

Biodegradable and Bio-based Green Blends from Carbon Dioxide-Derived Bioplastic and Poly(Butylene Succinate)

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Published online: 3 September 2016
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Abstract Conventional polymer materials from fossil fuels feature many unresolved questions regarding disposing and future resource availability. To substitute some of the established plastics with bio-based and biodegradable alternatives, new materials have to be developed and researched. The aliphatic biodegradable polyester poly(butylene succinate) offers good material properties and the perspective to be partially bio-based in the future. Poly(propylene carbonate) is an amorphous co-polymer of propylene oxide and carbon dioxide. The incorporation of carbon dioxide in the polymer offers a great way to reduce the excess CO₂ levels in the atmosphere and at the same time to add a bio-based component to the plastic. By melt blending and injection molding these two materials, partially bio-based, potentially biodegradable blends are generated. The blends' mechanical, thermal and morphological properties are studied, using DSC, DMA, TMA, SEM, and FTIR analysis as well as tests regarding impact, flexural and tensile properties. Furthermore, the shrinkage of PPC, PBS and their blends is examined. It was found that blending of these two materials, without any additives or fillers, is not very promising, as almost all mechanical and thermal properties are decreased compared to the neat

PBS. However, shrinkage of PPC can be eliminated when added into a PBS matrix and low contents of PPC might offer a possibility to increase the impact toughness of PBS.

Keywords Poly(propylene carbonate) · Poly(butylene succinate) · Biopolymer blending · Injection molding · Characterization

Introduction

Today, most consumer products like food packaging, clothes and fabrics, electrical devices or household items as well as industrial products and parts are made from or contain polymer materials. The worldwide production volume for plastics has risen to 299 million tons in 2013 [1], with most of it coming from conventional fossil based carbon sources.

Due to the importance of polymers in our everyday life and rising prices as a result of limited fuel reserves, bio-based alternatives become more and more attractive and competitive. Not only can these materials preserve the worldwide fossil fuel reserves by substitution of petroleum based carbon, but often offer additional benefits such as biodegradability [2, 3], biocompatibility [4] or the ability to fixate pollutants like carbon dioxide [5], which is suspected to be one of the main causes for climate change through global warming [6]. Additionally, the increasing usage of polymers leads to a huge environmental waste problem due to improper handling and disposal. Polymer pollution in the oceans is especially drastic. Reduced to small pieces, waste can find its way into fish and other animals where it causes diseases or death of valuable livestock. Biodegradable materials that disintegrate within a given time after usage

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could be a viable option to reduce waste and pollution, especially in short-term applications like packaging.

However, industries and manufacturers wish for materials with comparable characteristics to established polymers and bio-based or biodegradable alternatives often exhibit poor material properties compared to their fossil based equivalents. Therefore, to create a functional material with sufficient properties and bio-based carbon content, blending of established materials with promising bio-based materials or incorporation of natural fibers into the matrix is usually an attractive option.

The intention of this work is to find a possible use for poly(propylene carbonate) (PPC), a copolymer that reaches an estimated bio-based carbon content of about 25 % through the incorporation of carbon dioxide, offers good impact resistance and elongation at break, and is possibly biodegradable under the right conditions [7–10]. PPC will be blended with poly(butylene succinate) (PBS) an already established biodegradable polymer with good materials properties comparable to the widely used polyethylene (PE) [11]. Furthermore, PBS has the potential to be partially bio-based once succinic acid, which is needed for the synthesis of PBS, will be obtained from natural resources [12] like bacterial fermentation [13].

Blending of these materials could offer new partially bio-based, environment friendly blends with acceptable material properties, potential biodegradability and increased bio-based content.

Literature Review

Poly(propylene carbonate) (PPC) can be synthesized by copolymerization of carbon dioxide and propylene oxide, to create a co-polymer with good impact strength, high elongation at break and a bio-based carbon content of 25 % [5]. Due to its smooth degradation into H₂O and CO₂, PPC experiences an increasing demand with an annual production capacity of more than 10,000 t/year [14]. Today, it is usually used to increase the toughness of epoxide resins [15], as a binder in ceramic industries [16] and in combination with starch as biodegradable blends [17, 18]. However, the amorphous poly(propylene carbonate) exhibits several challenges such as poor mechanical properties and thermal stability [19], high shrinkage and low glass transition temperature of about human body temperature [14]. Furthermore, material properties of PPC can vary depending on the catalyst used during copolymerization and the resulting stereo- and regiochemistry [14].

Most publications about PPC offer no detailed information on the microstructure which makes comparison of different studies difficult [14]. The glass transition temperature of different PPC products varies from about 25 to

45 °C, which is directly related to the concentration of ether and head-to-tail linkages [20, 21]. To obtain a product with good and stable material properties, it is also desirable to create a perfect alternating co-polymer, which was only very recently achieved by using homogeneous catalysts [22, 23]. Decomposition of poly(propylene carbonate) into circular polycarbonate (cPC) starts at around 150–180 °C, which is not easily released from PPC therefore making measuring of the exact decomposition temperature difficult [24]. It occurs by unzipping and backbiting, with hydroxide and carbonate chain ends being the main factor for fast unzipping of the chain [25]. Desirable thermally stable poly(propylene carbonate) is therefore mainly achieved by end-capping PPC with maleic anhydride or incorporation of co-monomers to reduce unzipping [26]. The peak rate of decomposition, depending on the molecular weight of PPC, was found around 230–250 °C at which even thermally stable end-capped PPC decomposes [26]. At higher temperatures PPC also acts highly shear thinning [27].

A study about the mechanical properties with an alternating purified PPC showed a Young's modulus of 830 MPa with a tensile strength and an elongation-at-break as high as 21.5 Mpa and 330 %, respectively [28]. Thermally stable PPCs exhibit lower tensile strengths and Young's moduli [29]. High elongation makes the material elastic and tough and is the most desirable property of PPC. It was found that PPC with a high molecular weight above 50 kDa shows a high elongation at break of 330 % [28].

