Biodegradable Bottle Development and Testing

Evaluation of the Manufacturing Process and Performance Properties for Polyhydroxyalkanoate (PHA) Materials

California Department of Resources Recycling and Recovery

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Contractor's Report
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Acronyms and Abbreviations

DOE	Design of experiment
LDPE	Low density polyethylene plastic
PET	Polyethylene terephthalate plastic
PHA	Polyhydroxyalkanoate plastic
PHB	Polyhydroxybutyrate plastic
PHBV	Polyhydroxybutyrate valerate plastic
PLA	Polylactic acid plastic
PP	Polypropylene plastic

Executive Summary

The California Department of Toxic Substances Control and Department of Resources Recycling and Recovery (CalRecycle) initiated a research study with the CSU Chico Research Foundation to understand the plastics manufacturing process of producing bioplastic bottles from polyhydroxyalkanoate (PHA) materials and to understand the properties of the PHA bottles. The research goals were to identify PHA co-polymers that are suitable for plastic bottle manufacturing and to identify key performance properties of the bottle including clarity, rigidity or stiffness, impact resistance, moisture barrier, oxygen barrier, environmental stress crack, and scuff resistance. They are excellent materials for plastic applications and have properties similar to polypropylene. PHA bioplastics are biodegradable in aerobic and anaerobic environments under hot or cold temperatures. Thus, PHA plastics are biodegradable in both hot industrial compost and cold marine environments.

Three PHA materials were molded into extrusion blow molding bottles on a Rocheleau R4 lab machine. The three PHA materials included polyhydroxybutyrate valerate (PHBV) from Tianan Company, P(3HB-4HB) from Tianjin Company, and Mirel P(3HB-4HB) produced by Telles. Two of the PHA materials were molded into blow molded bottles with the use of additives for chain extension, nucleation, and processing. The PHA materials from Tianan and Tianjin are designed for injection molding processes for applications such as toothbrushes, planter cups, and biodegradable stakes, but not extrusion processes. Thermoforming grades were not available from these companies. Therefore, additives were incorporated for chain extension, nucleation, and processing. The Mirel P(3HB-4HB) materials were provided in thermoforming and injection grades and were blow molded into bottles without any additional additives.

The PHBV and P(3HB-4HB) plastics from Tianan and Tianjin companies were blended with common additives for extrusion. These additives can increase the melt strength of the plastics and increase the nucleation that leads to higher crystallinity. Also, additives can be used for processing aids to produce more bottles. In particular, the additives used were a Joncryl chain extender from BASF, Paraloid chain extender from DOW, boron nitride nucleating agent, and an Ecovio processing aid from BASF. BASF Joncryl and DOW Paraloid are chain extenders that improve the melt strength of bioplastic materials. Boron nitride is a nucleating agent that increases crystallinity and strength of bioplastics. The acrylic impact modifiers and nucleating agent were compounded with Tianjin PHA at concentrations of 0.5 to 1 percent. The bottles appeared more flexible, as a result of the additives, but became brittle after 24 hours due to the increased crystallinity.

Ecovio plastic was used to improve the processing of the bottles, which added thermal stability to the Tianan and Tianjin plastics. When the Tianan or Tianjin materials were left in the hot barrel for more than 5 minutes, the plastic seemed to degrade and did not produce any bottles. In other words, when the residence time of the blow molding operation was greater than 5 minutes, poor quality bottles were produced. Ecovio provided stability for the Tianan and Tianjin PHA materials and allowed longer residence time that increased the molding quality of the bottles.

The Mirel P(3HB-4HB) material was more thermally stable than Tianan PHBV or Tianjin P(3HB-4HB) materials, had the widest processing window of the three resins, and produced the most number of bottles. Due to smaller processing windows, we were able to produce a limited number of bottles with the P(3HB-4HB) from Tianjin and PHBV from Tianan. The

manufacturing process for these two materials required very tight control on the temperature. If the temperature was raised or lowered a few degrees, it significantly impacted our ability to produce bottles. Thus, it was very difficult to produce bottles with the Tianjin P(3HB-4HB) and Tianan PHBV materials.

Optimal blow molding conditions for Mirel P(3HB-4HB) were rear temperature of 320°F, front temperature of 300°F, block temperature of 300°F, injection pressure of 1000 psi, blow pressure of 60 psi, mold temperature of 120°F, and mold close time of 60 seconds. Optimum conditions were not found for Tianan PHBV or Tianjin P(3HB-4HB) due to their blow molding difficulties.

Mirel P(3HB-4HB) demonstrated superior mechanical properties to Tianan PHBV and Tianjin P(3HB-4HB). Both Tianan PHBV and Tianjin P(3HB-4HB) were blended with Ecovio resin to obtain tensile bars and blow molded bottles. Mirel P(3HB-4HB) tensile strength and impact strength exceeded Tianan PHBV and Tianjin P(3HB-4HB) blends by 10X and 5X, respectively. Mirel P(3HB-4HB) tensile modulus exceeded Tianan PHBV and Tianjin P(3HB-4HB) blends by 10X, respectively. Mirel P(3HB-4HB) elongation was comparable to Tianjin P(3HB-4HB) and greater than Tianan PHBV by 5X.

Mirel P(3HB-4HB) had lower water and carbonated water permeation than Tianjin P(3HB-4HB). Mirel P(3HB-4HB) had significantly less water absorption than Tianjin P(3HB-4HB). Mirel P(3HB-4HB) had higher moisture and oxygen barrier properties than Tianjin P(3HB-4HB). Tianan PHBV was not available for permeation testing due to molding difficulties.

Mirel P(3HB-4HB) was stiffer, stronger, and tougher than Tianan PHBV or Tianjin P(3HB-4HB). Mirel P(3HB-4HB), also, had higher scuff resistance than Tianjin P(3HB-4HB). All three PHA materials had low clarity properties and had an opaque color. Environmental stress crack resistance (ESCR) testing was not pursued because bottle caps were not available to run the test according to American Society of Testing and Materials (ASTM) standards.

Key Findings

- Mirel P(3HB-4HB) is an excellent opaque bottle material for the extrusion blow molding process.
- Tianjin P(3HB-4HB) and Tianan PHBV injection grade materials are not suitable bottle materials for the extrusion blow molding process.
- Additives improved their processing performance; however, the bottles produced an inferior quality compared to Mirel P(3HB-4HB) material.
- Mirel P(3HB-4HB) was superior to Tianjin P(3HB-4HB) and Tianan PHBV in processing and had the widest processing window.
- Mirel P(3HB-4HB) was superior to Tianjin P(3HB-4HB) and Tianan PHBV and produced the most number of bottles.
- Mirel P(3HB-4HB) was superior to Tianjin P(3HB-4HB) and Tianan PHBV in mechanical properties.
- Mirel P(3HB-4HB) was superior to Tianjin P(3HB-4HB) in permeability in water.
- Mirel P(3HB-4HB) was superior to Tianjin P(3HB-4HB) in permeability of soda water.
- Mirel P(3HB-4HB) was superior to Tianjin P(3HB-4HB) in scuff resistance.
- Mirel P(3HB-4HB) is available in multiple blends for injection molding, thermoforming, and extrusion.
- Tianjin P(3HB-4HB) and Tianan PHBV are available in only injection molding grades.

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Introduction

CSU Chico Research Foundation executed a research contract with the California Department of Toxic Substances Control and Department of Resources Recycling and Recovery (CalRecycle) to develop the manufacturing process for PHA bottles and to test the bottles with a series of performance and quality tests. Dr. Joseph Greene from the Department of Mechanical and Mechatronic Engineering and Sustainable Manufacturing at California State University Chico was the principal researcher. The research goals were to identify PHA co-polymers that are suitable for plastic bottle manufacturing and to identify key manufacturing and performance properties of the bottle that included clarity, rigidity or stiffness, impact resistance, moisture barrier, oxygen barrier, environmental stress crack, and scuff resistance.

Background

Plastic debris is accumulating in the oceans around the world endangering animal life, releasing toxic chemicals, and collecting floating toxins that can enter the food stream through fish. Ocean debris is an environmental concern for California and other coastline states. In 2008, volunteers in California collected 904,375 marine debris items from the shore and underwater near the beaches. Plastic debris is a major component of ocean litter. In California, more than 70 percent of marine debris collected from the beach was made from plastics.[1] Plastics can cause harm to sea life through starvation, suffocation, infection, drowning, and entanglement.

Plastics comprised the majority of collected waste in worldwide beach clean-ups in 2006, 2007, and 2008. In California, the five most common plastic debris items on beaches that account for 75 percent of the plastic debris are cigarette filters, food wrappers and containers, beverage caps and lids, bags, and food service items, e.g., cups, plates, and cutlery. These packaging and cutlery items are typically made from four common plastics: polyethylene, polypropylene, polystyrene, and polyethylene terephthalate.

Pre-production plastic pellets also account for significant amounts of plastic in the oceans from storm run-off of industrial areas. The fate of plastics in the oceans can lead to fragmentation and result in slurry of plastic particles that can degrade and release toxic chemicals such as phthalates, flame retardants, bisphenol-A (BPA), antimony oxide, heavy metal inks, and styrene monomer as the plastics break down.[2]

Plastics can be produced from natural or synthetic materials. Traditional plastics, with an annual world production of approximately 140 million tons[3] are typically made from petroleum-based products. Alternatively, biobased polymers are produced from natural materials, such as, starch from corn, potato, tapioca, rice, and wheat. Biobased polymers can also be made from oils, such as, palm seed, linseed, soy bean, etc., or fermentation products, like polylactic acid (PLA), polyhydroxyalkanoate (PHA), and polyhydroxybutyrate (PHB).[4]

PHA biodegradable plastics are made by bacteria. The bacteria typically eat corn syrup and then produce the PHA in their cells. PHA is harvested and the biodegradable plastic is purified and made into plastic pellets. PHA can be made from several monomers based on P3HB, P4HB, PHB, PHBV, and P(3HB-4HB), which are described in Figure 1. PHB is very common but is brittle and stiff and crystalline.[5] PHBV is also very crystalline and brittle.

PHA plastics can be made into bottles, bags, containers, and other consumable plastic applications. PHA typically has biobased and biodegradable additives. PHA is biodegradable under industrial composting conditions and is marine biodegradable.[6, 7]

Chemical Structure of PHA

PHA is a family of several plastics that include, P3HB, PHBV, and others. P3HB is the most common form of PHA. The structures are listed in Figure 1.

