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Poly[(*R*)-3-hydroxybutyrate]/Poly(styrene) Blends Compatibilized with the Relevant Block Copolymer

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ABSTRACT: A novel triblock copolymer PS-PHB-PS based on the microbial polyester Poly[(*R*)-3-hydroxybutyrate] (PHB) and poly(styrene) (PS) was prepared to be used as compatibilizer for the corresponding PHB/PS blends. It was prepared in a three-step procedure consisting of (i) transesterification reaction between ethylene glycol and a high-molecular-weight PHB, (ii) synthesis of bromo-terminated PHB macroinitiator, and (iii) atom transfer radical polymerization of styrene initiated by the PHB-based macroinitiator. Fourier transform infrared, gel permeation chromatography, ¹H-, and ¹³C-NMR spectroscopies were used to determine the molecular structure and/or end-group functionalities at each step of the procedure. Although thermogravimetric analysis showed that the block copolymer underwent a stepwise thermal degradation and had better thermal stability than their respective homopolymers, differential scanning calorimetry displayed that the PHB block in the copolymer could not

crystallize, and thus generating a total amorphous structure. Atomic force microscopy images indicated that the block copolymer was phase segregated in a well-defined morphological structure with nanodomain size of ~40 nm. Contact angle measurements proved that the wettability properties of the block copolymer were in between those of the PHB and PS homopolymers. Blends analyzed for their morphology and thermal properties showed good miscibility and had well-defined morphological features. Polymer blends exhibited lower crystallinity and decreased stiffness which was proportional to the amount of compatibilizer content in the blends. © 2012 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 50: 5151–5160, 2012

KEYWORDS: atom transfer radical polymerization (ATRP); blend compatibilization; block copolymer; poly[(*R*)-3-hydroxybutyrate]; polystyrene

INTRODUCTION Synthetic polymers currently used in industrial packaging are experiencing an explosive growth in municipal waste, and because of their recalcitrant nature, their disposal is considered problematic. Owing to the environmental concerns, consumer awareness, and stricter regulatory measures for the use and disposal of synthetic polymeric materials, there is a demand as well as an opportunity for alternative materials for use in packaging.¹ Bio-based polymers appear to be well suited to replace synthetic, nondegradable thermoplastics in packaging. Biodegradable aliphatic polyesters comprised in the family of polyhydroxyalkanoates (PHAs) such as poly(ε-caprolactone), poly(L-lactic acid), and microbial polyesters offer a great potential.² Among this last family PHAs, Poly[(*R*)-3-hydroxybutyrate] (PHB) has been studied most extensively and is relatively

easier to produce, and being a saturated polyester it behaves similarly to conventional thermoplastics.³ As a result, microbial PHB has attracted much attention as an environmentally degradable resin for a wide range of applications in packaging, agricultural, marine, and medical sectors.⁴ However, it has relatively high glass transition (5 °C) and melting temperatures (175–180 °C) that cause increased brittleness in PHB-based plastic items and results in a poor processing window. These feature combined with the fairly high production cost.⁵

Various approaches have been explored to improve the performance of PHB polymer materials.⁶ One approach is to incorporate other hydroxyalkanoate units into the polymer chain backbone to form random copolymers of (*R*)-3-hydroxybutyrate with (*R*)-3-hydroxyvalerate, 4-hydroxybutyrate, and

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so on.⁷ Another approach is to prepare miscible blends of PHB with other flexible biodegradable polymers or plasticizers of low molecular weight. In this regard, variety of PHB blends have been studied, which include binary blends with poly(vinyl acetate),^{8–15} poly(methyl methacrylate),^{16–18} poly(vinyl phenol),^{19–22} poly(ethylene oxide),^{23–30} poly(ethylene glycol),^{31–34} polylactide (PLA),^{35–45} cellulose derivatives,^{46–51} and various PHB synthetic stereoisomer analogues.^{52–55} New PHB-based materials can be produced by tweaking properties through blending of two or more polymers. However, most polymer blends are immiscible because of their high degrees of polymerization and intrinsic structural features. Consequently, the entropic term becomes small and the miscibility becomes increasingly dependent on the contribution of the enthalpic term. One promising approach for improving the physical properties and adjusting the degradation rate is to synthesize block copolymers based on PHB through chemical or biological routes. Low-molecular-weight telechelic PHB with hydroxyl at each end has been prepared by a transesterification reaction of alkane diols and a high-molecular-weight PHB.^{56–60} These telechelics could be used as macroinitiators in the synthesis of a block copolymer.^{61–70} Various methods are used for developing block copolymers which include controlled “living” free radical polymerization techniques, such as nitroxide-mediated polymerization,⁶² reversible addition-fragmentation chain transfer,⁶³ and atom transfer radical polymerization (ATRP).^{52,56,58,60,71–73} ATRP is one of the well-developed controlled polymerization and it has been attracting much attention as a new route to well-defined polymers with low polydispersities.

