Studies on Recyclability of Polyhydroxybutyrate-*co*-valerate Bioplastic: Multiple Melt Processing and Performance Evaluations

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Received 17 June 2010; accepted 22 December 2011
DOI 10.1002/app.36840
Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Recyclability of the bioplastic polyhydroxybutyrate-*co*-valerate (PHBV) was studied with multiple melt processing (five cycles), with their performances evaluated. A batch of PHBV was processed with a twin screw extrusion followed by injection molding. This operation was repeated five times and samples were collected from each cycle for characterization. For each cycle, the mechanical properties were characterized with tensile, flexural, and impact testing, along with dynamic mechanical analysis. The results showed that the mechanical properties are maintained for four cycles; but in the fifth cycle, there was slight decrease in the properties. Gel permeation chromatography studies revealed that the molecular weight of the polymer does not decrease drastically; however, a drop was observed after third, fourth, and fifth cycle (8.7% decrease after third cycle, 13.5% decrease after fourth cycle, and 16.6% decrease after fifth cycle). The differential scanning calorimeter showed that the glass transition and melting temperatures did not change upon reprocessing, but the degree of crystallinity was reduced as a consequence of melt processing. The thermal gravimetric analysis showed that the onset value of thermal decomposition decreased very slightly. It was observed by Fourier transform infrared spectroscopy that the chemical structure of PHBV was maintained without any side chain reaction during processing. Scanning electron microscopy studies from the fractured surfaces of Cycles 1 and 5 confirmed that the uniformity of PHBV surfaces was maintained after five cycles, coinciding with the mechanical tests. The density measurements revealed that there was no change in the density of PHBV. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: PHBV; recycling; mechanical properties; degradation

INTRODUCTION

Polymer recycling is one of the most important subjects of the current industry, besides producing biodegradable polymers, to increase the number of environment friendly materials. In the United States alone, recycling is done for more than 2 billion pounds of polymers. The two major recycled polymers are polyethylene terephthalate (PET) and high density polyethylene (HDPE).[1] Polymer recycling is easier than other types of material classes due to the thermoplastic properties of the polymers that can be reprocessed in extruders and injection molding machines.[2] An important issue in polymer recycling is the separation of the polymers in the waste and landfill areas. These polymers are heavily mixed in with other polymers and wastes. Thus, a large the issue is the separation of the polymers from other wastes as well as the separation of the polymers between each other. Near infrared technologies (NIR) help to separate the polymers.[3,4] It was shown that PET and polyvinyl chloride (PVC) could be separated using NIR.[3]

In industry, recycled polymers are subjected to multiple extrusions.[2] The reprocessing and recycling of polymers have adverse effects on the final properties due to the degradation caused by mechanical shear forces and thermal effects.[5] The study of multiple extrusions of plastics is an important study in understanding the changes in the properties of the polymers.

Biopolymers and bioplastics are a very important class of polymers that can be degraded under certain time periods and conditions.[6] The fluctuations in oil prices and dependency on oil resources motivate

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Contract grant sponsor: Ontario Ministry of Agriculture, Food, and Rural Affairs (OMAFRA, Alternative Renewable Fuels "Plus" Research Program); contract grant number: ARF24.

Contract grant sponsor: The Ministry of Economic Development and Innovation Ontario, Canada AUTO21 Network of Centres of Excellence program.

biologically-based materials and polymers in efforts to reduce petroleum-based polymers. Additionally, environmental concerns promotes the wide spread applications of the biobased polymers. Being degradable does not mean that they cannot be reused and recycled. The recyclability and reuse of these polymeric materials is just as important as the commercial petrochemical polymers. Polylactic acid (PLA) and polyhydroxybutyrate-*co*-valerate (PHBV) are two attracting biobased polymer families for future applications.[1]

PLA is an important type of biopolymer which takes attention by many different industries and is produced by a number of different producers. PLA is obtained by the polymerization of lactic acid obtained from agricultural resources such as corn.[7,8] It has high strength and high modulus with low percent elongation.

The recycling of PLA polymer was recently published.[2] The authors observed that there was slight decrease in the mechanical properties. Tensile strength and impact toughness decreased slightly with a decrease in the onset temperature of the polymers after certain cycles. They concluded that recycled PLA can be easily used as additive for the processing of PLA.