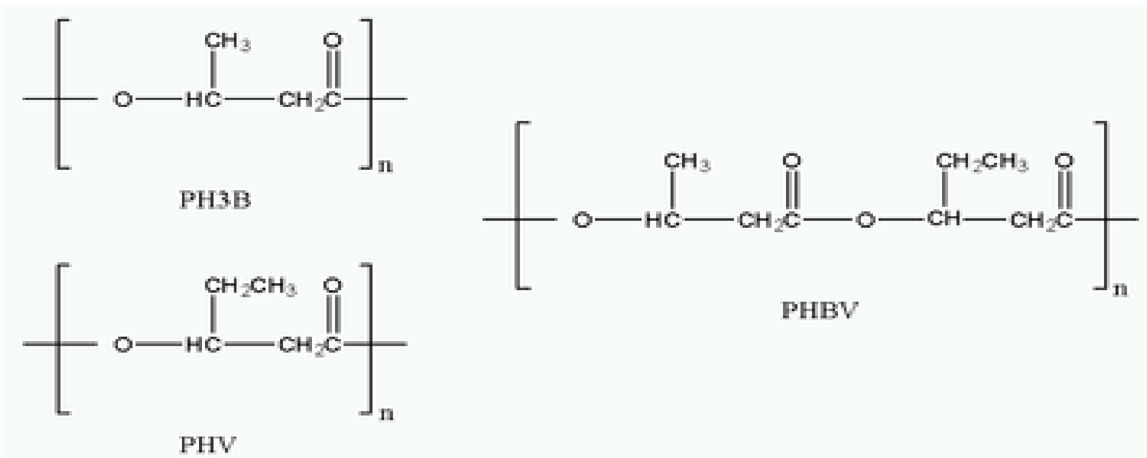


Figure 1. Structures of poly-3-hydroxyvalerate (PHV), poly-3-hydroxybutyrate (P3HB) and poly-3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV).[8]

PHA can be made from more than 100 monomers based on P3HB, P4HB, and PHB, and PHV. The PHA biopolymer can be made with increased ductility with changes to the polymer structure.[9] Chemical structures of PHA can affect the physical, mechanical, and processing properties of the plastic resin. Also, the molecular weight or polymer size of the PHA molecule can influence the mechanical and processing properties. Hence, some PHAs are more suited for injection molding applications and some PHAs are more suited for blow molding and thermoforming applications due to their chemical structure and molecular weight.

Typically, an injection molding grade of a plastic, like PHA, would not be suited for extrusion or blow molding applications. Similarly, an extrusion grade of a plastic, like PHA, would not typically be suited for an injection molding application. The difference in the injection and extrusion or thermoforming grades is related to the viscosity of the plastic as measured with the melt index test. This will be explained more fully for the three PHA plastics in the testing section of the report. Research of the chemical structure of PHA and the PHA polymer chain are beyond the scope of this project.

The PHA polymer can be made more ductile with additives and with using the stretch blowing process. The additives can be made from natural or petroleum sources. Biobased nucleating agents have been used with PHA.[10] PHA-based biodegradable bottles would need to be made from 99 percent or more biobased materials to be classified as biobased. Also, according to ASTM D7081, PHA bottles would need to convert 30 percent of the carbon to carbon dioxide during biodegradation process to be classified as marine biodegradable. Thus, the petroleum-based additives like Joncryl and Paraloid and Ecovio must be less than 1 percent to meet the biobased content criterion in ASTM standards.

Telles LLC, a joint venture between Archers Daniel Midland (ADM) Company and Metabolix Company, produces Mirel P(3HB-4HB) bioplastic at its $300 million commercial facility in Clinton, Iowa, that opened in 2010. The production capacity is 110 million pounds per year.[11] Our research evaluated P3001 thermoforming grade and P1004 injection molding grade PHA. Both materials were made into plastic bottles with the extrusion blow molding process. In January 2012, ADM Company ended its relationship with Metabolic Company and Telles LLC joint venture for PHA bioplastics was terminated. [12]

Tianjin Green Bio Company produces P(3HB-4HB) in Tianjin Economic-Technological Development Area, China in a facility that opened in 2010. The production capacity is 22 million pounds of PHA per year.[13] Tianjin produces one material of P(3HB-4HB), available in powder form, that can be used for injection molding applications. Tianjin does not produce a thermoforming grade.

Tianan PHBV is produced at Ningbo Tianan Biologic Material Co. Ltd in Ningbo, China in a facility that opened in 2000. Tianan produces one grade of PHBV for injection molding and none for thermoforming. The material is available in powder and pellet forms. The production capacity is 22 million pounds per year as reported in 2010.[14]

During the research project, we ran out of Tianjin P(3HB-4HB) and Tianan PHBV materials. Tianan PHBV was no longer available from Diamond Polymers, which discontinued the resin. PHBV is available from Tianan in China at a cost of $3,000 for 25 kg. Also, Tianjin P(3HB-4HB) is available in China at a cost of $1,500 for 25 kg. Purchasing additional PHA plastic would have exceeded the budget. Injection and thermoforming grades Mirel P(3HB-4HB) plastic were not available until March 2011, which was near the end of the research project. The lack of materials prevented additional molding and testing of the PHVB plastics and development of a thermoforming grade PHBV from Tianan and P(3HB-4HB) from Tianjin.

Blow Molding Testing Review

Thermoplastic materials can be made into plastic bottles with the blow molding process. Blow molding can involve two techniques: injection blow molding and extrusion blow molding. Injection blow molding plastic materials have lower viscosity and lower melt strength than extrusion blow molding materials. Typically, injection grade plastic materials will not have sufficient melt strength to properly produce bottles with extrusion blow molding processes. Melt strength, melt index, and density are important material properties that influence the quality of the plastic bottle. PET and PLA materials are tested for melt index and density. PET is tested for intrinsic viscosity, which is similar to the melt index test.

The melt index and intrinsic viscosity provide a measure of the flowability, or viscosity, of the plastic material as it fills the blow molding die. Melt index is used as a quality control test for polyethylene, polypropylene, and other plastics. Intrinsic viscosity is used as a quality control test for PET plastics. The viscosity of the plastic is influenced by the temperature of the die. The hotter the plastic, the lower the viscosity of the plastic and the faster it will fill the die. Also, the melt strength of the plastic is reduced as the plastic is heated.

ASTM has test methods for melt index (ASTM D5577) and intrinsic viscosity (ASTM D5525). PHA plastics have similar properties to polypropylene plastic. PLA plastics are similar to PET plastics. In our research, melt index of PHA plastic was measured to determine the melt strength of the plastic. The melt index test followed the ASTM test method.

Permeability is an important performance measure of the quality of blow molded bottles. Permeability is defined as the rate of mass transfer of liquids and gases through the plastic bottle membrane. The flow of water through the walls of the plastic bottles can be measured by recording the mass of the bottles over time. The mass of the bottle will be reduced as water passes through the walls and evaporates.

Similarly, CO_2 can be measured by filling the bottles with a carbonated water and then weighing the bottles over time. Test methods were developed for permeability in this research since no ASTM standards exist for the test procedure. Also, water soak tests indicated the propensity of the plastic material to absorb water, which can indicate permeability. If the plastic absorbs water, then it is likely to allow water to flow through the walls as in permeability.

Results

The project was broken down into four major phases that included a review of blow molding manufacturing processes, compounding of PHA formulations, producing PHA bottles, and testing of PHA bottles.

Phase 1: Blow Molding Manufacturing Review

Plastics can be made into bottles with the blow molding process. [15, 16, 17] Blow molding can involve injection blow molding, extrusion blow molding, or stretch blow molding process, depending on the plastic material properties. The injection blow molding process is used to produce polyethylene terephthalate (PET) and polylactic acid (PLA) plastic bottles. The PET or PLA plastic is injection molded into preforms in one operation and then subsequently cooled and then reheated in a separate operation to form the bottle. PHA does not have high enough melt strength nor is it tough enough to undergo the two-step injection blow molding process.

PHA is better suited for the extrusion blow molding process that has the plastic heated, extruded into a parison, and then blown into the bottle in a one-step process. A parison is the form of plastic melt that exits the extruder that air is blown through to make a bottle. It resembles a thick bubble that is blown into a shape of the bottle die. The extrusion blow molding process was achieved in the Chico State plastics laboratory with a Rocheleau machine that was installed in 2006.

The PHA materials were blow molded in a Rocheleau R4 Laboratory Blow Molder. The machine is shown in Figure 2. The R-4 utilizes a 38 mm feed screw with 24/1 L/D ratio. The R-4 machine has a reciprocating screw design that allows for fewer moving parts than continuous extrusion machines. The R-4 blow molder can have single or multiple parison dies. We used a single parison die with a 125 mm width and 280 mm height bottle.

Figure 2. R4 Rocheleau extrusion blow molding machine.

The molding parameters of PHA were optimized using design of experiment methodology for the three PHA plastics.

Phase 2: Compounding of PHA formulations

PHA is a plastic material with slow crystallization rate but is highly crystalline at room temperature and atmospheric pressure.[18] The slow crystallization rate of PHA can result in difficult blow molding results due to the low viscosity of the plastic as it leaves the blow mold extruder. The low viscosity of the PHA can be improved by blending it with additives of chain extension and nucleation in a twin screw extruder.

Materials

The PHA materials used in this study are all commercially available plastics.[19] The PHA materials were obtained from two foreign companies and one domestic company. Tianan from China supplied a PHBV and Tianjin from China supplied a P(3HB-4HB). U.S.-based Telles supplied a P(3HB-4HB). The mechanical properties of Mirel PHA[20] are listed in Table 1. The mechanical properties of Tianan (PHBV) [21] and Tianjin P(3HB-4HB) [22] are also listed in Table 1. The mechanical properties of the materials help the part designers and engineers select a material for an appropriate application. The values for yield strength, elongation, and modulus will identify how much stress the plastic can maintain for a plastic part application. The properties of the PHA are similar to polypropylene (PP) and should be successful in these types of plastic applications. Polyethylene is used more frequently for bottles than PP and will be used as a control in the research project. PHA properties are not similar to polycarbonate or polyester plastic and would not be successful in plastic applications for those plastics.

Table 1. Mechanical properties of PHA Plastics.