Due to its new and unique properties, different PPC based blends and possible fillers for PPC were researched regarding their impact on the material properties. It was found that glass fibers are well dispersed and improve the thermal properties but greatly reduce elongation at break [29], which is one of the most favorable qualities of PPC. The same observations were made for a blend of PPC, starch, calcium carbonate and EVOH [30]. A promising filler for PPC could be untreated calcium carbonate. With the addition of calcium carbonate the Young's modulus and yield strength were increased while keeping a high elongation of 300 % [31].

Several studies investigated the possible biodegradability of poly(propylene carbonate). PPC starts decomposing through erosion on its surface [14]. In a medium of pH 6 with lipases a weight loss rate of about 1 wt% per month was observed [7]. A study on a blend of PPC and a starch derivative, which degraded in a period of more than 14 months, showed that degradation can be slightly faster in soil [8]. A 200 µm compressed film of low molecular weight (~50 kDa) PPC disintegrated within 3 months at 60 °C [9]. On the contrary, a different study reported almost no effect on a PPC film after 6 months [8]. However, in the presence of water, PPC is affected by

hydrolysis at temperatures above its glass transition temperature [10].

Poly(butylene succinate) (PBS) is a highly crystalline, biodegradable aliphatic polyester with material properties that are comparable to polyethylene (PE) [11]. Due to its good material properties and biodegradability in lipase solution, activated sludge, soil, water and compost [11, 32, 33], PBS is already established with an estimated annual production capacity of 98,000 t/year [34]. It is the result of trans-esterification of succinic acid and 1,4-butanediol [11] and has the potential of a high bio-based carbon content once succinic acid is obtained from bacterial fermentation [13]. PBS has a melting point of about 115 °C and a heat deflection temperature of 97 °C [11]. Its Young's modulus ranges from 300 to 500 MPa varying with the degree of crystallinity [11]. The elongation at break of PBS depends on its molecular weight; for example it has been reported to be 10 and 270 % for two grades of PBS with molecular weights of less than 100,000 and more than 180,000, respectively [11].

While processing PBS, it is important to dry the material to a moisture content below 0.2 % to prevent hydrolysis [11]. This is usually achieved by air drying at 80 °C [19]. Drying PBS at higher temperatures as well as processing temperatures above 200 °C will result in a dramatic decrease of viscosity [11]. A high crystallization rate is necessary to create semi crystalline materials, therefore the addition of nucleating agents can be beneficial [35].

The combination of poly(propylene carbonate) and poly(butylene succinate) could offer a sustainable blend with satisfactory thermal and mechanical properties and the potential of biodegradability and a way to decrease harmful CO₂ emissions.

In 2007, Pang et al. [19] studied the miscibility and material properties of poly(propylene carbonate) and poly(butylene succinate) blends, with the intention of improving the material properties of PPC. The PPC/PBS blends were produced in a batch mixing process followed by compression molding the blends into sheets and cutting them into test bars for tensile testing and other characterization methods. It was found that with increasing PBS content the yield strength and the strength at break of the blend improved [19].

To examine the miscibility of the materials, a DMA study with compression molded neat PPC, neat PBS and blends with 30, 50 and 70 % PPC content was carried out [19]. The measured glass transition temperatures (T_g) of PPC and PBS were 34.4 and −24.3 °C, respectively [19]. Two glass transition temperatures were observable for all of the heterogeneous two-phase blends, which indicated that the two polymers are not miscible. A two-phase morphology was later observed with SEM microscopy to prove these observations [19]. While the melting

temperature stayed mostly unaffected at around 115 °C for all the blends, the crystallization temperature of PBS slightly increased with PPC contents of more than 10 wt% in the blend, which implied that PPC might acted as a nucleation agent in the PBS phase [19].

During MFI measurement it was observed that with increasing PBS content the flow properties of the blend increased. While PPC has a very low melt flow index of about 1 g/10 min [36], PBS has good flow properties at about 22 g/min [19].

Pang et al. [19] came to the conclusion that melt-blending PPC and PBS can produce completely biodegradable blends with satisfactory properties with mechanical properties, thermal stability and flow properties improved in comparison to the neat PPC.

In addition to what is so far reported in the literature, the present study is focused on more industrially prevalent processing techniques namely twin-screw extrusion to produce the blends followed by injection molding to produce test bars. The blends are characterized through several mechanical testing techniques including tensile, flexural and impact. More importantly, there is a focus on the high shrinkage that PPC undergoes after molding into the final shape. This is particularly important in injection molding which is a more common method for industrial applications because it is faster and allows more complex product shapes than compression molding.

Experimental

Materials

The poly(propylene carbonate) (PPC), used in this study was a QPAC[®] 40 obtained from Empower Materials (New Castle, USA) with an average number molecular weight (M_n) of 150,000–350,000 [36]. An injection grade poly(butylene succinate) (PBS), (Biocosafe 1903) with a melting temperature of about 115 °C was acquired from Yifan Xinfu Pharmaceutical Co. Ltd. In Zhejiang, China. PPC was dried at 50 °C using a vacuum oven for a period of 24 h to a moisture content of about 0.1–0.4 %. A longer drying time showed no further reduction of moisture content. Temperatures higher than 50 °C cause the pellets to stick to each other, making it very difficult to process. PBS was dried to a moisture content of about 0.2 % in a regular drying oven at 80 °C for 4 h. Longer drying times will degenerate the material causing a drastically increased melt flow index.

Processing Method

The pre-mixed pellets for different formulations were then processed using a “Haake MiniLab II” twin screw extruder

from Thermo Scientific, USA, at 150 °C and a rotation speed of 100 RPM. Blending was carried out for 3 min. After blending, the polymer melt had to be filled into a transfer device, which was then plugged into a “Haake MiniJet II” injection molding machine, from the same company. Using different molds, sample bars for measuring impact, flexural and tensile strengths were injected. Injection was carried out at 150 °C with an injection pressure between 170 and 200 bars for 6 s and a post pressure of 200 bar for 6 s. About 4–5 g of material were needed for each sample. Impact sample bars with the dimensions of 62.5 mm × 12.3 mm × 3.5 mm (length, width, thickness) were then notched, with a notched depth of 10 mm, the same day. Flexural samples had the dimensions of 88.3 mm × 12.3 mm × 2.2 mm (length, width, thickness). ASTM type V dumbbell-shape test bars were used for tensile testing.