Polyhydroxyalkanoate (PHA) is another important biopolymer family with a homopolymer and copolymer structure.[9,10] The PHBV is the copolymer form which is obtained from the bacterial resources, specifically from the bacteria *Alcaligenes eutrophus*.[11] Different feeding, glucose, and propionic acid ratios produce different copolymer compositions, with the valerate content being varied from 0 to 24%. The valerate content in the PHA family of polymers helps to increase the elasticity and processability.

In this study, PHBV polymer is processed five times with melt processing techniques, the changes in the properties are measured. The effect of reprocessing on the mechanical properties is the most important parameter for the reusability of the polymers, thus great importance is placed on observing these changes. The changes in the physical properties, chemical structure, and thermal properties are also very critical for the understanding of the reprocessability of PHBV.

EXPERIMENTAL

Materials

PHBV with 14% valerate content is used from Zeneca Bioproducts with the trade name Biopol D600GN and production batch code GL60DN19.

Processing

DSM Xplore 15 mL microcompounder (twin screw extruder) was used to melt process PHBV and samples for mechanical properties were prepared with the DSM Xplore 12 mL injection molding machine. The melt processing was repeated for five cycles. The processing temperature was 170°C in the microcompounder, the molten PHBV was transferred to the injection barrel at 170°C, and the samples were prepared with the mold temperature at 35°C and four bar pressure.

Mechanical properties

Tensile strength and tensile modulus values were determined according to ASTM D-638 standard using Instron 3382. At least three samples were tested and mean values were determined with standard deviations. Flexural strength and modulus were determined according to ASTM D790 standard using Instron 3382 with different grips. At least three samples were tested and mean values were determined with standard deviations. Izod notched impact testing was done with a Testing Machine according to ASTM D-256 standard. Due to high standard deviations, at least five samples were tested.

Dynamic mechanical analysis

Storage modulus values were determined using a DMA Q800 from TA Instruments in a temperature range of −50 to 140°C with a heating rate of 3°C/min, an amplitude of 0.01 μm and a frequency of 1 Hz.

Gel permeation chromatography

Viscotek GPC max VE2001 GPC with Viscotek Model 3580 differential refractive index (RI) detector was used to conduct the molecular weight measurements. Chloroform was used as the solvent used for the experiment with a flow rate of 1 mL/min. PHBV concentration was 0.75 mg/mL. The sample injection volume was 100 μL. Polystyrene standards were used for calibration.

Differential scanning calorimeter

The glass transition point, melting point, and enthalpy of crystallization were determined using a Q100 DSC from TA Instruments. The samples underwent a heat cool heat method, heating from −50to 200°C with a rate of 10°C/min. The glass transition point, melting point were derived from the second heating cycle and enthalpy of crystallization point was obtained from the cooling cycle.

Thermal gravimetric analysis

Q500 TGA from TA Instruments was used to conduct the TA experiments. The samples from each cycle was heated from room temperature to 600°C

with 20°C/min ramp rate to observe the mass loss upon heating and the onset temperature of degradation.

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) measurements were conducted with the Thermo Scientific Nicolet 6700, and an ATR attachment.

Scanning electron microscopy

Samples were coated with sputtering gold/palladium (60 : 40) to a final thickness of 20 nm with 20 mA for 2.5 min. The samples were examined with a Hitachi S-570 scanning electron microscope at 10 kV.

Density

The density of the samples was measured using an electronic densimeter MD-300S from Alfa Mirage. At least three replicates were measured and standard deviations were calculated accordingly.

RESULTS AND DISCUSSION

Tensile testing

The changes in mechanical properties after the reprocessing of PHBV with melt processing techniques are measured. The shear forces during the extrusion process, crystallization phenomena, and thermal effects influence the material properties of the polymers studied. The tensile test is a very important mechanical measurement, as it provides the maximum stress that the material can carry, the percent elongation, Young's modulus, and toughness values.[12] The tensile tests measures any changes after each processing cycle. The changes in tensile strength and modulus give very critical information regarding the reprocessability and recyclability of the material.[2]

The tensile test results showed that PHBV exhibited a typical brittle fracture with less than 10% strain values (around 5%). This happens for polymers that are tested above their glass transition temperature with quasi-viscous flow behavior.[13] The brittleness of these bacterial based polyesters arises from secondary crystallization. This secondary crystallization affects the mobility of the amorphous phase creating brittle polymers.[13] El-Taweel et al.[13] further relates the brittleness of the polyhydroxybutyrate (PHB) with the % crystallinity. It was understood that above 40% crystallinity, the polymers exhibited brittle fracture. Though after certain cycles of melt processing, crystallinity decreased from 59 to 46% (measured by differential scanning calorimeter (DSC)), the brittle behavior did not change.

