AQUEOUS SUSPENSIONS OF POLYHYDROXYALKANOATE AND THEIR APPLICATION AS FUNCTIONAL BARRIER COATINGS

by

SCOTT WAYNE TULL

(Under the Direction of Jason Locklin)

ABSTRACT

Polyhydroxyalkanoates (PHAs) are a class of naturally produced thermoplastic polyesters requiring no chemical modification or volatile solvent to be utilized as replacement for unsustainable petroleum based plastic coatings. PHA coatings on paperboard allow single use barrier coatings to have sustainable end of life through biological degradation and allow substrates to be cost effectively recyclable. In the work outlined it is shown how to formulate an aqueous coating from PHA particles utilizing surfactants, rheology modifiers, and heterogenous nucleating agents. Application of the volatile-solvent free aqueous PHA suspension on paperboard is shown to demonstrate ability to impart superior properties such reduction in gas and liquid permeability and ability to heat seal once applied to a substrate.

INDEX WORDS: Polyhydroxyalkanoate, biodegradable, aqueous suspensions, aqueous dispersion, barrier coating

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DEDICATION

I dedicate this to those who support me. Primarily my wife Julie.

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I love you Julie, thank you for being the rock I have always needed. Thank you, Mom and Dad, without you I would never be here.

Thank you, Jason Locklin, My PI. My beginnings under your guidance were assuredly rocky and difficult but you have always stuck with me and given me the advice I need. I aspire to be a leader you will respect. Sometimes sitting in your office venting about the illogical problems we deal with is the best part of my day and I hope I can still do it after graduating. Thank you to my committee members, Dr. Ritchie, Dr. Ferreira, and Dr. Handa for guiding me through my Ph.D. I know you were busy, but you always found time to meet and get me over the hill. Thank you again Dr. Ritchie for your guidance and wisdom.

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INTRODUCTION AND PRECEDENT FOR POLYHYDROXYALKANOATE COATINGS

1.1 Current Single Use Plastic Usage

Roughly within the span of one human life plastics have been wrapped into every aspect of modern life with plastic use increasingly dominating the packaging industry ever since the cost of single use was eclipsed by the reusable container market. Geyer et al estimated that only 30% of all plastic ever produced is currently in use, and of plastics used in 2015 only 9% was recycled[1]. Of that waste, synthetic polymers do not readily decompose, and so these damaging materials accumulate in landfills and in natural environments, which leads to countless issues for waste management and are potentially detrimental to worldwide health[2-4].

Modern packaging provides the ability for foods and other consumer goods to be efficiently sealed and distributed utilizing the design of single-use plastics. Single-use containers and packaging are composed of or coated in petroleum-based plastics, such as polyethylene, which provide performance properties such as gas and/or liquid barrier, printability, and heat sealability[5]. But once a single use plastic has been thrown away, it is commonly far cheaper and convenient to fabricate a new article from virgin plastic than to clean and recycle it [6, 7]. As landfills overflow with worthless environmentally persisting plastic accumulates, the need for more sustainable materials and end-of-life management grows. Biodegradable polymers such as polyhydroxyalkanoates (PHAs) can replace unsustainable petrol-based materials and offer value through exciting new end-of-life opportunities, such as fertilizer or fermentation feedstocks, for new polymer[8].

1.2 Single Use Plastic Barrier Coatings for Paperboard

Paper is widely available, biodegradable, and capable of being repulped and reused multiple times[9]. Because of its mechanical strength and flexibility, paperboard is a common single-use substrate for food containers, beverage cups, and napkins among many other numerous products. However, paperboard alone is water absorbent and highly permeable to water and oxygen vapors due to its polar chemical structure and porosity[10]. For paper to properly preserve food products from oxidation, moisture, microbial growth, and seal a cup from the penetration of hot liquids, it must be coated with another material capable of barrier properties such as aluminum or plastic[11]. Aluminum coatings provide excellent barrier but are difficult to compound, have poor acid resistance, encounter difficulty in printing, and do not heat seal[12].

Most paperboard products are coated in plastic to provide functional properties necessary to their application. Examples of coated paperboard applications and the coating materials that provide necessary functional properties are shown in Table 1.1. Materials such as ethylene vinyl alcohol, a common oxygen gas barrier coating, must be combined with other coating materials such as extrusion-coated, low-density polyethylene to provide water barrier and heat sealability[13].

Table 1-1: Examples of Coating Paperboard Applications and the Coating Material that Provides Necessary Functional Properties.

Paperboard Coating Example	**Suitable Coating**
Container blocking oxygen gas vapor from spoiling the food it contains	Ethylene vinyl alcohol (EVOH)
Wrapper impeding food grease penetration and subsequent spoilage.	Fluorocarbon
Hot serve beverage cup preventing penetration of hot coffee through paper cup.	Low-density polyethylene Polyurethane and Alkyd Resin
Spice enclosed into packet by heat sealing coated substrate.	Low-density polyethylene

Other coatings for paperboard, such as recycled PET suspensions, see use as a water barrier, but provide little gas barrier and heat sealability [14, 15]. Polyurethanes and alkyd resins are advantageous as moisture and water barrier coatings, but they suffer from high cost, require harmful volatiles solvents to produce, and limit end-of-life[16-18]. Low-density polyethylene (LDPE) is the most versatile paperboard coating and provides barrier to oil, grease, and water, as well as printability and heat sealability[19]. LDPE is cheap in comparison to other coatings with high performance, but the true cost of LDPE is not noticed until the coated paperboard is discarded.

Even though paperboard is recyclable through repulping processes, LDPE coated paperboard rarely is recycled. This is due to the complications of contaminating paper fibers by sticky masses in the repulping process[20, 21]. Further, many paperboard products, such as hot serving cups, typically suffer from large amounts of waste during the coating process when the ends and sides of the coated paper are cut off, and the waste that has already been coated in polymer is not easily re-pulped and reincorporated as a raw material because of the remaining plastic coating on the paper fibers. Separation of sticky LDPE from paper fibers requires volatile organic solvent recovery followed by purification steps[22].

1.3 Aqueous Suspension PHA Coatings

To reduce amounts of waste accumulated in landfills, the use of environmentally persisting plastics should be replaced with a biodegradable plastic alternative such as polyhydroxyalkanoates (PHAs.) PHAs are a class of hydrophobic thermoplastic polyester produced by bacteria that naturally degrade in the environment[23, 24]. A PHA polymer’s physical properties are based on the concentration of the copolymers that comprise it, allowing for PHAs to tailor material properties to the application requirements[25, 26]. Choosing a PHA chemistry that results in physical properties similar to LDPE allows PHAs to be a coating solution for all performance barrier requirements, printability, and even heat sealability.

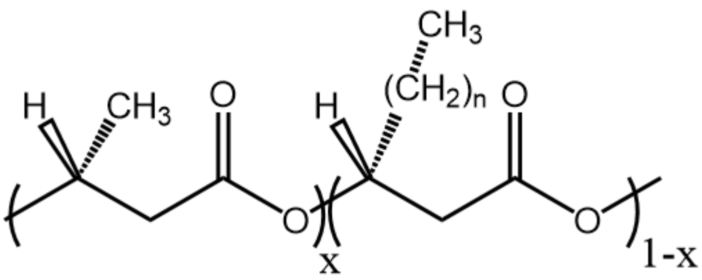

Figure 1-1: Chemical structure of PHA copolymers where x is the repeat units of 3-hydroxybutyrate and a comonomer with pendant chain length determined by n.

By dispersing PHA polymer particles in water, it is possible to produce a volatile-solvent free waterborne suspension capable of imparting superior barrier properties once coated and cured onto a substrate. Since polyesters such as PHA polymers are alkaline labile any coated paper fibers are recoverable and can be easily recycled using existing technology by degrading the polymer in a base bath during the re-pulping process[27]. Replacing a conventional single-use plastic coating with PHA could then provide cost savings by allowing for unused coated paper cuttings to be recyclable.

Herein, we discuss a method for producing an aqueous PHA suspension capable of spreading uniformly on paperboard through a multitude of coating methods such as gravure or Mayer rod. A dispersion is a two-phase system where one phase is dispersed in another phase. As shown in table 1.2, the dispersion term encompasses a wide range of potential mixtures such as emulsions, foams, and colloidal suspension.

Table 1-2: Description of Potential Dispersions Based on the Phase type of Dispersion Media and Dispersed Phase.

Dispersed Phase	Dispersion Media		
	Solid	**Liquid**	**Gas**
Solid	Solid gel/suspension	Colloidial suspension	Solid aerosol
Liquid	Gel	Emusion	Liquid aerosol
Gas	Solid Foam	Foam	N/A

Properties of a dispersion coating are influenced by the particle size of the dispersed phase. When the dispersed phase is 1nm-1µm in size solid particles, the dispersion is characterized as a colloid, while a suspension is a dispersion of particle size >1µm. A distinction between colloid and suspension is that dispersions of particles > 1µm are susceptible to sedimentation due to gravity. Dispersions of particles in the colloid range do not sediment from gravity due to Brownian motion, and whether or not a colloid will sediment is dependent on solid-liquid interface interactions. Further description of solid-liquid interface interactions and their impacts on dispersion coatings will be discussed in subsequent chapters.

A waterborne coating must be homogeneous and be able to precisely coat its substrate before melting the polymer to make a uniform film, and enough material should be distributed to provided barrier properties. To create a stable waterborne PHA coating, a means to distribute the polymer particles successfully is necessary in order to break up agglomerates and allow for each separate particle to be wetted. This is accomplished using a high level of shear, typically from sonication, rotor-stator mixers, or very high shear impellers. To produce a shelf-stable dispersion, the following food-safe components are necessary to the formulation:

- Dispersing Surfactants
- Wetting Agent
- Defoaming Surfactant
- Rheology modifier

1.4 Dispersing Surfactants

Surfactants, also called surface-active agents, are amphiphilic chemicals possessing both hydrophilic and hydrophobic functionality[28]. These chemicals act to reduce surface tension between the liquid phase (water) and solid phase (PHA granules), which allow the particles to be wetted and subsequently dispersed. Surfactants are generally regarded as a formulator's most versatile tool. Most consumer products such as paints, lotion, and even ice cream is formulated with a surfactant, and many contain more than one surfactant.

While all surfactants utilize their amphiphilic nature to reduce interfacial tension, not all surfactants are interchangeably usable. Surfactants can differ chemically, being designated as nonionic, ionic, or zwitterionic. Whether or not a surfactant is usable in an application can sometimes be determined by the type of surfactant. Further, surfactants are typically characterized based on hydrophilic-lipophilic balance and critical micelle concentration, which are useful in understanding specific roles a surfactant can have in the formulation of a suspension coating. The main roles of surfactants in the application of aqueous PHA suspensions are that of a wetting agent, solubilizing agent, or defoamer.

Surfactant hydrophobicity is influenced by the chain length of its non-polar portion of its tails, which is typically aliphatic hydrocarbon or alkyl ether, such as polyethylene oxide. Fluorocarbon and siloxanes are sometimes used as surfactant hydrophobic tails but have issues with toxicity and environmental persistence. The hydrophobicity of a surfactant’s head is determined by chemistry involving charge and hydrogen bonding. Surfactants are typically segregated as nonionic, ionic, or zwitterionic. Nonionic surfactants have no charge on their polar head, ionic surfactants are either cationic or anionic in charge, and zwitterionic are both cationic and anionic.

Ionic surfactants are the most common class of surfactants and are found commonly in soaps and detergents because of their tendency to foam. Ionic surfactants stabilize foam through electrostatic repulsion between two sides of a bubbles film, and additionally produce increased concentrations of counterions, which, through osmotic pressure, prevent the thinning of foam films[29]. When ionic surfactants form a micelle, the surface is coated in counter ions, thereby creating an electrical double layer and stabilizing the micelle against van der Waals attraction due to electrostatic repulsion. Derjaguin–Landau–Verwey–Overbeek (DLVO) theory uses van der Waals and electrical double layer theory to rationalize why some colloids are stabilized and others aggregate. The stabilization is explained by van der Waals attraction drawing particles together being weaker than the repulsion encountered when a stabilized particle is a within two times the thickness of the electrical double layer [30-32].

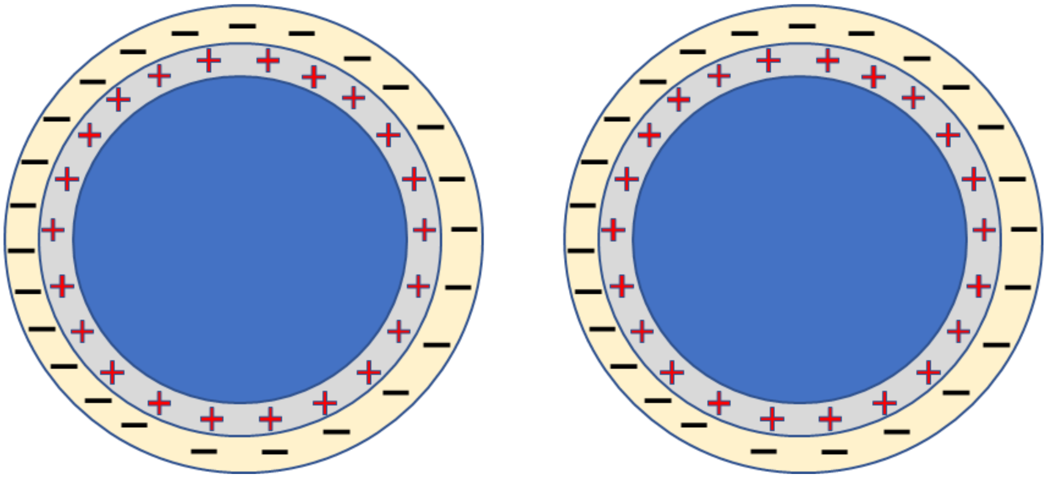

Figure 1-2: Ionic Surfactants micelles Coating Hydrophobic particles.

Zwitterionic surfactants are also charged but are defined as being both cationic and anionic on the polar head. Zwitterionic surfactants can be either anionic, cationic, or both which depends on pH and level of protonation of the molecule. Because of this, suspensions stabilized by zwitterionic surfactants are prone to instability at high or low pH. While zwitterionic surfactants are useful in some applications their use is not considered in this application. A better choice is that of non-ionic surfactants, which are uncharged and advantageously produce less stable foams than their ionic counterparts[33].

Since non-ionic surfactants are uncharged, they do not rely upon the electrical double layer, and instead adsorbed non-ionic surfactants stabilize utilizing steric stabilization. When two particles adsorbed with non-ionic surfactant come into proximity below two times the thickness of the surfactant adsorbed, the particles will encounter steric repulsion[34, 35]. Compression of the adsorbed surfactant layers creates an increase in concentration of the solvated polar surfactant “heads” and the concentration gradient osmotic pressure drives the flow of water in between the compressed layers of adsorbed surfactants. Whether the particles aggregate or are stabilized and remain in suspension can be determined using equation 1-1, the Gibbs-Helmholtz thermodynamic equation.

$$\Delta \boldsymbol{G_R} = \Delta \boldsymbol{H_R} - \boldsymbol{T}\Delta \boldsymbol{S_R} \qquad \textbf{Eq 1-1}$$

Where ΔH_R is the change in enthalpy, ΔS_R is the change in entropy, and T is the absolute temperature. If the Gibbs free energy change ΔG_R is positive upon the overlap of adsorbed layers, then the particles remain stabilized[36].