At present, poly(styrene) (PS) is a material of choice for use in packaging and many single-use disposable products, owing mainly to its lower cost and favorable properties such as low thermal conductivity, transparency, and ideal rheological characteristics. One consistent drawback, however, is its nonbiodegradability, and despite many efforts to recycle and reuse, PS remains a major contributor to municipal waste that tends to accumulate. New and innovative options are needed to overcome this challenge. One possible option is to prepare PS-based products containing a second biodegradable polymer component, which will help reduce the amount of PS in municipal waste.

Though PHB and PS have quite similar processing temperatures, these polymers are basically incompatible, as reflected by their phase separation. Phase-separation problems in binary blends can be overcome to some extent by the presence of suitable block or graft copolymers that can act as compatibilizers.^{74–78} Studies have been conducted in our laboratory where PS and PHB were compatibilized by using commercially available compatibilizing agents based on PS random copolymers containing methyl methacrylate or maleic anhydride comonomers.^{79,80} However, an excessive amount of compatibilizer was required to achieve good compatibilization in blends owing to the random character of the copolymers. In view of that, a new strategy was planned to compatibilize PHB/PS-based blends where a triblock copolymer is synthesized from PHB using ATR copolymerization of styrene.

EXPERIMENTAL

Materials

Biocycle® PHB ($M_w = 425 \text{ kg mol}^{-1}$, $(M_w/M_n) = 2.51$) was kindly supplied by PHB Industrial S.A., Brazil. Styrene (S) monomer was purchased from Sigma-Aldrich, St. Louis, MO. Anisole, diethylene glycol dimethyl ether (diglyme), sodium metal, 2,2'-Bipyridyl (Bipy), ethylene glycol, copper (I) bromide, α -bromoisobutyryl bromide, and dibutyltin dilaurate were all reagent grade and purchased from Sigma-Aldrich Chemical, St. Louis, MO. PS (Empera 124 N) with a melt volume-flow rate of $12 \text{ cm}^3 10 \text{ min}^{-1}$ was purchased from INEOS Styrenics International SA, Marl, Germany. All other reagents used in this study were purchased from Sigma-Aldrich, St. Louis, MO.

The high-molecular-weight natural-origin PHB was purified by dissolution in chloroform for 24 h, removal of the chloroform-insoluble material by filtration, precipitation of the filtered chloroform solution into methanol, and washing of the filtrate with diethyl ether. The molecular weight of this starting material was measured as $M_w = 217 \text{ kg mol}^{-1}$, $(M_w/M_n) = 1.70$ by gel permeation chromatography (GPC) analysis. Anisole and diethylene glycol dimethyl ether (diglyme) were kept at 100°C over sodium metal for 4 h and then distilled under reduced pressure. Styrene was washed with 5% NaOH and distilled water. After drying over Na_2SO_4 , it was distilled under reduced pressure before use. Triethylamine (TEA) was refluxed over KOH and distilled under nitrogen. Copper (I) bromide (CuBr) was purified by washing with glacial acetic acid followed by methanol. Chloroform was washed with distilled water several times and then distilled from CaCl_2 before use. All other reagents were used as received.

Preparation of Telechelic PHB-Diol

PHB-diol prepolymer was prepared by transesterification using PHB and ethylene glycol with dibutyltin dilaurate as the catalyst in diglyme as reported previously.^{56,60,65} In total, 10 g of PHB was heated in a solution containing 100 mL of diglyme and 20 mL of ethylene glycol at 140°C under nitrogen atmosphere, to which 300 mg of dibutyltin dilaurate was added successively. After heating for 7 h, the reaction was stopped by cooling to 50°C . The resulting solution was washed twice with distilled water and the product was extracted with chloroform. The organic phase was dried with anhydrous Na_2SO_4 and filtered. The resulting polymer was precipitated in low-boiling petroleum ether and separated by filtration. Precipitate was dried in a vacuum oven and a white solid polymer sample recovered. The total yield was roughly 30%. The chemical structures of the PHB-diols were confirmed by GPC, Fourier transform infrared (FTIR), and ^1H NMR spectroscopy.

FTIR (film): $\nu (\text{cm}^{-1}) = 3400\text{--}3600$ (ν , —OH stretching), 2967 (ν , C—H aliphatic), 1723 (ν , C=O), 1200–1147 (ν , C—O).