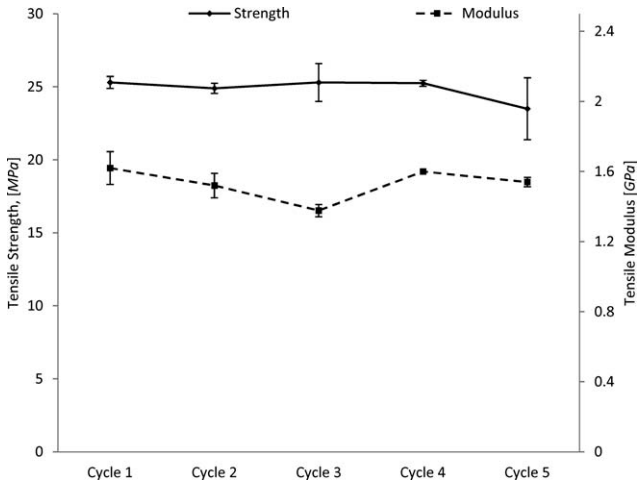

Figure 1 Effect of reprocessing on tensile strength and modulus.

The results showed that the tensile strength values did not change until Cycle 5 (Fig. 1, the long bars show the strength values and the circles show the modulus values). There was a slight decrease in the fifth cycle (7.1%). Some fluctuations were seen in the mean values but the tensile strength values were in the same range. The percent elongation values did not change much, as stated the crystallinity is above 40% for all the cycles. This was a very important result for the recycling of PHBV. As the strength was maintained through the five cycles, it was concluded that the material could withstand similar stress values and the recycled material could be reused as virgin material, or mixed with new materials in the production line as filler.

In an earlier study conducted with polylactic acid,[2] it was shown that after reprocessing, the tensile strength (5.2% decrease in tensile strength after 10 times processing) which was in the range of this study. The chains in PHBV are less susceptible to chain scission and break down,[15] and for PHBV it was observed that the properties were not altered in the initial cycles but was decreased for the final one. The infrared spectra measurements confirm this observation of stability after certain cycles (discussed in the later sections). In another study, the tensile strength was studied with two different screw speeds, it was observed that higher screw speeds decreased the properties and screw speed at 110 rpm which is similar to this study, did not change the properties significantly.[16]

The tensile modulus values were in the same range (Fig. 1). Similar observations for polylactic acid reprocessing were reported previously, showing that the modulus values were within the same range.[17] Their conclusion was that the increase in crystallinity accompanied with the decrease in molecular weight maintained the modulus values to

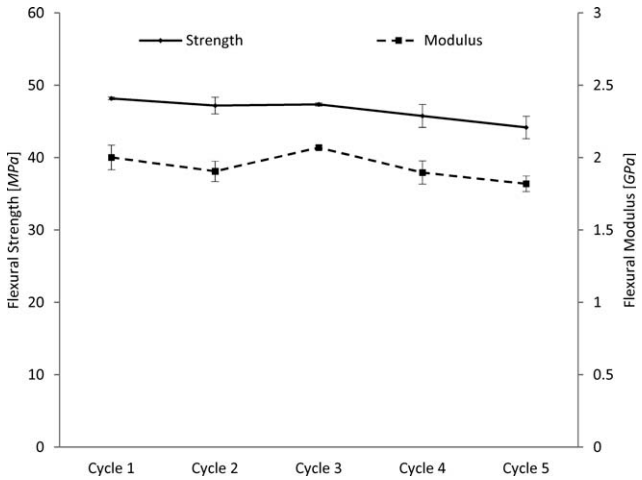

Figure 2 Effect of reprocessing on flexural strength and modulus.