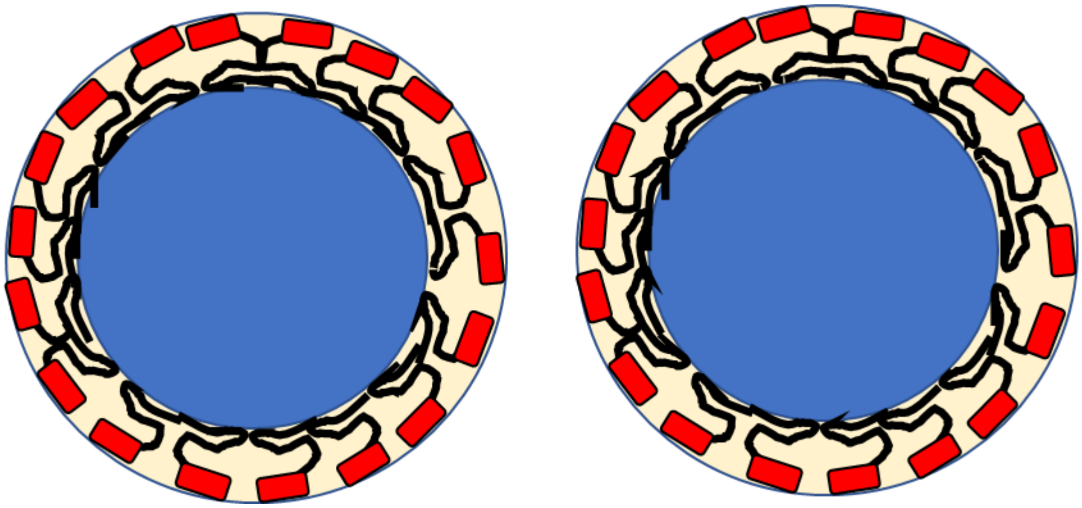

Figure 1-3: Non-ionic surfactant micelles coating hydrophobic particles.

1.4.1 Hydrophilic-Lipophilic Balance

When discussing a surfactant and its properties the hydrophilic-lipophilic balance (HLB) should be considered. First introduced by William Griffin and the Atlas Powder Company in the 1940s, the HLB system of surfactant classification can be used to determine which surfactant is best to disperse a solid or liquid in water[37, 38]. Their classification system has since been improved in many ways, but it is still based upon the amphiphilic nature of surfactants and uses a weight percent between a surfactants hydrophilic head and hydrophobic tail. The system is devised such that the higher an HLB, the more polar the surfactant. Calculated HLB is generally a good indicator of how a surfactant will function but does not consider the charge on a surfactant.

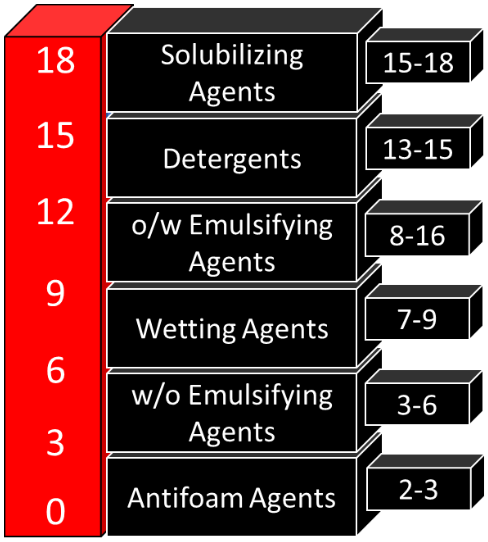

Figure 1-4 Hydrophilic-Lipophilic balance and the use of surfactants that fall within those ranges [37].

1.4.2 Critical Micelle Concentration

Upon introduction into water, surfactants rapidly reduce surface tension between the air and water interface by alignment of their hydrophobic “tail” into the air. Surface tension γ continues to decrease from ~72 mN^{-1} until around 30-40 mN^{-1} where a critical concentration of surfactant has been reached[39]. At this critical point, interfacial and bulk properties abruptly change as surfactant molecules associate and form larger units called micelles that are in equilibrium with monomer surfactant molecules. The concentration is known as the critical micelle concentration (cmc.)

The cmc is observed by adding surfactant to water while observing surface tension, which experiences a sudden plateau at the cmc. Surfactants have varying cmc values that are dependent on ionic strength, temperature, and the chemistry of that surfactant. Generally, the cmc is decreased as the surfactants alkyl portion (hydrophobic) is increased in chain length[40]. When the concentration of surfactant is greater than the cmc, surfactant hydrophobic tails coat polymer particles, forming micelles around individual granules with only polar heads in contact with water. This lowers the interfacial tension between the particles to be dispersed and the dispersant solvent water.

There are many surfactants with diverse chemistry to choose from, but it is important to keep in mind the end application when selecting components of a formulation. Since the target application is that of a food-contact, single-use paper coating, the generally regarded list (GRAS) was used to determine which surfactants would be best for the formulation of a food contact paper coating[41]. Since PHA granules are uncharged and ionic surfactants tend to stabilize foam more than nonionic surfactants, nonionic surfactants were chosen for the purpose of dispersing hydrophobic PHA granules.

1.5 Wetting Surfactant

In addition to dispersing agents, wetting agents are a necessary tool in many formulations. Wetting agent HLBs fall in the range of 7-9 and typically have shorter aliphatic chains containing branched structure than dispersing agents[42]. The most basic function of a wetting agent is to assist in the displacement of air from a solid surface by a liquid, typically water, by reducing the interfacial tension at the interface between solid and liquid phases[43, 44]. To do this, these surfactants preferably orient between aqueous and air phases[45]. This is important in the first step of suspension production where adsorbed air on each particle must be displaced. Additionally, wetting is acutely important in the application of coatings where the application substrate must take a large amount of coating over a vast surface area in a short time[46]. In the application of coating, if wetting is accomplished more efficiently then less imperfections are possible, and so the coating is thereby more effective.

1.6 Defoaming Surfactant

In general surfactants create foam, some more so than others, but when adding surfactant to a suspension to stabilize and disperse hydrophobic PHA particles a consequence is the additional foam and problems that come along with it. To alleviate this, a formulation should include a defoamer, also called antifoam, which typically has a low HLB of 2-3. As indicated by the low HLB number, defoamers are poorly soluble in water and typically require other surfactants help disperse them. Luckily, most suspensions containing defoamers contain several other surfactants as well. The concentration that works for one defoamer may not work for all, but typically less than 0.5% weight of the total formulation is included as a defoamer.

The chemical structure of effective defoamers is typically different from other surfactants. While defoamers are still contain both polar and non-polar regions, the polarity of the polar head is reduced (as reflected in the HLB number) and is typically sandwiched between two identical nonpolar tails[47]. This is referred to as a gemini surfactant. An example of a gemini surfactant is the 2,4,7,9-tetramethyl-5-decyne-4,7-diol shown in figure 1-3.

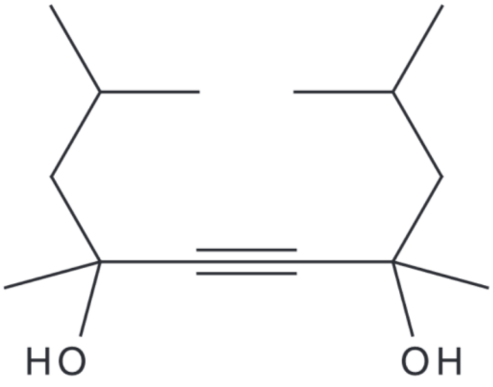

Figure 1-5: Chemical structure of the gemini surfactant 2,4,7,9-tetramethyl-5-decyne-4,7-diol (TMDD.)

1.7 Rheology Modifier

Modern coating technology has developed around the use of aqueous latexes out of necessity to avoid the previous convention of relying on hazardous and environmentally problematic volatile solvents. But with the change in solvent from volatile organic, the surface tension of water becomes a brutal conundrum. There is only one liquid having higher surface tension than water, which is liquid mercury[48]. A majority of additives for waterborne coating formulations such as surfactants are intended to cope with surface tension and the variety of problems surface tension causes. Another functional tool that must be added to help rectify the problems encountered is a rheology modifier.

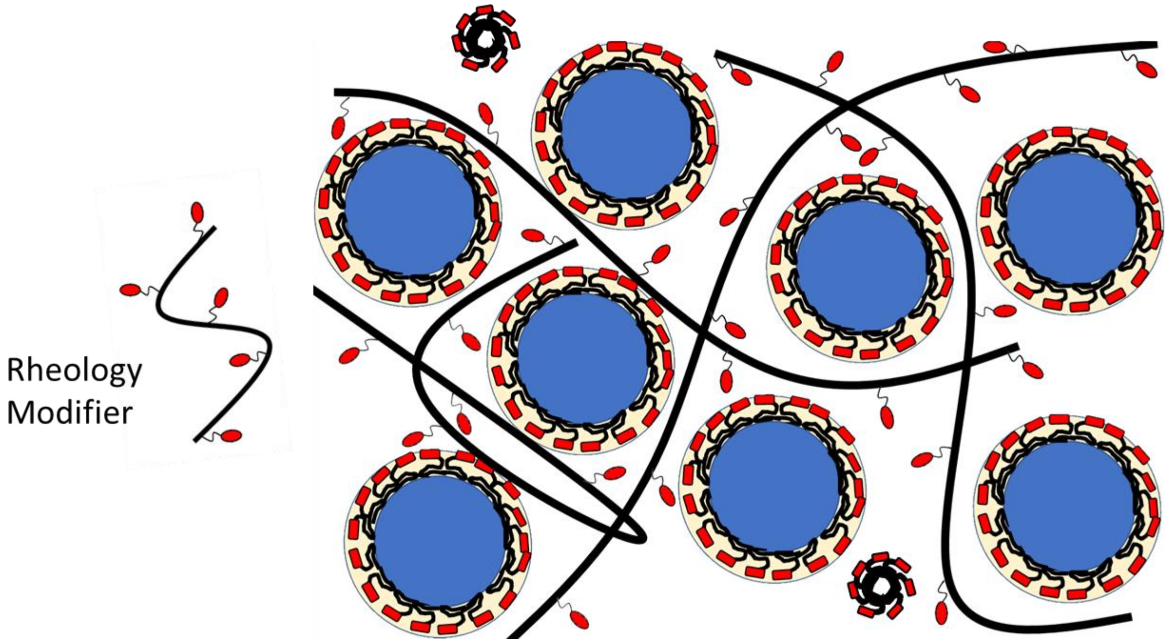

Figure 1-6: A depiction of a rheology modifier showing how it may thicken by creating a superstructure throughout a suspension of hydrophobic particles.

Rheology modifiers change the resistance to flow of a suspension, thereby making it thicker, and is defined mathematically by equation 4-1 [49].

$$\boldsymbol{\eta} = \frac{\tau}{\dot{\gamma}} \qquad \textbf{Eq 1-2}$$

Where η is the viscosity, τ is shear stress (Pa), and the rate of shear $\dot{\gamma}$ is equal to the fluid velocity divided by the distance between planes of shear. The selection of a rheology modifier is based on application requirement such as shear rate, pH, and chemical compatibilities. Typically, a rheology modifier makes up less than 1.0% of the total suspension weight. In figure 1-6 a depiction of a rheology modifier shows how it may thicken by creating a superstructure throughout the suspension. PHA particles are shown in blue, which are coating in surfactant having a red hydrophilic head, and each micelle of PHA is separated by the high molecular weight chains of the rheology modifier. This shows how the rheology modifier also protects the suspension from agglomeration and subsequent sedimentation by forming a web like superstructure.

Rheology modifiers of organic polymer structure are usually characterized as either conventional thickeners or associative thickeners. While there is some overlap in functionality between conventional and associative thickeners, conventional thickeners are high molecular weight (greater than 10^5 g/mol) water soluble polymers that thicken through flocculation and hydrodynamic interactions. Conversely, associative thickeners are typically lower molecular weight water soluble polymers that contain hydrophobic groups that are capable of “associating” with other suspended hydrophobic materials such as aliphatic polymer particles[50, 51].

1.7.1 Mechanism of Thickening by Rheology Modifiers

The hydrodynamic mechanism is a function of molecular weight, chain entanglement, swelling, and chain stiffness. Since conventional thickeners have high molecular weights, when they are solvated by the water of a coating, the thickener polymer chains take up large portions of hydrodynamic volume, thereby effectively increasing viscosity by “tying” up a significant portion of previously free water[52]. Generally, dissolving higher molecular weight thickeners gives higher molecular weights, though, while cellulosic thickeners tend to have lower molecular weight than thickeners with more flexible chains such as polyethylene oxide, they may not be any less effective as a thickener.

Another mechanism a conventional rheology modifier utilizes to thicken suspensions is to create regions of depletion flocculation, where the suspended phase is concentrated in “packets” of flocculation. This occurs by the suspended phase concentrating and displacing thickener chains, and results in the suspended phase being driven closer and closer as water is driven out to further solvate the displaced thickener chains[53, 54]. These depletion flocculants can be viewed through optical microscopy and in some cases can be felt between your fingertips [55].

Associative rheology modifiers may be able to thicken through hydrodynamic and flocculation mechanisms depending on the molecular weight of their water-soluble polymer, but most associative thickeners are below 50,000g/mol. The primary mechanism of associative thickening is through hydrophobic regions of the polymer associating with the suspended phase[56]. Interestingly, ionic polymer surfactants have overlap with associative thickeners and can act to increase viscosity through association while dispersing hydrophobic materials[57]. Additionally, since associative thickeners are usually of lower molecular weight they are less inclined to act through depletion flocculation and consequently suspensions thickened by associative thickeners have higher gloss and appearance[58].

Selection of a rheology modifier for PHA suspensions should consider the target application is that of a food contact single use paper coating. A useful tool in selection is that of the generally regarded list (GRAS) [41]. Additionally, any additive added to a biologically degradable PHA suspension should also be at least partially degradable in the environment. For these reasons an advantageous choice to improve coating viscosity and stability is that of bacterial produced guar and xanthan gum[59, 60].

1.8 Suspension Method

In order produce a uniform polymer film from an aqueous polymer dispersion, the dispersed phase must be free of agglomerates and of uniform particle size distribution. The natural granule form of PHA created by bacterium are typically a micron in size with a narrow particle size distribution. But once hydrophobic PHA particles are harvested from the cell and cleaned up, they harshly agglomerate and do not readily separate without intense shear. In order to break up agglomerates of PHA granules, and finely distribute and implement the dispersion system a cavitation mixing system is used.[61]

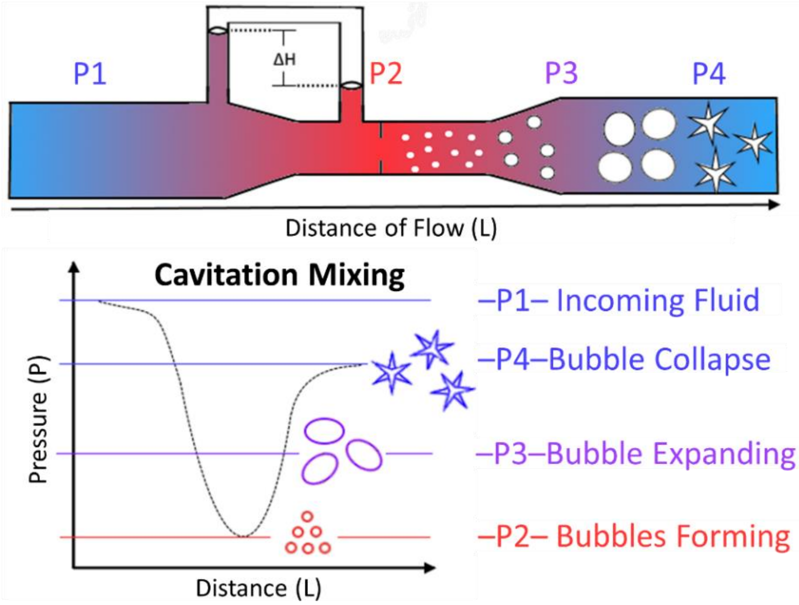

Figure 1-7 The energy necessary to mechanically break up agglomerates and separate polymer particles is supplied by hydrodynamic cavitation.