Description	Mirel P3001	Mirel 1003	Tianjin Sogreen P(3,4) HB	Tianan ENMAT Y1000P
Specific gravity, g/cc	1.29	1.4	1.2	1.25
Yield strength, MPa	19	26	14 - 33	31 – 36
Elongation at break, %	13	3	10 - 775	2.5 - 4
Flexural modulus, GPa	1.48	3.4	0.5 – 1.8	3.5 – 4.2
Heat Distortion Temperature, °C	116	132	85 - 134	N/A

Additives

Additional additives are needed to improve the melt strength and crystallinity of Tianan PHBV and Tianjin P(3HB-4HB). Additional additives were not needed with Telles P(3HB-4HB). The melt strength can be increased with the addition of Joncryl chain extender from BASF and Paraloid chain extender from DOW Chemical. The crystallinity of PHA can be improved with addition of boron nitride nucleating agent. Boron nitride increases the nucleation of the plastic and causes the crystallinity to increase. The processing of PHA can be improved with additions of Ecovio processing aid from BASF. Ecovio increases the melt strength of the PHA plastic and improves the ability of the PHA to be blown into a bottle.

The additives cannot exceed 1 percent of the PHA polymer concentration to maintain PHA's biobased polymer designation. Typically, 0.5 percent chain extender and 0.5 percent nucleating agent are blended with PHA powder.

Ecovio material is a film grade that was obtained from Roplast Industries in Oroville, Calif. and was produced by Heritage Bag Company of Texas. Ecovio is a blend of 80 percent Ecoflex, 10 percent PLA, and 10 percent talc. Ecovio is compostable but not ocean biodegradable. It also is only 10 percent biobased.

Compounding Experimental Set-up

Compounding is necessary to convert the Tianjin P(3HB-4HB) and Tianan PHBV powders into plastic pellets for the blow molder. The additives and PHA materials are compounded in a twin screw extruder with BASF Joncryl additive or DOW Chemical Paraloid 515 acrylic impact modifier and boron nitride nucleating agent and then extruded into pellets. The pellets were dried overnight at 105°C before molding them into bottles.

The twin screw extruder, American Leistritz Model ZSE-18HP twin-screw extruder system, with 40:1 L/D is shown in Figure 3. In the feed zone, the particles are conveyed away from the hopper and fed into the heated barrel. In the transition zone, particles are melted and the melt is homogenized, completing a process that started at the end of the feed zone. This section is designed to enhance the friction and contact with the barrel. Finally, in the metering zone, screw section is designed to act efficiently as a pump by generating pressure in the now homogenously molten mass of plastic.

The temperatures of the eight zones were between 160°C and 190°C. The screw rpm was between 30 and 66. The side-stuffer speed was 30 rpm. The water bath was warmed to 45°C with hot water from the sink and then warmed with a barrel heater. The P(3HB-4HB) and PHBV extrudate was cut into pellets at the take-up roll. The Joncryl and Paraloid additives caused the PHA plastic to swell at the exit of the die. The P(3HB-4HB) was more elastic than the PHBV and caused the cutter to jam if processed too quickly. The compounding time of the P(3HB-4HB) was approximately the same as for PHBV with Joncryl or Paraloid additive.

Ecoflex was added to the Tianjin P(3HB-4HB) and Tianan PHBV powders to improve processing of the materials into bottles. Both materials have very low viscosity and low melt strength that prevented the successful production of blow molded bottles. The viscosity was measured with a melt index test.

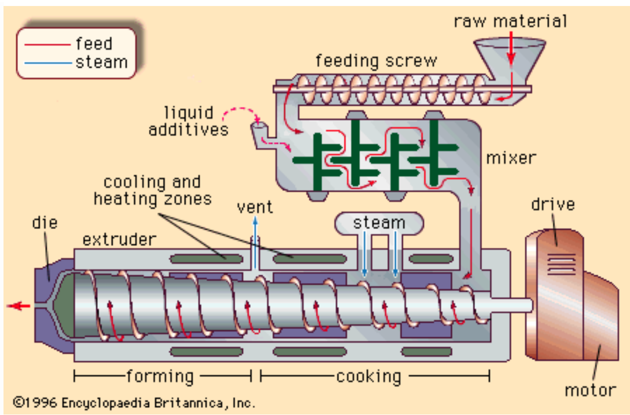


Figure 3. Leitztriz twin screw extruder with 40:1 L/D and 18 mm diameter. [23]

Design of experiment (DOE) methodology was used to determine the optimum compounding parameters of PHA materials, additives, and processing conditions. The Taguchi L8 design of experiment was used as a guide for the blending of the additives. Several DOE's were run with the L8 experimental design. Approximately 20 experimental trials were run with different molding parameters. A typical L8 experimental design is listed in Table 2.

Table 2. Design of Experiment (DOE) layout of Taguchi L8 design.

	PHA plastic	**Ecoflex**	**Joncryl or DOW Acrylic Additive**	**Boron nitride Nucleating**
Experiment #	**type**	**%**	**%**	
1	PHBV- Tianan	25.0	0	0
2	PHBV- Tianan	25.0	0.5	0.5
3	PHBV- Tianan	50.0	0	0.5
4	PHBV- Tianan	50.0	0.5	0
5	PHA- Tianjin	25.0	0	0.5
6	PHA- Tianjin	25.0	0.5	0
7	PHA- Tianjin	50.0	0	0
8	PHA- Tianjin	50.0	0.5	0.5

The extruded pellets from the DOE were then used in the blow molding machine to produce plastic bottles. The parameters were modified with additional adhesion promoters and nucleating agents to produce full-sized bottles.

Phase 3: Blow Molding Results

The PHA materials were blow molded in a Rocheleau R4 Laboratory blow molder. Initially, only Tianjin P(3HB-4HB) and Tianan PHBV materials were available. The low melt strength and low thermal stability of the Tianjin P(3HB-4HB) and Tianan PHBV materials caused the blow molded bottles to be a very poor quality. Ecovio was added to improve the processing of the Tianjin P(3HB-4HB) and Tianan PHBV materials. A minimum of 40 percent Ecovio was necessary to produce blow molded bottles from Tianjin P(3HB-4HB) or Tianan PHBV. The addition of Ecovio created an thermoforming grade for Tianjin P(3HB-4HB) and Tianan PHBV materials. This blend was tested in the tensile tests and compared to the thermoforming grade of Mirel P(3HB-4HB).

A. Tianjin P(3HB-4HB) and Tianan PHBV molding results

Tianjin P(3HB-4HB) and Tianan PHBV were molded into several bottles as shown in Figures 4, 5, and 6. Figure 4 and Figure 5 show a few representative bottles made without Ecovio. Figure 6 shows a few representative bottles made with 40 percent Ecovio. PHA thermally degraded in the barrel and provided significant amounts of scrap as shown in Figure 7. The molding conditions are listed in Table 3. The DSC for the Tianjin P(3HB-4HB) and Tianan PHBV are provided in the Appendix.

Differential Scanning Calorimetry (DSC) illustrates that the melting points of Mirel P(3HB-4HB) is 175°C, Tianjin P(3HB-4HB) is 155°C, and Tianan PHBV is 175°C. The DSC results, listed in the Appendix, also show that P(3HB-4HB) has two melting point bumps in the curve indicating the two blends of 3HB and 4HB. PHBV is more uniform with one melting point indicating single polymer type. DSC results can help identify the melting point of the plastic material and help provide temperature settings for the blow molding machine.

Table 3. Processing information for Tianjin P(3HB-4HB) and Tianan PHBV.

Molding Parameter	Setting
Injection Pressure	500 psi
Blow pressure	70 psi
Rear Temperature	290 to 300 °F
Front Temperature	277 to 285 °F
Shut Off Block Temperature	215 to 225°F
Head Temperature	215 to 225°F
Mold Temperature	100°F

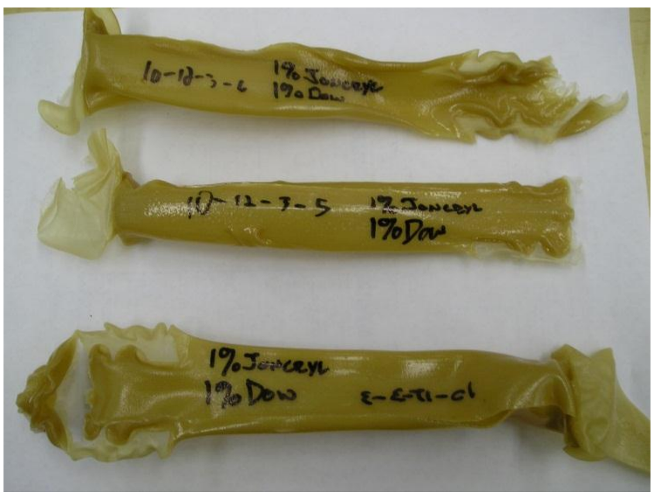


Figure 4. Tianjin P(3HB-4HB) bottles with 1 percent Parloid and 1 percent Joncryl additive.

Figure 5. Tianan PHBV bottles with 1 percent Joncryl additive.

Figure 6. Tianjin P(3HB-4HB) bottles with 1 percent Paraloid additive and 40 percent Ecovio.

Figure 7. PHA scrap produced during blow molding of Tianjin P(3HB-4HB) and Tianan PHBV.

B. Mirel P(3HB-4HB) molding results

Mirel P(3HB-4HB) was available in injection grade and thermoforming grade. The plastic pellets from injection and thermoforming grades were made into bottles using an extrusion blow molding process at molding conditions outlined in a Taguchi DOE. Mirel P(3HB-4HB) was blow molded on a Rocheleau R4 extrusion blow molding machine. The resin was a thermoforming grade. Figure 8 shows examples of Mirel P(3HB-4HB) bottles with quality rating of 4 out of 5.

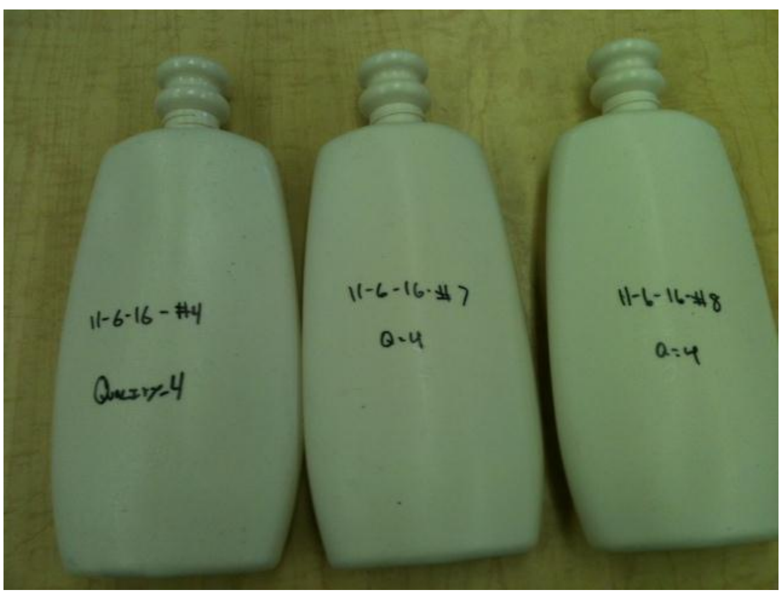


Figure 8. Mirel P(3HB-4HB) bottles.