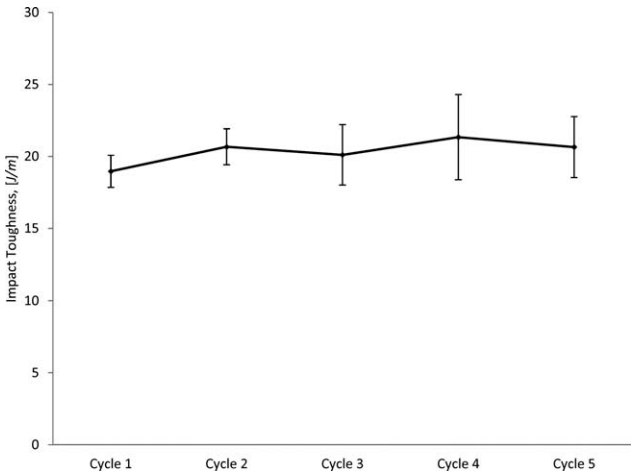

Figure 3 Effect of reprocessing on toughness.

a similar range. Another study also showed that the modulus values were not significantly altered for the polylactic acid and flax composites.[16] For this study, the crystallinity decrease and molecular weight decrease were very slight, which is reflected in the modulus values and other mechanical properties. It can be concluded that there is no significant change in the modulus value, this is also very critical for the reusability of these important classes of bioplastics.

Flexural testing

The samples collected from each cycle were subjected to flexural testing along with the tensile testing. Flexural testing was used to understand the mechanical properties subjected to bending load as a comparison to tensile loading. The results of flexural strength and modulus are shown in Figure 2. (The full lines show the strength and the dotted lines show the modulus values.) It was observed that the flexural strength remained in a similar range especially for the first three cycles, as seen in the tensile loading. There was a slight decrease after third cycle with the fourth and fifth cycles. For the fifth cycle, a decrease of 8.33% was observed. This small change in the properties was consistent with the tensile data as well. The values were within a certain range, thus showing good data for recyclability. This shows that PHBV can be easily reprocessed and manufactured into desired products.

Impact strength

Impact strength values are critical for some applications such as automotive bumpers. The results were very promising for the impact values (Fig. 3), as the mean values were in the same range showing almost identical values with small fluctuations. One other important result of this research was the consistency of the mechanical properties measured with three different methods, tensile testing, flexural testing, and impact toughness. All of the measurements demonstrate that the reprocessing cycles did not affect the mechanical properties of PHBV. This offers many new possibilities of recycling. This stability in the impact toughness values are consistent with a study conducted with polycarbonate, in which they observed a very slight decrease after five cycles.[19]

Dynamic mechanical analysis

Dynamic mechanical analysis gives very important information on the modulus values with respect to changes in the temperature during testing. The dynamic mechanical analysis (DMA) testing was conducted with a three-point bending clamp, and similar modulus values were obtained with the flexural testing. With DMA, PHBV samples from five

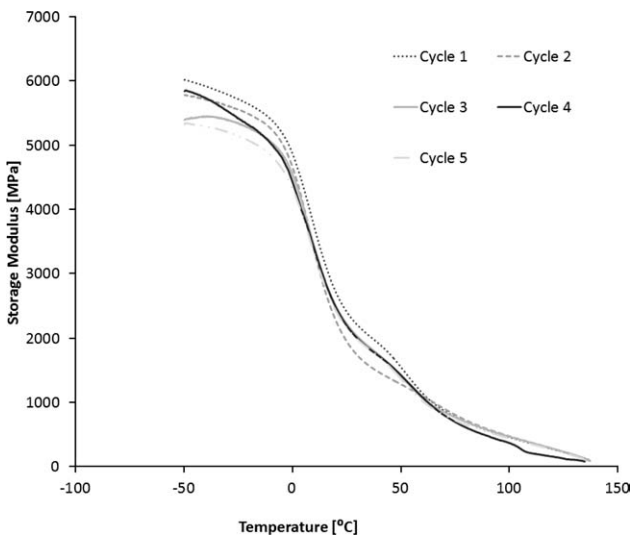

Figure 4 DMA-storage modulus from Cycles 1 to 5.