Cavitation is characterized by a rapid decrease in pressure to a point at which a phase transition creates vapor filled bubbles, and a subsequent increase in pressure rapidly collapses the vapor in a shockwave of energy. This energy drives the mechanical forces necessary to create a uniform dispersion[62]. Figure 1-5 shows how hydrodynamic cavitation can be created utilizing a volume constriction during fluid flow, which is more efficient than sonication cavitation. But in order to produce hydrodynamic cavitation a large amount of material is necessary to pump and move through the volume constriction quickly[63]. Sonication provides similar energies to hydrodynamic cavitation but does not require fluid movement other than agitation to circulate material. Because of this, sonication cavitation is useful to disperse PHA suspensions on the small scale

(<5 gallons), while hydrodynamic cavitation is useful to disperse PHA suspensions on a large scale (>5 gallons.)

1.9 Objectives and Dissertation Outline

This dissertation is written to address the necessary components of an aqueous suspension of hydrophobic polyhydroxyalkanoate (PHA) particles for use as a functional barrier coating of paperboard. PHA aqueous suspension functional barrier coating is capable of imparting superior barrier properties to water, water vapor, and function as a heat sealable adhesive. The remainder of the thesis is divided into five chapters discussing the development and application of such a coating.

Chapter 2 discusses PHA polymer properties for a suspension coating and its advantages as a functional barrier coating of paperboard. A specific copolymer of PHA, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) containing 5-8% comonomer is chosen because of its melting transition below thermal degradation and above the temperature of most food service. The dispersibility of hydrophobic PHA particle size is discussed as a function of the particle size by volume. The influence of dispersed PHA weight percent on film structure recovery is examined, and the best loading of PHA into suspension was determined. Impact of PHA coatings on a substrates barrier to water is determined using the Cobb value and water vapor transmission rate. Lastly, a method of determining PHA heat sealability is detailed and PHAs potential as a heat sealable coating is discussed.

Chapter 3 details a system of surfactants and their necessity in order to dispersing hydrophobic PHAs in water. Surfactant chemistry is discussed, and nonionic surfactants are chosen to disperse PHA. The hydrophilic lipophilic balance is used to formulate a dispersant system for PHA using a mixture of a highly polar and a nonpolar nonionic surfactant. The lowest necessary concentration of that surfactant system to disperse 45% weight amount of surfactant used is then determined using rheology. Lastly, a thermally induced repeatable thickening phenomenon encountered is presented and a solution is given.

In Chapter 4 a rheology modifier xanthan gum is identified as suitable for application with PHA. The addition of this rheology modifier provides further stability to a PHA suspensions and was found to greatly reduce sedimentation of dispersed particles over time. Superior xanthan gum rheology modified PHA suspensions are discussed as a means to reduce coating defects prior to ovening, which is shown to be determinable by a the 3-interval thixotropy test capable of simulating the coating procedure.

In chapter 5 reduced nucleation kinetics of PHA copolymers is discussed as a dilemma. Polarized optical microscopy and differential scanning calorimeter are used to determine improvement in nucleation rates of dried PHA suspensions. Nucleation rates are greatly improved by using homopolymer polyhydroxybutyrate as a heterogenous nucleating agent. This system is revised by adding a second nucleating agent capable of increasing the temperature processing window.

Lastly, chapter 6 summarizes the previous chapters and discusses future directions and work that are important to the success of an aqueous suspension coating of PHA on paperboard.

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CHAPTER 2

APPLICATION AND CAPABILITIES OF POLYHYDROXYALKANOATE AS AN AQUEOUS SUSPENSION COATING CAPABLE OF FUNCTIONAL BARRIER PROPERTIES[1].

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[1] Tull, Scott. "Application and Capabilities of Polyhydroxyalkanoate as an Aqueous Suspension Coating Capable of Functional Barrier Properties." To be submitted to ACS Biomacromolecules

Abstract:

To reduce the amount of waste accumulated in landfills the use of environmentally persisting plastics can be replaced with a biologically degradable plastic alternative such as polyhydroxyalkanoate (PHA.) PHAs copolymers are a wide class of aliphatic thermoplastic polyester produced by bacteria that naturally degrade in the environment. The single use application of paperboard coatings is exceedingly un-recycled, generally due to the difficulty in reclaiming paper fibers from the most common barrier coating of low-density polyethylene (LDPE.) This can be alleviated by the replacement of common performance barrier coatings on paperboard with PHA, which provides advantageous end of life properties and the ability to efficiently recover and reuse paper fibers. Additionally, application of PHA as a paperboard coating requires no volatile organic solvents or costly extrusion coating due to the particle size of PHA directly out of the cell being idea for suspension in water. A medium chain length PHA comonomer poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) was chosen based on melting point and shown to have advantageous functional barrier properties.

2.1 Introduction

Low cost and readily available paperboard provides mechanical strength and flexibility to a majority of packaging products though it suffers from high permeability to water and oxygen vapors due to its high porosity and polar chemical structure [1]. The issue of permeability with paper is typically remedied through surface treatment such as barrier coating which provide necessary improvement allowing coated paperboard to contain greasy food or boiling liquid[2]. Many paper products are extrusion coated in polyolefin such as low-density polyethylene, a low-cost material, but not without consequence to papers end of life.

Once paperboard is coated in polyolefin its end of life is greatly limited due to polymer encapsulating paper fibers. Further, the use of fresh paper fibers and virgin LDPE plastic is far cheaper the cost to recycle used materials, and so paper cups are rarely recycled[3]. As an alternative to extrusion coatings, water based suspension coatings typically require less processing and utilize water in place of volatile organic solvents. Unfortunately, waterborne coatings suffer from compromises such as the high water permeability of ethyl vinyl alcohol or the high cost of polyurethane which also has limited functional properties such as heat sealability [4, 5].

For a polymer to be capable of aqueous suspension coatings the polymer must be either soluble or capable of suspension in water. Further, aqueous suspension stability and uniformity of produced films are dependent on particle size[6]. The dispersed phase of suspensions must be free of agglomerates and of uniform particle size distribution near the colloid range of 1nm-1μm [7]. The natural granule form of PHA created by bacterium is advantageous for creating a aqueous dispersion, since PHA granules produced are typically a 1-2μm in size with a narrow particle size distribution[8]. Having as fine a particle size as possible increases the stability of the suspension. Additionally, reducing particle size also reduces film formation temperature[9]. This gives PHA an advantage over materials that are produced as large particles and must be reduced to a small particle size through highly inefficient milling methods.

Polyhydroxyalkanoate (PHA) is a material with great potential as a waterborne coating for paperboard. Coatings of PHA are capable of flexibility without cracking due to a low glass transition. PHA melts above the temperature of food service allowing film formation during production of the article but remaining solid for consumer use. Since PHA is produced near the colloid range in vivo it is capable of stable suspensions with minimal processing. Literature reported barrier properties to water vapor and liquid are encouraging compared to commodity plastics[10, 11]. Additionally, the thermoplastic nature of PHA allows for functional advantages such as heat sealing and reprocess ability.

2.2 PHA Polymer Properties:

PHA adds value to the substrate through environmentally conscious coatings requiring no volatile organic solvents or petroleum products, while PHA coated substrate also have an end of life capable of recycling or biological degradation. PHA polymer is the backbone that holds the parts of a coating together upon application and subsequent curing, but it must be able to be dispersed and remain in suspension until after application on the intended substrate. This requires a polymer having particle size distribution capable of long-term suspension stability.

PHA properties are influenced by the chemistry of the monomers that make up the polymer. An intimate understanding of chemical influence of PHA monomer on PHA final properties is important to be able to choose and tailor a copolymer appropriate to the application at hand. In the case of PHA suspension coatings on paperboard with intended application as single use beverage containers or food containers, a coating must be able to provide properties such as water penetration resistance, reduction to water vapor transmission rate, and ability to heat seal. The following sections summarize PHA as a material capable of stable suspension and coatings improving paperboard.

2.2.1 PHA Comonomer

PHAs are classified by their monomer carbon chain length as either short chain length (SCL) or medium chain length (MCL), which have 3-5 or 6-15 carbons in length[12]. Copolymers can also be created which contain multiple monomers, which can include both SCL and MCL monomers. Monomers incorporated into the polymer are determined by many variables such as feedstock, growth conditions, and organism genetics[13, 14]. A homopolymer can be produced by feeding a single monomeric building block such as hexanoic acid, or a copolymer can be created by feeding a fatty acid source such as canola and using an organism capable of incorporating multiple monomers[15].

Material properties such as melting point (T_m), crystallinity (X_c), glass transition temperature (T_g), and physical properties of the polymer are dependent on monomer chain length. Further, by incorporating differing amounts of more than one copolymer allows for fine tuning of the thermal and physical properties by controlling the abundance and length of pendant aliphatic chains extending from the polymer’s backbone, especially copolymers combining both SCL and MCL such as poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)[16]. PHA polymers produced from varying carbon sources such as waste products and oils typically are found to exist as a blend of many different comonomer-fraction components, or potentially many different comonomers incorporated in a compositional distribution. For example, when a PHA polymer is fractionated by solvent/nonsolvent techniques, it can contain a distribution of polymer chains mostly composed of low comonomer content and some varying amount of polymer chains composed of high comonomer content[17]. This compositional distribution can have large effects on polymer properties, such as broadened or multiple melting points, crystallization rates, and mechanical properties due to immiscibility[18].

2.2.2 Thermal Properties

PHA thermal properties are heavily dependent on polymer composition and copolymer. Highly crystalline pure homopolymer polyhydroxybutyrate (PHB) experiences a melting transition at 175°C but thermogravimetric analysis reveals that PHB begins to degrade at that same temperature[19, 20]. PHA degradation is heavily influenced by the presence of water or air and chemical formation of crotonic acid through advantageous deprotonation and beta elimination pathways, which can then accelerate degradation by further deprotonation or transesterification[21]. This degradation causes fouling of material properties such as retarding crystallization, diminishing barrier to liquids or gasses, and destruction of mechanical properties[22-24]. Because of this, applications seeking to use homopolymer PHB as a thermoplastic have found limited success due to degradation occurring while the material is melted.

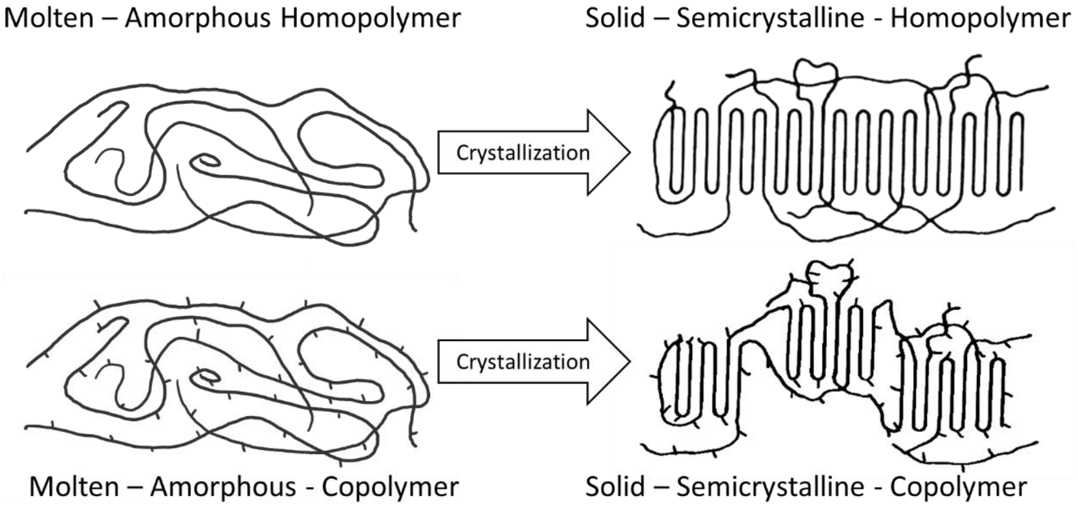
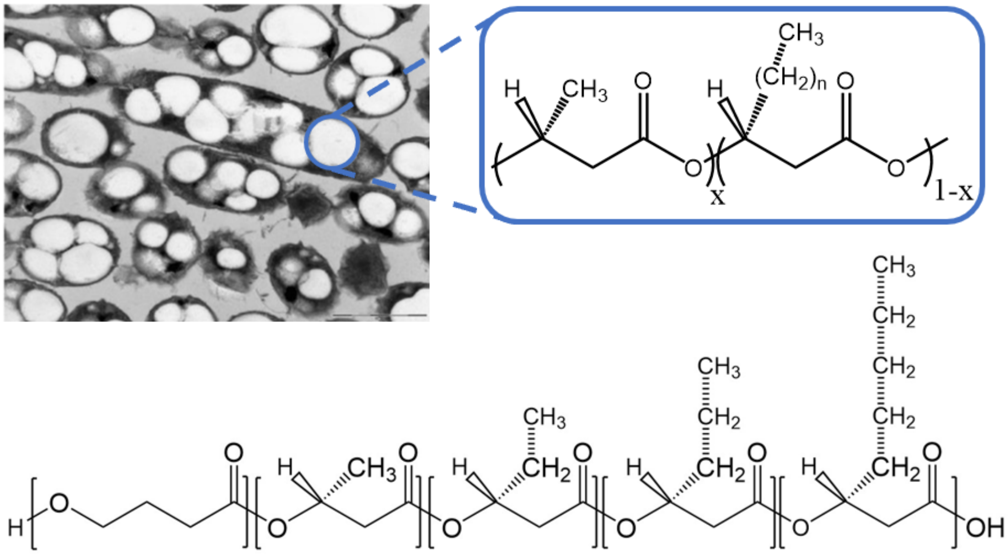


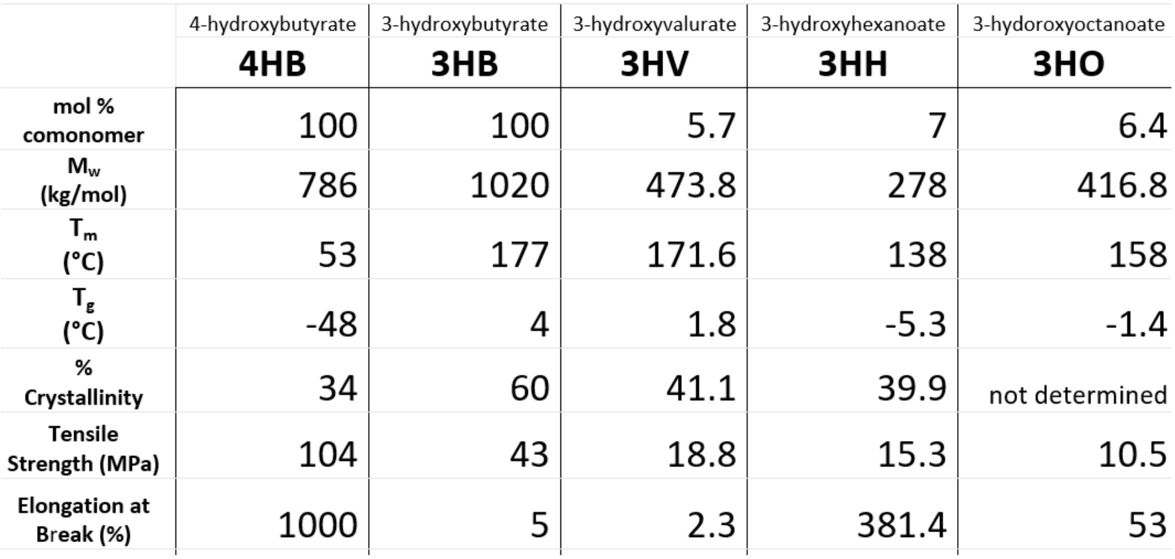
Figure 2-1: The formation of lamella during crystallization of PHB and PHA copolymers, where the point defects of comonomer as shown excluded from the lamella.