A Design of Experiment (DOE) was used to establish optimal conditions for quality of bottles. The DOE produced 10 parts at each experiment for a total of 80 parts. The bottles were rated for

1 (poor) to 5 (excellent) upon molding. The rating values are as follows: “1” was for a partially filled bottle, “2” was for a mostly filled bottle, “3” was for a completely filled bottle with holes in it, “4” was for a completely filled bottle with thin sections or bubbles, and “5” was for a completely filled bottle with consistent thickness. The design of experiment is listed in Table 4. The DOE tested 40 bottles at each of the low settings and 40 bottles at each of the high settings for each processing parameter in the columns.

The DOE results are displayed in Figure 9 and show that the conditions with the highest quality were higher rear temperature, high front temperature, high mold temperature, low injection pressure, and longer close time. The significant factors for quality are ones with the largest slope between the low and high settings. The significant factors for controlling quality are Rear Temperature, Injection Pressure, and Mold Temperature. The other process parameters were less significant.

Table 4. Taguchi Design of Experiment.

	Rear Temp	Front Temp	Mold Close time	Block/Head Temp	Blow Pressure	Injection Pressure	Mold Temp
Experiment	°F	°F	sec	°F	psi		
1	290	260	30	250	30	1000	80
2	290	260	30	280	60	1500	110
3	290	280	60	250	30	1500	110
4	290	280	60	280	60	1000	80
5	300	260	60	250	60	1000	110
6	300	260	60	280	30	1500	80
7	300	280	30	250	60	1500	80
8	300	280	30	280	30	1000	110

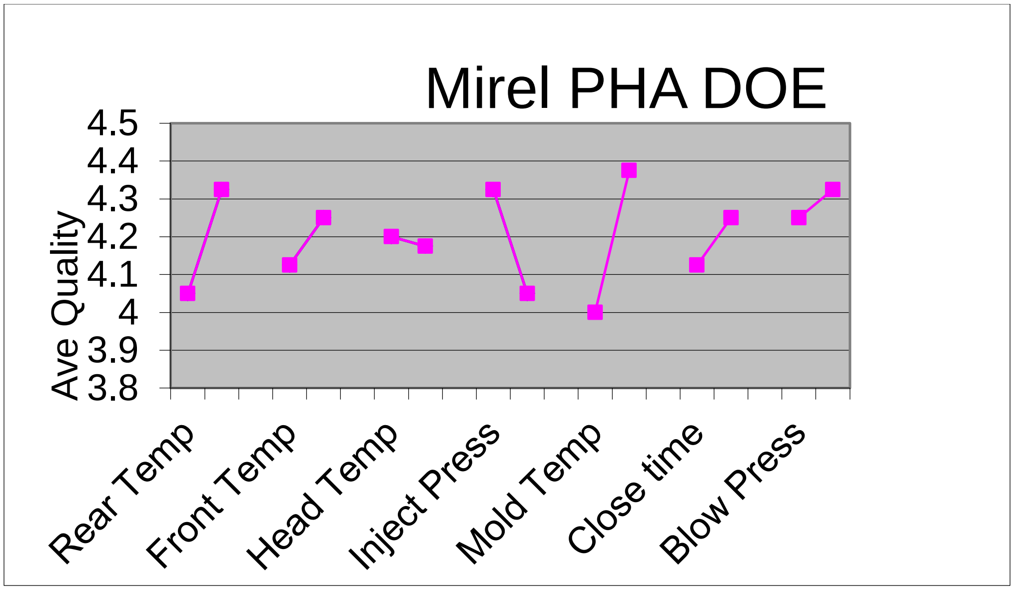


Figure 9. Mirel DOE blow molding results for quality.

The optimal conditions that yielded the highest quality are listed in Table 5. The optimal conditions are rear temperature of 320°F, front temperature of 300°F, block temperature of 300°F, injection pressure of 1000 psi, blow pressure of 60 psi, mold temperature of 120°F, and mold close time of 60 seconds.

Table 5. Optimum processing information for Mirel P(3HB-4HB).

Molding Parameter	Setting
Injection Pressure	1000 psi
Blow Pressure	60 psi
Rear Temperature	320 °F
Front Temperature	300 °F
Shut Off Block Temperature	300°F
Head Temperature	280°F
Mold Temperature	120°F

Melt Index Testing

The quality of the molded bottles can be improved with knowledge of the melt index of the materials. Melt index is an indication of the viscosity of the material or the ability of the material to flow at temperature while under load of a 2.6 kg weight. The melt index was measured with a LMI 4002 series melt flow indexer. Melt index is a measure of flow at temperature in 10 minutes. The melt index units are g of flow in 10 minutes. The melt index of the Tianjin P(3HB-4HB) is listed in Figure 7 and the melt index of the Mirel P(3HB-4HB) is listed in Figure 8. The melt index values of the Mirel thermoforming grade were very similar to the values of the Mirel injection molding grade. Both materials in Figures 7 and 8 are the same PHA polymer type of P(3HB-4HB). The Mirel P(3HB-4HB) has more thermal stability than the Tianjin P(3HB-4HB) and produced higher quality bottles. The melt index of Tianan was not tested due to lack of availability of material. All of the Tianan plastic material was used to produce bottles.

Figure 10 shows that Tianjin PHA is less thermally stable than Mirel PHA. The viscosity of Tianjin reduces dramatically after 175° C. Thus, the maximum temperature to blow mold Tianjin bottles would be 175° C. Figure 11 clearly shows that Mirel PHA is very thermally stable over arrange of temperatures from 170 to 195° C.

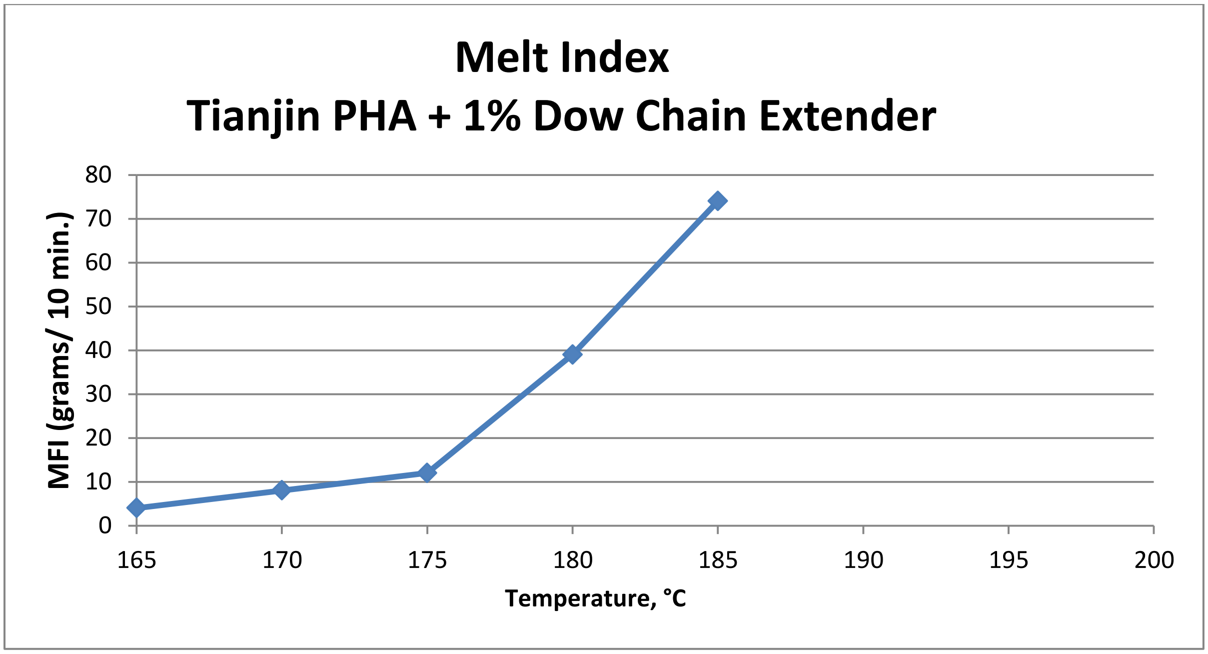


Figure 10. Melt index for Tianjin P(3HB-4HB).

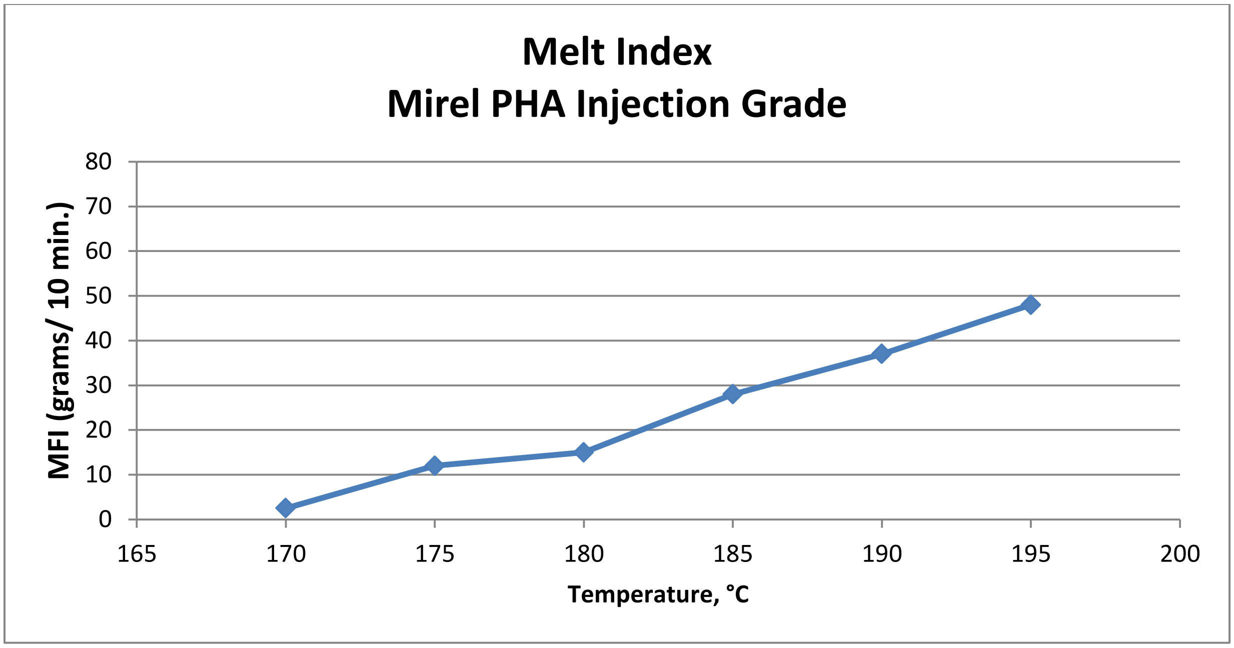


Figure 11. Melt index for Mirel P(3HB-4HB).

