FINAL REPORT

Polyhydroxyalkanoates (PHA) Bioplastic Packaging Materials

SERDP Project WP-1478

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14. ABSTRACT

The objectives of our project were to demonstrate the use of biodegradable PHA natural plastic for foamed packaging and stretch/shrink film applications. PHA packaging foams and stretch-shrink films were produced and tested for functional performance and biodegradability.

Biodegradable PHA foam was made at greater than 15X expansion using a variety of blowing agents. We successfully demonstrated polymer branching and that certain stretch films were suitable for hand stretching.

High melt-strength and melt-elasticity PHA polymers were produced using blends of branched, long chain-length PHA polymers with linear PHA polymers.

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Acronyms and Definitions

ASTM – American Society of Test Methods
ISO – International Standardization Organization
PHA – Polyhydroxyalkanoates
P3HB - polymer of 3-hydroxybutanoic acid
DoD – Department of Defense
GPC - Gel Permeation Chromatography
MSB - magnetic suspension balance
TSS - total suspended solids
ThOD - Theoretical Oxygen Demand
COD - Chemical Oxygen Demand
NSRDEC – Natick Soldier Research and Development Engineering Center
CEFPACK - Center for Flexible Packaging
CAEFF - Center for Advanced Engineering Films and Fibers
T cr - recrystallization temperature
Tg - Glass Transition Temperature
Tm - Melting Temperature
Mw - weight averaged molecular weight
LLDPE – linear low density polyethylene
NAFTA – North American Free Trade Agreement
ADM – Archer Daniels Midland
PLA – poly lactic acid
DSC – Digital Scanning Calorimetry

Acknowledgements

The work accomplished in this project would not be possible without the funding and support of the Strategic Environmental Research and Development Program (SERDP). SERDP’s commitment to sponsor the development of environmental technologies that support the long-term sustainability of the Department of Defense is vital to solving our nation’s environmental challenges. We acknowledge and thank the entire SERDP organization for their support.

We are also very appreciative of the support and guidance provided by Dr. Jo Ann Ratto as the technical liason for the project. Jo Ann brings a wealth of experience in DoD technical development, specifically in the area of biodegradation testing. She has worked with Metabolix on the development of PHA bioplastics for over 10 years, and we look forward to continuing collaborations in the future.

Finally, we’d like to acknowledge the assistance of Dr Bhuwneesh Kumar, University of Toronto. Dr. Kumar ably guided our foaming trials, and his expertise significantly accelerated our success in developing PHA foaming technology.

Executive Summary

Polyhydroxyalkanoates (PHA) are a family of biobased, biodegradable natural plastics that can functionally replace over 50% of the plastics used today. PHAs represent the best candidates for broad replacement of current plastic packaging materials due to their durability in use and their wide spectrum of properties. They range in properties from strong, moldable thermoplastics to highly elastic materials to soft, sticky compositions, and can be made as resins or as latex with excellent film-forming characteristics. Their moisture barrier properties are superior to other biodegradable materials. Breakthroughs in polymer processing techniques made at Metabolix allowed PHA formulations to be processed on existing polymer processing equipment. In addition to these attributes, PHAs are biodegradable in aquatic (oceans, rivers, and wetlands), soil, and municipal waste treatment environments, and they can be both hot and cold composted.

PHA natural polymers represent an environmentally benign route to the replacement of conventional fossil fuel-based thermoplastics such as polystyrene and polyolefins.

Project Objectives Achieved. The objectives of our project were to demonstrate the use of biodegradable PHA natural plastic for foamed packaging and stretch/shrink film applications. PHA packaging foams and stretch-shrink films were produced and tested for functional performance and biodegradability.

The overall objectives we achieved included the following:

- Polymer branching, a key enabling technology for producing long-chain length PHA polymers, was successfully demonstrated.
- High melt-strength and melt-elasticity PHA polymers were produced using blends of branched, long chain-length PHA polymers with linear PHA polymers.
- These developments enabled the successful demonstration of the applicability of biodegradable PHA for foamed packaging and stretch/shrink film applications.

PHA biodegradable plastic was successfully formulated into foam and film grades as illustrated below.

Figure 1 PHA Foam Peanuts

Key to the foam grade formulation development was achieving high melt strength and maintaining the melt strength through the foaming process. The primary technique developed to achieve high melt strength was long chain branching via organic peroxide used during the reactive extrusion. This technique is similar to the process originally developed for polyolefin foam grades. Considerable optimization of the peroxide choice and reactive processing conditions was required due to the difference in chemical structure of PHA from polyolefin's and due to the complex thermal stability issues inherent in PHAs.

It was also found that standard talc foam cell nucleants were useful in minimizing cell size which resulted in a better foam structure.

The foam processing conditions, while unique for PHA, were found to be as expected based on polystyrene and polyolefin experience. In general, the primary extruder conditions were optimized to efficiently melt the polymer and to mix in the blowing agent while minimizing thermal and shear degradation of the polymer. The second extruder conditions were optimized to cool the melt to the minimum temperature without inducing crystallization. Standard dies and standard die setups were found to be successful.

PHA foam strand suitable for cutting into foam peanuts was also successfully made.

Based on what we learned above, PHA foam with expansion ratios up to 15X were made. In other words, the polymer was 15 times greater than the density of the foam. The density of the foam was measured according to the procedure within the foam characterization section. The density of the polymer is 1.25 and fixed for PHA resins.

The implications of these findings are important to note. Different foam expansion ratios enable different applications. Low expansions use more material but are much stronger. Very high expansions are most cost efficient, but don't have sufficient strength for some applications.

Our goal was to achieve as wide a range of expansion ratios as possible to meet multiple application needs. A key sub-goal of the project was to develop packaging peanuts which are typically high expansion ratios (30X). We were not successful in getting to those high expansion values. However, the medium expansion ratios we achieved are ideal for semi-structural applications such as foam food plates.

While we successfully made blown and cast films with the branched PHA formulations, we also learned that these films do not exhibit any shrink even at temperatures very close to their melting point. This is attributed to the slow crystallization kinetics of PHA and the consequently low levels of orientation frozen-in during the film fabrication step. The only way to produce oriented PHA films is through a solid-state orientation process. Through experimentation using a TM Long stretcher, we determined the approximate conditions (temperature and stretch rate) to produce oriented PHA film.

Project Objectives Not Met. The as-made PHA films were found to lack the tensile strain-hardening character to sustain stretch wrapping application using the machine-wrap process because of the high stretching rate typical of this process. However, because of the high tensile elongation of the PHA films, we think they would be suited for hand-wrap applications.

Very low density foam / very high expansion ratio foam was not achieved. Specifically 30X expansion is typical for foam peanuts and this was not achieved.

It was also not possible to stretch our film at high speed commercial rates. We were only able to achieve stretching at slow / hand stretching rate.

Next Steps/Future Developments. After completion of the project, we will continue working on improving production of shrink film. Metabolix will fund this post-SERDP work. Specifically, we will attempt to undertake the production of oriented film specimens for the shrink film market. We have identified a lab that can conduct tests to determine the suitability of PHA films in hand-wrap application and this process will be initiated. We will continue to work on issues related to strain hardening behavior to enable stretch film applications.

Also in post-SERDP activity, the stretching parameters learned from the TM Long experiments will be employed in a film line with inline orientation capability to produce oriented film specimens that can be tested in the shrink tunnel at Clemson. These experiments will probably be completed by the end of 2009 and will be funded by Metabolix.

Metabolix has entered into a strategic alliance with ADM, one of the world's largest bio-processing companies to construct a 50,000 ton/year PHA manufacturing plant in the Midwest. In post-SERDP activity funded by Metabolix, we will work with them to scale-up the foaming process to produce commercial products.

Objectives

The objective of this project was to demonstrate the use of biodegradable PHA natural plastic for foamed packaging and stretch/shrink film applications. PHA packaging foams and stretch-shrink films were produced and tested for functional performance and biodegradability.