^1H NMR (CDCl_3): δ (ppm) = 5.10–5.30 (owing to —CH— protons of PHB), 4.13–4.34 (owing to $\text{—OCH}_2\text{CH}_2\text{OH}$ protons of Eg and $\text{HOCH}(\text{CH}_3)$ protons), 3.73–3.93 (owing to $\text{—OCH}_2\text{CH}_2\text{OH}$ protons of Eg), 2.32–2.81 (owing to $\text{—CH}_2\text{—}$ protons, of PHB), and 1.11–1.48 (owing to $\text{—CH}_3\text{—}$ protons of PHB).

Preparation of the Macroinitiator Br-PHB-Br

This reaction was adopted following the method described by Zhang et al.⁶⁰ Briefly, PHB-diol prepolymer (1 g) was added to 25 mL of chloroform in a 50-mL flask under nitrogen atmosphere and stirred. In all, 0.323 g (3.2 mmol) of TEA was added. Subsequently, α -bromoisobutyryl bromide (0.735 g, 3.2 mmol) was added dropwise to the solution cooled in an ice bath. The reaction mixture was stirred at room temperature for 2 days. The precipitated byproduct was removed by filtration, and the solution was washed thoroughly with 5% aqueous NaHCO₃ several times. The organic part was further washed with water and dried overnight over anhydrous Na₂SO₄ and solvent was removed with a rotary evaporator. The residue was purified by precipitation from CHCl₃ solution into methanol. This procedure was repeated three times before product was recovered. The resulting white, solid sample was dried for 2 days *in vacuo* (yield, 63%).

¹H NMR (CDCl₃): δ (ppm) = 5.01–5.36 (owing to $-\text{CH}-$ protons of PHB), 4.28–4.41 (owing to $-\text{CH}_2-$ protons of Eg residue), 4.07–4.25 (owing to $-\text{CH}_2-$ protons of Eg residue), 2.22–2.67 (owing to $-\text{CH}_2-$ protons of PHB), 1.94–1.86 (owing to $-\text{C}(\text{CH}_3)_2\text{Br}$ protons of the end group), 1.11–1.33 (owing to $-\text{CH}_3-$ protons of PHB).

¹³C NMR (CDCl₃): δ (ppm) = 19.5–20.8 (owing to $-\text{CH}_3$ carbons of PHB), 30.7 (owing to $-\text{C}(\text{CH}_3)_2\text{Br}$), 40.0–41.8 (owing to $-\text{CH}_2$ carbons of PHB), 55.3 (owing to $-\text{C}(\text{CH}_3)_2\text{Br}$ carbons of the end group), 61.5–64.5 (owing to $-\text{OCH}_2\text{CH}_2\text{O}-$ carbons of Eg residue), 67.0–69.0 (owing to $-\text{CH}-$ carbons of PHB), and 169.0–170.3 (owing to $-\text{C}=\text{O}$ carbons of PHB).

Preparation of PS-PHB-PS Triblock Copolymer by ATRP

In a typical preparation, 0.25 g (0.096 mmol) of Br-PHB-Br macroinitiator, 2.2 mL (19.23 mmol) of styrene, and 2,2'-bipyridine (0.045 g, 0.289 mmol) was dissolved in anisole (9 mL) in a dry Schlenk flask. The homogeneous solution was purged with nitrogen for 10 min. After additional three freeze-thaw pump cycles, 0.014 g (0.096 mmol) of CuBr was added. After four freeze-thaw pump cycles, the polymerization was allowed to proceed for 66 h at 115 °C under nitrogen. When the reaction was stopped, the polymer mixture was dissolved in chloroform and then washed with water until discoloration of the water. The solvent was removed under vacuum, and the polymer was purified by repeated precipitations from chloroform solutions into methanol (yield, 23%, $M_w = 8400$, $M_w/M_n = 1.58$, $\text{DP}_n = 62$). The chemical structure of the PHB-PS block copolymer was confirmed by FTIR, ¹H NMR, and ¹³C NMR spectroscopy.

FTIR (film): ν (cm⁻¹) = 3080–3000 (ν , C–H aromatic), 2930 (ν , C–H aliphatic) 1722 (ν , C=O), 1610 (ν , C=C aromatic), 1200–1150 (ν , C–O), 759 and 699 (δ , C–H aromatic).