Mechanical Tests

The impact bars were tested for their notched Izod impact strength according to ASTM D256. Both, notching cutter and impact monitor were manufactured by Testing Machines Inc., USA. Tensile properties were measured, according to ASTM D638 using a universal testing machine by Instron, USA, model 3382, with a 5 kN load cell and at a rate of 10 mm/min. The flexural test was conducted according to ASTM standard D790 in three-point bending mode and a rate of 9.6 mm/min. All mechanical properties were measured 48 h after processing of the materials, at room temperature (23 °C) and a relative humidity of 50 %.

MFI Measurement

The test was carried out in a melt flow indexer complied with ASTM 1238 and manufactured by Qualitest, USA, model 2000A. Because PPC degrades at 180 °C, melt flow index (MFI) analysis for PPC as well as all the blends was carried out at 150 °C. To ensure comparability, PBS was also tested at 150 °C. The polymers were kept in the barrel for 7 min before starting to extrude and cut. The extrusion through the MFI die was done with an applied weight of 2.16 kg.

Heat Deflection Temperature

Heat deflection temperature (HDT) was measured using a dynamic mechanical analyzer (DMA) by TA Instruments, USA, model Q800, in a range between 35 and 100 °C and a temperature ramp of 2 °C/min. Impact test bars were used as samples for the HDT testing. The constant load to apply a stress of 0.455 Mpa was calculated according to ASTM D648 using the width and thickness of the samples. The

HDT was reported as the temperature that yields a strain of 0.1889 %, equivalent to what generates a deflection of 0.25 mm in a sample with dimensions required by ASTM D648.

Dynamic Mechanical Analysis

The same equipment was used for dynamical mechanical analysis (DMA) to determine the glass transition temperatures of the pure materials and blends. For DMA, the samples were ramped from −50 to 80 °C at 3 °C/min while being exposed to a dynamic deflection amplitude of 15 μm with a frequency of 1 Hz. The results were analyzed with the Universal Analysis 2000 software, version 4.5A, from TA Instruments.

Differential Scanning Calorimetry

Further thermal analysis regarding melting and crystallization temperatures as well as crystallinity were conducted using differential scanning calorimeter (DSC), Q200 from TA Instruments, with two heating runs. Small samples of about 5–20 mg were heated up to 250 °C at a rate of 10 °C/min, to erase the thermal history of the materials, then cooled down to −70 °C at a rate of 5 °C followed by a second heating cycle at a rate of 10 °C/min. The results were analyzed with the Universal Analysis 2000 software, version 4.5A, from TA Instruments.

Using the acquired DSC data and following formula, crystallinity of the PBS phase in the blend systems can be calculated.

$$c = 100 \times \frac{\Delta H_m}{\Delta H^0 \times x} \quad (1)$$

where c is the degree of crystallinity, ΔH_m is the measured melting enthalpy, ΔH^0 is the theoretical melting enthalpy of 100 % crystalline PBS, and x is the PBS content.

The melting enthalpy is specified by the integral of the melting peak in the DSC graph and was measured with Universal Analysis 2000 from TA instruments. Completely crystalline PBS has a theoretical melting enthalpy of 110.3 J/g [37, 38].

Thermo-Mechanical Analysis

The coefficient of linear thermal expansion (CLTE) was measured with a thermo-mechanical analyzer (TMA) from TA Instruments, model Q400, in a range between 50 and 75 °C with a temperature ramp rate of 5 °C/min. In the experiment, a probe is placed on a small flat sample cut from a flexural bar and the displacement of the probe during temperature ramp is recorded. A regression line

through the linear part of the resulting expansion graph is considered as the CLTE.

Due to the requirement of measuring a linear part of the graph and the relatively low melting temperature of PBS, a range smaller than 50 °C, which is given by ASTM standard E831, had to be chosen. The results were analyzed with the Universal Analysis 2000 software, version 4.5A, from TA Instruments.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was carried out for PBS and samples of the 80/20, 70/30 and 50/50 formulations with a “Phenom ProX” SEM by Phenom-world, The Netherlands. Previously tested impact samples were gold coated on the fracture surface with an Emitech K550 sputtering device from Quorum Technologies, United Kingdom, for 2 min at a coating rate of 7 nm/min.

Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectra were recorded using a Nicolet 6700 from Thermo Scientific, USA. A number of 32 scans per sample were conducted in attenuated total reflection (ATR) mode with a resolution of 4 cm⁻¹. OMNIC Spectra software, version 1.0.0.1591, from Thermo Scientific was used to analyze the results.

Results and Discussion

Mechanical Properties

Figure 1 shows tensile stress at yield of neat polymers and their blends. PPC, as a ductile polymer, suffers from a low strength at yield. PBS features a tensile strength at yield

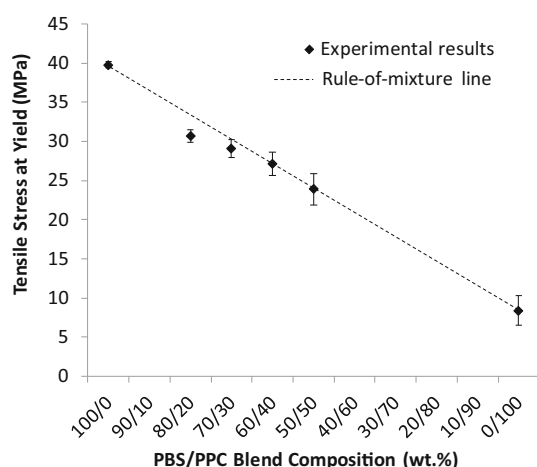


Fig. 1 Tensile stress at yield of neat polymers and different blends

which is about 5 times higher than PPC, thus a decrease in tensile strength is expected with the addition of PPC. As shown in Fig. 1, the blends follow the rule of mixture with a slight deviation and tensile strength linearly decreases with increased PPC content. Strain hardening effects were observable for PBS and PPC during tensile testing, which is why tensile stress at break was about 10 % higher than tensile stress at yield. The same observations were made for all the blends.