Phase 4: Testing Results

Mirel P(3HB-4HB), Tianjin P(3HB-4HB), and Tianan PHBV materials were tested for tensile properties and impact properties. Tianjin P(3HB-4HB), and Tianan PHBV were blended with Ecovio, melt strength additive, and nucleation additive. Tensile bars were tested with a MTS tensile test machine, MTS QT/50, with 10,000 pound Load Cell and Q-test software. The samples were pulled in a tensile mode at a rate of 1.5 inch/min at room temperature according to ASTM D638. The noise factor on the load cell is 0.1 percent at full scale or 10 lbs. force. The tensile results for the PHA plastics are listed in Table 6 and Figures 12, 13, and 14. Mirel thermoforming and injection grade plastics were significantly stronger and stiffer than Tianjin and Tianan PHA plastics. The tensile properties are lower for Tianan and Tianjin PHA plastics because they were blended with Ecovio plastic causing a reduction in tensile properties. The blend with Ecovio is needed to produce bottles with the Tianan PHA and Tianan PHBV. Thus, the mechanical properties are comparing the properties of materials than can be blow molded into bottles.

Table 6. Tensile properties of PHA plastics.

Resin	Yield Strength, psi Average	Tensile Modulus, psi Average	Elongation, % Average
Mirel Injection Grade	3640	112,216	9.92
Mirel Thermoforming Grade	3717	91,076	15.90
Tianjin PHA-40/Eco-60	1,466	19,956	8.60
Tianjin PHA-25/Eco-75	1,711	18,342	19.09
PHBV-50/Eco-50	954	84,319	1.70
PHBV-25/Eco-75	1,754	60,845	4.83

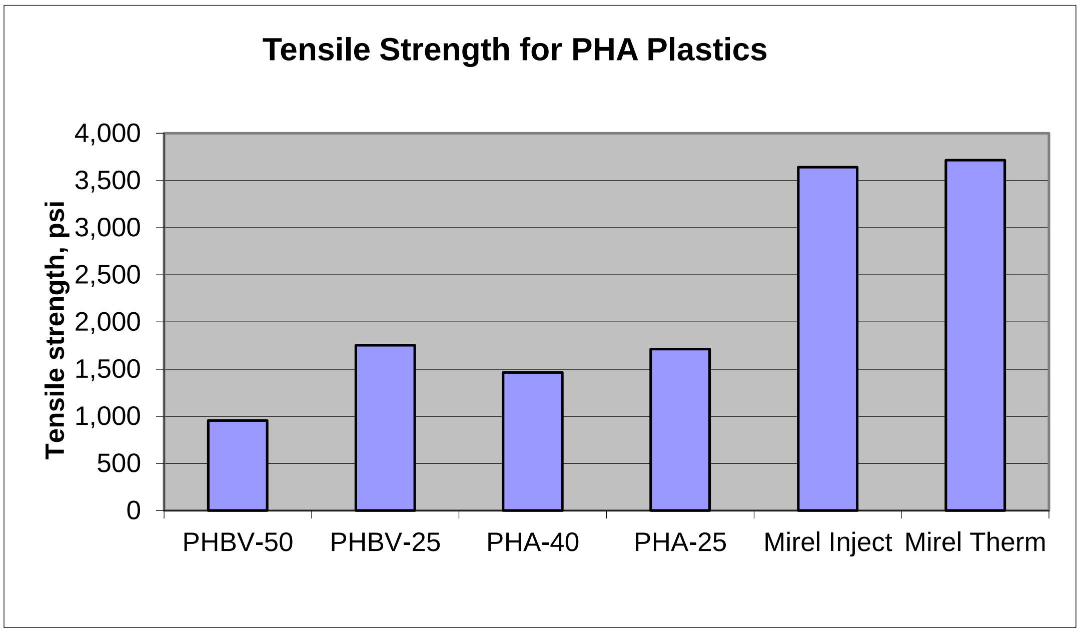


Figure 12. Tensile strength of Tianan PHBV, Tianjin PHA, and Mirel PHA plastics.

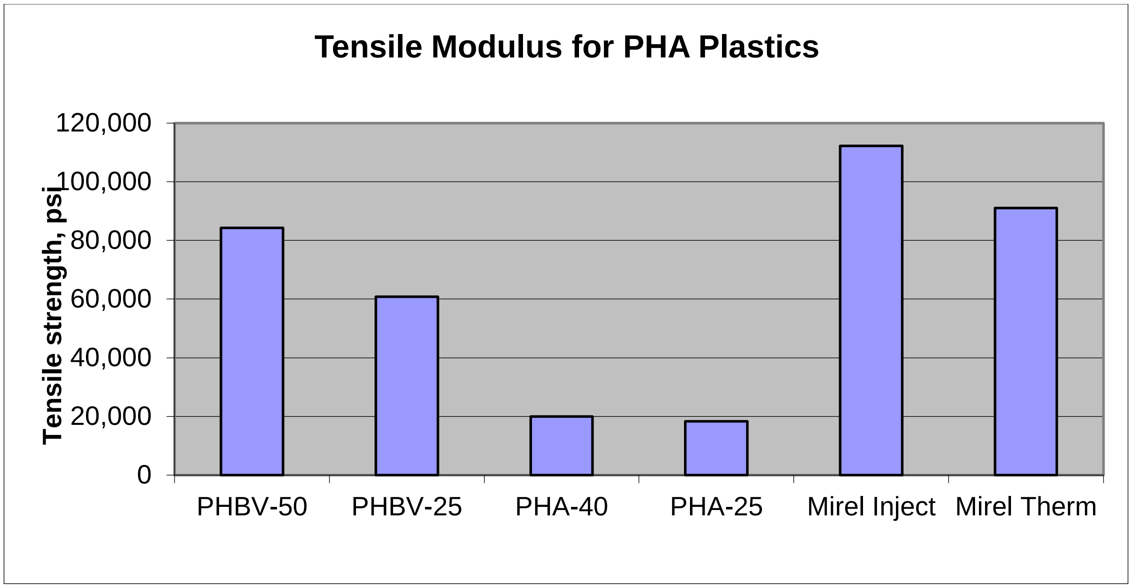


Figure 13. Tensile modulus of Tianan PHBV, Tianjin PHA, and Mirel PHA plastics.

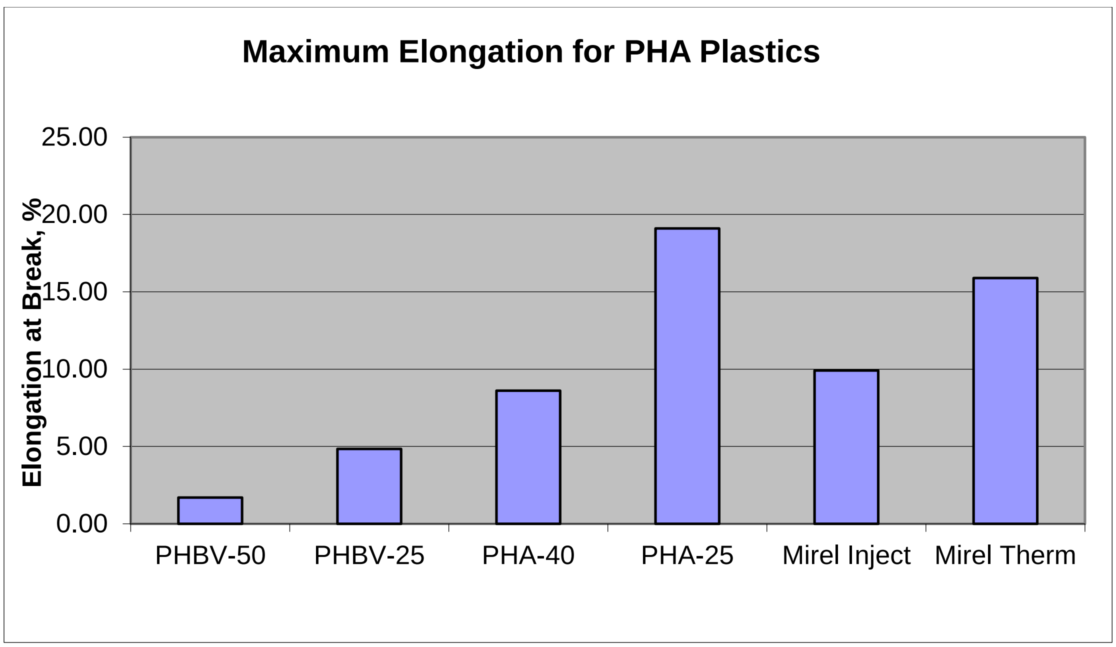


Figure 14. Tensile elongation of Tianan PHBV, Tianjin PHA, and Mirel PHA plastics.

The PHA plastics were tested on an Izod impact test machine. The impact strength results for 10 samples of each plastic are listed in Table 7.

Table 7. Impact properties of Tianan PHBV, Tianjin PHA, and Mirel PHA plastics.

Resin	Impact Strength, ft-lbs Average
Mirel Injection Grade	4.28
Mirel Thermoforming Grade	5.92
Tianjin PHA-40/Eco-60	1.04
Tianjin PHA-25/Eco-75	1.27
Tianan PHBV-50/Eco-50	0.12
Tianan PHBV-25/Eco-75	0.54

Mirel P(3HB-4HB) had significantly higher (5X) impact strength than Tianjin P(3HB-4HB) or Tianan PHBV.