Fortunately, upon incorporation of other monomers, a copolymer melting transition can be dropped well below the decomposition onset by disrupting crystallinity. This effect is most pronounced when an MCL monomer is blended into a mostly SCL monomer polymer, where the pendant side chain is left unincorporated into the bulk crystallinity[25]. This phenomenon of reduced crystallinity through “defects” of MCL copolymers being excluded from crystallized SCL lamella is depicted in figure 2-2[26-30]. For example, inclusion of 10% SCL monomer 3-hydroxyvalerate (3HV) results in a polymer melting at 163.2°C, while inclusion of 10% MCL monomer 3-hydroxyhexanoate (3HH) reduces the melting transition to 127°C. A summary of different PHA copolymers and the impact of copolymer content on material properties is shown in Figure 2-3 where pure or comonomers with PHA are indicated by mol % comonomer[28-31]. By utilizing the phenomenon of comonomer inclusion depressing melting temperature, a PHA can be melted below its thermal decomposition onset, allowing thermal processing and use as a thermoplastic.

While the melting and crystallization may change drastically upon addition of comonomers, glass transition temperatures changes are more subtle. The glass transition (Tg) of homopolymer PHB begins at 4°C and tends to vary between -10 and 10°C in poly(3-hydroxybutyrate-co-3-hydroxyvalurate) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) copolymers depending on comonomer molar ratios[32]. This is advantageous since copolymers can be more flexible but does not largely impact applications since the polymers Tg is always below room temperature.

Incorporation of MCL copolymers advantageously depresses a PHA melting transition by disrupting crystallization. But as crystallization is disrupted by increasing MCL copolymer the PHA relative crystallinity is reduced. This reduction in relative crystallinity results in a disadvantage of reduced crystallization rates. Both the crystallization onset and peak are depressed by comonomer incorporation into PHAs, and if too high of MCL comonomer is incorporated cold crystallization will be exhibited[33].





	4-hydroxybutyrate **4HB**	3-hydroxybutyrate **3HB**	3-hydroxyvalurate **3HV**	3-hydroxyhexanoate **3HH**	3-hydoroxyoctanoate **3HO**
mol % comonomer	100	100	5.7	7	6.4
M_w (kg/mol)	786	1020	473.8	278	416.8
T_m (°C)	53	177	171.6	138	158
T_g (°C)	-48	4	1.8	-5.3	-1.4
% Crystallinity	34	60	41.1	39.9	not determined
Tensile Strength (MPa)	104	43	18.8	15.3	10.5
Elongation at Break (%)	1000	5	2.3	381.4	53

Figure 2-2 Structure of different PHA monomers and the properties of their polymers when pure or comonomers with PHA as indicated by the mol % comonomer. Note that molecular weight is given for comparable.

Cold crystallization is crystallization that occurs upon heating after the polymer has been previously cooled below its glass transition and is a result of incomplete polymer crystallization for a particular heating rate and time[34].

When a PHA is slow to crystallize this can negatively affect the materials application. For example, a PHA may be tacky and act as an adhesive before crystallization, resulting in unwanted adhesion to processing equipment or materials.

2.2.3 Mechanical Properties

Mechanical properties of PHAs are based on the comonomer unit, percentage comonomer, and comonomer sequence distribution. Pure homopolymer polyhydroxybutyrate is highly brittle, but by utilizing copolymerization physical properties similar to polyolefin, polyethylene, and polypropylene can be achieved[35, 36]. Incorporation of comonomer reduces T_g due to an increase in segmental motion between polymer chains, which greatly increases flexibility of PHA copolymers. If the incorporated comonomer is increased in length, such as hexanoate to a decanoate, a large decrease in young modulus is observed [37]. Copolymers such as poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) show a much longer elongation at break than poly(3-hydroxybutyrate-co-3-hydroxyvalurate)[27]. Tensile experiments show similar results to melting point depression where incorporation of MCL monomers have a much greater effectiveness over SCL monomers, and in general a higher tensile strength is traded for a substantial increase in elongation at break, and toughness[38]. By controlling the amount and type of copolymer in a PHA, a PHA copolymer properties can be tailored similar to conventional polymers such as low-density polyethylene or isotactic polypropylene[39].

2.2.4 PHA Particle Size

Particle size, chemical, and physical properties of polyhydroxyalkanoate (PHA) are based on the organism used, media chemistry, and growth conditions[40]. When the polymer is ready to be harvested PHA producing cells are lysed then cellular and growth material must be removed to purify polymer granules. Upon lysis PHA is an amorphous granule of polymer, once cellular material is cleaned from the polymer granule it can begin to crystallize from the outside in[41]. While a PHA has not yet developed its crystalline shell, the amorphous granule is deformable and liquid like flow is possible enabling separate amorphous granules to coalesce[42]. However, once the outer crystalline granule shell has formed the particle size is locked in. Because of this, the process to purify and render PHA polymer usable has a significant impact on the particle size distribution of PHA.

Dispersion properties such as film formation and dispersion stability are based on the properties of the dispersed particle. Important particle properties include particle size, shape, chemistry, and surface charge. As observed by optical microscopy particles are capable of being varying degrees of oval/spherical shape. Since PHA particles are made up of aliphatic polyester the particles are hydrophobic in nature. Because of this PHA particles do not readily disperse in water without help from surface active agents[43].

Since PHA particles are not typically mono disperse it is important to describe a PHA particle size in terms of its particle size distribution. A useful metric of particle size distribution is the volume weighted distribution, where the contribution of a particles diameter in the distribution is related to the particles volume[44]. From this we can draw convenient parameters based on maximum particle size for a specific percentage volume of the sample population. For example, median particle size by volume (D50 or Dv50) defines the maximum particle diameter below which 50% of the sample volumes exist. D10, D50, and D90 are commonly used evaluate a particle size distribution[45].

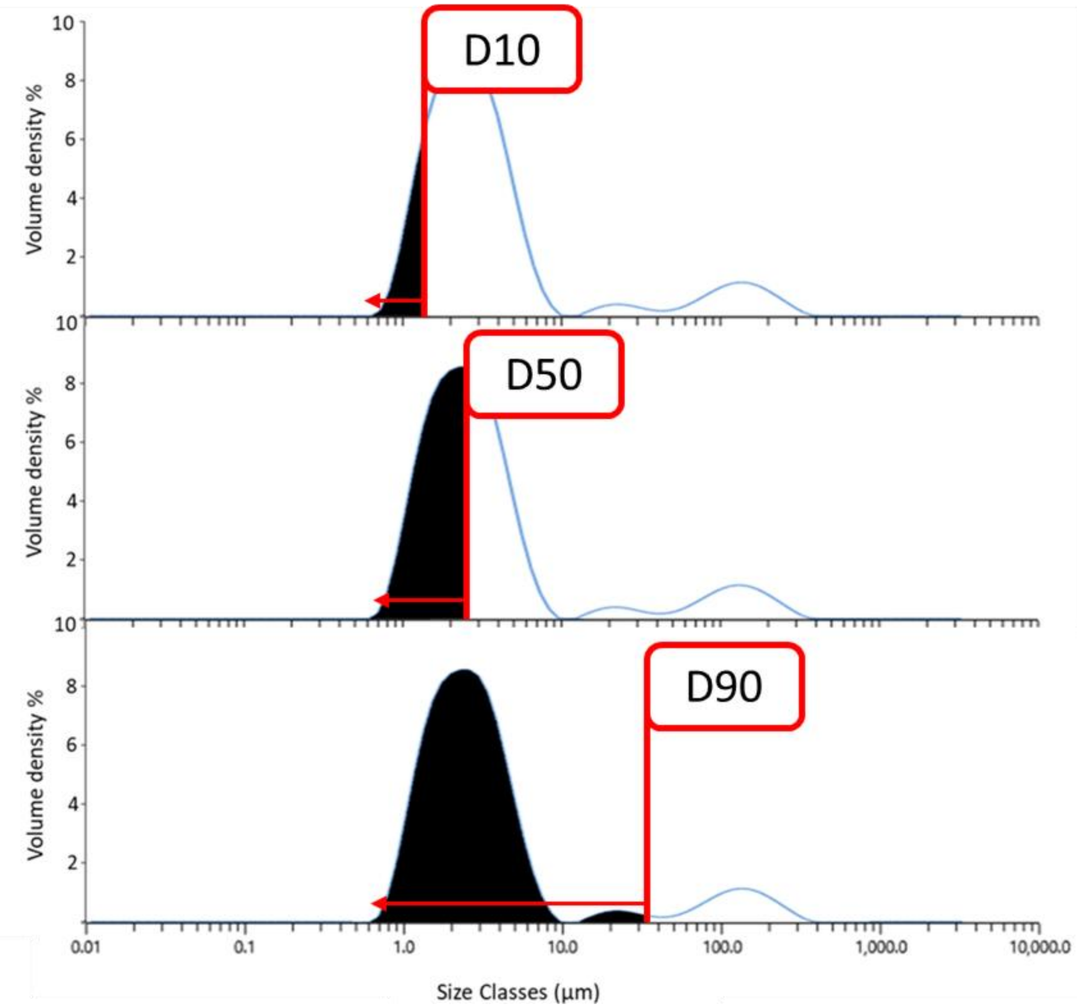


Figure 2-3: Graphical depiction of percentage volume below a specific particle diameter. For example, D50 refers to a particle diameter 50% of all measured particles of the population are smaller than.

When a PHA flocculates, it falls out of suspension in the dispersion and forms a solid layer of sedimented polymer on the bottom of the container. This can be estimated using equation 2-1 where if value on the left of equation is greater than the right value (kT), sedimentation of particles occurs[46].

$$\frac{4}{3}\pi R^3 \Delta\rho g L > kT \qquad \textbf{Eq 2-1}$$

Where R is the particle radius, Δρ is the difference in density between the particle and the medium, g is acceleration due to gravity, L is the vessel length, k is the Boltzmann constant, and T is the absolute temperature. As shown in the equation, particle radius R is cubed, having significant impact on whether sedimentation will occur. The sedimented layer is highly difficult to shear apart and redisperse due to compaction and surface area, sometimes even harder to disperse than the original polymer granules.

2.2.5 Coating Barrier Properties

When selecting packaging for perishable goods it is important to keep in mind the permeability of the packaging. How able a material is to prevent transmission of liquids or gasses is defined as that material's barrier properties[47]. Liquids that are of particular interest are water and grease, while gasses of interest are oxygen or water vapor. The relative importance of barrier properties is determined by the intended application of a coated substrate. For example, a coffee cup should have improved barrier to water or oil and grease, but gas transmission is of little importance. Tests for barrier properties follow industrial standards such as ASTM or TAPPI.

Coat weight of PHA coatings added to the substrate is an important metric effecting the properties imparted by that coating. Adding more coat weight can improve barrier properties by increasing the thickness of PHA binder a liquid or gas must pass through to penetrate the article. There are many methods used to evaluate coat weight during the application process such as infrared sensors, but because complications by PHAs low IR absorbance the most reliable method of coat weight measurement is gravimetric[48]. For coated laboratory substrates the sample is weighed before coating and then weighed again after conditioning at ambient temperature and humidity, then coat weight can be calculated using equation 2-2.

$$\boldsymbol{coat\ weight\ (gsm) = \frac{M_f - M_i}{A} \times 100^2} \qquad \textbf{Eq 2-2}$$

Where is M_f the mass of the sample after coating in grams, M_i is the initial mass in grams, A is the surface area coating is applied to in cm^2, and 100^2 is the factor to convert from cm^2 to m^2.

Susceptibility to water penetration is determined by the water absorption Cobb test and is expressed in a Cobb value or the mass of water absorbed in a duration of time by $1m^2$ of paper under 1cm of water[49]. The duration of the test is noted and should be given with the measured Cobb value, and in general a lower Cobb value with a longer test duration implies less water absorptiveness.

The value is calculated for a 10cm^2 ring sample using the equation 2-3 where M_f and M_i are the substrate final mass and initial mass, respectively.

$$\boldsymbol{Cobb\ value\ (gsm) = \left(M_f - M_i\right) \times 1000} \qquad \textbf{Eq 2-3}$$

Water vapor transmission rate (WVTR) is defined as the rate of water permeation through a film of known thickness at a certain temperature and humidity. WVTR is calculated by equation 2-4:

$$\boldsymbol{WVTR\ (g/m^2 \cdot 24hr)\ =\ \frac{M_{water}}{A \times T}} \qquad \textbf{Eq 2-4}$$

Where WVTR is expressed in terms of g/m^2/24 hr, is the mass of water found passing through the sample, A is the surface area of sample tested in m^2, and T and is the time in days. WVTR is commonly tested according to ASTM F1249 where a film is pressed and sealed between two chambers and variable controlled % relative humidity nitrogen test gas passes through passes through one chamber, which permeates through the sample over time and enters the other chamber[50]. The other chamber contains carrier gas of ultra-high purity nitrogen gas passes through and collecting any water vapor that passes through the sample, the water vapor is carried to the infrared sensor and measured. A problem commonly encountered when measuring WVTR of coated substrates is that of the edge effect, where since the coating is not applied to substrate edges an increased permeation through the porous substrate is observed. To avoid the edge effects of a substrate the coating polymer is prepared as a film and evaluated without the substrate.

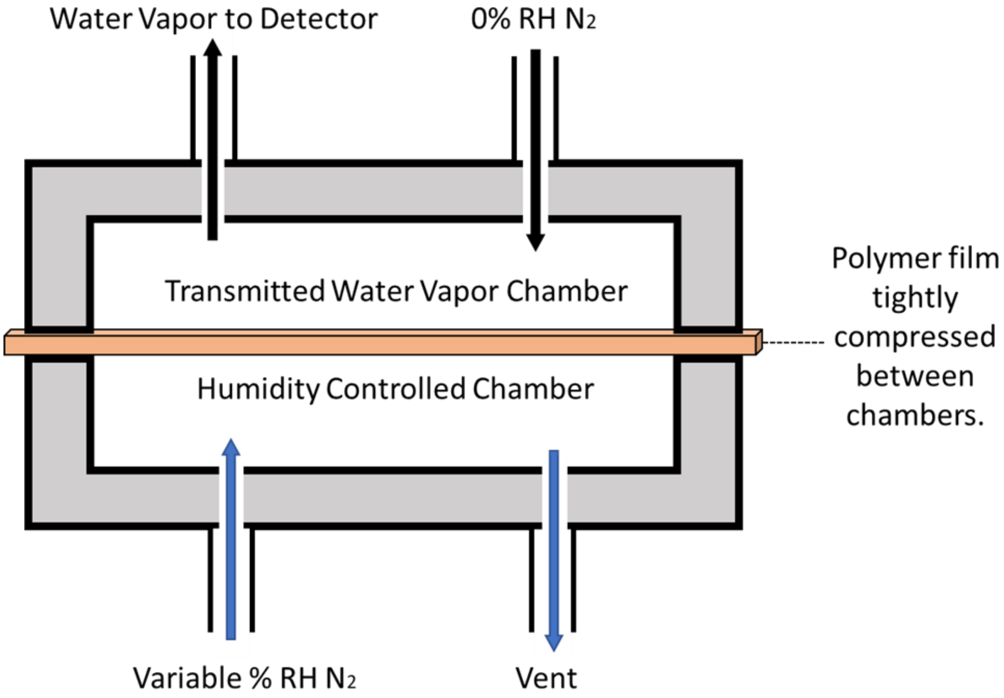


Figure 2-4 Water Vapor Transmission Rate measurement of polymer film substrates as specified in ASTM F1249.

2.2.6 Heat Sealing of PHA coatings

During the paper coating process, the paper is unwound from a roll, coated, the coating is cured, and the paper is rerolled. For the paperboard to take the form of a finished article such as a food to go container or a beverage cup it must be converted. To form the coated paperboard into shape the paper is cut, creased, and folded[51]. Food containers and boxes must be sealed to retain shape and provide barrier properties to its contents. Defects in the seal lead to mechanical failure of the formed article or breech in contamination by liquids, gasses, or microbial contamination[52].

Thermoplastic coated paperboard allows for a formed article to be sealed through the process of heat sealing. This involves heating the coated substrate layer, joining of substrates under pressure, and subsequent cooling to solidify the coating and seal the substrates together. The use of a thermoplastic thereby eliminates the necessity of a separate adhesive to adhere coated paper substrates together. Typically used heat sealing polymers are waterborne acrylate or extruded polyolefin[53, 54]. Waterborne coatings can utilize the porous nature of paper advantageously by penetrating further into the substrate and improves adhesion mechanical strength between adhered substrates[55].