¹H NMR (CDCl₃): δ (ppm) = 6.21–7.9 (owing to aromatic ring, (i) 5.01–5.43 (owing to $-\text{CH}-$ protons, *b* of PHB), 4.12–4.26 (owing to $-\text{CH}_2-$ protons, *e* of Eg residue), 3.92–4.04 (owing to $-\text{CH}_2-$ protons, *d* of Eg residue), 2.23–2.72 (owing to $-\text{CH}_2-$ protons, *a* of PHB), 0.77–2.03 (owing to

FIGURE 1 ¹H NMR spectra of PS-PHB-PS triblock copolymer.

$-\text{CH}_3-$ protons *c* of PHB and to $-\text{CH}-$ and $-\text{CH}_2-$ protons *g* and *h* of PS backbone) (Fig. 1).

¹³C NMR (CDCl₃): δ (ppm) = 19.3 (owing to $-\text{CH}_3$ carbons of PHB), 39.7–41.3 (owing to $-\text{CH}_2-$, $\text{CH}-\text{Ar}$ of styrene and $-\text{CH}_2$ carbons of PHB), 68.5 (owing to $-\text{CH}-$ carbons of PHB), 125–130 (owing to aromatic ring), 144.6–147 (owing to aromatic ring), and 168.6–170.0 (owing to $-\text{C}=\text{O}$ carbons of PHB).

Preparation of PHB/PS Blends by Solution Casting

PHB/PS blends compatibilized with PS-PHB-PS triblock copolymer were obtained by solution casting. In brief, 0.1 g of the blend PHB, PS, and copolymer in a series of weight ratios (45:45:10, 40:40:20, and 33.3:33.3:33.3) was dissolved in chloroform (5% wt/v). This solution was used for casting films on Teflon plates. The plates were left at room temperature to achieve complete evaporation of chloroform. Vacuum drying was further applied to completely remove any possible solvent remaining in the films.

Characterization

¹H NMR and ¹³C NMR measurements were performed in CDCl₃ solution, using a Varian Gemini VRX 200 or a Bruker AC250 (250.133 MHz) instrument.

FTIR spectra were recorded with a Spectrum One Perkin-Elmer FTIR spectrophotometer with 4 cm⁻¹ resolution. For this, polymer films were deposited on a KBr crystal plate.

The number and weight average molecular weights of the polymers, M_n and M_w , respectively, were determined by size exclusion chromatography (SEC) with a Jasco PU-1580 liquid chromatography equipped with two PL gel 5 μm Mixed-D columns, a Jasco 830-RI refractive index detector, and a Perkin-Elmer LC75 UV detector. PS standards (0.4–400 kg mol⁻¹) were used for calibration.

Pyrolysis was performed in a thermogravimetric analysis (TGA) Q500 Series of the TA Instruments. Generally, sample size was about 7 mg. Samples were scanned from 30 to 500

SCHEME 1 ATRP production of PS-PHB-PS triblock copolymer.

$^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere at a flow rate of 60 mL min^{-1} using a platinum sample pan of $50\text{ }\mu\text{L}$.

Differential scanning calorimetry (DSC) traces were performed in a Mettler-Toledo instrument TA 4000 System consisting of the DSC-30 module and Star software. Samples of 5–10 mg were weighed in $40\text{ }\mu\text{L}$ aluminum pan and an empty pan was used as reference. Measurements were performed under nitrogen at a flow rate of 30 mL min^{-1} according to the following protocol: (1) First and second heating scans from -20 to $200\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$; (2) Cooling scan from 200 to $-20\text{ }^{\circ}\text{C}$ at $100\text{ }^{\circ}\text{C min}^{-1}$. The melting enthalpy of 146 J g^{-1} was used to determine the degree of crystallinity⁸¹ of PHB.

Surface morphologies were recorded on small-sample fragments sandwiched between two microscope cover glasses and observations were made using a Nikon-polarized optical microscope (Optiphot-Pol) equipped with a Mettler FP82 hot stage. The samples were heated up to $200\text{ }^{\circ}\text{C}$, kept at this temperature for 2 min, compressed to decrease film thickness, and cooled down to room temperature and kept at that temperature for 30 min for crystallization.

Atomic force microscopy (AFM) experiments under ambient conditions were performed in the tapping mode on a commercial Multimode system equipped with a Nanoscope IV controller (Veeco Instruments) using silicon cantilevers with a nominal force constant of $\sim 30\text{ N m}^{-1}$ from Veeco (type RTESP) at a resonance frequency of about 320 kHz.

Static contact angles were measured using the sessile drop technique with a FTA200 Camtel goniometer, using water as probing liquid.