The overall objectives we achieved included the following:

- Polymer branching, a key enabling technology for producing long-chain length PHA polymers, was successfully demonstrated.
- High melt-strength and melt-elasticity PHA polymers were produced using blends of branched, long chain-length PHA polymers with linear PHA polymers.
- These developments enabled the successful demonstration of the applicability of biodegradable PHA for foamed packaging and stretch/shrink film applications.

The objectives we achieved, specifically related to foam packaging, included:

- A blowing agent for PHA foaming was found and demonstrated.
- A foaming process was developed that achieved medium density foam suitable for foam food service items.
- Samples of foamed "peanuts" were produced.

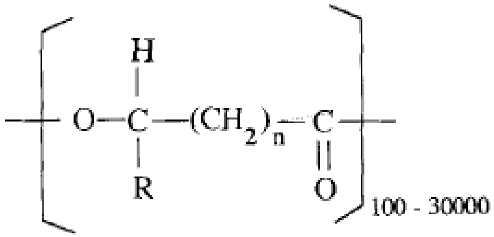
We also were able to demonstrate successful film production.

Background

The current practice of producing plastics from ever-depleting fossil fuel resources is not sustainable. PHA natural polymers represent an environmentally benign route to the replacement of conventional fossil fuel-based thermoplastics such as polystyrene and polyolefins.[1] Since the starting raw material (sugar) is photosynthesized from carbon dioxide and water, the polymer (exclusive of energy used in fermentation and melt processing) represents no net generation of carbon dioxide to the atmosphere. PHA polymers are formulated for use using environmentally benign additives such as plasticizers and fillers (e.g. talc as mineral filler).

Foamed products are a major source of plastics packaging in the market today. Foam packaging is dominated by polystyrene, with a small amount of polyolefin foam. Plastic packaging materials represent a significant portion of the world's plastics consumption. In North America alone, by 2006, consumption of plastic shrink/stretch film is estimated to be over 1.5 billion pounds (lbs) per year[11] and foamed product consumption at 8.5 billion lbs per year[12]. While these materials are low-cost and effective for many Department of Defense (DoD) packaging applications, the logistics of managing and packaging waste in remote areas and foreign countries is becoming increasingly problematic and costly for the military. Of the 288 million pounds of nonhazardous solid waste generated by approximately 20,000 troops each year in the Balkans, 66 million lbs were nondegradable plastic waste. Expanding this waste generation to Iraq with approximately 135,000 troops, approximately 446 million lbs of nondegradable plastic waste is generated each year[7]. Virtually all of the foam used in packaging applications goes into landfill, where it is one of the highest volume contributors. Similarly, polystyrene sheet foam used for packaging electronics or other equipment is a constant source of problems for DoD applications when disposal of the sheets is either expensive or logistically complicated[3].

Polyhydroxyalkanoates (PHA) are a family of biobased, biodegradable natural plastics that can functionally replace over 50% of the plastics used today[4]. PHAs represent the best candidates for broad replacement of current plastic packaging materials due to their durability in use and wide spectrum of properties. They range in properties from strong, moldable thermoplastics to highly elastic materials to soft, sticky compositions, and can be made as resins or as latex with excellent film-forming characteristics[5]. Their moisture barrier properties are superior to other biodegradable materials. In addition to these attributes, PHAs are biodegradable in aquatic (oceans, rivers, and wetlands), soil, and municipal waste treatment environments, and they can be both hot and cold composted. The generic structure of PHAs are documented in Figure 2.



$$\left[-O-\underset{R}{\overset{H}{\underset{|}{\overset{|}{C}}}}-(CH_2)_n-\underset{\underset{O}{\|}}{C}- \right]_{100 - 30000}$$

		Polymer
n = 1	R = hydrogen	Poly(3-hydroxypropionate)
	R = methyl	Poly(3-hydroxybutyrate)
	R = ethyl	Poly(3-hydroxyvalerate)
	R = propyl	Poly(3-hydroxyhexanoate)
	R = pentyl	Poly(3-hydroxyoctanoate)
	R = nonyl	Poly(3-hydroxydodecanoate)
n = 2	R = hydrogen	Poly(4-hydroxybutyrate)
n = 3	R = hydrogen	Poly(5-hydroxyvalerate)

Figure 2: Generic Structure of PolyHydroxyAlkonates (PHAs)

PHAs are well suited to meet the challenges of the foam marketplace. PHAs are hydrolytically stable, a key attribute for foam applications that involve exposure to moisture or high humidity environments. Other biobased packaging foams, primarily starch peanuts, are water soluble and become sticky in humid environments contaminating the item being protected. This is especially unsuitable when protecting electronic components. Similarly, polylactic acid (PLA) plastics have been shown to having poor hydrolytic stability.

Stretch and shrink films are one of the mainstays of the industrial packaging industry. By 2006 the market for stretch and shrink polyolefin films is projected to be 2.5 billion lbs in North America, with stretch film representing about 1.66 billion lbs and shrink films approximately 0.84 billion lbs[6]. Stretch and shrink film utilized as pallet wrap is one of the largest growing areas and represents a major challenge for disposal. Having a pallet wrap material that is biodegradable will save DoD energy and money in collection of the waste and bringing material back to source for disposal. In addition, PHAs offer the only opportunity for marine degradable packaging while being water resistant and having good barrier properties. The primary use of stretch/shrink film in the DoD is pallet-wrap, where large volumes of the film need to be either disposed of or transported back from forward locations[7].

Prior to undertaking this project, Metabolix developed PHA formulations with the proper physical and rheological properties which allowed us to produce PHA foam and film packaging products. The fundamental physical properties of PHAs, e.g., modulus, tensile strength, elongation at break, and barrier properties are in ranges suitable for both these applications.

It is important to understand that the challenge in producing foam products suitable for packaging revolves around stabilizing the foaming process during the melt extrusion stage. The primary technique developed to achieve high melt strength was long chain branching via organic peroxide used during the reactive extrusion[8]. This technique is similar to the process originally developed for polyolefin foam grades. The technical project approach we applied was established based on addressing this challenge.

This process included nucleating and blowing stable gas cells and then stabilizing the entire foam structure by crystallization of the polymer with resulting increase in the modulus. A balance between elastic and viscous polymer melt properties was required to achieve stable cell growth. Cell nucleating agents create high numbers of small cells which leads to low density foams. Tailoring the rheological properties of PHAs through long chain branching was key to achieving an acceptable foaming process.

A challenge that we had to recognize related to the stretch film portion of the project included the fact that PHA packaging foams and stretch/shrink films share a primary technical goal of needing high melt strength and melt elasticity. Metabolix's strategy for obtaining these characteristics was to develop long chain branched PHA polymers. While some initial scouting work on long chain branching was done prior the project, the optimization was done during the project. This is also true for our crystallization work.

Judicious blending of long chain branched polymer and linear polymer, combined with tailoring of composition and molecular weight of the base polymer, allows the rheology of PHAs needed to impart high melt strength and melt elasticity. Once branching is introduced, the rheological and crystallization behavior of the branched PHAs can be characterized and optimized for each application. Each foam application can be classified in terms of the foam density, as shown in Table 1.

Table 1: Classification of Polyolefin Foams by Density

Category	Expansion Ratio	Foam Density (pcf)
Structural foam SF	< 2	> 30
High density HD	5 - 10	6- 12
Medium density MD	11 - 20	3 – 6
Low density LD	21 - 50	1.2 – 3
Ultra low density ULD	51 - 100	0.6 - 1.2

A challenge with meeting military specifications for foams in general is that the specifications were originally developed based on polyurethane foams that can easily achieve ultra-low density with good compressibility because of the high rigidity of polyurethane itself. Many food applications such as disposable food plates are of a medium density, specifically, polystyrene foam.

Pallet-wrap products, which are typically stretch or shrink film, require PHA formulations which have the proper mix of tensile and tear strength, puncture resistance, and elasticity to match the performance of existing polyolefin films. Typical stretch films are not monolithic structures. Rather, they are coextruded, uni-axially orientated films comprising multiple layers, each providing a different contribution to the overall physical performance of the composite film. Metabolix achieved the desired properties by judicious co-extrusion of different formulations comprising blends of branched, crystalline and amorphous PHA polymers.