During tensile testing, the blends of PBS and PPC maintained a high elongation at break ranging from 160 to 190 % although the results were lower than those of both neat polymers (see Table 1). Elongation was higher with increased PPC content.

PPC features a higher Young's modulus than PBS of about 930 MPa, but contrary to what was expected, the addition of PPC did not increase the Young's modulus of the blends. Figure 2 shows that the modulus for blends with 20, 30 and 40 % PPC content is at around 660 MPa, which is lower than the values of both neat polymers. A 50/50 blend showed even lower data. This decrease in modulus is likely caused by poor miscibility and adhesion between the two blends.

Analogous to tensile properties, flexural modulus generally decreased with increasing the PPC content in the blend (Fig. 3). An exception was the PBS/PPC 60/40 blend with a flexural modulus of 744 MPa, which is about 8 % higher than the next best blend. After repetition of the experiments, similar values were found. Because of its low glass transition and softening temperatures, PPC bent under its own weight at room temperature when mounted on the 3-point bending supports and no flexural modulus could be recorded.

As discussed so far in this section, the tensile and flexural properties of the blends showed large standard deviations and rather unexpected results regarding the rule of mixture, especially for tensile and flexural moduli. The observed behavior could be due to the huge difference in the CLTE, discussed in the following sections, of the two polymers that can adversely affect the interfacial adhesion between the two phases in the blends.

Table 1 Elongation at break

PBS/PPC (wt%)	Elongation at break (%)	Standard deviation (%)
100/0	215.2	±39.4
80/20	166.8	±16.4
70/30	171.6	±34.2
60/40	179.5	±14.7
50/50	189.7	±27.2
0/100	324.9	±25.9

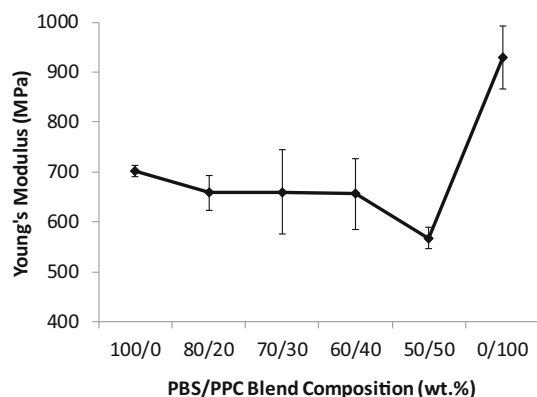


Fig. 2 Young's moduli of neat polymers and different blends

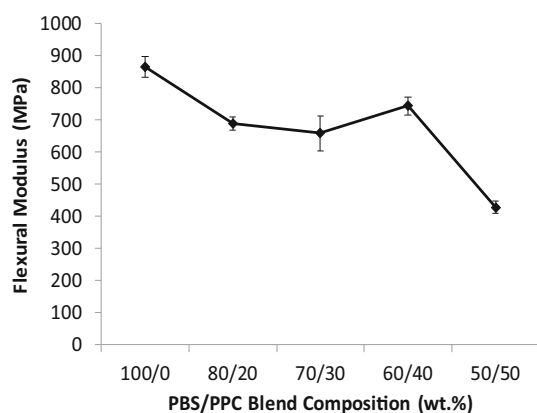


Fig. 3 Flexural modulus of different formulations

Figure 4 shows that a low percentage of PPC in the blend can improve the notched Izod impact properties. While neat PBS and neat PPC both feature an impact strength of about 26 J/m, a blend with 20 % PPC content reached an impact strength of 32 J/m. The major factor for this improvement has to be the blends morphology which is discussed later in details. It was observed that PPC forms many small droplets in the PBS matrix which hinder the

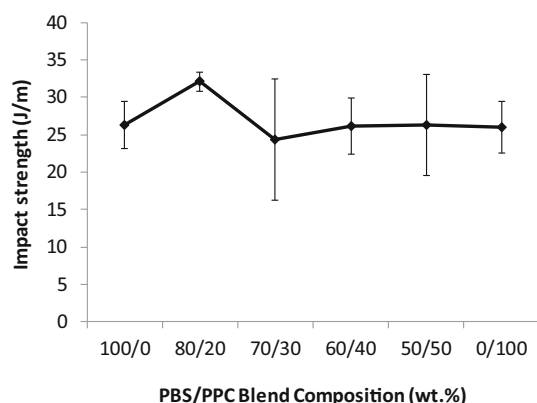


Fig. 4 Notched Izod impact strengths of different formulations

crack to take a direct path during the breaking process, therefore consuming and increasing energy needed for a break. In the blends with higher PPC content, bigger droplets with more space in between are formed, which are easier avoided by the crack and don't absorb as much energy. This is why impact strength values of the higher PPC content blends are converging near the value of neat PPC. The 70/30 blend, which seems to be on the verge between small and bigger droplets, supports this theory.

Because bigger and smaller droplets can be found in this case, the acquired data becomes inconsistent resulting in a high standard deviation. These observations were later supported by SEM images (see “SEM” section).

Thermal Properties

Using a differential scanning calorimeter (DSC), analyses of thermal transition properties were carried out. As shown in Table 2, the addition of the amorphous polymer PPC to the blend had no effect on the melting temperature. The process of melting is defined as the first-order phase transition of crystalline or semi-crystalline materials. Therefore, amorphous polymers don't exhibit melting and the melting temperature is solely based on the crystalline phase of PBS.

PPC does, however, lower the crystallization temperature from about 91 °C exhibited by neat PBS and a blend with 20 % PPC content to 58 °C with 50 % PPC content. The heat deflection temperature was drastically reduced with increasing PPC content. A 50/50 blend exhibited an HDT as low as 34.3 °C making it unusable for any consumer based application. HDT for neat PPC could not be measured due to its even lower softening temperature.