TABLE I
Change of Molecular Weight after Reprocessing

Sample	M_w (Da)	M_w/M_n
Raw PHBV	337,028	1.977
Cycle 1	331,652	1.482
Cycle 2	336,794	1.748
Cycle 3	307,680	2.146
Cycle 4	291,687	1.471
Cycle 5	281,216	1.982

cycles were tested in a temperature scale between −50 and 140°C. The room temperature flexural modulus values were around 1.9 MPa from the flexural modulus and the DMA modulus values at room temperature was also around 2.0 MPa showing the consistency of the data. DMA also confirmed that PHBV could be recycled without loss in the mechanical properties. The DMA curves are plotted in Figure 4.

Gel permeation chromatography

Gel permeation chromatography is used to understand the effect of processing and reprocessing conditions on the molecular weight of the polymers.[19–21] Gel permeation chromatography data supports all findings of the mechanical tests, confirming the reliability of the data. As expected, there was a slight decrease in the molecular weight due to thermal processing accompanied with shear; however, the decrease was not significant. For the first and second cycles, the molecular weight remained almost within the same range. For the third cycle, there was a decrease of 8.7% in the M_w value. For the fourth and fifth cycles, the percent decrease was 13.5 and 16.6%, respectively. The results are tabulated in Table I. As the decrease was not very significant, the mechanical properties do not change much. A 16.6% decrease in the molecular weight is reflected in a 7.1% decrease in the tensile strength. As it is widely known in the polymer literature, the tensile strength is a function of the weight-average molecular weight and is often most influenced by large molecules in the polymer. The longer polymer chains help transfer the load from tensile strain more effectively to the polymer backbone by strengthening the intermolecular interactions. Therefore, the decrease in the molecular weight is confirmed with the decrease in the tensile strength for the fifth sample.

Hinsken et al.[21] reported that reprocessing polypropylene (PP) and HDPE reduced molecular weight of the polymers with different percentages. There was drastic change in the molecular weight of PP due to chain scission whereas in the HDPE case, the molecular weight was reduced very slightly showing a similar trend to our observations. Gel permeation chromatography (GPC) results were in agreement with the mechanical property measurements, and this shows that PHBV can be reprocessed and recycled with melt processing techniques without a significant loss in the molecular weight.

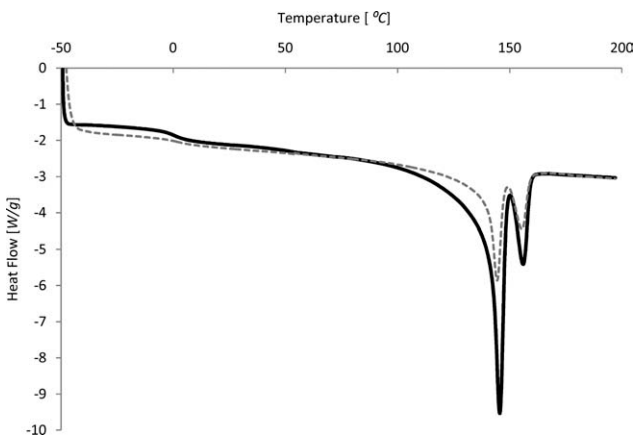

Figure 5 DSC melting and melt-crystallization thermograms of reprocessed PHBV for Cycles 1 and 5.

Differential scanning calorimeter

Nonisothermal DSC runs for raw PHBV and the five cycles were conducted. The enthalpy of melting decreased from 59.23 for Cycle 1, to 46.10 J/g for Cycle 5. The DSC curves for Cycles 1 and 5 are shown as representative to other cycles as well (Fig. 5). The enthalpy of melting was calculated by the TA Instrument software.

Using the following formula, the degree of crystallinity X_c % was calculated[20] and is summarized in Table II. ΔH_f is the enthalpy of melting.

$$X_c(\%) = \frac{\Delta H_f}{\Delta H_{f^o} \times w} \times 100 \quad (1)$$

where ΔH_{f^o} is 109 J/g for PHBV.[22]

During the melt processing of PHBV, the chains and crystals of PHBV were reoriented, and during the cooling stage, the crystals were reformed. As the molecular weight of PHBV decreased slightly during the melt processing the crystal structures were also influenced. The rearrangement of the crystals showed that the crystallinity of PHBV was reduced

TABLE II
Change of Crystallinity after Reprocessing

Sample	X_c (%)
Raw PHBV	54.2
Cycle 1	54.4
Cycle 2	52.8
Cycle 3	48.5
Cycle 4	48.8
Cycle 5	42.7