The cross-section morphologies of films were recorded using a JEOL (JSM-5600LV) scanning electron microscope (SEM) at

the required magnification and with accelerating voltage of 14 kV. Samples were cut from a compression molded sheet prepared by heating the powder at $175\text{ }^{\circ}\text{C}$ and applying pressure of 100 MPa for 2 min at the same temperature. The film samples frozen in liquid nitrogen were fractured and sputtered with gold before SEM observation.

RESULTS AND DISCUSSION

Synthesis of PS-PHB-PS Triblock Copolymer

The synthesis of the PS-PHB-PS triblock copolymer, as shown in Scheme 1, was completed via a three-step process: (i) high-molecular-weight bacterial PHB was converted into low-molecular-weight telechelic PHB-diol; ii) the PHB-diols reacted with β -bromoisobutyryl bromide to form PHB-Br as the macroinitiator species; and finally, this macroinitiator was used to carry out ATRP of styrene monomer to prepare the block copolymer.

The synthesis of telechelic PHB-diols involved the transesterification of bacterial PHB ($M_w = 217\text{ kDa}$, $M_w/M_n = 1.70$) with ethylene glycol and dibutyltin dilaurate as the catalysts.

TABLE 1 Trend of Molecular Weight Properties of PHB-Diols as A Function of Transesterification Reaction Time

Name	M_w (kDa)	M_n (kDa)	M_w/M_n
PHB-Eg-0 h	217	127	1.70
PHB-Eg-1 h	76	43	1.78
PHB-Eg-3 h	25	16	1.53
PHB-Eg-4 h	16	10	1.54
PHB-Eg-5 h	11	5.5	2.01
PHB-Eg-6 h	9.2	4.8	1.91
PHB-Eg-7 h	8.6	5.4	1.58

FIGURE 2 GPC of Br-PHB-Br and PS-PHB-PS triblock copolymer.

The aim of this step was to prepare PHB with one free terminal hydroxyl group at both ends, which can be used for the preparation of linear block copolymers in the next step by chain-extending reactions. The reaction was followed up by using SEC and the data are summarized in Table 1. The reaction had abrupt behavior and the starting material PHB-0 degraded within 1 h down to 33% of the original molecular weight. Oligomers with lower M_w were obtained when the reaction was continued for 7 h. The M_n of the final PHB-diol was about 6000 g mol^{-1} as determined from ^1H NMR, which is comparable to the M_n of 5400 g mol^{-1} determined by the SEC analysis. The apparent discrepancy between the values of the molecular weights evaluated by SEC and NMR results from the fact that the former technique provided approximate values of M_n as the block copolymers have different hydrodynamic volumes from those of the PS standards used for calibration. The PHB-diol formation was confirmed by ^1H NMR spectrum, which showed characteristic peaks at 3.73–3.93 and 4.13–4.34 ppm owing to the two methylene groups of ethylene glycol. These results are in complete agreement with those reported in a previous study by Saad et al.⁶³

Telechelic PHB-diol was further functionalized by a reaction with α -bromoisobutyryl bromide (Scheme 1) to include active initiating species for ATRP. The reaction was carried out at 0°C in chloroform in the presence of TEA to avoid cleavage of the PHB chain. The complete substitution of the hydroxyl groups was confirmed both by ^1H NMR and by ^{13}C NMR spectra. The ^1H NMR spectra showed the disappearance of the signal at 3.73–3.93 ppm owing to CH_2OH of the PHB-diol and the appearance of a new signal at 4.28–4.41 ppm owing to the formation of an ester bond in PHB-Br. The signal at 1.9 ppm was contributed from the methyl protons of the 2-bromo-2-methylpropionyl fragments introduced in the chain end of PHB-Br. The ^{13}C -NMR spectra also confirmed the complete functionalization of the biodegradable PHB polyester with bromine compound by the presence of methyl carbons ($-\text{CH}_3$) and methine carbons ($-\text{CBr}$) of the end groups [$-(\text{C}(\text{CH}_3)_2\text{C}=\text{Br})$] at 30.7 and 55.3 ppm, respectively.