Materials and Methods

Specific PHA formulations were designed for each application. For foamed PHAs, a suitable blowing agent and a foam cell nucleant were selected, and a foam extrusion process identified. For stretch and shrink films, film orientation introduced during processing was a necessary requirement for achieving our target properties. Once the formulation and processing parameters were identified, prototype PHA foams and stretch/shrink films were produced and converted to useful packaging products. Mechanical performance and composting and biodegradability testing was then performed.

Raw Materials

PHAs were produced in a biological fermentation process using renewable and sustainable agricultural feedstocks rather than petrochemical feedstocks. These feedstocks sugars can be derived from corn or from other biomass components including lignocellulosics.

The primary polymer utilized was P3HB ~ homo-polymer of 3-hydroxybutanoic acid. The molecular weight of the polymer recovered from the fermentation is quite high, often in excess of 1 million.

To achieve the desired foam processing and properties, various additives were formulated into foam grades. These included:

- Low levels of mineral fillers to nucleate foam cell growth. Talc was used.
- Peroxide branching agents were used to introduce long chain branching to enhance the melt strength.
- Plasticizers and lubricants were added at low levels for die slip and mold release characteristics.

Compounding Methods

The formulations were compounded on a 27 mm MAXX Leistritz twin-screw extruder, with the temperatures on the extruder zones set at: 150 / 175 / 175 / 175 / 170 / 170 / 170 / 170 / 170 / 180 / 180 ºC. The processing parameters are identified in Table 2.

Table 2: Extrusion Process Data

Process Data	
Rate (lbs/hr)	60
Screw RPM	90
Melt Temp (ºC)	200
Melt Pressure (psi)	1200
S-drive Torque (%)	55

In Monsanto’s patent US 6201083B1, they describe the use of peroxides to introduce branching into PHAs for additional melt-strength particularly for coatings and films. They also cite the use of peroxides such as dicumylperoxide and also bis-azides and radiation. In their US 6248862 patent they introduced branching sites via polyols in the fermentation process. The basic concepts have been well tried in other polymers including polyesters and nylons. These patents were reassigned to Metabolix in 2002. These same compounding methods were applied.

The main challenge for a reactive extrusion approach to branch PHAs is the concomitant thermal degradation of the PHA in the melt. Branching of small molecules (less than 20,000 g/mole) does little to enhance the overall polymer melt strength. In general, long chain branches have to be > 3 time M_e, where the entanglement molecular weight, M_e, for PHAs is estimated at being around 7000 g/mole.

Characterization Methods

Measurement of molecular weight was estimated by Gel Permeation Chromatography (GPC) using a Waters Alliance HPLC System equipped with a refractive index detector. The column set was a series of three PLGel 10 µm Mixed-B (Polymer Labs, Amherst, MA) columns with chloroform as mobile phase pumped at 1 ml/min. The column set was calibrated with narrow distribution polystyrene standards.

The PHA sample was dissolved in chloroform at a concentration of 2.0 mg/ml at 60C. The sample was filtered with a 0.2 µm Teflon syringe filter. A 50 µ-liter injection volume was used for the analysis.

The chromatogram was analyzed with Waters Empower GPC Analysis software. Molecular weights are reported as polystyrene equivalent molecular weights.

Measurements of crystallinity and crystallization behavior were performed using a Perkin Elmer DSC to characterize the non-isothermal melt-crystallization kinetics of the subject PHB copolymers. In this test, the specimen (cut from a disc compression molded at 165 °C for one minute) was placed and crimped in the DSC sample pan. This test specimen was then exposed to 200 °C for one minute to melt all of the crystals; it was then cooled to 160 °C at 40 °C/min and maintained at 160 °C for about 1 minute. The specimen was then cooled to -50 °C at a rate of about 10 °C/min. As the polymer undergoes crystallization, an exothermic peak in the "heat flow versus temperature" trace becomes evident. The peak-temperature of this exotherm was noted as the recrystallization temperature or Tc. A higher Tc generally means faster crystallization kinetics.

Measurements of torsional rheology (G') were performed using parallel plate rheometry. All oscillatory rheology measurements were performed using a TA Instruments AR2000 rheometer employing a strain amplitude of 1%. First, pellets (or powder) were molded into 25 mm diameter discs that were about 1200 microns in thickness. The disc specimens were molded in a compression molder set at about 165 °C, with the molding time of about 30 seconds. These molded discs were then placed in between the 25 mm parallel plates of the AR2000 rheometer, equilibrated at 180 °C, and subsequently cooled to 160 °C for the frequency sweep test. A gap of 800-900 microns was used, depending on the normal forces exerted by the polymer. The melt density of PHB was determined to be about 1.10 g/cm^3 at 160 °C; this value was used in all the calculations.

Specifically, the specimen disc was placed between the platens of the parallel plate rheometer set at 180 °C. After the final gap was attained, excess material from the sides of the platens were scraped. The specimen was then cooled to 160 °C where the frequency scan (from 625 rad/s to 0.10 rad/s) was then performed; frequencies lower than 0.1 rad/s were avoided because of considerable degradation over the long time it takes for these lower frequency measurements. The specimen loading, gap adjustment and excess trimming, all carried out with the platens set at 180 °C, takes about 2 ½ minutes. This was controlled to within ± 10 seconds to minimize variability and sample degradation. Cooling from 180 °C to 160 °C (test temperature) was accomplished in about four minutes. Exposure to 180 °C ensures a completely molten polymer, while testing at 160 °C ensures minimal degradation during measurement.

During the frequency sweep performed at 160 °C, the following data was collected as a function of measurement frequency: $|\eta^*|$ or complex viscosity, *G'* or elastic modulus (elastic or solid-like contribution to the viscosity) and *G''* or loss modulus (viscous or liquid-like contribution to the viscosity). For purposes of simplicity, we used *G'* measured at an imposed frequency of 0.25 rad/s as a measure of "melt strength". Higher *G'* translates to higher melt strength.

<u>Measurements of apparent solubility's blowing agents</u> of N_2, CO_2, HFC-134a, and n-Butane in the PHA melt employed a magnetic suspension balance (MSB), while the swollen volume predicted by the Simha–Somcynsky (SS) equation of state (EOS) was used to account for the buoyancy effect. (Park, 2008) The swollen volumes of the polymer/gas mixture, as well as the gas solubility and diffusivity for PHA are discussed in Section 7. Since the PHA degrades easily for prolong heating, each test was done individually at a particular set of pressures and temperatures.

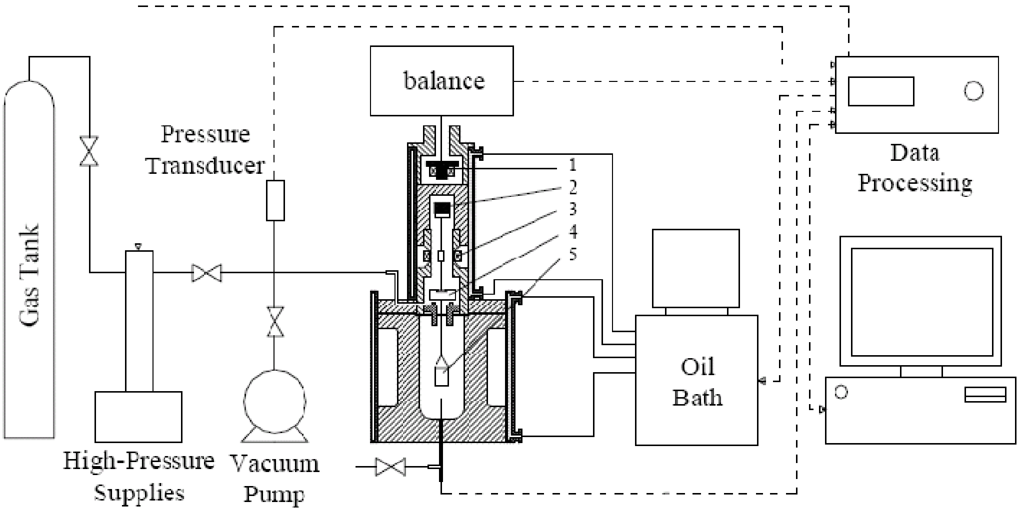


Figure 3: **Schematic of Overall MSB System** (1. Electromagnet, 2. Permanent magnet, 3. Position sensor, 4.Coupling device; 5. Sample holder)

Upon the completion of the sorption uptake curve measurement, the diffusivity (i.e., diffusion coefficient) of each gas in the polymer melt was estimated from the sorption uptake curve (measured weight gain W_g versus time t) during the gas dissolution kinetic process. Fick's second law was applied in this study for the extraction of the diffusion coefficient from the sorption curve, which was obtained from MSB.