Increasing PPC content also had an influence on the melt flow properties of the blends. PPC exhibits a very low melt flow index of 0.9 g/10 min. This value, given by the technical data sheet, was hard to reproduce due to the bad flow properties and stickiness of the material. The lowest recorded data of a sample with 0.25 % moisture content was 2.1 g/10 min at 150 °C and 2.16 kg weight. However, the trend shown by the blends and neat PBS prove that an MFI of about 0.9 g/10 min reported in the technical data-sheet for PPC is reasonable.

Shrinkage and Thermal Expansion

One of the major problems with processing neat PPC is that it undergoes heavy shrinkage when processed on its own. An injection molded type V tensile sample (ASTM D638) with a gauge length of 25.4 mm shrunk to less than 22 mm gauge length within 48 h. The main shrinkage occurred within minutes after removing the sample from the mold. After the initial shrinkage, shrinking continued at a lower

Table 2 Thermal properties and melt flow index

PBS/PPC (wt%)	HDT (°C)	Melting temperature (°C)	Crystallization temperature (°C)	Glass transition temperature (°C)	MFI (g/10 min) (150 °C)
100/0	95.0 ± 0.9	114	90.8	−17	6.0 ± 0.03
80/20	82.5 ± 0.9	115.5	91.4	—	3.43 ± 0.006
70/30	62.2 ± 3	115	85	—	3.44 ± 0.11
60/40	45.6 ± 3.3	113.5	67	—	1.65 ± 0.06
50/50	34.3 ± 2.8	113	58	—	1.69 ± 0.18
0/100	—	—	—	41.9	0.9*

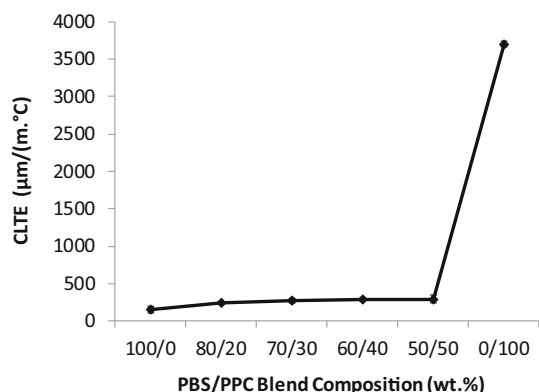
* Data sheet value

rate but could still be observed more than 2 months later. The shrinking the samples undergo while cooling down from processing temperatures to room temperature can be directly related to thermal expansion of the material. To study the expansion behavior of PPC and its influence on the blends, the CLTE was determined using TMA (thermo-mechanical analysis) in a temperature range from 50 to 75 °C (see Fig. 5).

As expected, it was found that PPC exhibited a very high thermal expansion of 3699.9 $\mu\text{m}/(\text{m}\cdot^\circ\text{C})$, compared to PBS with only 153.4 $\mu\text{m}/(\text{m}\cdot^\circ\text{C})$. However, the shrinking effect of PPC can be almost completely eliminated by blending it with PBS. The coefficients of linear thermal expansion of all blends are very close to neat PBS and no shrinkage could be observed on macroscopic level over time.

DMA

To determine the glass transition temperature (T_g) of polymers, it is necessary to study their unique viscoelastic behavior using dynamic mechanical analysis (DMA). During a cyclic deformation, DMA measures the stored energy, also known as storage modulus which represents the elastic response of the polymer, and the energy dissipated as heat, known as loss modulus. The loss modulus

**Fig. 5** Coefficient of linear thermal expansion (CLTE)

represents the viscous part of the polymer and increases when glass transition sets in. At the same time, the storage modulus decreases while the polymer undergoes glass transition. The energy dissipation or damping capability of a polymer is defined as the quotient of the loss modulus over the storage modulus and is known as tan delta. The peak of the resulting tan delta graph is considered as the glass transition temperature.

Storage modulus graphs of the neat PBS and the PBS/PPC 50/50 blend are shown in Fig. 6a. The curve for the blend showed two distinct glass transitions in storage modulus, one in the range of -40 to 0 °C and another one in the range of 20 – 40 °C. The former transition completely matches with the one observed for the neat PBS.

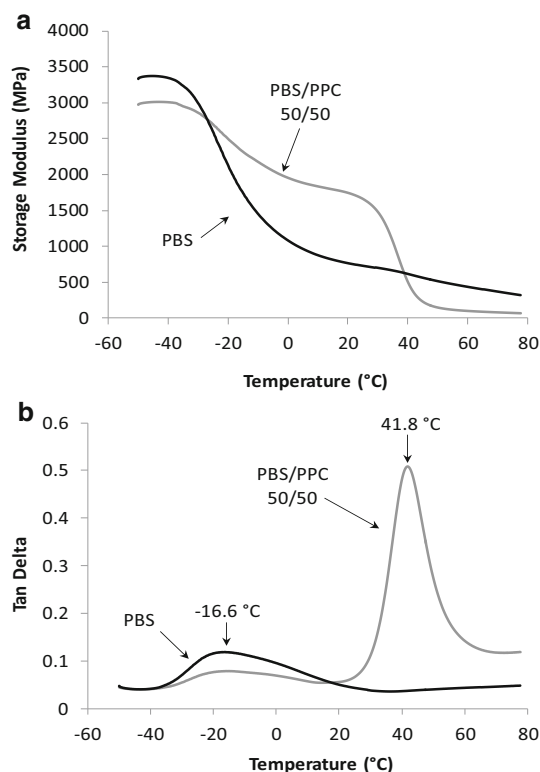
**Fig. 6** DMA graphs of the neat PBS and the PBS/PPC 50/50 blend; **a** storage modulus and **b** tan delta