Water and CO_2 Permeability

Mirel P(3HB-4HB) and Tianjin P(3HB-4HB) materials were tested for permeation of water and carbon dioxide by filling the blow molded bottles with water or with carbonated water. The experimental apparatus is displayed in Figure 15. Tianan PHBV was not available for permeability or water absorption testing.

Permeability of water, O_2, and CO_2 are often measured for plastics. The permeation results are similar for O_2, and CO_2 gases since both carbon dioxide and oxygen are non-polar fluids. Permeation of water would be different since water is a polar fluid. During the test, the fluid passed through the plastic and evaporated into the air. The mass of each bottle was measured for seven days and then once per week for four weeks. LDPE bottles were used as a control since it is a more common plastic bottle material than PP. PET was not used since it requires an injection blow molding process and not an extrusion blow molding process. CO_2 is more important permeation gas than O_2 since carbonated water is used in bottle soda market for plastic bottles. We substituted testing for carbon dioxide rather than oxygen in this research.

The PHA samples were tested for water and carbon dioxide permeability. [24] The blow molded bottles were filled with water or carbonated water. The mass of the bottles were recorded daily for the first week and then weekly for the first month. The results are displayed in Figures 16 and 17.

Figure 15. Permeation test experimental apparatus.

Mirel P(3HB-4HB) had lower water permeation than Tianjin P(3HB-4HB). Thermoforming grade Mirel P(3HB-4HB) had half the water permeation of Tianjin P(3HB-4HB). Injection grade Mirel P(3HB-4HB) had equivalent water permeation to Tianjin P(3HB-4HB). Mirel P(3HB-4HB) had 4X more water permeation than LDPE. Tianjin P(3HB-4HB) had 10X more water permeation than LDPE.

Mirel P(3HB-4HB) had lower carbonated water permeation than Tianjin P(3HB-4HB). Injection and thermoforming grades of Mirel P(3HB-4HB) had half the carbonated water permeation than Tianjin P(3HB-4HB). Mirel P(3HB-4HB) had 4X more carbonated water permeation than LDPE. Tianjin P(3HB-4HB) had 10X more carbonated water permeation than LDPE.

Based on these results, Mirel P(3HB-4HB) would have higher moisture and carbon dioxide barrier properties than Tianjin P(3HB-4HB). Barrier properties are an important characteristic of blow molded bottle materials. Carbonated water barrier performance would be an important characteristic for plastic bottles produced for soft drink products. Likewise, water barrier performance would be an important characteristic for plastic bottles produced for bottled water products.

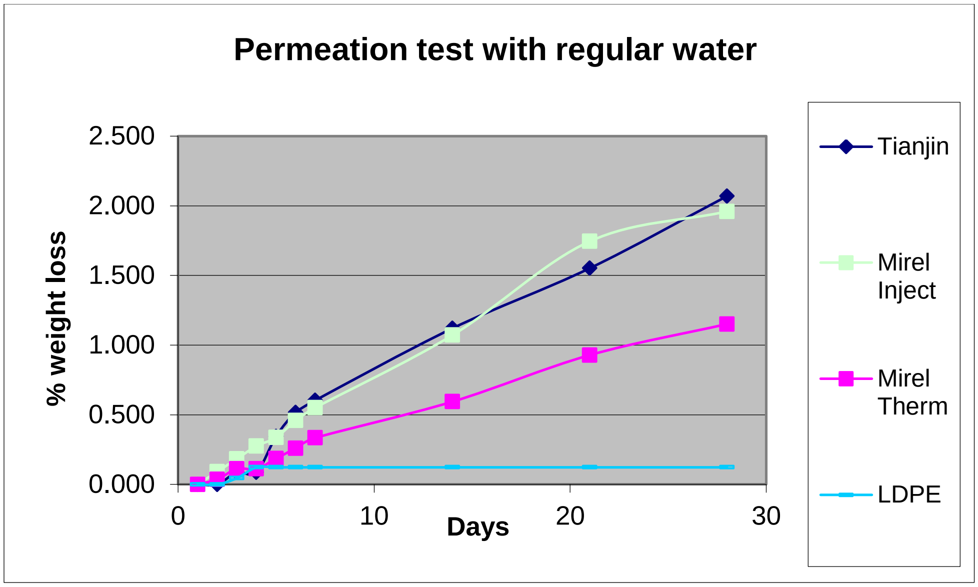


Figure 16. Permeation test with water for PHA plastics.

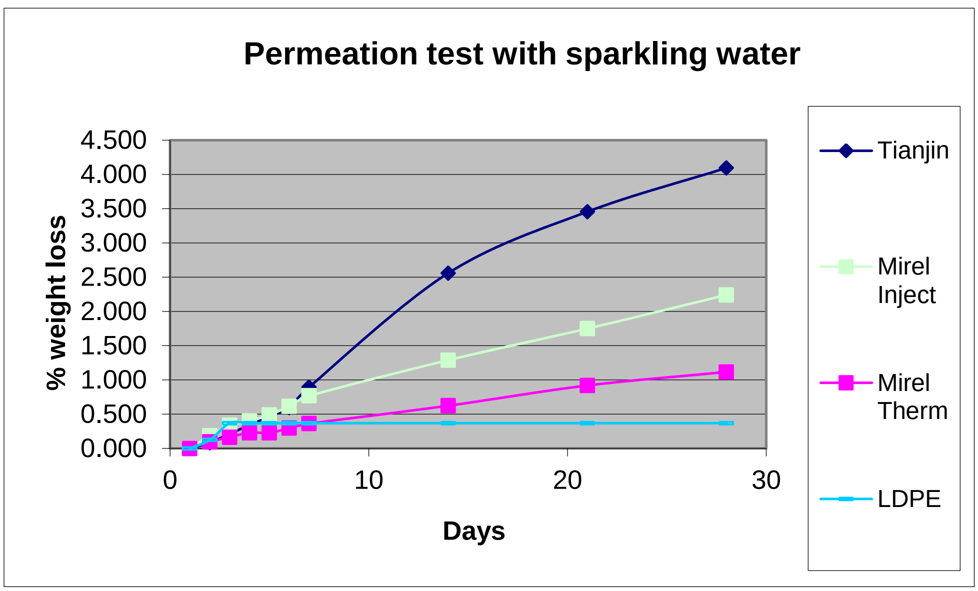


Figure 17. Permeation test with sparkling carbonated water for PHA plastics.

Water Absorption

Mirel P(3HB-4HB) and Tianjin P(3HB-4HB) materials were tested for water absorption by placing strips of bottles from each material in a tub of water at room temperature. Water absorption should correlate to the water permeation tests. Thus, absorption of water for the plastics should have similar results as permeation of water through the plastic. Experimental apparatus is displayed in Figure 18. The mass of the plastic strips were measured for seven days and then once per week.

The water absorption result is displayed in Figures 19.

Mirel P(3HB-4HB) had lower water absorption than Tianjin P(3HB-4HB). Injection grade and thermoforming grade Mirel P(3HB-4HB) had one-quarter the water absorption of Tianjin P(3HB-4HB). Thermoforming grade Mirel P(3HB-4HB) had equivalent water absorption of injection grade Mirel P(3HB-4HB) . Mirel P(3HB-4HB) had 7X more water permeation as LDPE. Tianjin P(3HB-4HB) had 22X more water permeation than LDPE.

The water absorption test method was a more efficient method of indicating the PHA plastic material's response to the presence of water than the permeability measurement method of mass loss from the previous section of this report.

Figure 18. Water soak test experimental apparatus.

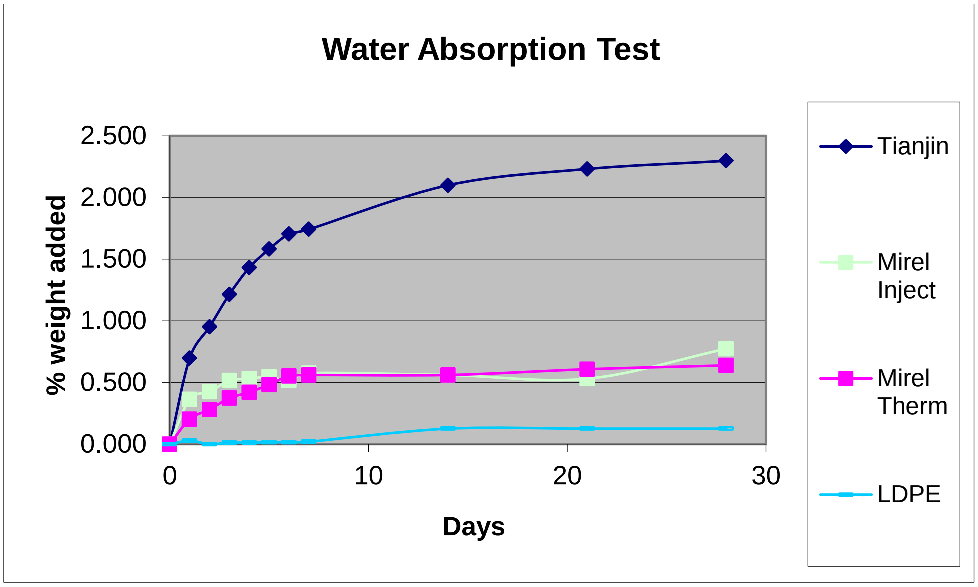


Figure 19. Water absorption test with PHA plastics.

Scuff Resistance

Scuff resistance of the Mirel P(3HB-4HB) and Tianjin P(3HB-4HB) was measured according to ASTM D7027-05. Tianan PHBV bottles were not available due to lack of plastic material. The ASTM standard is a test method for "Evaluation of Scratch Resistance of Polymeric Coatings and Plastics Using Instrumented Scratch Machine." A scratch test machine was not available, but the testing was conducted with a manual scratch method according to the specifications in the test. The test places an indenter on the plastic substrate with a prescribed force over a test distance and time. The requirement is to identify the amount of force necessary to cause a white indentation in the plastic.

In our case we tested the Mirel and Tianjin bottles by placing a mass on a Type D durometer and scratching the plastic for 100 mm in one second. The Type D durometer is a pointed metal piece on the end of a hardness dial. Type D durometer records the hardness of soft plastic and rubber materials. The durometer's steel point had a diameter of 1.3 mm and a length of 4.5 mm. The durometer was held with the mass until it touched the plastic bottle. The durometer was then moved along the plastic without imparting very much downward force. The force applied was 2 N, 10 N, 20 N, and 50 N. Scratches and white color were noted in the plastic bottles at each force. Figures 20 and 21 list the test results for the scratch testing with 2 N (222g) and 50 N (5kg).