Foam Extrusion Methods

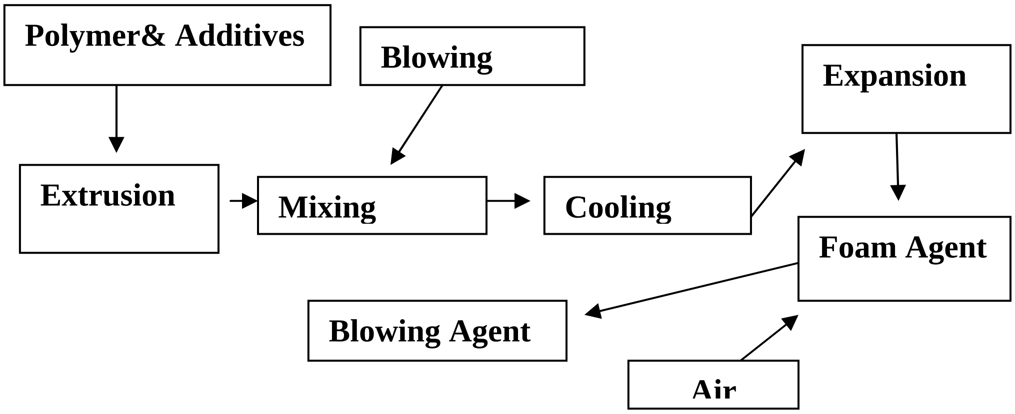


Figure 4: Basic Process for Making Thermoplastic Foams

Figure 4 illustrates the basic process for making the thermoplastic foams. The first requirement was to melt the polymer and add the physical blowing agent into the polymer melt. The pressure exerted by the extrusion process and polymer melt had to exceed that of the incoming blowing agent, otherwise the blowing agent would simply exit via the extruder feed section[9]. Care had to be taken to generate as small a gas bubble as possible to help in the mixing of the blowing agent in the polymer melt. Ideally the blowing agent would have high solubility at the high polymer melt temperature, but low solubility at lower temperatures at die exit to facilitate cell nucleation and growth. As soon as the blowing agent was added, there would be a static mixing section to facilitate good blowing agent mixing. It was very important that the blowing agent be dispersed as well as possible, often at the molecular level, to create a uniformly distributed foam cell structure.

Thereafter follows a cooling step to both obtain uniform temperature distribution throughout the melt (sometimes called gel) and desired temperature for optimum rheology for foaming. In most industrial foam lines this secondary cooling is achieved by using another extruder, hence the term "tandem extrusion foam process". In polymers the rheology, or viscosity, is highly temperature dependent and thus if temperature gradients are too high, non-uniform density foams result.

The critical requirements for foaming at the die exit are illustrated in Figure 5. Obviously there must be generated sufficient internal pressure (ΔP) above atmospheric pressure and resistance to polymer flow from a blowing agent to nucleate cells. The resistance to the cell nucleation and growth arises from the requirement of the polymer to flow around the growing cells, and also the kinetics of gas transport to the growing site. Nucleation itself is little understood, but is generally recognized to be mostly heterogeneous in nature. The cell nucleation density can be further controlled using particles such as talc or chalk. Care has to be taken that the heterogeneous particle does not interfere with cell wall strength. In most cases the cell grows around a particle because of the lower strength of the particle-polymer interface.

Of note, it was important to control the extensional flow of the polymer due to die entrance and exit geometries as the polymer chain orientation and internal strain energy can influence the local flow behavior of the polymer melt around a growing cell.

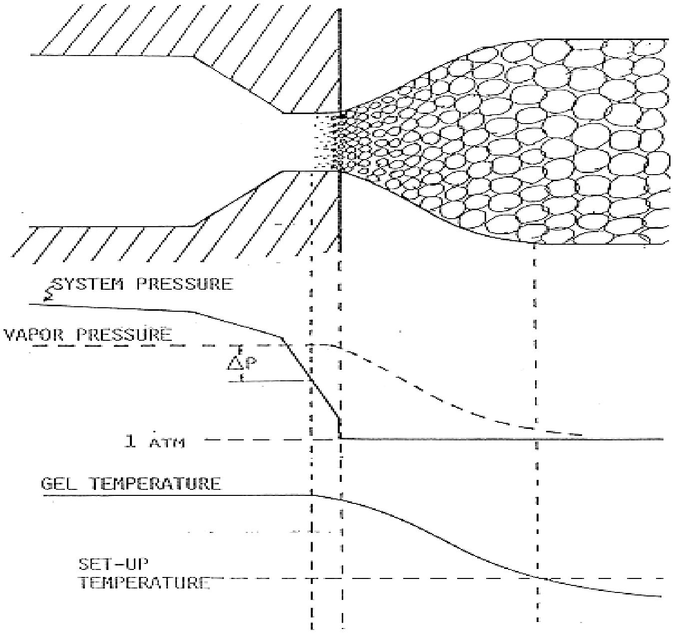


Figure 5: Basic Requirements for Cell Nucleation, Growth, and Stabilization

As the foam expands there is an adiabatic cooling from the blowing agent. If the melt strength of the cell wall is lower than the blowing agent pressure, cell bursting is observed. At densities of around 30 kg/m^3 cell wall thicknesses may well be in the range of a micron. Hence, it is often said that “strain-hardening” is a requirement for good polymer foam stability. This is usually achieved through branching of the resin. Another way to get foam stabilization with semi crystalline polymers such as PHA and polypropylene is through re-crystallization.

For dimensional stability and higher cushioning capability, closed cell foams are produced so that the internal bubble pressure is employed in addition to the polymer solid-state properties. Nitrogen usually permeates into the cells fairly rapidly (hours and days). This means if a blowing agent has a low permeance the cells may expand over days, and vice-versa. In

PHAs, as with polypropylenes, a further change in properties may occur over several weeks due to additional slow crystallization at room temperature.

To develop an approximate set of the processing parameters necessary to foam PHA a small Brabender melt plastometer was used (Figure 6). It consisted of a 5 hp extruder driver, equipped with a ¾ inch diameter tapered screw and speed control gearbox. A positive displacement pump was used for injecting the blowing agent to the polymer melt. A gear pump (Zenith PEP-II 0.3 cc/rev), was used to control both the back pressure in the melt and die pressure. A heat exchanger for cooling the polymer melt contains homogenizing static mixers. The die used was a simple filamentary die with overall diameter 1.25 mm and a 45° entrance, land length was 15mm. Pressure transducers and thermocouples were at each stage.