A material capable of providing good heat sealability should have a melting well below paper scorching temperatures and low molten viscosity to flow between substrate paper fibers[56]. For paperboard coating heat seals to be considered acceptable the paper fiber must be torn and the coating should not delaminate without tearing paper[57]. Delamination is caused by poor bonding between the PHA coating and the substrate, and in case of paper coatings requires that the molten coating penetrate and bind paper fibers on both substrates. Additionally, the coating must have enough strength that the substrate mechanically fails before the heat sealable coating mechanically fails. Lastly, crystallization of PHA binder should be fast enough to set up in the time required by the application.

2.3 Materials:

Span 80, tween 20, and xanthan gum were acquired from VWR chemical. 18.2mΩ deionized water produced at the New Materials Institute at UGA. The

New Materials Institute of the University of Georgia produces polyhydroxyalkanoate copolymers on campus. These polymers were processed using detergents and other surfactants then dried and characterized.

2.4 Experimental:

2.4.1 Differential Scanning Calorimetry

DSC experiments were performed on a TA instruments Discovery 250 DSC. Thermal transitions such as melting peak, crystallization peak, and glass transitions of PHA were determined through differential scanning calorimetry (DSC.) Samples were heated from 25°C to 180°C at a ramp rate of 10°C/min and were then cooled to -20°C at -10°C/min. A second heat up was performed on some samples to investigate crystallization behavior and whether a material experienced cold crystallization.

2.4.2 Nuclear Magnetic Resonance Spectroscopy

PHA polymers were dried under vacuum before samples were dissolved in deuterated chloroform at a concentration of 5 mg/mL. Samples were characterized using a Varian/Agilent DD 600MHz using standard proton nuclear magnetic resonance (NMR) spectroscopy protocol and 64 scans. Data was then worked up using Mestrelab Mnova software to assign and integrate peaks. To calculate percent 3-hydroxyhexanoate in a copolymer a simple ratio was used as shown in equation 2-5.

$$\%\,\boldsymbol{3HH} = \frac{\boldsymbol{I_{3HH}}}{\boldsymbol{I_{3HB}}} \times \mathbf{100} \qquad \textbf{Eq 2-5}$$

Where %3HH is the percentage of 3HH comonomer relative to 3-hydroxybutyrate (3HB) monomer, I_{3HH} is the peak integration for 3HH monomer methyl protons, and I_{3HB} is the peak integration for 3HB monomer methyl protons.

2.4.3 Cryogenic Scanning Electron Microscopy

Two PHA suspensions were chosen based on their particle size distribution and submitted to the USDA for cryo-SEM analysis.

2.4.4 Laser Diffraction Particle Size Analysis

A Malvern Mastersizer 3000E equipped with a Hydro MV automated dispersion unit was used to analyze the particle size distribution of PHA polymers. This unit allows for measurement of up to 600mL of dispersant and is capable of sonication and agitation to keep sample in suspension and deagglomerated. Deionized water was used to fill the measurement cell and mixing chamber. Sample of PHA suspension were added until the Mastersizer measured an obscuration of 10%. An RI of 1.6 was chosen for PHA and measurements were taken in triplicate.

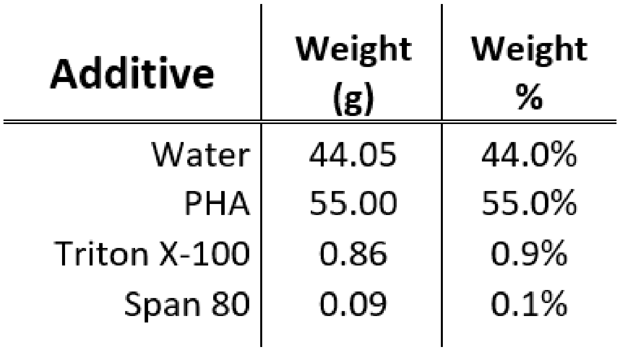
2.4.5 PHA Suspension Preparation

Once suspension mixture components were weighed out, they were combined and mixed under high shear to achieve homogeneity. To break up agglomerates of PHA granules and finely distribute the suspension's additives a sonication cavitation mixing system is used. The apparatus used to provide cavitation is a Sonomechanics BSP-1200 with a 1200-watt source. To combat heat up of suspension dispersant and prevent boiling the sonicator was run in 30 second intervals, cooling to room temperature after each sonication interval.

2.4.6 Dispersibility Testing

Multiple polyhydroxyalkanoate materials of similar comonomer content and physical properties were acquired and evaluated based on their particle size distribution using laser diffraction. The maximum particle diameter below which 90% of the sample volumes exist (D90) was calculated and recorded for each of the PHA materials analyzed. A suspension of each polymer was then produced at the same weight percent loading of PHA and suspension additives according to table 2-1.

Table 2-1. PHA particle size dispersibility testing formulation for PHA suspensions.



Additive	Weight (g)	Weight %
Water	44.05	44.0%
PHA	55.00	55.0%
Triton X-100	0.86	0.9%
Span 80	0.09	0.1%

Once a suspension was produced for a PHA sample, the sample was passed through a coarse mesh of 500µm. The laser diffraction particle size distribution was determined again to verify the dispersed particle size distribution. The remainder of each sample was characterized based on the total amount of PHA solids dispersed using a gravimetric moisture balance, which evaporated all volatiles by heating the suspension to 150°C and calculated the % solid using equation 2-6.

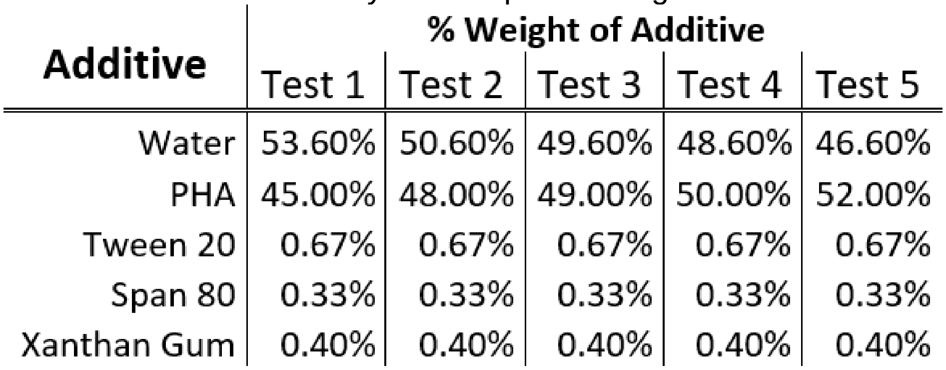
$$\% \boldsymbol{Solids} = \mathbf{100} - \left(\frac{\boldsymbol{Weight\ Loss}}{\boldsymbol{Starting\ Weight}} \times \mathbf{100}\right) \qquad \textbf{Eq 2-6}$$

Where the weight loss is the weight lost by drying, starting weight is the initial sample weight, the fraction is converted into percentage by multiplying by 100, and is subtracted from 100 to convert to a weight percent solids.

2.4.7 Optimum PHA Weight Percent for Coatings

PHA suspension coatings were produced using additive formulations shown in table 2-2. Once the suspensions were prepared, they were stirred covered overnight using stir bar to remove any air bubbles created when the suspension was produced.

Table 2-2. PHA suspension coatings produced to evaluate the influence of suspended PHA % wt. on stability of film upon coating.



Additive	**% Weight of Additive**				
	Test 1	Test 2	Test 3	Test 4	Test 5
Water	53.60%	50.60%	49.60%	48.60%	46.60%
PHA	45.00%	48.00%	49.00%	50.00%	52.00%
Tween 20	0.67%	0.67%	0.67%	0.67%	0.67%
Span 80	0.33%	0.33%	0.33%	0.33%	0.33%
Xanthan Gum	0.40%	0.40%	0.40%	0.40%	0.40%

After overnight deaeration, PHA suspension samples were tested on a TA discovery hybrid rheometer set up with 40mm parallel plates geometry equipped with a solvent trap to retain humidity and reduce coating evaporation during testing. Amplitude and frequency sweeps were performed to determine linear viscoelastic range for each sample. The 3-interval thixotropy test was then performed as follows:

1. Low oscillatory shear to simulate behavior at rest.
2. High rotational shear to simulate structural breakdown during application.
3. A second low oscillatory shear to simulate structure regeneration after application.

The low oscillatory shear amplitude and frequency were chosen in the linear viscoelastic region after performing both an amplitude and frequency sweep. The high rotation shear step RPM was chosen to be 2000RPM. Plots of recovery over time were created using a calculated recovery % as shown in equation 2-7.

$$\% \boldsymbol{Recovery} = \mathbf{100} - \left(\frac{G'_1 - G'_3}{G'_1} \times \mathbf{100}\right) \qquad \textbf{Eq 2-7}$$

Where G'$_1$ is the average storage modulus from the low oscillatory shear step 1, G'$_2$ is the storage modulus during the low oscillatory shear step 3 at a specific time.

2.4.8 WVTR Preparation and Testing:

In order to eliminate substrate edge effects a carver pressed film of the coating material is prepared and measured in place of the coated substrate. Polymer films were prepared on a dual heated platen carver press. The platens were set at 160°C and were allowed 60 minutes to reach equilibrium. A PHA having 6.5% 3HB was chosen and three blends of PHA were produced. To produce a film, 2.5g of the PHA was sandwiched between nonstick paper. The press was actuated until reaching 5000psi pressure over 10 seconds and then 50 seconds were allowed for the polymer to fully melt and form a film. The press was then opened, and the film was placed under a flat and heavy aluminum block overnight.

After 24 hours samples were removed from beneath the heavy aluminum block and film thickness was measured in five different places using Mitutoyo calipers. Carver pressed samples of PHA were then tested using a Labthink C390 water vapor transmission rate test system. PHA film Test specimen were chosen based on having at least 10cm by 10cm of uniform film with no apparent imperfections. The tests were performed in accordance with ASTM F1249 using a cell condition of 90% RH and 25°C.

2.4.9 Heat Sealing of PHA Coatings

A heat sealer was designed according to heat seal samples specified in ASTM F2029 for making laboratory heat seals for determination of heat sealability[58]. The heat sealer relies on a 40mm bore and 25mm stroke dual guided air rod cylinder pushing a platen of width 25mm by 15mm against a cold platen of the same width. The top platen is heated using a cartridge heater moderated by a PID temperature controller. Guided air cylinder pressing is actuated and timed by a pneumatic solenoid moderated by a KT-V Koyo timer.

A PHA suspension was produced using the same formulation as in table 2-1. The coating was applied using mayer rod coating and cured at 170°C for 50 seconds. Coatings were let equilibrate overnight and then coat weight was calculated. Samples were then sandwiched coated side to uncoated paper and heat sealed using the designed apparatus. After heat sealing samples were conditioned for 1 second at room temperature and then torn to determine whether fiber tear, delamination, or no seal was noted.

2.5 Results and Discussion

Since there are a breadth of PHA copolymers and copolymer ratios it is important to choose a PHA material with properties necessary for the intended application. Shown in figure 2-5, the New Materials Institute of the University of Georgia can produce PHA polymer of varying chemical and thermal properties. Determination of comonomer content ratio was determined by NMR spectroscopy. Figure 2-5 Shows a proton NMR plot where the ratio of comonomer methyl protons is used to calculate 3HH comonomer %. For PHA paperboard coatings in food service application a target of 5-8% 3HH poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) copolymer was chosen in order to have a melting transition peak of 140-143°C.

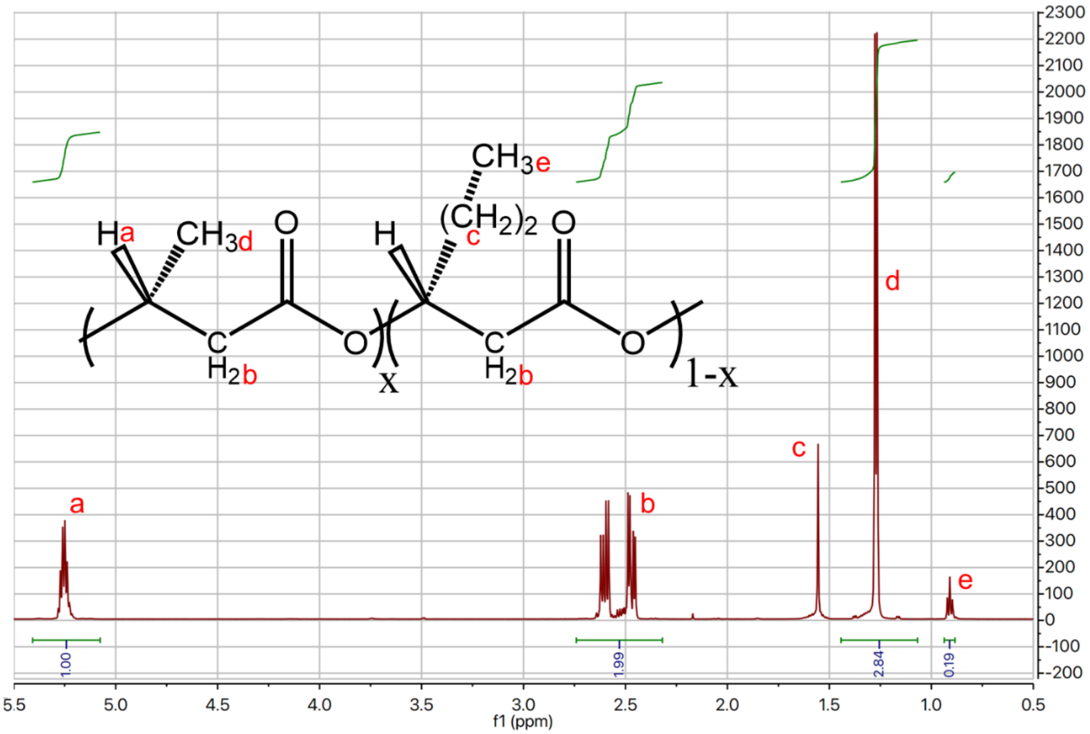


Figure 2-5 Proton NMR of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) with peak assignments.

. A melting transition peak of 140-143°C is optimal since it allows the coated paperboard finished product to have a wide range of applications requiring high or low heat, such as hot beverage and frozen food containers. A PHA polymer that undergoes melting transition below 150°C is molten far enough below the autocatalytic decomposition point such that thermal degradation is limited. Additionally, between 5-8% 3HH PHA polymers crystallize fast enough that the crystallization peak occurs above 60°C and no cold crystallization is observed.

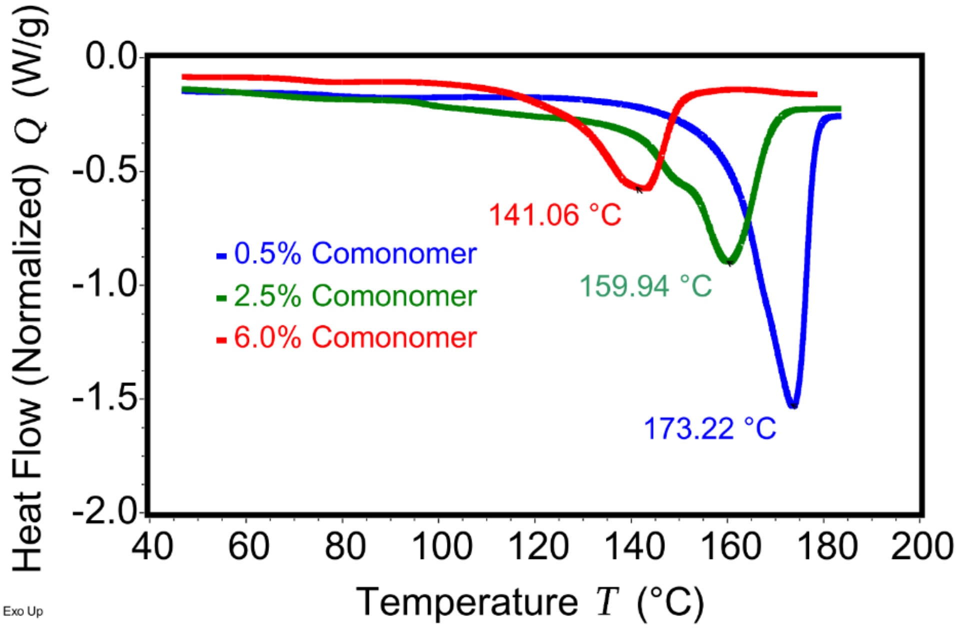


Figure 2-6: First heat up melting transition DSC plot for poly(3-hydroxyalkanoate-co-3-hydroxyhexanoate) with varying amount of 3-hydroxyhexanoate comonomer percentage.