TABLE III
Change of T_g and T_m after Reprocessing

Sample	T_g (°C)	T_m (°C)
Raw PHBV	1.65	156.25
Cycle 1	2.3	156.17
Cycle 2	1.12	156.47
Cycle 3	1.43	155.87
Cycle 4	0.99	155.69
Cycle 5	2.38	155.7

due to the melt processing. Herein, the crystallinity of PHBV material decreased contributing to less tensile strength and less resistance to external forces, which was observed by the tensile test measurements. This finding was contrary to previous findings for polylactic acid[2,17] and polypropylene[23] where they observed increased crystallinity after certain reprocessing of the polymers. This might be arising from the differences in the polymers studied. For polylactic acid polymers, they propose that reprocessing creates new nucleation sites which are not the case for PHBV.[15] In Table III, T_g and T_m values for different cycles are shown. It was observed that T_g and T_m values were also in the same range and were not affected. This shows the reprocessability of the material and will help in reusing and recycling PHBV for many different purposes.

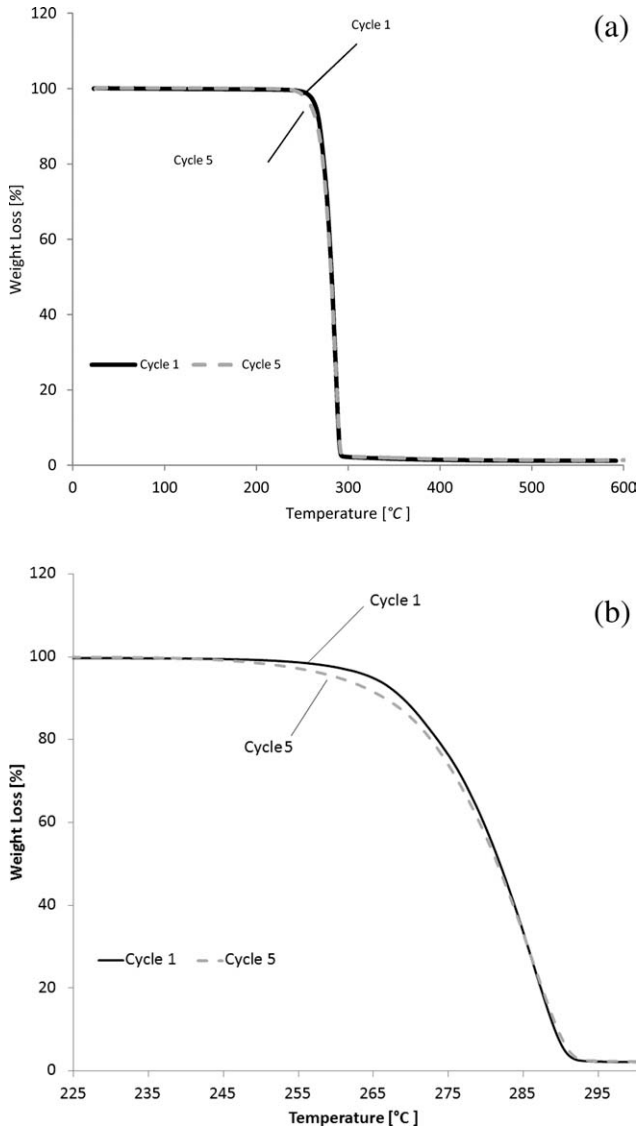

Figure 6 TGA curves showing thermal degradation for Cycles 1 and 5.

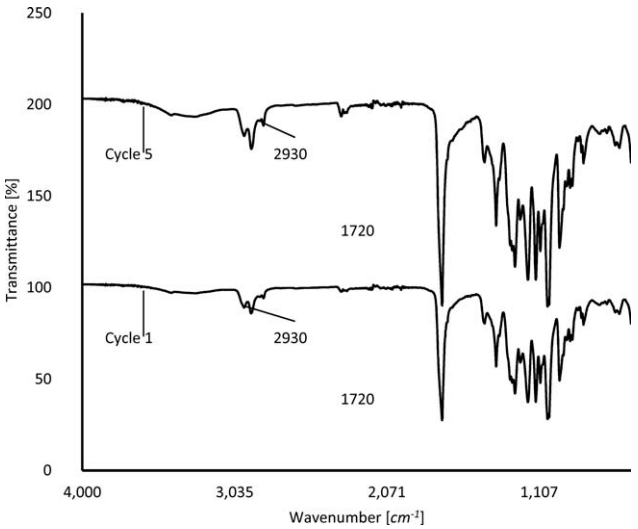

Figure 7 FTIR peaks for Cycles 1 and 5.