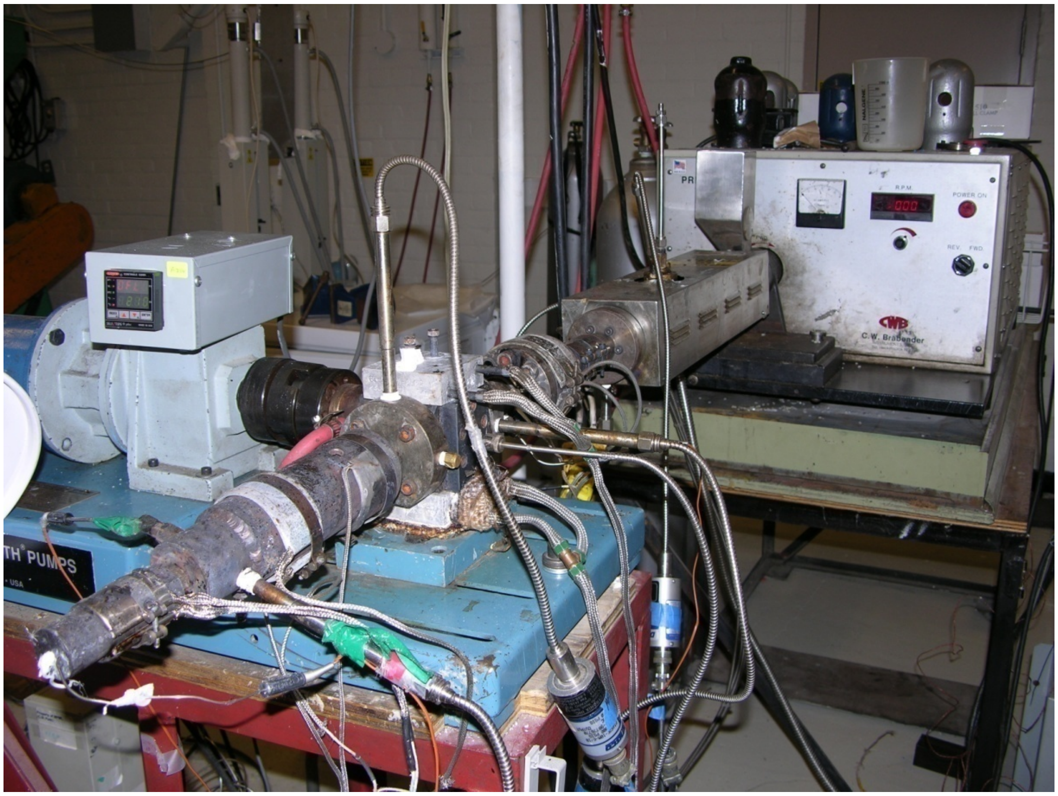


Figure 6: **Small Scale Brabender Plastometer Foam Line**

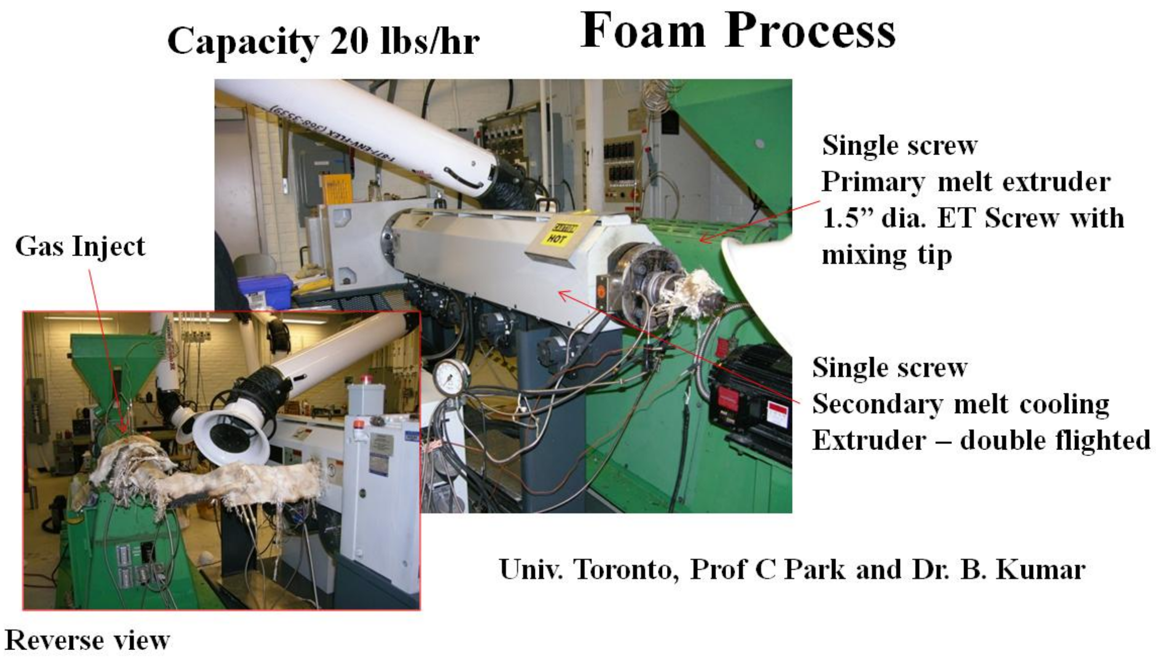


Figure 7: U. Toronto Tandem Foam Line

After screening runs on the brabender line, a larger “tandem line” for foam was used at the University of Toronto (figure 7) to find the optimal process conditions. The tandem line has 1½” primary extruder with a Barr ET screw and a pineapple mixing tip. The gas inject is about 2/3 of the way down the first screw barrel. The melt is fed to a second extruder outfitted with a 2” double flighted cooling screw.

Foam Characterization Methods

Measurements of foam density were performed following ASTM D792 procedure. This involved measuring the weight of a foam sample both in air and under water, and calculating the density according to the equation:

$$\rho_{\text{foam}} = \rho_{\text{water}}\ (\text{weight of foam in air}) / (\text{weight of foam in air - weight of foam under water})$$

where the density of water is taken as 1 gr/cm^3.

Expansion Ratio is the polymer density (1.2 g/cm^3) divided by the Foam Density.

Measurements of foam cell size were estimated visually via a light microscope.

Film Processing & Characterization Methods

To evaluate stretch and shrink film, the equipment at the Center for Flexible Packaging (CEFPACK) and the Center for Advanced Engineering Films and Fibers (CAEFF) at Clemson University was used. These centers have reasonable lab-scale equipment to evaluate the potential of PHA film in both stretch-wrapping and in shrink film applications.

The TM Long stretcher at Clemson was employed to produce oriented film specimens for the shrink tunnel experiments.

A branched PHA formulation was converted into blown film at the Killion Laboratories in Houston, TX. Specifically, a 1.5 inch Davis Standard extruder (smooth-bore feed section) equipped with a barrier screw was employed. The four zones of the extruder were set at: 175/170/165/160 (°C) and the extruder was operated at a screw speed of about 70 rpm for the production of the PHA film. The film was produced using a 2.5 inch spiral mandrel die (all die zones set at 160 °C with the die tip set at 165 °C) with two feed-ports and a die gap of about 40 mils (1 mm). The film blow-up ratio was about 2.7 and the final thickness was about 2.0 mils (50 microns). See Figure 8.

Figure 8: Davis Standard Extruder (Killion Laboratory, Houston,Tx)

The tensile stress-strain properties of the above films were measured according to ASTM D882, using an Instron tensile tester (Model 3345) shown in Figure 9. The PHA films were also subjected to stretching using a TM Long Biaxial Stretcher at the Clemson University Center for Advanced Engineering Films and Fibers.

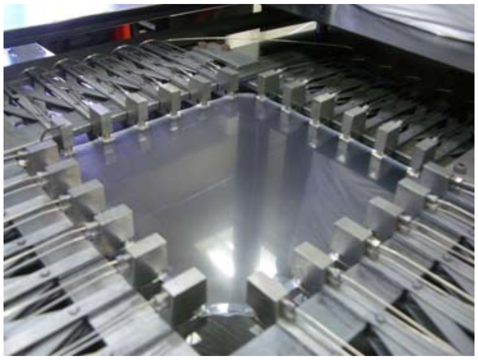


Figure 9: Long Biaxial Stretcher (Clemson University Center for AEF&F)

The shrink wrap experiments were performed using a shrink tunnel equipped with variable temperature oven and line-speed. The stretch wrap (machine wrap) testing was carried out at the Clemson University Center for Flexible Packaging using a commercial stretch wrapper used to wrap pallets and boxes (Uline semi-automatic stretch wrap machine) with adjustable stretch ratio (Figure 10).