2.5.1 Impact of PHA Particle Size on Dispersibility

Laser diffraction particle size tested PHA suspensions show high variability in particle size distribution as shown in Figure 2-7. From these results its apparent that some PHA polymers produced are tight in distribution such as copolymer 3, some have a couple of particle size modes such as copolymer 1, and some PHA have multimodal distributions containing particle diameters up to 0.8mm. To further understand these results samples having high D90 (wide particle size distribution) and samples of low D90 were submitted to the USDA for cryo-SEM testing.

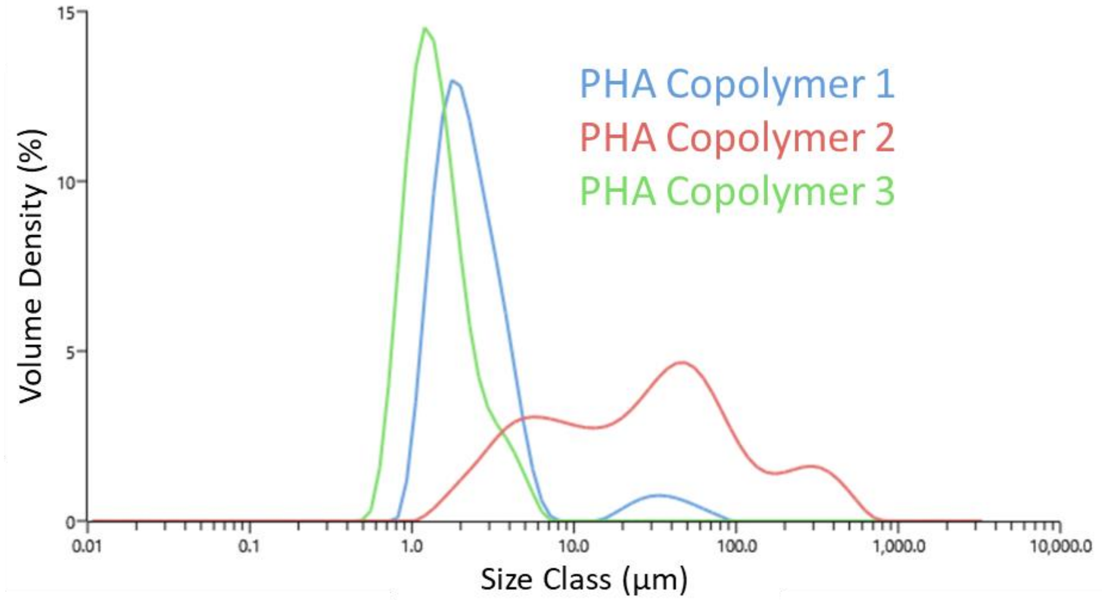


Figure 2-7: Particle size distribution of PHAs as measured by laser diffraction.

As shown in figure 2-8 and 2-9 the results of the USDA cryo-SEM show that PHA samples with wide particle size distribution are drastically different in aspect ratio than monomodal narrow particle size PHA. Both samples submitted to the USDA were prepared as PHA suspensions similarly, but they dispersed differently. The sample having high aspect ratio shown in 2-9 was unable to mix into a homogenous suspension and was found to be unstable to sedimentation. The next testing performed compared PHA samples based on their D90 particle size distribution and dispersed to a high PHA weight percent in order to determine how dependent PHA dispersibility is on D90 particle size.

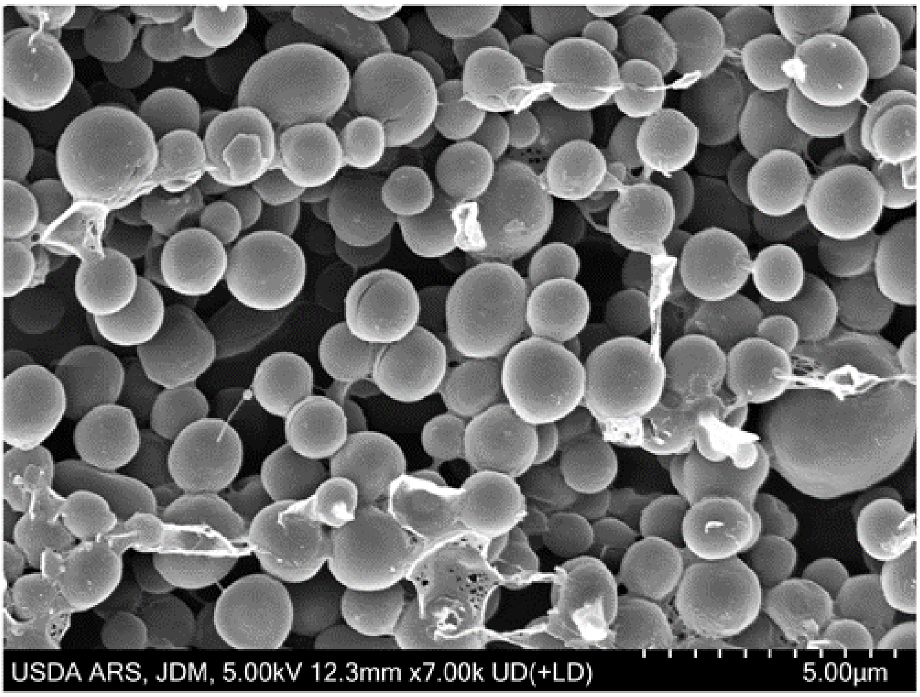


Figure 2-8 PHA granules imaged by cryo SEM.

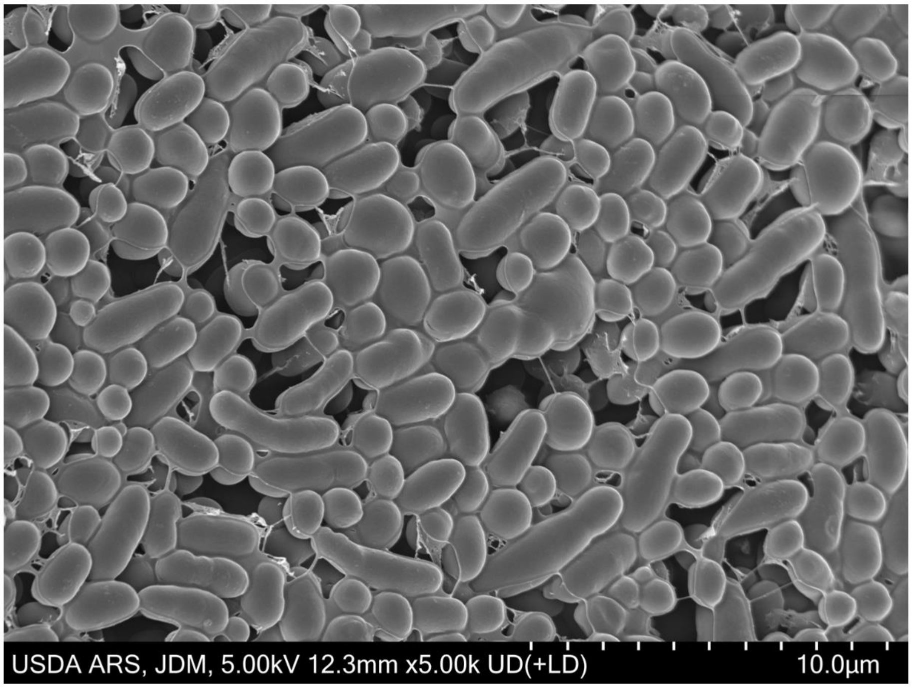


Figure 2-9 PHA granules imaged by cryo SEM showing coalesced PHA granules.

As seen in table 2-3 the results of the dispersibility study show PHA weight % capable of suspension is dependent on D90 particle size distribution. It is possible to disperse a multimodal PHA of D90 greater than 10μm but reaching 50% weight of the dispersion is not possible. As particle size is increased further outside the colloid range of 1nm-1μm the particle becomes increasingly difficult to disperse. A dispersion with wide particle size distribution such as a D90 of 50μm will readily flocculate on the order of only 24 hours before settling 90 percent of dispersed polymer. As shown in the plotted experimental results in figure 2-10 PHA with D90 of > 100μm are not dispersible higher than 40% weight and may not be dispersible at all.

Table 2-3: Dispersed PHA particles, the percent volume diameter data for that PHA sample, and the total dispersed polymer (%weight of suspension.)

PHA Particle Sample	**D10 (μm)**	**D50 (μm)**	**D90 (μm)**	**Suspended PHA (% wt)**
PHA Copolymer 1	1.29	2.16	4.53	54.4
PHA Copolymer 2	3.69	28.6	192	28.5
PHA Copolymer 3	0.857	1.37	2.88	56.1

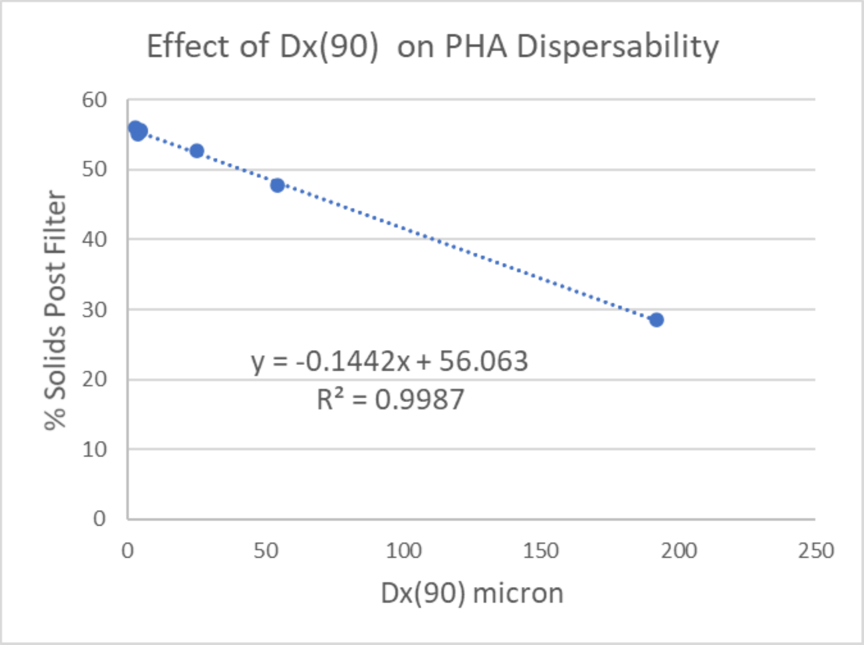


Figure 2-10: Effect of a PHA D(90) on its dispersibility.

Since the PHA particles used are uncharged the most influential dispersion property of a PHA particle is its size. Because of this the total volume fraction of PHA capable of being dispersed in a coating is related to the particle size distribution. It is possible to disperse volume fractions of PHA that are up to 50% weight of the total suspension, but in order to reach 50% weight of the total suspension the PHA used must have a monomodal particle size distribution. After multiple iterations of testing, it was found that a PHA with D90 less than 10µm monomodal particle size is paramount to production of a shelf stable containing a high-volume fraction of PHA.

A second experiment was conducted to investigate the influence of percentage of PHA suspended on stability of film upon coating. For a waterborne coating to produce a high-quality film the coating must be able to response appropriately to shear and regenerate its structure. The regeneration of structure should not be too fast to allow the coating to fill in any surface irregularities such as peaks and voids, known as leveling. Coating structure regeneration also should not be too slow as to allow “sagging” defects from gravity spreading the coating too thin and causing pits or tears[59]. Sagging and leveling are indicators of poor coating structural regeneration and were evaluated using a 3 interval thixotropy test[60].

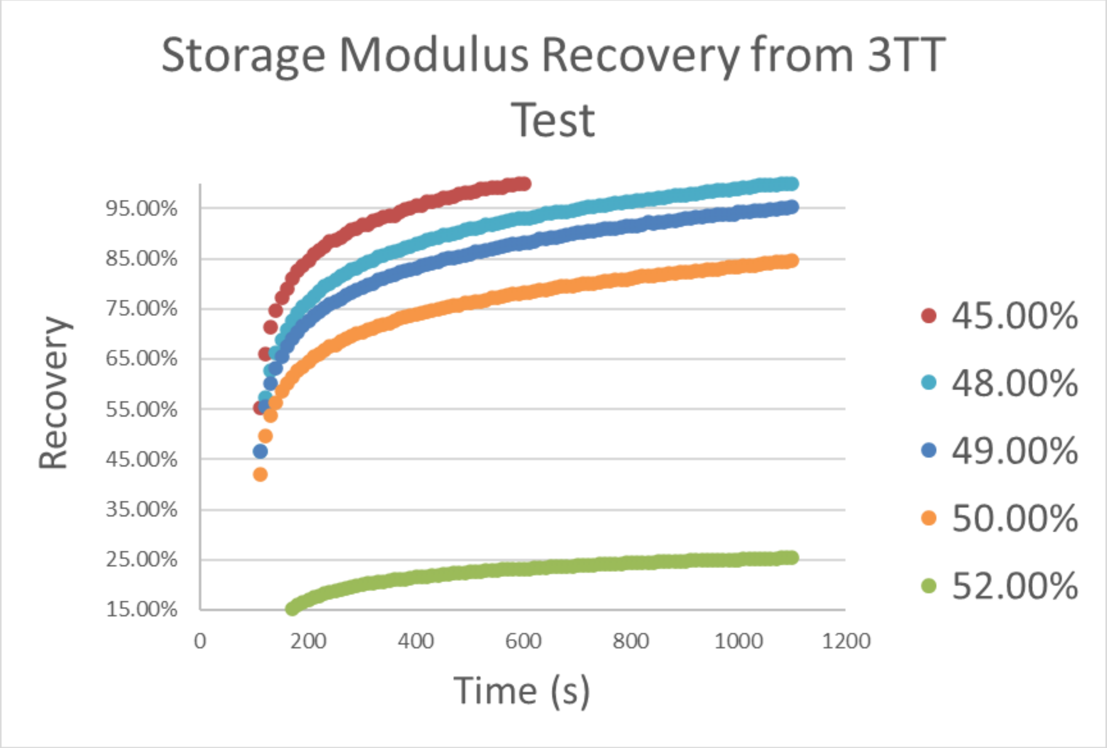


Figure 2-11: Storage Modulus Recovery of PHA suspensions of various viscosity from 3-interval thixotropy test.

A 45% weight PHA suspension is the only suspension able to fully recover its structure, while the other coatings such as 48 and 49% weight never fully recovered structure. As PHA percent weight is increased the coating is less able to recovery its structure, potentially due to instability of the suspension. Based on the results of the 3-interval thixotropy test recovery results a 45% PHA suspension is the best choice in order to avoid sagging imperfections and have the ability to level and fill in any imperfections caused by coating.

2.5.2 Barrier Properties

Two different PHA suspensions were coated onto two different paper substrates using Mayer rods size 3, 4, or 14. PHA suspension DC0618002 was used to coat a based coated paperboard with two different coat weights. Alternatively, PHA suspension 800020200215 was coated onto an uncoated substrate with either one coat or two separate coats. By using different Mayer rods, the 800020200215 single and double coatings were of similar gsm coat weight.