Figure 20. Scratch testing for Mirel P(3HB-4HB).

Figure 21. Scratch testing for Tianjin P(3HB-4HB).

The scratch test results found that the Mirel P(3HB-4HB) plastic had a white scratch at 20 N force and the Tianjin P(3HB-4HB) plastic had a white scratch at 10 N force. The Mirel and Tianjin Mirel P(3HB-4HB) plastics did not have a white scratch at 2 N force but did have a white scratch at 50 N force. Thus, Mirel P(3HB-4HB) is more scratch- and scuff-resistant than the Tianjin P(3HB-4HB)

Environmental Stress Crack Resistance (ESCR)

ESCR resistance can be measured according to ASTM D5419-09. The ASTM standard is a test method for "Environmental Stress Crack Resistance of Threaded Plastic Closures." Plastic closures in this case refer to bottle caps. The test method requires the use of plastic bottles and caps. The bottle is filled with a fluid that can cause stress cracking, e.g., detergents, oils, shampoos, etc.

Then the cap or closure is added to the top of the bottle and the assembly is placed in an oven at 50°C. The bottles and caps are inspected daily for leaks or cracks. The test was not run on our bottles since we did not have caps to secure the tops of the bottles. Future ESCR testing can be done if caps are built for the bottle.

Conclusions

Injection and thermoforming grades of Mirel P(3HB-4HB) had superior processing properties to Tianan PHBV and Tianjin P(3HB-4HB) and would make excellent blow molded plastic bottles. Tianan PHBV or Tianjin P(3HB-4HB) plastic materials are injection-molding grade and would not make a satisfactory blow molded bottle with the extrusion blow molding process. Mirel P(3HB-4HB) had superior thermal properties to Tianjin P(3HB-4HB) and would provide a more thermally stable bottle. Mirel P(3HB-4HB) would not produce a clear bottle and should not be considered a replacement for PET or PLA for plastic beverage bottles. Mirel P(3HB-4HB) can be a replacement for polyethylene and polypropylene plastic bottles for shampoo, oils, detergents, etc.

Mirel P(3HB-4HB) has superior mechanical properties to Tianan PHBV or Tianjin P(3HB-4HB). Tianan PHBV or Tianjin P(3HB-4HB) were blended with Ecovio resin to obtain tensile bars and blow molded bottles. Mirel P(3HB-4HB) tensile strength and impact strength exceeded Tianan PHBV and Tianjin P(3HB-4HB) blends by 10X and 5X, respectively. Mirel P(3HB-4HB) tensile modulus exceeded Tianan PHBV and Tianjin P(3HB-4HB) blends by 10X. Mirel P(3HB-4HB) elongation was comparable to Tianjin P(3HB-4HB) and greater than Tianan PHBV by 5X.

Mirel P(3HB-4HB) had lower water and carbonated water permeation than Tianjin P(3HB-4HB). Mirel P(3HB-4HB) had significantly less water absorption than Tianjin P(3HB-4HB). Mirel P(3HB-4HB) had higher moisture and carbon dioxide barrier properties than Tianjin P(3HB-4HB).

Mirel P(3HB-4HB) is stiffer, stronger, and tougher than Tianan PHBV or Tianjin P(3HB-4HB). All three materials have low clarity properties and have an opaque color.

The research was limited by the availability of the Mirel P(3HB-4HB), Tianan PHBV, and Tianjin P(3HB-4HB) plastic resins. Metabolix Company informed our research team that Mirel P(3HB-4HB) resins are being developed to improve the properties for bottle applications and to produce a Mirel blow molding resin. Tianan PHBV and Tianjin P(3HB-4HB) plastic resins were injection molding grade and not blow molding grade. Thus, their performance in the blow molding process was poor. The plastics from Tianan and Tianjin would perform better with injection molding applications, such as toothbrushes, cosmetic cases, containers, or agricultural stakes.

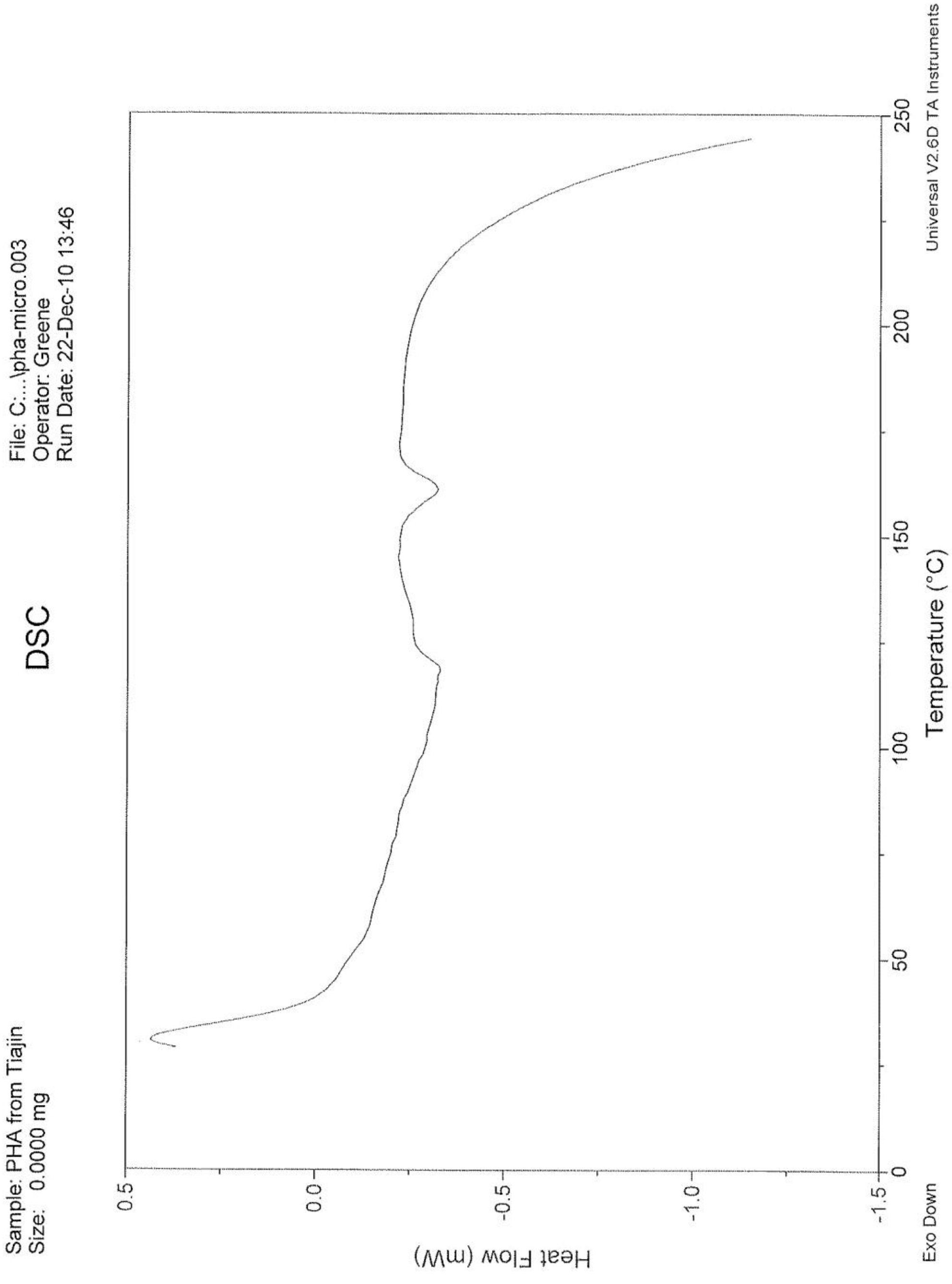
Future Research Work

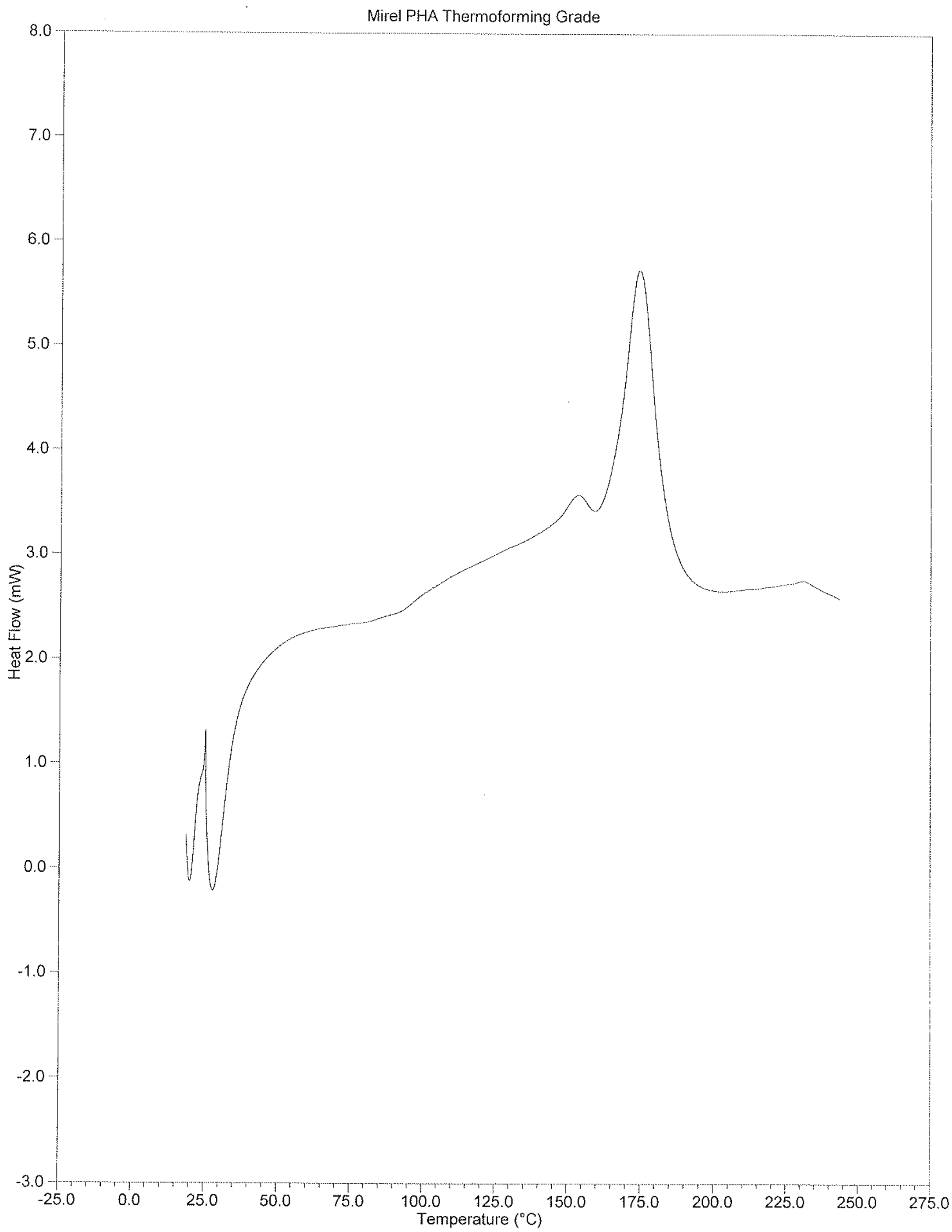
Future research is needed to optimize biodegradable materials for blow molded bottles. Tianjin P(3HB-4HB) and Tianan PHBV materials are useful for injection molding applications but need additional development for extrusion, thermoforming, and blow molding applications. Mirel P(3HB-4HB) material properties and processing conditions can be improved and adapted for blow molding applications with additional research that can optimize the processing conditions and improve mechanical and barrier properties. Additional testing of Mirel, Tianan, and Tianjin PHA materials is needed for stress crack resistance according to ASTM standards.