PS-PHB-PS block copolymer was synthesized via ATRP of styrene using Br-PHB-Br as macroinitiator and cuprous bromide (CuBr)/2,2'-bipyridine complex as catalyst, in the presence of anisole as solvent at 115°C . The amount of CuBr and 2,2'-bipyridine used was calculated based on ratios between Br-PHB-Br/ CuBr /2,2'-bipyridine:1/1/3. To minimize the impact of water and oxygen on polymerization, the reaction was performed under a nitrogen atmosphere and anhydrous conditions. The block copolymer was separated and purified from the reaction mixture by several extractions with water, followed by repeated precipitation in methanol. Conversion of monomer increased with extension of polymerization time approaching about 71 wt % within 66 h. The formation of PHB-PS block copolymer was confirmed both by ^1H NMR and by ^{13}C NMR spectra. Resonances observed at 6.21–7.90 ppm in the ^1H NMR spectrum of the PHB-PS copolymer (Fig. 1) were owing to aromatic ring of the styrene, whereas resonance from 1.86 to 2.03 ppm was owing to the methylene protons of PS backbone. These observations were further confirmed by ^{13}C NMR, indicating the presence of aromatic ring at 30, 125–130, and 145–147 ppm. The relative PHB and PS content in the copolymer was evaluated from the integrated areas of the ^1H NMR signals at 6.21–7.90 ppm (aromatic ring *i* of PS) and 5.30 ppm ($-\text{CH}-$ protons *b* of PHB). Consistently, the length of the PS blocks was calculated from the known length of PHB block. Figure 2 shows the SEC traces of the Br-PHB-Br macroinitiator and the triblock copolymer PS-PHB-PS-derived therefrom. The monomodal shape of the block copolymer curve suggested the absence of residual homopolymers and the complete initiation of the macroinitiator during the ATRP process.

Thermal Properties of PS-PHB-PS Block Copolymer

Thermal analyses also confirmed the formation of block copolymer structure (Table 2). In general, PHB decomposed in a single degradation step. The temperature of 2% weight loss (T_d) in the sample was considered as the onset of degradation. The T_d of neat PHB was 233°C , whereas the temperature of maximum degradation rate (T_{p1}) was 274°C . The residual weight of the PHB measured at 490°C was 0.4 wt%. The thermal decomposition of the macroinitiator Br-PHB-Br also occurred in a single degradation step. The T_d of Br-PHB-Br was 238°C . On the other hand, two-step thermal degradation was observed in the block copolymer PS-PHB-PS with a significant increase in T_d value (17°C) compared to neat PHB. The first step of degradation was in the range of 240 – 320°C mostly owing to the decomposition of PHB. The second step was in the range of 320 – 500°C ,

TABLE 2 TGA Data of PHB, PS, and PS Triblock Copolymer^a

Sample	T_d ($^\circ\text{C}$)	T_{p1} ($^\circ\text{C}$)	T_{p2} ($^\circ\text{C}$)	R_{490} (%)
PHB	233	274	–	0.40
PHB-Br	238	289	–	0.71
PS-PHB-PS	250	283	415	0.38

^a T_d is the decomposition temperature defined at 2 wt % of weight loss; T_p is the first derivative peak; and R_{490} is the residual weight at 490°C .

TABLE 3 DSC Parameters (second Heating) of PS-PHB-PS Triblock Copolymer^a

Code	T_{g1} (°C)	T_{g2} (°C)	T_{cc} (°C)	$T_{m,PHB}$ (°C)	$X_{c,PHB}$ (%)
PHB	3.8	–	24	179	61
PHB-Br	10	–	33	116, 134, 140	19
PS-PHB-PS	2	136	–	–	–

^a T_g , T_{cc} , and T_m are the glass transition, cold crystallization, and melting temperatures, respectively, and X_c is the degree of crystallinity.

representing the decomposition of the more thermally stable PS component. The significant changes were also apparent in the thermal properties of the block copolymer attributed to the reaction between PHB and PS (Table 2). The temperature of T_{p1} for copolymer was increased from 274 to 283 °C for PHB. The presence of the second derivative at 415 °C indicated the formation of the block copolymer. As the copolymer has a greater amorphous content than neat PHB, it is expected that the copolymer will have a higher thermal stability. In this regard, copolymers with higher degree of crystallinity have shown to be less thermally stable.^{60,82} The residue recovered after the thermal degradation of the

copolymer (0.38%) was more or less equivalent to the residue resulted from the neat PHB (Table 2).

The neat PHB polymer is mostly amorphous soon after quenching (second heating), as suggested by the equivalent areas of cold crystallization and melting peaks. It behaves as a typical crystalline polymer⁸³ as indicated by its glass transition temperature (T_g) and the cold crystallization temperature (T_{cc}) of 3.8 and 24 °C, respectively. The PS, on the other hand, behaves as an amorphous polymer with T_g of 89 °C, much higher than that of the PHB (Table 3). T_{ms} of Br-PHB-Br were 116, 134, and 140 °C. The presence of different melting temperatures once again indicated the partial disruption of crystalline structure of PHB. Moreover, the lower temperature peak can be attributed to the fusion of the crystallites formed upon cooling the melt, whereas the higher peaks may be owing to the fusion where spherulites are recrystallized and perfected during the subsequent heating. In the PS-PHB-PS block copolymer, the T_m peak of PHB could not be observed, indicating that PHB crystalline phase was not formed. This was also confirmed with the TGA data as indicated earlier. However, two T_g s were found; T_g at lower temperature (2 °C) attributed to the PHB block and T_g at higher temperature (136 °C) attributed to the PS block. The crystallinity of neat PHB was 61% which decreased to