Thermal gravimetric analysis

Figures 6a and 6b show the weight loss graphs of Cycles 1 and 5 overlaid. The thermal gravimetric analysis (TGA) curve is magnified (Fig. 6b) to show the very minute decease of the degradation onset temperature. Only a 0.7°C change for the degradation onset temperature was observed after five cycles (Table IV). All the degradation onset temperatures from the different cycles are tabulated in Table IV showing almost the same degradation onset temperature. Zenkiewicz et al.[2] observed slight decrease (7.4°C) for the onset temperature for polylactic acid after 10 cycles.

Fourier transform infrared analysis

FTIR measurements are presented only for Cycles 1 and 5 (Fig. 7). The other cycles are not shown here as there was no change in FTIR spectra between

TABLE IV
Change of T_d after Reprocessing

Sample	T_d (°C)
Cycle 1	262.41
Cycle 2	262.57
Cycle 3	262.32
Cycle 4	262.05
Cycle 5	261.70

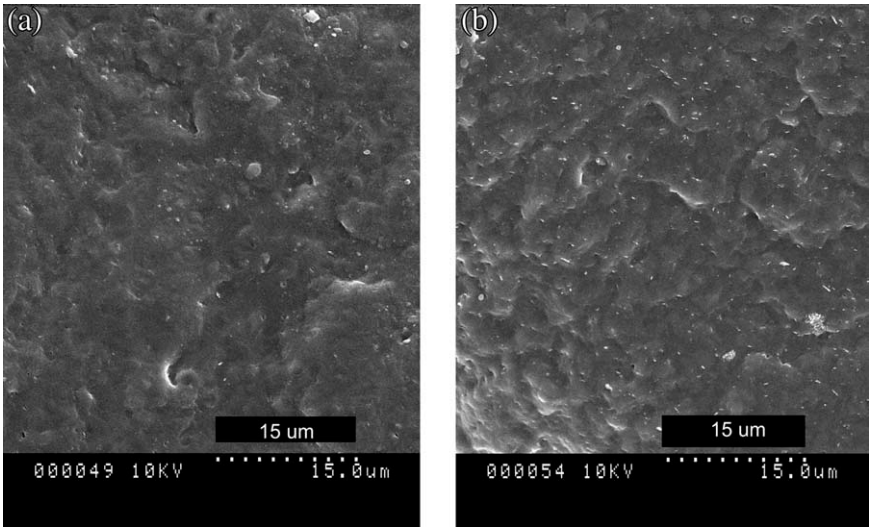

Figure 8 SEM pictures of fractured surfaces for Cycles 1 and 5.

Cycles 1 and 5. FTIR measurements showed that chemically all the bonds were stable. There was no bond breakage or new bond formation that could influence the material properties. The specific peaks such as 2930 and 1720 cm^{-1} of PHBV are shown in Figure 7. The first peak corresponds to the CH_2 stretching, whereas the second peak corresponds to the C=O bonds.[24,25] Guerrica-Echevarria et al.[16] observed the similar results with five times of reprocessing polypropylene. They have concluded that there was no side reaction besides chain chission during the processing. This data showing the chemical stability supports the recyclability of the polymers and the PHBV.

Scanning electron microscopy

The scanning electron microscopy (SEM) pictures [Fig. 8(a,b)] further support all the above findings that the material properties do not change significantly even after five cycles. Two SEM images of Cycles 1 and 5 are shown. The arrows in the figures show the similar regions of two different samples. It can be clearly seen that the fractured surfaces are almost identical, which shows that the type of fracture is same. The image of the fifth cycle is more important in understanding the degradation of this biopolymer. It can be seen with this melt processing conditions, PHBV does not degrade significantly. In another study conducted with polylactic acid and flax fiber composites, SEM pictures showed that the polymer matrix was not changed but the flax fibers were significantly broken down after six cycles.[16]

The density measurements showed that there was no change in the density of PHBV (1.23 g/cm^3) with a standard deviation of less than 0.005 g/cm^3 for each cycle. The results are not shown.