Table 3 Change of crystallinity of PBS with increasing PPC content

PBS/PPC (wt%)	Crystallinity (%) (processing thermal history)	Crystallinity (%) (DSC thermal history)
100/0	59 ± 3.7	61.6 ± 1.8
80/20	63.5 ± 1.9	60.4 ± 1.3
70/30	62.2 ± 5.3	55.9 ± 2.4
60/40	63.9 ± 1.9	58.8 ± 0.8
50/50	61.7 ± 2.3	59.5 ± 3.2

Figure 6b demonstrates the tan delta graphs of the neat PBS and the blend. The glass transition temperatures (T_g) found for the neat PBS was $-16.6\text{ }^{\circ}\text{C}$. The same peak maximum was observed for the glass transition of the PBS in the PBS/PPC 50/50 blend while the one for PPC in the blend was observed at $41.8\text{ }^{\circ}\text{C}$. As compared to the tan delta curve of the neat PBS, the blend had lower tan delta value or damping capability at sub-zero temperatures while it showed significantly higher tan delta value at temperatures above the room temperature due to the presence of PPC in the blend. With known T_g for the neat materials, DMA can be used to find out whether two polymers are miscible or not. In the DMA analysis of the 50/50 blend (see Fig. 6), the two glass transition temperatures observed for the two polymers suggest that PPC and PBS are not miscible. These observations match with the SEM images made in a following experiment (see “SEM” section).

Morphology

Crystallinity

To further examine whether PPC has an influence on the crystallinity of PBS and acts as a nucleating agent or not, the crystallinity of the blends and neat PBS was calculated.

By taking the PBS content into the calculation, the results in Table 3 only picture the crystallinity of the PBS phase. The results show that neat PBS exhibits a crystallinity of 59 % before deleting the processing thermal history and a slightly higher crystallinity of 61.6 % in the second heating run. PBS phases in all blends display a stable crystallinity around 60 % with variances that lie within standard deviations. Using Tukey’s method, it was proven that the crystallinity values for the first run show no significant difference, statistically. In the second heating run, the 70/30 blend exhibit a significant difference compared to neat PBS. A small decrease of crystallinity can be observed in all cases after erasing the thermal history. Overall a nucleating effect of PPC on PBS couldn’t be proved. As an amorphous polymer, PPC doesn’t feature any crystalline structures that could act as nucleation points. In another point, the amorphous nature of PPC, generally, did not impose any hindrance to the crystallization of PBS.

SEM

Scanning electron microscopy was conducted for samples of PBS and three different blend formulations (see Fig. 7). While the PBS sample shows a homogenous surface, a characteristic behavior for immiscible blends is observable in the 70/30 and 50/50 blends. A two phase microstructure is observable and following the aspiration for a minimal surface area, PPC forms droplets in the PBS matrix. The PPC represents the discontinuous phase due to its higher viscosity in comparison to PBS. As predicted, these droplets increase in size with increasing PPC content. It is not obviously visible if 50/50 is the turnover point from a PBS matrix to a PPC matrix, however, the 50/50 blend is very close to a co-continuous morphology and the fracture surface pattern of the sample suggests that the turnover takes place at higher PPC content.

The 80/20 blend, however, offers an anomaly in its structure. PPC seems to be well dispersed in particles of varying form and size. Poly(propylene carbonate) fragments are often not arranged in spheres or droplets but rather form patches of irregular shapes. In certain areas PPC even seems to agglomerate to form larger clusters (see Fig. 8). With a PPC content which is only 10 % higher, the 70/30 blend doesn’t exhibit this phenomenon anymore.

This irregular distribution of seemingly randomly formed particles is presumed to be the main reason for the improvement of impact properties in the 80/20 blend. While breaking, the crack is forced to avoid PPC areas to find the path of lowest energy, which increases the necessary energy compared to a crack with a rather straight path.

Fourier Transform Infrared Spectroscopy

Due to the existence of C=O double bonds in both neat polymers used, FTIR analysis in Fig. 9 shows a very prominent peak at the equivalent wavelength of 1710 cm^{-1} . Another prominent peak is the C–O single bond peak at around 1150 cm^{-1} . Both peaks can be found in the neat polymers as well as all blends. O–H groups are very rare in both polymers and only appear on the terminal chain ends. FTIR shows only scatter for the O–H group area of $3000\text{--}3700\text{ cm}^{-1}$. No new peaks or peak shift can be observed in any of the blends, which proofs that no bonding effects take place during blending.

Conclusion

Blends of poly(butylene succinate), PBS, and poly(propylene carbonate), PPC, can be easily injection molded which produces a material with lower carbon footprint than the neat PBS. However, blending of the two immiscible polymers reduced almost all mechanical and thermal

Fig. 7 Scanning electron microscopy for different PBS/PPC blends **a** 100/0, **b** 80/20, **c** 70/30, and **d** 50/50. Ratios are based on wt%. All scale bars show 10 μm