FIGURE 3 Optical micrographs of (a) Br-PHB-Br, (b) PS-PHB-PS triblock copolymer, (c) PS45-PHB45-C10, and (d) PS45-PHB33-C33 blends. SEM micrographs of (e) PS45-PHB45-C10 and (f) PS33-PHB33-C33 blends.

FIGURE 4 AFM images of (a) and (b) PS-PHB-PS triblock copolymer at different scales and compatibilized PS/PHB blends of (c) PS45-PHB45-C10, (d) PS33-PHB33-C33.

19% in Br-PHB-Br until its complete disappearance in the block copolymer was also noted, this further confirming the formation of the copolymer structure. The disappearance of crystallinity in the copolymer may occur during its cooling from the molten state, because of possible physico-chemical interferences between the PS and the PHB blocks, thus preventing the crystallization of PHB. However, when the PHB components of the copolymer were first crystallized at higher temperature, the PS blocks in the copolymer were excluded and confined between the PHB lamellae, thus, restricting the mobility of PS segment and consequent crystallization of PHB segment.

Morphology of PS-PHB-PS Block Copolymer

The morphology of PS-PHB-PS copolymer was studied using polarized optical microscope. PHB is known to have a crystalline morphology and form nucleated spherulites which exhibit a typical banded structure.^{84,85} The PS-PHB-PS copolymer which is devoid of crystallinity showed no spherulite formation but only few spots compared to Br-PHB-Br [Fig. 3(a, b)].

The AFM clearly shows the phase images of the PS-PHB-PS block copolymer films after being annealed at 120 °C for 24

h [Fig. (4a, b)]. Arrays of laterally regular lamellar structures were visible on the surface of the block copolymer owing to phase separation. Domains were homogeneously distributed along the surface and were often truncated. The length of these domains ranged between 100 and 700 nm, with a diameter of 44 nm and a height ranging between 1 and 5 nm.

Contact Angle Measurements of PS-PHB-PS Block Copolymer

The contact angle measurements were made to examine the wettability properties of the block copolymer. Copolymer samples were spin-coated on glass slides from chloroform and static contact angles (θ) were measured using water as

TABLE 4 Contact Angle Data of the PS-PHB-PS Triblock Copolymer

Sample	Contact angle (°)
PHB	76 ± 1.1
PS	99 ± 1.1
PS-PHB-PS in CHCl ₃	85 ± 0.8
PS-PHB-PS in toluene	95 ± 1.3

^a Errors were calculated at 95% of confidence of Student's *t*-test.

a standard Interrogating liquid (Table 4). Although the contact angles of PHB and PS were 76 and 99°, respectively, that of the copolymer PS-PHB-PS was in between these two values (85°). This indicated almost a balanced mix of the different block onto the surface of the film in the presence of water.

Morphology of PHB/PS Blends

Fractured surfaces of PHB/PS blends containing the triblock copolymer as compatibilizer at three different concentrations (10, 20, and 33%) were examined for surface morphology under the scanning electron microscopy (Fig. 3). Although PS appears to form the matrix, PHB was randomly dispersed as filler in the form of small beads. Phase separation was distinctly apparent, particularly, in blends with 10% [Fig. 3(e)] and 20% of compatibilizer not shown in Figure 3. Blends with one third compatibilizer by weight, however, were much smoother, indicating compatibility and better adhesion between the two incompatible homopolymers [Fig. 3(f)]. Samples examined by the AFM after annealing at 120 °C provided similar results where phase separation was distinctly apparent at lower compatibilizer concentration 10% [Fig. 4(c)] and 20% not shown in the figure but not in blends with 33% of compatibilizer, again suggesting a better compatibilization between PHB and PS at higher block copolymer loadings [Fig. 4(d)].