CONCLUSION

In this study, it was shown that biopolymers, like the petrochemical polymer counterparts, can also be processed multiple times with no significant loss in the properties. Thus, the biopolymers are not just biobased and degradable, but they are also recyclable. The reprocessability was confirmed with four different mechanical tests (tensile, flexural, impact, and DMA), GPC measurements, DSC, TGA, FTIR analysis, SEM images, and density measurements. All the measurements have shown that the material properties are maintained except for a slight decrease in the fifth cycle. It was understood that PHBV can be reused with many processing cycles in the melt extrusion processes as virgin or additive to new batch products.

References

1. Cornell, D. D. J Polym Environ 2007, 15, 295.
2. Zenkiewicz, M.; Richert, J.; Rytlewski, P.; Moraczewski, K.; Stepczynska, M.; Karasiewicz, T. Polym Test 2009, 28, 412.
3. Scot, D. M. Meas Sci Technol 1995, 6, 156.
4. Kulcke, A.; Gurschler, C.; Spöck, G.; Leitner, R.; Kraft, M. J Near Infrared Spectrosc 2003, 11, 71.
5. Duigou, A. L.; Pillin, I.; Bourmaud, A.; Davies, P.; Baley, C. Compos A 2008, 39, 1471.
6. Mohanty, A. K.; Misra, M.; Drzal, L. T. Natural Fibers, Biopolymers, and Biocomposites; CRC Press: Boca Raton, FL, 2006, p 1.
7. Gupta, B.; Revagade, N.; Hilborn, J. Prog Polym Sci 2007, 32, 455.
8. Wang, S.; Ma, P.; Wang, R.; Wang, S.; Zhang, Y.; Zhang, Y. Polym Degrad Stabil 2008, 93, 1364.
9. Singh, S.; Mohanty, A. K.; Sugie, T.; Takai, Y.; Hamada, H. Compos A 2008, 39, 875.

10. Singh, S.; Mohanty, A. K. Compos Sci Technol 2007, 67, 1753.
11. Kose, G. T.; Kenar, H.; Hasirci, N.; Hasirci, V. Biomaterials, 2003, 24, 1949.
12. Callister, W. D. Materials Science and Engineering: An Introduction, 7th ed.; Wiley: New York, 2006, p 138.
13. El-Taweel, S. H.; Stoll, B.; Hohne, G. W. H.; Mansour, A. A.; Seliger, H. J Appl Polym Sci 2004, 94, 2534.
14. Iannace, S.; Ambrosio, L.; Huang, S. J.; Nicolais, L. J Appl Polym Sci 1994, 54, 1531.
15. Sadrmohaghegh, C.; Scott, G. Eur Polym J 1995, 16, 1037.
16. Guerrica-Echevarria, G.; Eguiazaibal, J. I.; Nazaibal, J. Polym Degrad Stabil 1996, 53, 1.
17. Pillin, I.; Montrelay, N.; Bourmaud, A.; Grohens, Y. Polym Degrad Stabil 2008, 93, 321.
18. Le Duigou, A.; Pillin, I.; Bourmaud, A.; Davies, P.; Baley, C. Compos A 2008, 39, 1471.
19. Abbas, K. Polym Eng Sci 1980, 20, 376.
20. Renstad, R.; Karlsson, S.; Albertsson, A. C. Polym Degrad Stabil 1997, 57, 331.
21. Hinsken, H.; Moss, S.; Pauquet, J. R.; Zweifel, H. Polym Degrad Stabil 1991, 34, 279.
22. Weihua, K.; He, Y.; Inoue, Y. Polym Int 2005, 54, 780.
23. Martins, M. H.; Aurelio De Paoli, M. Polym Degrad Stabil 2002, 78, 491.
24. Ke, Y.; Wang, Y.; Ren, L.; Lu, L.; Wu, G.; Chen, X.; Chen, J. J Appl Polym Sci 2007, 104, 4090.
25. Grøndahl, L.; Chandler-Temple, A.; Trau, M. Biomacromolecules 2005, 6, 2200.