Figure 10: Stretch Wrap Machine (Clemson University Center for Flexible Packaging)

Biodegradation Testing Methods

Biodegradation testing was conducted at two outside laboratories. The first one tested biodegradation in a marine environment according to ASTM D6691 at U.S. Army NSRDEC in Natick MA under the direction of Dr. Jo Ann Ratto (Biodegradation of Materials Supplied by Metabolix Telles, 2008). The second tested biodegradation both in a hot composting environment according to ASTM 6400 / ISO EN13432, and in an aqueous aerobic biodegradation environment according to ASTM D5271 / ISO 14851, at Organic Waste Systems in Gent Belgium under the direction of Dr. Bruno De Wilde.

ASTM 6691 Laboratory Testing

Biodegradation in the marine environment was examined through respirometry experimentation (ASTM D6691-01) where an inoculum of 13 marine microorganisms was added to the test samples in a synthetic sea water solution at 30ºC. Columbus Instruments respirometers were used to measure carbon dioxide evolution (mineralization) as a function of time. Glucose, a known biodegradable material, was used in three sample chambers in order to confirm that the respirometer was operating properly. Chambers containing only the synthetic seawater solution and inoculum were used as a negative baseline control. Please see ASTM D6691-01 for a more detailed description of the experimental procedure.

ASTM D6400 / ISO 13432

The composting bin test simulates as closely as possible a real and complete industrial composting process at pilot plant scale composting bins of 200 liters capacity. The test items were mixed with the organic fraction of fresh, pretreated municipal solid waste (biowaste) and introduced in an insulated composting bin after which composting spontaneously starts. Like in full scale composting, inoculation and temperature rise happens spontaneously. The composting process was controlled through aeration and moisture content. The temperature and exhaust gas composition were regularly monitored. The compositing process was continued until fully stabilized compost was obtained (3 months).

Specimens for evaluation were in the form of sheets, in various thicknesses, and dimensions of 10 cm X 10 cm. They were added to the biowaste at a level of 1%. The test was performed in duplicate and lasted 12 weeks.

At the conclusion of the composting test, the compost was sieved at 2, 5, and 10 mm size. Disintegration of the test specimens was evaluated very precisely by manual selection. If possible a mass balance was calculated on the basis on the basis of wet and dry weight. The compost obtained at the end of the composting process was used for further measurements, specifically chemical analysis for heavy metals and ecotoxicity testing.

The test is considered valid only if:

- The maximum temperature during composting is above 60°C and below 75°C,
- The daily temperature remains above 60°C during at least one week and above 40°C during at least four weeks,
- The pH increases to above 7.0 during the test and does not fall below 5.0,
- After twelve weeks the blank compost has Rottegrad IV-V and a volatile fatty acid content of less than 500 mg/kg.

More details about the testing procedure can be found in ASTM D6400 *“Standard Specification for Compostable Plastics”* or ISO EN 13432 *“Requirements for packaging recoverable through composting and biodegradation – Test scheme and evaluation criteria for the final acceptance of packaging”.*

ASTM D5271 / ISO 14851

The aqueous biodegradation test determines the biodegradation of test items under laboratory conditions by a consortium of bacteria from different sources. The test material was brought into a chemically defined (mineral) liquid medium, essentially free of other organic carbon sources and spiked with micro-organisms.

During seventy days, the biodegradation of the test specimens was tested together with a cellulose reference item in an aquatic, aerobic biodegradation test using a mixture of wastewater sludge, compost, and soil extract as inoculum without any pre-adaptation to the test item.

The test was executed at ambient temperature (21°C) and considered valid if:

- The degree of biodegradation of the reference material is > 60% at the end of the test, and
- The BOD of the blank at the end of the test does not exceed an upper limiting value obtained by experience (the value depends on the amount of inoculum and is, for

example, for 30 mg total suspended solids (TSS) per liter about 60 mg/l as inter-laboratory tests have shown).

During the aerobic biodegradation of organic materials in an aqueous medium, oxygen was consumed and carbon was converted to gaseous mineralized carbon (in the form of carbon dioxide). Part of the organic material was assimilated for cell growth. Sodium hydroxide (NaOH) pellets trap the CO_2 released and the induced pressure drop was directly related to the consumed oxygen and hence the biodegradation of the test item.

The amount of biodegradation is expressed as the ratio of the BOD (corrected for the blank) to the Theoretical Oxygen Demand (ThOD) or Chemical Oxygen Demand (COD) of the used test item.

More details on the testing procedure can be found in ASTM D5271 *"Standard test method for assessing the aerobic biodegradation of plastic materials in an activated sludge wastewater treatment system"* or ISO 14851 "*Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium – Method by measuring the oxygen demand in a closed respirometer".*

Results and Accomplishments

Branching Technology

Table 3 lists the GPC results for samples after undergoing the same thermal treatment in the reactive extruder. CES 071011-0 is the starting granule molecular weight before extrusion.

Table 3: Branching of PHA

	% Peroxide	T cr	Tg	Tm	Mw	Mn	Mw/Mn
CES 071011-0		none	-0.01	169	619,573	266,811	2.32
CES 071011-1	0	109.22	-2.34	163.9	530,119	226,023	2.35
CES 071011-2	0.05	108.62	-5.94	162.6	560,855	245,445	2.29
CES 071011-3	0.1	108.21	-5.53	162.8	565,942	211,523	2.68
CES 071011-4	0.2	108.06	-5.23	155.2	647,610	255,676	2.53
CES 071011-5	0.15	107.98	-6.06	155.1	598,001	251,668	2.38

Table column explanatory details:

% peroxide is the amount of peroxide added in the compounding operation based on the weight of the total formulation.

T cr is the recrystallization temperature as measured in a Differential Scanning Calorimeter (DSC).

Tg and Tm are the Glass Transition Temperature and Melting Temperature respectively, also measured on the DSC.

Mw and Mn are the weight averaged molecular weight and the number averaged molecular weight respectively, measured by Gel Permeation Chromatography (GPC).

Mw/Mn is the ratio of the two number as is also referred to as the polydispersity index

The data set (-1 to -5) shows how adding more peroxide to the formulation causes an increase in molecular weight from the branching reaction. The -0 sample is the raw resin before extrusion. Just the act of extruding the material causes molecular weight loss (compare -0 with -1).

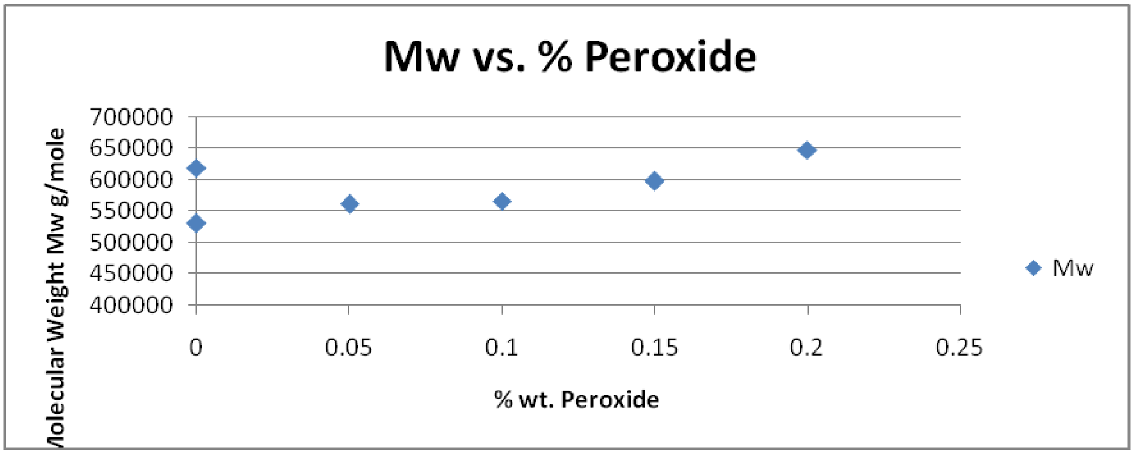


Figure 11: Molecular Weight Change on Branching

Molecular weight build-up due to free-radical chain transfer is also concurrent with fragmentation due to chain scission. Thus the molecular weight distribution, as measured by M_w/M_n often increases. The accuracy of GPC Mw, and particularly M_n values can be ±5% so it can be said that there is a general trend toward a broadened molecular weight distribution with increasing peroxide content as seen by these results. If one assumes the entire molecular weight increase is due to coupling of chains then one can estimate that about 20% of the chains are coupled at 0.2% wt. peroxide addition. Thus, these branched resins are in fact blends in which a minor phase is branched.