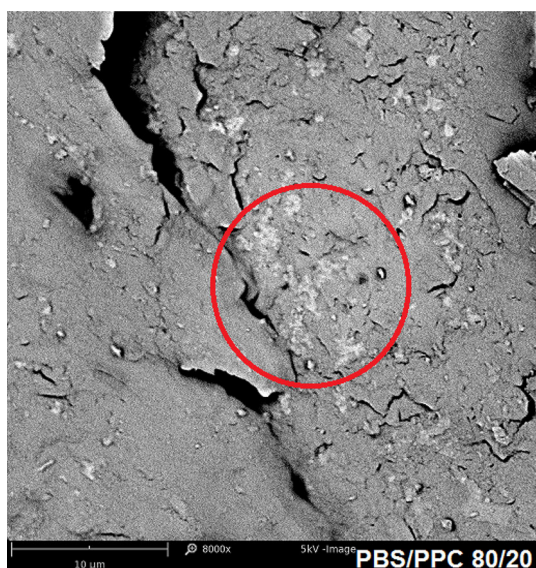
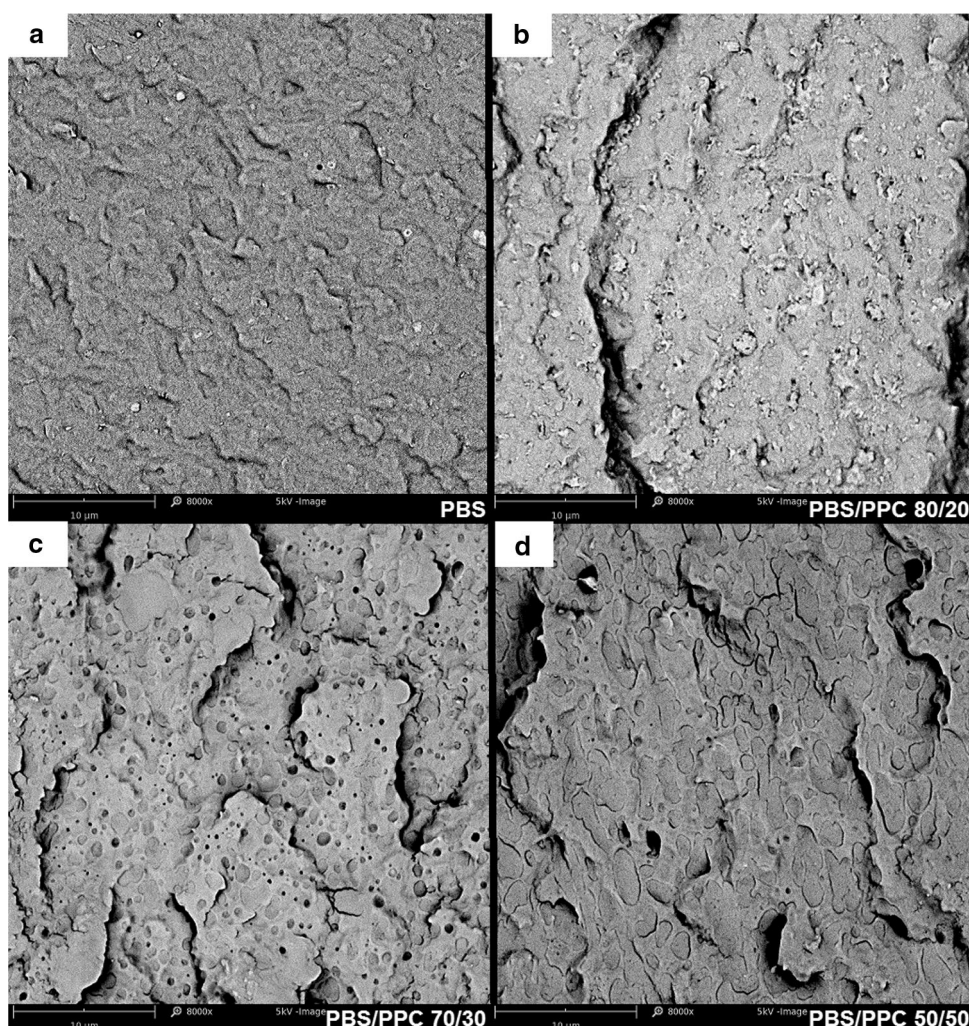


Fig. 8 Agglomerated particles of PPC visible on SEM image of PBS/PPC 80/20 blend (wt%)

properties compared to neat PBS. A small amount of PPC added to PBS could be a viable option to increase the impact strength. A more detailed study about the influence of low PPC content blends on the impact properties of PBS, may offer interesting and promising results. As an amorphous polymer, PPC has no crystalline structures that could act as nucleating points. Even though the shrinkage of PPC was eliminated by blending, blends of PBS with higher PPC content were not beneficial, due to the overall decreased properties.

These reasons hinder PBS and PPC blends to be competitive at the current stage. To create blends that feature better properties and have possible real-life applications, additives have to be incorporated into the blends to improve phase adhesion and miscibility of the polymer as well as improve the thermal stability. Moreover, an improvement of mechanical and thermal properties can be achieved by adding certain fillers like fibers or nano-materials. With the inclusion of additives, the biodegradability might be affected, which makes a biodegradability study

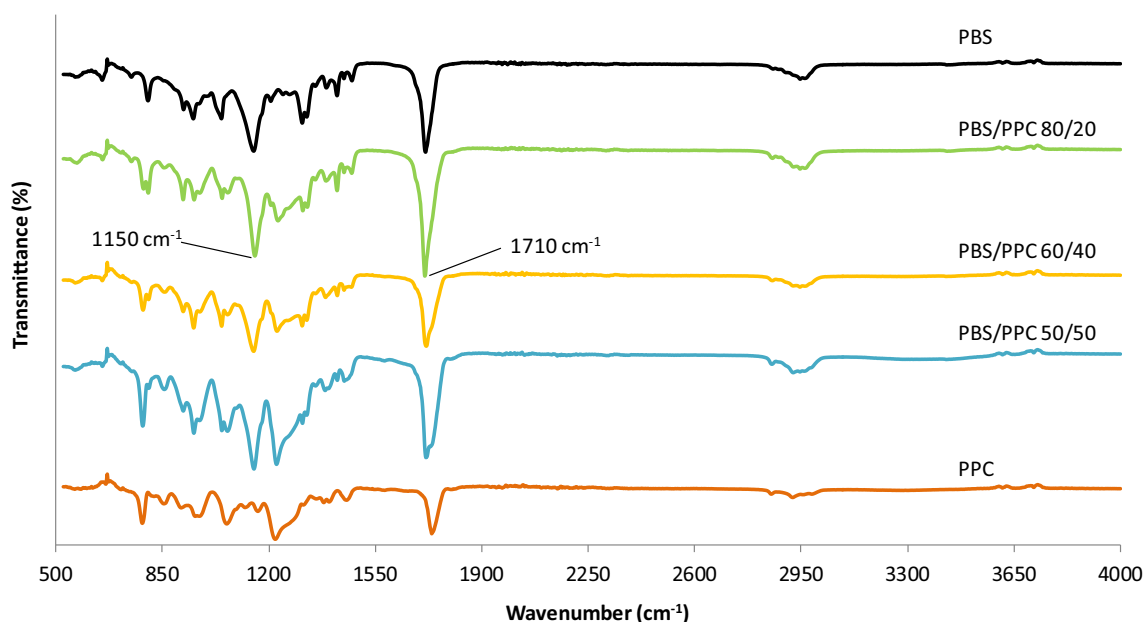


Fig. 9 FTIR transmittance of neat materials and different blends

regarding PBS and PPC blends with and without additives relevant for future work.

