, M., Fair, N., Benson, R. S., Thermal and mechanical properties of poly(lactic acid) and poly(ethylene/butylene succinate) blends. *J. Environ. Polym. Degrad.* 1997, *5*, 225–235.

[94] Park, J. W., Im, S. S., Phase behavior and morphology in blends of poly(L-lactic acid) and poly(butylene succinate). *J. Appl. Polym. Sci.* 2002, *86*, 647–655.

[95] Shibata, M., Inoue Y., Miyoshi M., Mechanical properties, morphology, and crystallization behavior of blends of poly(L-lactide) with poly(butylene succinate-co-L-lactate) and poly(butylene succinate). *Polymer* 2006, *47*, 3557–3564.

[96] Harada, M., Ohya, T., Iida K., Hayashi, H. *et al.*, Increased impact strength of biodegradable poly(lactic acid)/poly(butylene succinate) blend composites by using isocyanate as a reactive processing agent. *J. Appl. Polym. Sci.* 2007, *106*, 1813–1820.

[97] Bhatia, A., Gupta, R. K., Bhattacharya, S. N., Choi, H. J., Compatibility of biodegradable poly (lactic acid) (PLA) and poly (butylene succinate) (PBS) blends for packaging application. *Korea-Australia Rheol. J.* 2007, *19*, 125–131.

[98] Yokohara, T., Okamoto, K., Yamaguchi, M., Effect of the shape of dispersed particles on the thermal and mechanical properties of biomass polymer blends composed of poly(L-lactide) and poly(butylene succinate). *J. Appl. Polym. Sci.* 2010, *117*, 2226–2232.

[99] Qiu, Z. B., Ikehara, T., Nishi, T., Poly(hydroxybutyrate)/poly(butylene succinate) blends: miscibility and nonisothermal crystallization. *Polymer* 2003, *44*, 2503–2508.

[100] Qiu, Z. B., Ikehara, T., Nishi, T., Miscibility and crystallization behaviour of PHBV and PBSU. *Polymer* 2003, *44*, 7519–7527.

[101] Wang, R. Y., Wang, S. F., Zhang, Y., Wan, C. Y. *et al.*, Toughening modification of PLLA/PBS blends via *in situ* compatibilization. *Polym. Eng. Sci.* 2009, *49*, 26–33.

[102] Sonnenschein, M. F., Guillaudeu, S. J., Landes, B. G., Wendt, B. L., Comparison of adipate and succinate polyesters in thermoplastic polyurethanes. *Polymer* 2010, *51*, 3685–3692.