The upper point on the zero peroxide axis (Figure 11) is the molecular weight of the base resin, before compounding. Just running the resin through the compounding process results in a molecular weight loss as shown by the lower point on the zero peroxide axis. As peroxide is added to the compound process, the molecular weight increases from the branching reactions.

Blowing Agent Technology

The best blowing agent from our experiments was shown to be HCFC 134a. The most preferred blowing agent from a green perspective was CO_2.

The solubilities of nitrogen, carbon dioxide, n-butane and HFC134a, in PHA (polyhydroxyalkanoate) melt were determined at temperatures 160, 165 and 170°C and pressures up to 20 MPa using a magnetic suspension balance (MSB). The Simha-Somcynsky (SS) equation of state (EOS) was applied to predict the amount of volume swelling in the PHA/gas mixture due to gas dissolution. The experimentally measured “apparent solubility” from the MSB was then corrected accordingly by taking into account the swollen volume. After the measurement of the gas sorption curve in the PHA melt, the theoretical sorption model based on Fick’s second law was adopted to estimate the diffusion coefficients of all of these four blowing agents in PHAs at

160, 165 and 170°C respectively. The solubility of N_2, CO_2, n-butane and HFC134a increased as the pressure increased. It was observed that HFC134a has the highest solubility whereas N_2 has the lowest solubility in PHA melts (Figure 12). It should be noted that in cases of N_2 and HFC134a at 160°C, the PHA seemed to be partially solid. So the results at this temperature (160°C) for these two blowing agents (BAs) might not be reliable. For the case of HFC134a, the PHA melt was completely molten at 165 and 170°C. It was not clear if there was a crystallizing effect of the blowing agent in the PHA for the case of N_2, CO_2, and n-butane. The PHA melt seemed to have some crystalline section at 165 and 170°C, and that these crystalline sections have some effects on the foaming behaviors.

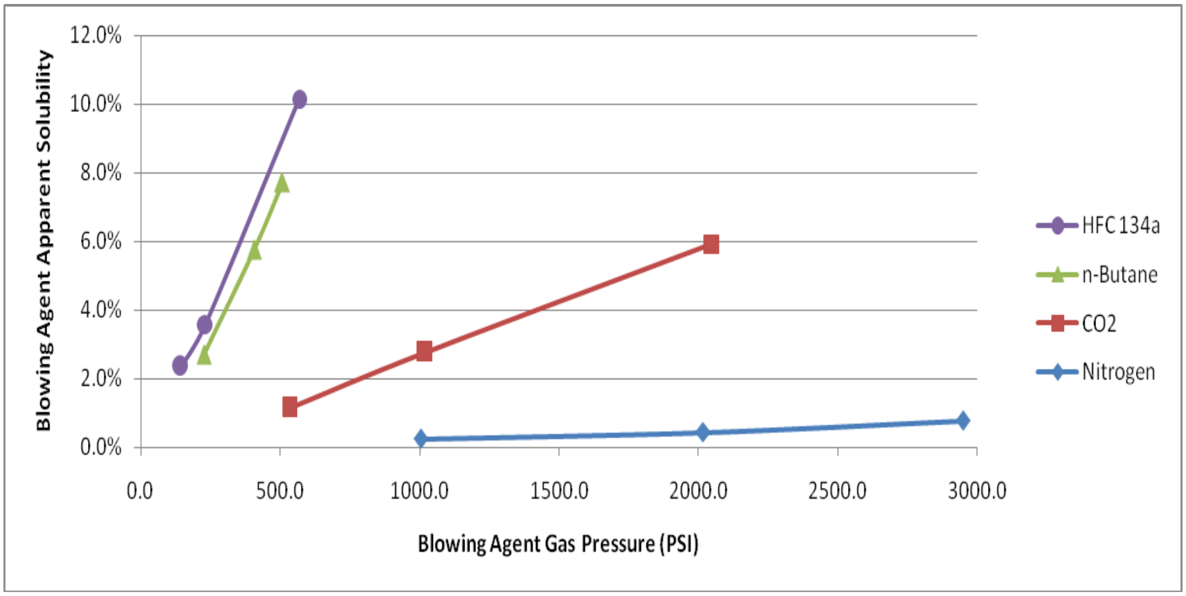


Figure 12: **Blowing Agent Solubility - Park, C. (2008) *"Gas Solubilities in PHA.* Toronto."**

It was found that the order of magnitude in diffusion coefficients for various blowing agents in PHA is given by n-butane<HFC-134a<N_2<CO_2. The diffusivity at 160°C is very low compared to 165 or 170°C. It should also be noted that since at high pressures and temperatures the swelling effect is a dominating factor (thickness of the sample changes), the diffusivity data are not consistent.

Foaming Results

Key to success in foaming was understanding the critical role of melt strength and using samples of polystyrene as targets. Initially it was thought that foam expansion was being limited by die design. This turned out to not be the case, as improved grades foamed well at trials conducted at the University of Toronto (see Figure 13).

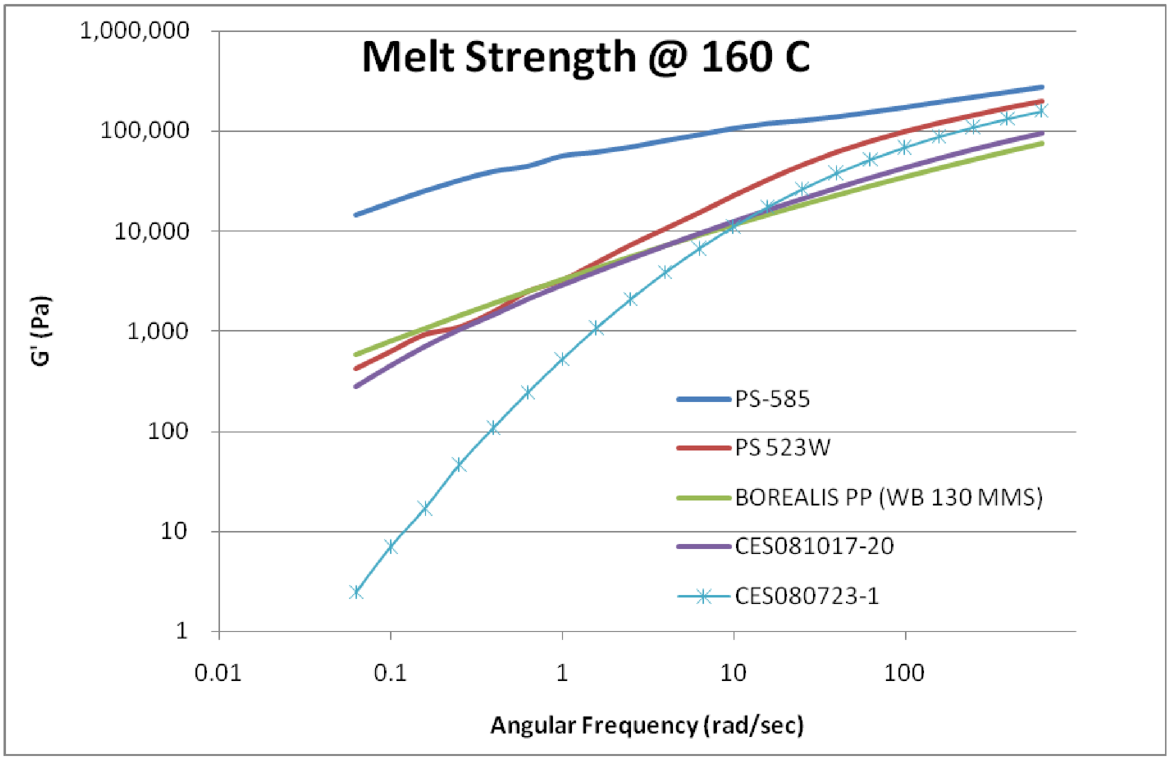


Figure 13: Melt Strength of Incumbent Materials

With the understanding of the critical role of melt strength, foam was prepared with materials of various degrees of melt strength and expansion ratios:

	CES080824-11	CES080824-9	CES080824-26	CES080824-27
G' (Pa)	9.2	29.4	499	998
Foam Expansion Ratio	1.6	4.8	7.1	15

Samples collected in the University of Toronto trials resulted in piles of foamed strands. Improvements are shown in Figure 14, with the improved product on the right side picture showing same height as old product (left side), but with 3x width and 1/3 weight, indicating better foaming expansion, up to 15x expansion ratio.

Figure 14: Initial foam strands (left) and improved foam strands (right)

Stretch & Shrink Film Testing

Optimization of the branching technology development outlined in the previous section enabled us to make PHA film using both the cast and blown film process. An optimized formulation of branched PHA, with melt rheological characteristics similar to that of a metallocene-catalyzed LLDPE blown film grade, was converted into blown film using a 1.5 inch Killion extruder equipped with a 2.5 inch spiral mandrel blown film die. A blown film roll, with 50 microns thickness and 260 mm width was set aside for subsequent stretch and shrink performance characterization.

The PHA blown film was subjected to a shrink wrap test in the shrink tunnel at Clemson University. While the film displayed some shrink at temperatures close to its melting point, the extent of shrinkage was inadequate. Typical shrink values obtained for the PHA film were about 10-20%, while the shrink wrap applications generally require shrinkage of greater than 50%. The fundamental reason why the shrink was minimal was due to the very low levels of orientation frozen-in during the film fabrication step. PHA generally crystallizes at very slow rates compared to polyethylene or polypropylene. Consequently, even though a considerable extensional strain is imposed during the film blowing process, the molecules are able to relax before the onset of crystallization -this minimizes the orientation in the as-made film.

Therefore, the next step was to focus on using film with a higher level of orientation frozen-in either during film fabrication or during post-fabrication stretching. Solid-state orientation, at temperatures just below the melting point, is a process that can create high levels of orientation. After many efforts to properly grip the film specimens in the TM Long machine, we were able to identify the temperature and strain rate required to produce oriented PHA film. Film specimens with high levels of orientation were produced; however, these specimens (post-orientation) were too small to be tested in the shrink tunnel.

Because of the promising tensile properties of the PHA film, specifically its tensile elongation to break (> 450% @ ASTM D882 conditions), its potential in stretch wrap applications was explored. We also attempted pallet wrapping with a PHA blown film roll. The PHA film broke in a brittle fashion during every pallet-wrapping attempt. It appeared that the film did not have adequate tensile strain-hardening character. An annealed (post-fabrication annealing at 120 C for 15 min) roll of PHA film fared marginally better even though that was far from acceptable.

The above experiments indicated that the PHA film we have is highly inadequate for pallet wrapping applications. While pallet wrapping is the largest volume segment of the stretch film industry, it appears like the "hand-wrap" segment of the stretch film industry is a reasonably large one. In fact, while approximately 40% of the stretch film industry in the NAFTA region is fulfilled by hand-wrap films, approximately 60% of the stretch film industry in Asia is of the hand-wrap kind.

Biodegradation Testing

The extreme corner points representing the limits of PHA formulation space were evaluated by Organic Waste Systems on Gent Belgium against both ASTM D6400 and ASTM D5271 test protocols.

All the PHA formulations pass ASTM D6400 through a specimen thickness of 0.82 mm. In addition, the PHA had no negative effect on either the composting process or on the physic-chemical quality of the compost produced[10].

When tested via ASTM D5271 protocols, all the PHA formulations showed a biodegradation percentage above 90% within a period of six months. They can be considered as completely biodegradable under the biodegradation criteria defined in ASTM D6400 (compostability norms). It should be noted that this complete biodegradation was obtained at ambient temperature and was therefore also representative of wastewater conditions, home composting, and soil conditions.

Finally, the foam grade itself was evaluated against ASTM D6691 marine respirometry and was found to degrade similar to the glucose control material, fully degrading within 120 days.

Conclusions

Polyhydroxyalkanoate biodegradable plastic was successfully formulated into foam and film grades.

Key to the foam grade formulation development was achieving high melt strength and maintaining the melt strength through the foaming process. The primary technique developed to achieve high melt strength was long chain branching via organic peroxide use during reactive extrusion. This technique is similar to the process originally developed for polyolefin foam grades. Considerable optimization of the peroxide choice and reactive processing conditions was required due to the difference in chemical structure of PHA from polyolefin's and due to the complex thermal stability issues inherent in PHAs.

It was also found that standard talc foam cell nucleants were useful in minimizing cell size which resulted in a better foam structure.

The foam processing conditions, while unique for PHA, were found to be as expected based on polystyrene and polyolefin experience. In general, the primary extruder conditions were optimized to efficiently melt the polymer and to mix the blowing agent while minimizing thermal and shear degradation of the polymer. The second extruder conditions were optimized to cool the melt to the minimum temperature without inducing crystallization. Standard dies and standard die setups were found to be successful.

Using the above learning's, PHA foam with expansion ratios up to 15X were achieved. PHA foam strand suitable for cutting into foam peanuts was successfully made.

While we have successfully made blown and cast films with the branched PHA formulations, we have learned that these films do not exhibit any shrink even at temperatures very close to their melting point. This is attributed to the slow crystallization kinetics of PHA and the consequently low levels of orientation frozen-in during the film fabrication step. So, the only way to produce oriented PHA films is through a solid-state orientation process. Through experimentation using a TM Long stretcher, we have now determined the approximate conditions (temperature and stretch rate) to produce oriented PHA film

The as-made PHA films were found to lack the tensile strain-hardening character to sustain stretch wrapping application using the machine-wrap process because of the high stretching rate typical of this process. However, because of the high tensile elongation of the PHA films, we think they might be better suited for hand-wrap applications.

Future Development of the Product

Over the next few months, we will attempt to produce oriented film specimens for the shrink film market. We have now identified a lab that can conduct tests to determine the suitability of PHA films in hand-wrap applications and will initiate this process.

In the future, we will work on product formulation and film processing to improve the ability of PHA film to be used in this application. We will shift our focus to the hand-wrap portion of the stretch film application space and continue to optimize the PHA film formulation with a goal of producing suitable stretch films in the near future.

The stretching parameters learned from the TM Long experiments will be employed in a film line with inline orientation capability to produce oriented film specimens that may be tested in the shrink tunnel at Clemson. These experiments will probably be completed by the end of 2009.

In addition, Metabolix has established a strategic alliance with Archer Daniels Midland (ADM), one of the world's largest bioprocessing companies, to construct a 50,000 ton/year PHA manufacturing plant in the Midwestern U.S.

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11. Thedinger, Bart, “Solid Growth Ahead for Stretch & Shrink Film,” *Plastics Technology.* December, 2003.

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Appendices

Supporting Data

No additional data collected during this research project warrants archiving.

List of Scientific/Technical Publications

No Scientific or Technical information was published in peer-reviewed journals. No technical reports were submitted for publication. A poster entitled “PHA Bioplastic Packaging Materials” was presented at the SERDP-ESTCP “Partners in Environmental Technology Technical Symposium and Workshop” in 2006, 2007, and 2008. No textbook or book chapters were published from this work.

Other Technical Material

None.