Table 2-4 Results of 2-minute Cobb testing for PHA coatings of varying gsm coat weight[61].

PHA	Rod Size	Coat Weight, gsm	2-minute Cobb, gsm
DC0618002	4	7.82 ± 1.96	4.92 ± 1.13
DC0618002	14	18.91	2.1
800020200215	14	17.38 ± 0.43	28.13 ± 3.66
800020200215	3,3	16.87 ± 1.44	5.17 ± 0.78

Once sample coat weight was determined a 2-minute Cobb test was performed to determine the level of improvement the coating had on water permeability of the paper substrate. The results of 2-minute Cobb testing and their value based on how the paper substrate was coated are shown in table 2-4. Results of PHA suspension DC0618002 show a decrease in water permeability when higher gsm coat weight is applied. But on an uncoated and porous substrate a coating penetrates deep into the paper and provides little barrier as shown by the 800020200215 PHA suspension coating. It is only when two discrete coatings are applied to the porous substrate that a drastic decrease in water permeability is noted.

As shown in figure 2-12 the carver pressed films of PHA allowed 3.3± 0.15 g/m^2/24 hr of moisture to permeate into the testing chamber. While PHA was not found to be less permeable to water than other common single-use plastics, it is comparable. Table 2-5 shows the WVTR of commodity plastics such as polypropylene, high density polyethylene, and polyethylene terephthalate with WVTR rates of 1.7-2.0, 0.8-1.4, and 2.9-3.6g/m^2/24 hr respectively.

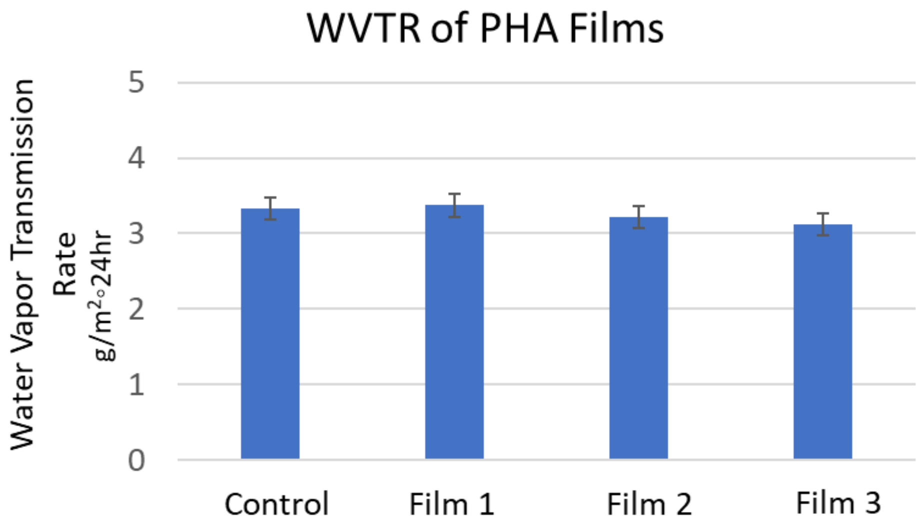
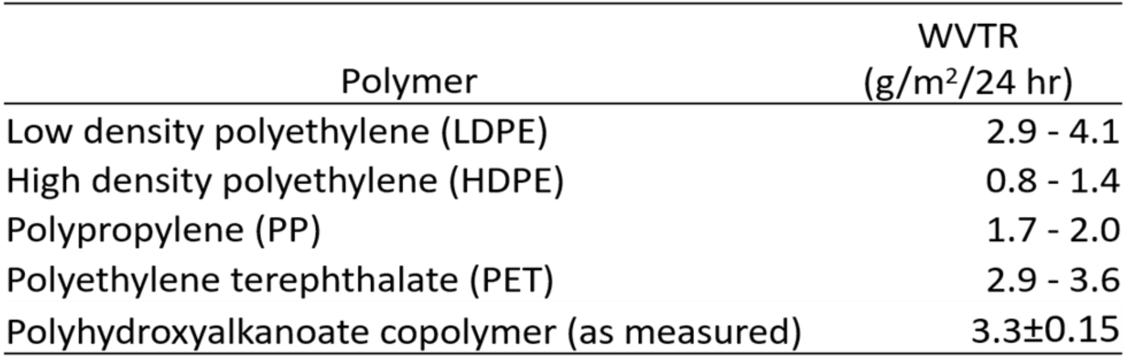


Figure 2-12: Water vapor transmission rate measured of PHA Films.

Though PHA may be far outside the range of metallized films, this shows PHA is applicable in many single use food containers. The WVTR of a PHA film may be improved by the addition of materials that create a more torturous path of transmission of water vapor through the film, such as calcium carbonate or crystalline materials that are suitable as fillers.

Table 2-5: Comparison of PHA WVTR to literature reported values of commodity plastics[62].



Polymer	WVTR ($g/m^2/24$ hr)
Low density polyethylene (LDPE)	2.9 - 4.1
High density polyethylene (HDPE)	0.8 - 1.4
Polypropylene (PP)	1.7 - 2.0
Polyethylene terephthalate (PET)	2.9 - 3.6
Polyhydroxyalkanoate copolymer (as measured)	3.3±0.15

2.6 Heat sealing of PHA Coatings on Paperboard

After tearing heat sealed samples it is apparent whether or not the two substrates were properly heat sealed based on the presence of torn paper fibers. A sample with fiber tear demonstrates substrate failure, meaning the coating correctly penetrated both substrate layers and crystallized before being torn. A sample with delamination shows coating failure, meaning the coating failed to adhere properly to either side of the substrate and broke free without any penetration into the substrate. Lastly, a no seal result should be checked for tackiness, which demonstrates a lack of crystallization in the given time.

Figure 2-13: Picture of Heat Sealer Designed according to ASTM F2029 for testing heat sealing of paper coatings and example of heat seal sample demonstrating full fiber tear.

For PHA paper coatings it was found important to dial in the interface temperature and time to melt the polymer just enough to flow into both substrates without overheating. Once the coating has penetrated both substrates it can be crystallized and provided necessary adhesion strength. If the coating is overheated crystallization is destroyed, and even if the coating can penetrate both substrates it will not crystallize in the necessary time. PHA coatings on paperboard were heat sealed at a surface temperature of 200°C with a pressing time of 1.0 seconds and pressure of 100 psi. If temperature were increased by

10°C degrees the coating would not crystallize within 1 second and was found to still be tacky, and if the temperature were decreased by 10°C the coating would not melt enough to seal.

When heat sealing paperboard PHA coatings between two substrates the substrates can be sealed with either one of the substrates being coated or both paper substrates being coated. In the case of only one substrate being coated the PHA coating must adhere to a new surface of paper, while in the case of both substrates being coated the polymer is adhering to the polymer of another paper coating. During testing of a PHA coating on a paperboard it was found that the substrate would not fiber tear upon heat sealing coated to uncoated if the coatings were not greater than 8gsm in coat weight. In the case of heat sealing coated to coated it was found that the same coating coat was necessary. Though, when the substrate was changed to a separate paperboard it was found that that substrate required at least 12gsm of coating to heat seal. This shows the necessity of troubleshooting based on what is necessary for a specific substrate.

2.7 Conclusions

Surprisingly some PHA have high aspect ratio, which contributes to lower dispersibility and limits suspension coating ability. The difference in PHA particle size distribution and morphology is unrelated to the production of a stable suspension, but it was determined that a D90 particle size of less than 10µm is necessary to produce stable suspensions. A PHA particle having D90 greater than 100µm is unable of reaching 40% weight PHA in suspension, and higher may be incapable of suspension at all. It was found that suspensions having 45% weight PHA are the highest percent PHA suspensions capable of stability and coating structure recovery post substrate application. When % PHA solids are increased above 45%, the coating is no longer able to fully recover its structure and fill defects created during substrate application.

Through analysis of many PHA polymers it was found that a PHA copolymer of 5-8% 3HH poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) is ideal for application in paper coatings. Since this PHA copolymer experiences a melting transition peak of 140-143°C it is able to be used in food service application such as hot beverage containment. The ability of this polymer coating to provide barrier properties and hold a hot beverage is evidenced by its ability to decrease water liquid (Cobb test) and vapor permeability (WVTR test.) Additionally, PHA coatings provide heat seal functionality similar to other thermoplastic coatings such as low-density. These key indicators show PHA has great promise to replace unsustainable and environmentally catastrophic single use barrier coatings having no end-of-life benefit.

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CHAPTER 3

OPTIMIZATION OF AQUEOUS POLYHYDROXYALKANOATE DISPERSIBILITY AND SUSPENSION STABILITY USING NONIONIC SURFACTANTS[2].

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[2] Tull, Scott. “Optimization of Aqueous Polyhydroxyalkanoate Dispersibility and Suspension Stability Using Nonionic Surfactants.” To be submitted to ACS Applied Materials & Interfaces

Abstract:

Polyhydroxyalkanoates (PHAs) are a class of aliphatic thermoplastic polyester produced by bacteria that naturally degrade in the environment. The particle size of PHA as produced in vivo is advantageous for suspension in water without the need for costly extrusion coating, but the formulation of aqueous suspensions of hydrophobic particles requires complex mixtures of surfactants and additives to keep the particles from aggregation and sedimentation. Further, for the waterborne coatings to have necessary barrier properties it must produce a uniform film having minimum defects. This requires perfect flow of the suspension coating on the substrate previous to drying. The stability of a PHA particle suspension is shown to be based on a proper hydrophilic-lipophilic balance, surfactant chemistry, and ideal surfactant concentration. Additionally, a curious issue of repeatable thermally induced thickening even during PHA suspension is described. This is determined to be related to the cloud point of polyethylene glycol-based surfactants such as Triton X-100 and a remedy is offered as using ionic surfactant or cooling the PHA suspension during processing.

3.1 Introduction

A complex problem is encountered in modern suspensions when attempting to disperse hydrophobic materials into a polar solvent such as water. To produce a functional and stable dispersion or emulsion an intimate knowledge of the interface between dispersant solvent and disperse phases is necessary. Aliphatic polymers such as PHA granules are highly hydrophobic and possess a large amount of surface area with low surface energy that must be wet by the dispersant. Subsequently, upon addition into water PHA granules stay clumped together or float at the surface. If a suspension of particles can be created, individual particles tend to aggregate or sediment due to gravity and van der Waals attraction. And once a particle encounters another and aggregates the chances of encountering another PHA granule is increased. A typical solution to these problems is to adsorb a surfactant onto the surface of the particle to be dispersed[1].

Surfactants act to reduce surface tension between the liquid phase (water) and solid phase (PHA granules), which allow the particles to be wetted and subsequently dispersed. Additionally, nonionic surfactants stabilize dispersed aqueous suspensions by providing a barrier against van der Waals fueled aggregation. When non-ionic surfactant adsorbed particles come into close contact, the adsorbed surfactant layers of each particle compress and buffer the hydrophobic particles from touching, a phenomenon known as steric stabilization[2, 3].

Since the target application is that of a food contact single use paper coating, the generally regarded list (GRAS) was used to determine which surfactants would be best for the formulation of a food contact paper coating[4]. Nonionic surfactants were chosen for the purpose of dispersing hydrophobic PHA granules since ionic surfactants tend to stabilize foam more than nonionic surfactant[5]. Potential nonionic surfactants to disperse a PHA suspension are chosen based on the hydrophilic-lipophilic balance system (HLB.) HLB ranks surfactants based on the weight percentage ratio between their hydrophilic "head" and hydrophobic "tail." In this system a surfactant having an HLB of 14 is highly hydrophilic, while an HLB of 1 is highly hydrophobic.

When choosing a surfactant to disperse and stabilize oil-in-water emulsions an HLB of 8-18 is typically used[6]. Since PHA is a hydrophobic aliphatic polymer, a similar range is chosen for surfactant selection to determine the level of HLB required to disperse PHA particles of unknown hydrophobicity. A formulation is not necessarily limited to only one surfactant. Many formulations include multiple wetting agents, a solubilizer, and multiple oil in water emulsifiers. Because of this it is important to understand the HLB of the entire composition as a whole. This can be done using a weighted average calculation such as equation 3-1.

$$\boldsymbol{HLB_{Total}} = \frac{\boldsymbol{X_A \times HLB_A + X_B \times HLB_B}}{\boldsymbol{M_A + M_B}} \qquad \textbf{Eq 3-1}$$

Where HLB_{Total} is the HLB of the surfactant mixture, X_A is the weight fraction of surfactant A, HLB_A is the HLB of surfactant A, X_B is the weight fraction of surfactant B, and HLB_B is the HLB of surfactant B.

3.2 Materials:

Span 80, tween 20, triton X-100, and sodium dodecyl sulfate (SDS) were acquired from VWR chemical. 18.2mΩ deionized water is produced in lab and is used for all experiments. A polyhydroxyalkanoate copolymer poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) containing 6.33 % 3-hydroxyhexanoate comonomer was produced at the New Materials Institute of the University of Georgia.

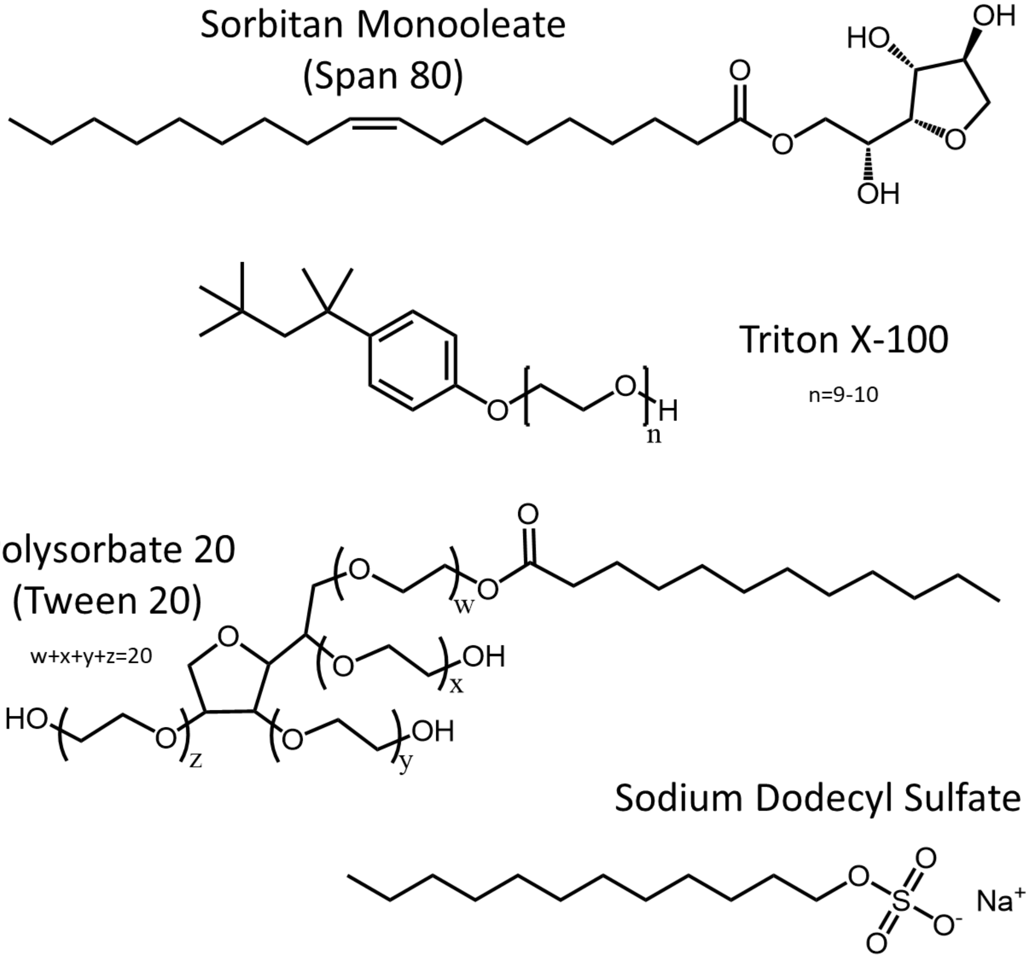


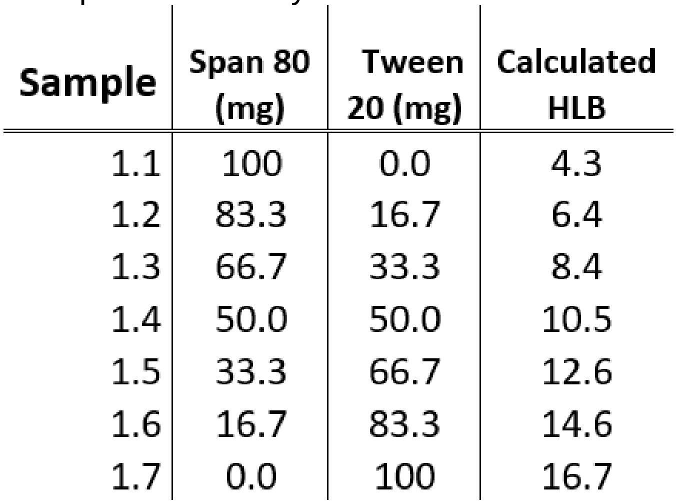
Figure 3-1. Chemical Structure of sorbitan monooleate (span 80), triton X-100, polysorbate 20 (tween 20), and sodium dodecyl sulfate.