Examination of blends under polarized optical microscope showed large spherulites in PHB which decreased with increased amount of compatibilizer [Fig. 3(c, d)]. Generally, spherulites contribute toward the PHB crystallinity; therefore, any decrease in spherulites concentration at higher compatibilizer content indicates lower crystallinity in the material. This could be owing to the fact that nucleating action of PHB decreased by increasing the amount of compatibilizer. Furthermore, the radius of the spherulites was reduced, thus overcoming brittleness of the film sample.⁸⁶

Thermal Analysis of PHB/PS Blends

In general, all blends had <1% residue with only negligible variability (Table 5). The onset temperature of decomposition (T_{onset}) of PS was 386 °C which was about 145 °C, 126 °C higher than the neat PHB and PS-PHB-PS copolymer, respectively. T_{onset} of all formulations containing compatibilizer had a higher T_{onset} than the neat PHB. Moreover, the

TABLE 5 TGA Data of PHB-PS Blends^a

Code	T_{onset} PHB (°C)	Tonset PS(°C)	T_{p1} (°C)	T_{p2} (°C)	R_{490} (%)
PHB	241	–	274	–	0.4
PS	–	386	–	415	0.1
PS-PHB-PS	260	386	283	415	0.38
45 P-45 S-10 C	268	392	285	416	0.65
40 P-40 S-20 C	270	392	287	418	0.72
33 P-33 S-33 C	269	392	285	418	0.62

^a T_{onset} is the onset decomposition temperature; T_p is the first derivatives peak; and R_{490} is the residual weight at 490 °C.

TABLE 6 DSC Parameters (second Heating) of PHB-PS blends^a

Code	T_{g1} (°C)	T_{g2} (°C)	T_{cc} (°C)	$T_{m,PHB}$ (°C)	$X_{c,PHB}$ (%)
PHB	3.8	–	47	179	61
PS-PHB-PS	2	136	–	141	–
45 P-45 S-10 C	1.9	95	50	174	33
40 P-40 S-20 C	1	130	51	174	27
33 P-33 S-33 C	–0.2	130	48	173	22

^a T_g , T_m , and T_c are the glass transition, melting, and cold crystallization temperatures, respectively, and X_c is the degree of crystallinity.

T_{onset} values for the PS in all formulations with compatibilizer remained unchanged compared to the neat PS. The peak degradation temperature (T_p) data clearly indicated that the PS-PHB-PS copolymer or compatibilizer was composed of two well-separated weight-loss steps centered around 283 and 415 °C, owing mostly to the thermal degradation of neat PHB and neat PS, respectively. In formulations with added compatibilizer, all blends showed analogous behavior, with two weight losses, resulting from thermal degradations of the PHB and PS backbone. In conclusion, the thermal stability of blend was somewhat in between those of PHB and PS components.

In DSC second heating scan, all samples exhibited their characteristic glass transition, cold crystallization, and melting temperatures. PHB exhibited one glass transition temperature T_g at 3.8 °C. Comparing the thermograms and calorimetric parameters (Table 6), the T_g of the PHB appears to be influenced by the concentration of the compatibilizer present in the blend. With addition of a compatibilizer, a decrease in the T_g s was observed in all the blends. The T_g values in the blends were comparable to the neat PHB material. These results indicated that the PS chains in the compatibilizer apparently penetrated into the amorphous region of PHB.

Neat PHB displayed a cold crystallization at about 47 °C. The DSC curve showed that the addition of the compatibilizer enhanced the cold crystallization process (i.e., the crystallinity that develops during the DSC heating scan), particularly, in blends containing 20% compatibilizer. This indicated the presence of a large fraction of the crystal phase that melted away but recrystallized in a second thermal scan.⁸⁷

The presence of compatibilizer in the blends caused a reduction in the T_m in all formulations. This decrease in the T_m was apparently owing to the interaction between the compatibilizer and the crystalline PHB.⁸⁷ The decrease in the T_m was accompanied by a substantial decrease in the crystallinity (Table 6). The X_c values for all the blends with compatibilizer decreased compared to that of neat PHB. This indicated that compatibilizer addition strongly impacted the crystallizing ability of the bacterial polyester in the blends.

CONCLUSIONS

Triblock PS-PHB-PS copolymer was successfully synthesized using ATRP reaction. The synthesized copolymer had

properties quite similar to that of the PS, which offers promises for this material for use in products manufactured by industrial, medical, and packaging sectors. A synthesized PS-PHB-PS-based compatibilizer was found to be useful for compatibilization of PS and PHB polymeric blends. At one-third concentration by weight, the PS-PHB-PS, compatibilizer, was found to be more effective in promoting a better dispersion and interfacial adhesion between PS and PHB. The T_g values of the blends components decreased with the increase of the compatibilizer content, indicating PS chain penetration into the amorphous region of PHB. Addition of compatibilizer affected the crystallizing ability of the bacterial polyester in the blends.

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