Acknowledgments The authors are thankful to the Ontario Ministry of Agriculture Food and Rural Affairs (OMARA)—University of Guelph Bioeconomy-Industrial Uses Research Program (Project # 200369); the Natural Sciences and Engineering Research Council (NSERC), Canada, for the Discovery Grants (Project # 400322); and the Ministry of Research and Innovation (MRI), Ontario Research Fund—Research Excellence Round 4 Program (Project # 050231 and 050289), for their financial support to carry out this research work. Furthermore the authors would like to thank the German Ministry for Science and Culture of Lower Saxony, the Volkswagen Foundation and Niedersächsisches Vorab for their support.

References

- PlasticsEurope (2014) <http://www.plasticseurope.org/information-centre/press-releases/press-releases-2014/china-leads-global-plastics-production-while-europe-ranks-second.aspx>. Accessed 4 Aug 2015
- Mohanty AK, Misra M, Hinrichsen G (2000) *Macromol Mater Eng* 276–277:1–24
- Sivan A (2011) *Curr Opin Biotechnol* 22:422–426
- Kawaguchi T, Nakano M, Juni K, Inoue S, Yoshida Y (1983) *Chem Pharm Bull* 31:1400–1403
- Ree M, Bae JY, Jung JH, Shin TJ (1999) *J Polym Sci* 37:1863–1876
- Solomon S, Plattner G-K, Knutti R, Friedlingstein P (2009) *Proc Natl Acad Sci USA* 106:1704–1709
- Inoue S, Tsuruta T, Takada T, Miyazaki N, Kambe M, Takaoka T (1975) *Appl Polym Symp* 26:257–267
- Du LC, Meng YZ, Wang SJ, Tjong SC (2004) *J Appl Polym Sci* 92:1840–1846
- Luinstra GA (2008) *Polym Rev* 48:192–219
- Jung JH, Ree M, Kim H (2006) *Catal Today* 115:283–287
- Xu J, Guo B-H (2010) *Biotechnol J* 5:1149–1163
- Bechthold I, Bretz K, Kabasci S, Kopitzky R, Springer A (2008) *Chem Eng Technol* 31:647–654
- Song H, Lee SY (2006) *Enzyme Microb Technol* 39:352–361
- Luinstra GA, Borchardt E (2012) Material properties of poly(propylene carbonates). In: Rieger B, Kunkel A, Coates GW et al (eds) *Synthetic biodegradable polymers*. Springer, Berlin, pp 29–48
- Okamatsu T, Kitajima M, Hanazawa H, Ochi M (1999) *J Adhes Sci Technol* 13:109–125
- Sterzel H-J, Ter Maat JHH, Ebenhoeck J, Meyer M (1992) United States Patent US5145900 A
- Ramis X, Cadenato A, Salla JM, Morancho JM, Vallés A, Contat L, Ribes A (2004) *Polym Degrad Stab* 86:483–491
- Ge XC, Xu Y, Meng YZ, Li RKY (2005) *Compos Sci Technol* 65:2219–2225
- Pang MZ, Qiao JJ, Jiao J, Wang SJ, Xiao M, Meng YZ (2008) *J Appl Polym Sci* 107:2854–2860
- Lu X-B, Wang Y (2004) *Angew Chem Int Ed Engl* 43:3574–3577
- Quan Z, Min J, Zhou Q, Xie D, Liu J, Wang X, Zhao X, Wang F (2003) *Macromol Symp* 195:281–286
- Coates GW, Moore DR (2004) *Angew Chem Int Ed Engl* 43:6618–6639
- Kim HS, Kim JJ, Lee SD, Lah MS, Moon D, Jang HG (2003) *Chemistry* 9:678–686
- Li XH, Meng YZ, Zhu Q, Tjong SC (2003) *Polym Degrad Stab* 81:157–165
- Varghese JK, Na SJ, Park JH, Woo D, Yang I, Lee BY (2010) *Polym Degrad Stab* 95:1039–1044
- Peng S, An Y, Chen C, Fei B, Zhuang Y, Dong L (2003) *Polym Degrad Stab* 80:141–147
- Thorat SD, Phillips PJ, Semenov V, Gakh A (2004) *J Appl Polym Sci* 93:534–544
- Du L, Qu B, Meng Y, Zhu Q (2006) *Compos Sci Technol* 66:913–918
- Chen W, Pang M, Xiao M, Wang S, Wen L, Meng Y (2009) *J Reinf Plast Compos* 29:1545–1550
- Du FG, Bian SG, Xiao M, Wang SJ, Qiao JJ, Meng YZ (2008) *J Polym Eng* 28:435–448

31. Li XH, Tjong SC, Meng YZ, Zhu Q (2003) *J Polym Sci Part B Polym Phys* 41:1806–1813
32. Kim H-S, Yang H-S, Kim H-J (2005) *J Appl Polym Sci* 97:1513–1521
33. Fujimaki T (1998) *Polym Degrad Stab* 59:209–214
34. Endres H-J, Siebert-Raths A, Behnsen H, Schulz C (2014) *Biopolymers facts and statistics*. IfBB—Institute for Bioplastics and Biocomposites, Hanover
35. Dong T, He Y, Zhu B, Shin K-M, Inoue Y (2005) *Macromolecules* 38:7736–7744
36. Empower Materials Inc. <http://www.empowermaterials.com/>. Accessed 10 Aug 2015
37. Correlo VM, Boesel LF, Bhattacharya M, Mano JF, Neves NM, Reis RL (2005) *Mater Sci Eng A* 403:57–68
38. Phua YJ, Lau NS, Sudesh K, Chow WS, Mohd Ishak ZA (2012) *Polym Degrad Stab* 97:1345–1354