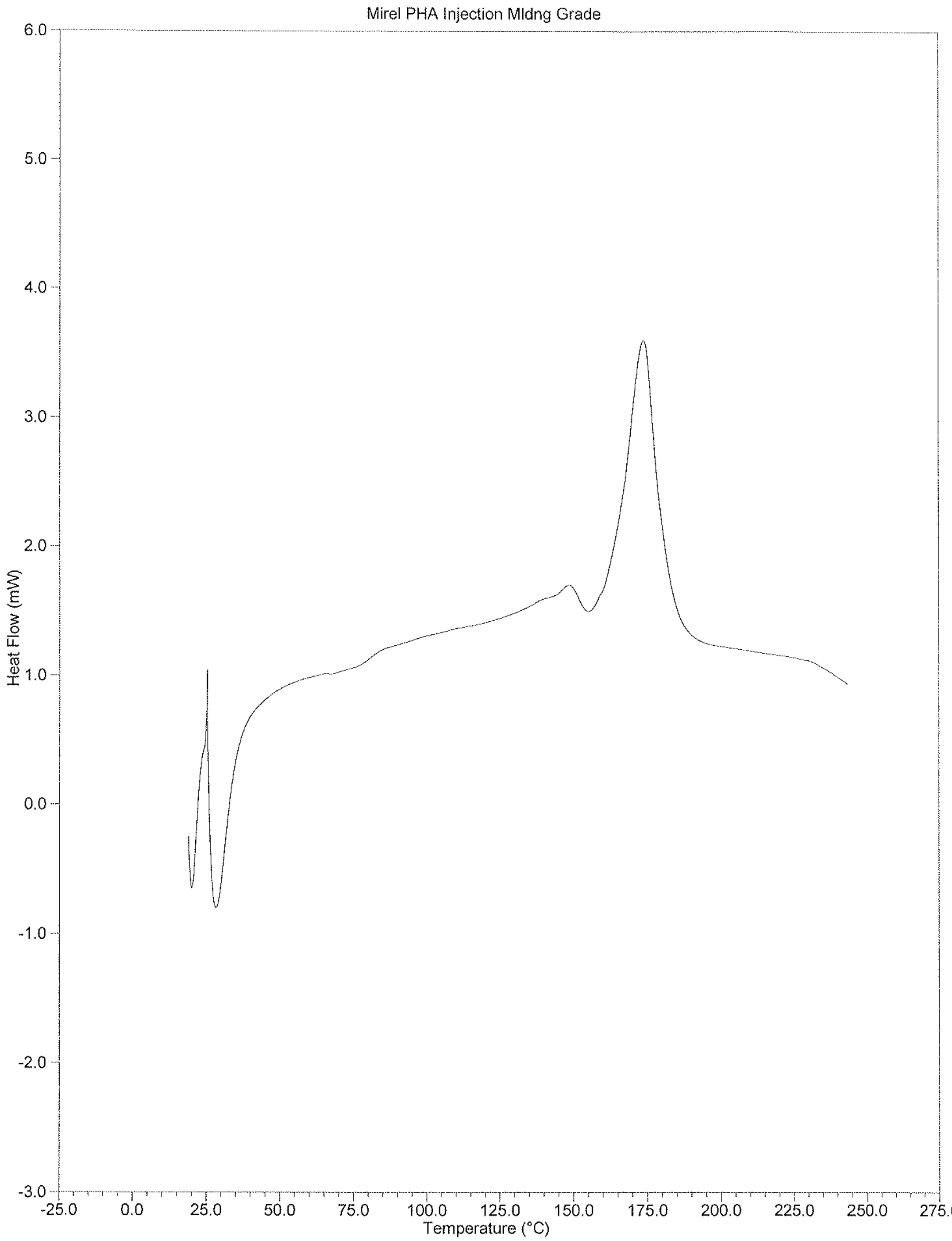
Additional work is needed for an injection molded bottle cap made from PHA plastics. Currently, plastic caps for bottles are made from polypropylene, which is not compostable or marine biodegradable. Thus, a marine biodegradable bottle of today would have a PP plastic cap. This could cause environmental problems to sea life if the caps enter marine waters.

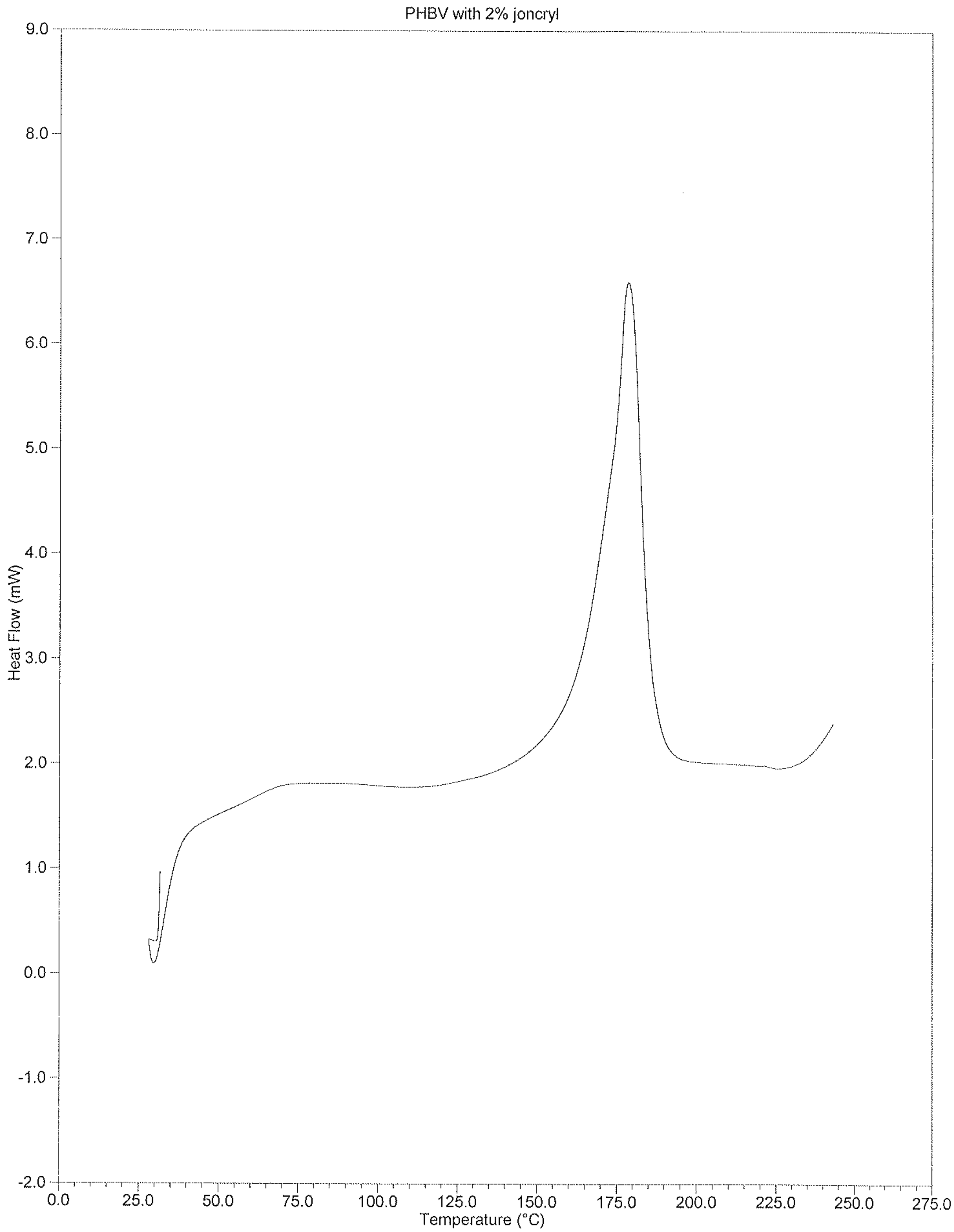
Additional work is needed to produce PHA from low-cost organic sources that are non-food based crops, like food waste and agricultural waste. The PHA developed from these waste sources would need to be analyzed and characterized with mechanical and chemical tests.

Appendix


DSC
Sample: PHA from Tiajin
Size: 0.0000 mg
File: C:...\pha-micro.003
Operator: Greene
Run Date: 22-Dec-10 13:46
Heat Flow (mW)
0.5
0.0
-0.5
-1.0
-1.5
Exo Down
0
50
100
150
200
250
Temperature (°C)
Universal V2.6D TA Instruments


Mirel PHA Thermoforming Grade
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
Heat Flow (mW)
-25.0
0.0
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
Temperature (°C)


Mirel PHA Injection Mldng Grade
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
Heat Flow (mW)
-25.0
0.0
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
Temperature (°C)


PHBV with 2% joncryl
Heat Flow (mW)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
0.0
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
Temperature (°C)

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