3.3 Experimental:

3.3.1 Influence of Surfactant Mixture on PHA Dispersibility

Suspensions of PHA were produced in 20mL scintillation vials by first weighing out amounts of span 80 and tween 20 as shown in table 3-1. The amounts of span 80 and tween 20 proscribed were calculated using equation 3-1, to give HLB values of 4.3, 6.4, 8.4, 10.5, 12.6, 14.6, and 16.7. Once surfactants were measured into the vial with the proscribed weights, 8.9g deionized water was added and the vials were capped tightly and sonicated in an ultrasonic bath for 20 minutes.

Table 3-1. 10 wt. % PHA suspensions produced to study impact of HLB on PHA dispersibility and suspension stability.



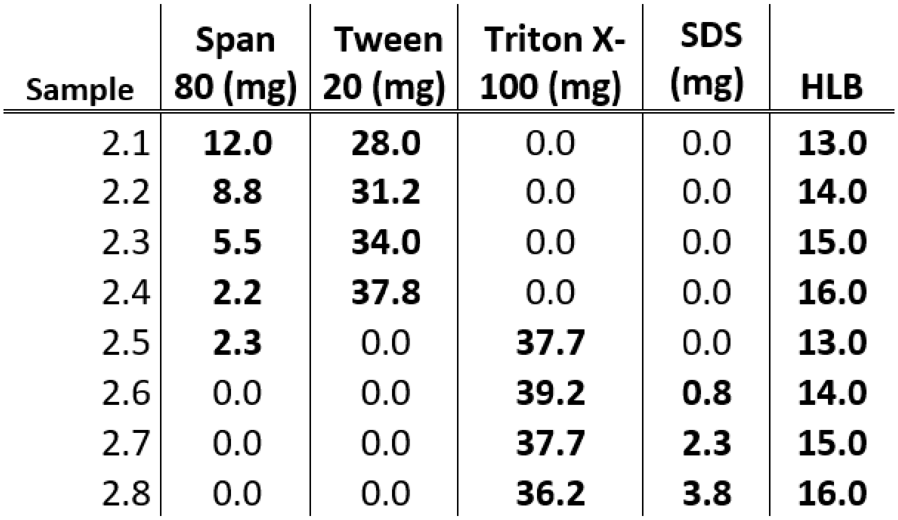
Sample	Span 80 (mg)	Tween 20 (mg)	Calculated HLB
1.1	100	0.0	4.3
1.2	83.3	16.7	6.4
1.3	66.7	33.3	8.4
1.4	50.0	50.0	10.5
1.5	33.3	66.7	12.6
1.6	16.7	83.3	14.6
1.7	0.0	100	16.7

After 20 minutes all vials were removed from the ultrasonic bath and 1.0g of PHA was added to each of the seven vials (10% weight PHA.) The vials were then capped tightly again and returned to the ultrasonic bath for 60 minutes. Samples were then left alone for 24 hours. After 24 hours it was determined whether the PHA was still in suspension.

A second dispersibility experiment was conducted with three different surfactants: Span 80 (HLB = 4.3), tween 20 (HLB = 16.7), triton x-100 (HLB = 13.5), and sodium dodecyl sulfate (HLB = 40.) For this experiment suspensions were produced in 20mL scintillation vials by first weighing out amounts of surfactant as shown in table 3-2. The amounts of surfactant proscribed were calculated using equation 3-1, to give HLB values between 13 and 16. Once surfactants were measured into the vial with the proscribed weights, 4.6g deionized water was added and the vials were capped tightly and sonicated in an ultrasonic bath for 20 minutes.

After 20 minutes all vials were removed from the ultrasonic bath and 1.0g of PHA was added to each of the vials. A tip sonicator was used to sonicate each sample for 10 seconds each, careful not to touch the walls of the vial. After 10 seconds the sample was allowed to cool for 5 minutes and then checked for agglomerates and visual viscosity. If the PHA was dispersed, another 1g of PHA was added and sonication with rest time was performed again. This was repeated for each sample until either 50% weight of PHA was dispersed into stable suspension with no agglomerates, or not all of the 1g PHA added was dispersed through sonication, whichever came first. Observations were taken based on level of dispersibility and visual viscosity, and then samples were left alone for 24 hours. After 24 hours it was determined whether the PHA was still in suspension.

Table 3-2. 50 Wt.% PHA suspensions produced to study impact of HLB and surfactant chemistry on PHA dispersibility and suspension.

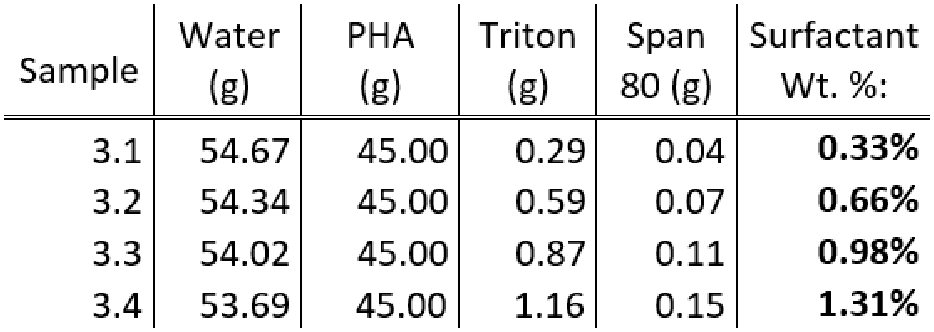


Sample	Span 80 (mg)	Tween 20 (mg)	Triton X-100 (mg)	SDS (mg)	HLB
2.1	**12.0**	**28.0**	0.0	0.0	**13.0**
2.2	**8.8**	**31.2**	0.0	0.0	**14.0**
2.3	**5.5**	**34.0**	0.0	0.0	**15.0**
2.4	**2.2**	**37.8**	0.0	0.0	**16.0**
2.5	**2.3**	0.0	**37.7**	0.0	**13.0**
2.6	0.0	0.0	**39.2**	**0.8**	**14.0**
2.7	0.0	0.0	**37.7**	**2.3**	**15.0**
2.8	0.0	0.0	**36.2**	**3.8**	**16.0**

3.3.2 Surfactant Concentration Necessary to Stabilize PHA suspension:

A series of suspensions were produced, each with varying total concentration of surfactant as shown in table 3-3. Total weight PHA was kept constant, and water was decreased to accommodate the varying surfactant weight. using of 45% PHA was chosen and kept constant while increasing concentration of surfactant mixture. The surfactant mixture used was triton X-100 (HLB = 13.5) and span 80 (HLB = 4.3) for a combined of HLB 12.9, and 4 different percent weight of surfactants were used: 0.33, 0.66, 0.98, and 1.31% weight. Surfactant was added to deionized water and sonicated with a horn sonicator for 15 seconds before adding PHA weight over 30 seconds while further sonicating. The suspension was allowed to cool over 5 minutes then sonicated for an addition 30 seconds to reach homogeneity.

Table 3-3. PHA suspensions of varying total surfactant concentration produced to study minimum of surfactant necessary to stabilize 45 wt. % PHA.



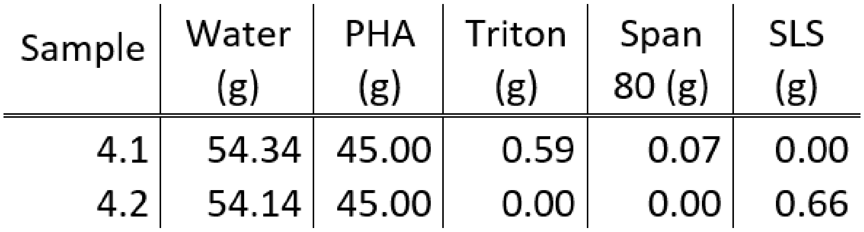
Sample	Water (g)	PHA (g)	Triton (g)	Span 80 (g)	Surfactant Wt. %:
3.1	54.67	45.00	0.29	0.04	**0.33%**
3.2	54.34	45.00	0.59	0.07	**0.66%**
3.3	54.02	45.00	0.87	0.11	**0.98%**
3.4	53.69	45.00	1.16	0.15	**1.31%**

To test the prepared suspensions a TA discovery hybrid rheometer was used. Samples were tested on a 40mm parallel plate geometry with solvent trap to retain humidity and limit evaporation from PHA suspension samples. Rotational flow sweeps were then performed on each PHA suspension sample while maintaining 25°C. The viscosity of each sample over the duration of the test for each sample was then plotted to consider suspension stability.

3.3.3 Unexpected Reversible Thickening Event of PHA Suspensions

To test an unexpected reversible thickening event, several PHA suspensions were produced using either nonionic triton-100 and span 80, or sodium dodecyl sulfate as shown in table 3-4. Sample 4.1 uses only triton X-100 and span 80 in a blend producing HLB of 12.9, while in sample 4.2 the same suspension as sample 4.1 was mixed, but only ionic surfactant SLS was added in place of triton X-100 and span 80. To prepare suspensions, surfactant was added to deionized water and sonicated with a horn sonicator for 15 seconds before adding PHA weight over 30 seconds while sonicating. The suspension was allowed to cool over 5 minutes then sonicated for an addition 30 seconds to reach homogeneity.

Table 3-4. PHA suspensions produced to test surfactant effects on PHA suspension reversible thickening.



Sample	Water (g)	PHA (g)	Triton (g)	Span 80 (g)	SLS (g)
4.1	54.34	45.00	0.59	0.07	0.00
4.2	54.14	45.00	0.00	0.00	0.66

3.4 Results and Discussion

3.4.1 Influence of Surfactant Chemistry and HLB on PHA Dispersibility

The surfactant concentration necessary to achieve stabilization of dispersed particles can be predicted using the cmc of surfactants, particle surface area, and dispersed particle chemistry [7]. This is useful in producing expectations in cases in which one surfactant is used, but when multiple surfactants are included, the prediction becomes more challenging. Since utilization of multiple surfactants was found to be beneficial for stability and wetting, an empirical way to determine the best surfactant concentration is necessary.

In the first test to determine optimum surfactant HLB to stably disperse PHA into suspension, 10% weight of polymer was used. Each of the samples 1.1 through 1.7 were produced with different HLB by varying the amount of span 80 and tween 20, giving HLB of 4.3, 6.4, 8.4, 10.5, 12.6, 14.6, and 16.7. While 10% weight PHA this is not the target level of polymer to produce functional barrier coatings on paperboard, this concentration of PHA in suspension gave indications on how well the surfactant blend dispersed PHA.

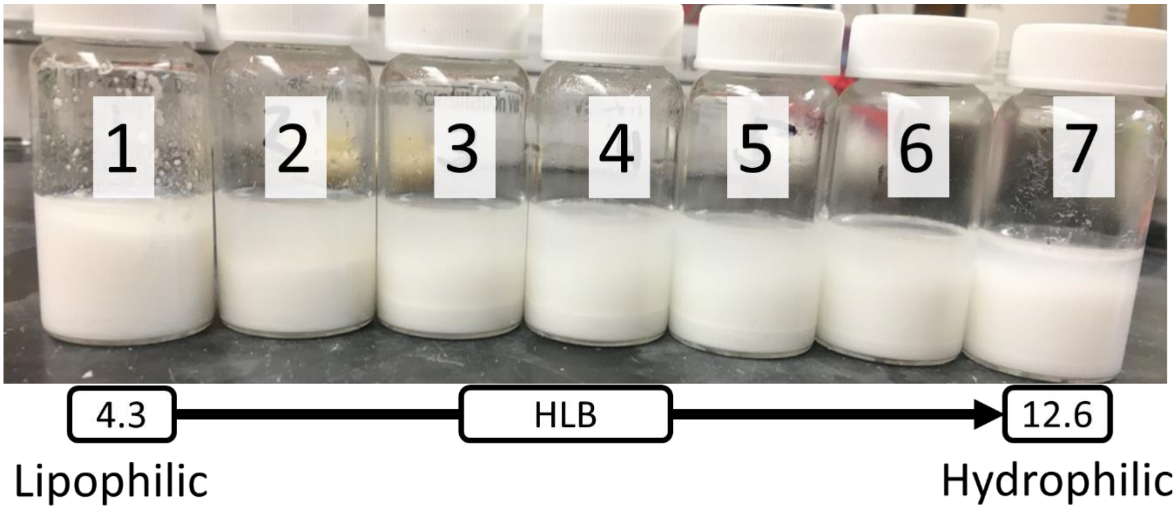


Figure 3-2: Experiment determining the impact of HLB on PHA dispersibility and stability in suspension.

When dispersing the polymers using an ultrasonic bath, in the first 10 minutes it was readily apparent that only samples 1.5, 1.6, and 1.7 had suspended and were flowable in viscosity. Samples 1.1, 1.2, 1.3, and 1.4 were all HLB 10.5 or below, showing a higher HLB is more capable of dispersing the PHA polymer quickly. To further test the samples and determine if lower HLB are even capable of dispersing PHA, the vials of suspension mixture were vortexed for 30 seconds each. While vortexing the samples experienced increased shear to help mix the surfactant into the PHA and break apart agglomerates of hydrophobic particles. The samples were then returned to the ultrasonic bath, and after 50 minutes all samples were more or less dispersed, though an apparent difference in viscosity was noted. All samples were waterlike in viscosity when the vial was upended except for samples 1.1, which seemed thicker more viscous like a milkshake. The samples were then left to sit for 24 hours on the lab bench.

After 24 hours enough time has passed for a large number of PHA particles to have fallen out of suspension, either through agglomeration due to van der Waals attraction or through gravity pulling the particles to the bottom of the vial. Before moving the samples, they were each examined for the level of sedimentation, which can be seen in figure 3-2. Though the suspension is turbid it is possible to see a sediment layer on the bottom of each vial, and if the samples are ranked by the level of sediment at the bottom then the lowest sediment samples were the suspensions mixed with highest HLB. Sample 1.1 felt grittier and heterogenous between gloved fingers, and though it appears most turbid this is because it never was fully dispersed. Sample 7.1 is the suspension with the highest HLB (16.7), but when compared to the next highest (14.7) it was noted that sample 1.7 possessed a greater clear layer of fluid and was falling out of suspension faster than sample 1.6. This is likely due to hydrophobic PHA requiring balance in HLB of surfactant dispersant mixture, and sample 1.7 contains only a highly polar surfactant (tween 20.) When a nonpolar surfactant (span 80) is included, such as in sample 1.6, the suspension of PHA was found to be more stable to the effects of sedimentation. Though, after another 24 hours all samples had sedimented to showing gravity overtook Brownian motion, likely because particles are greater than 1 micron in size.

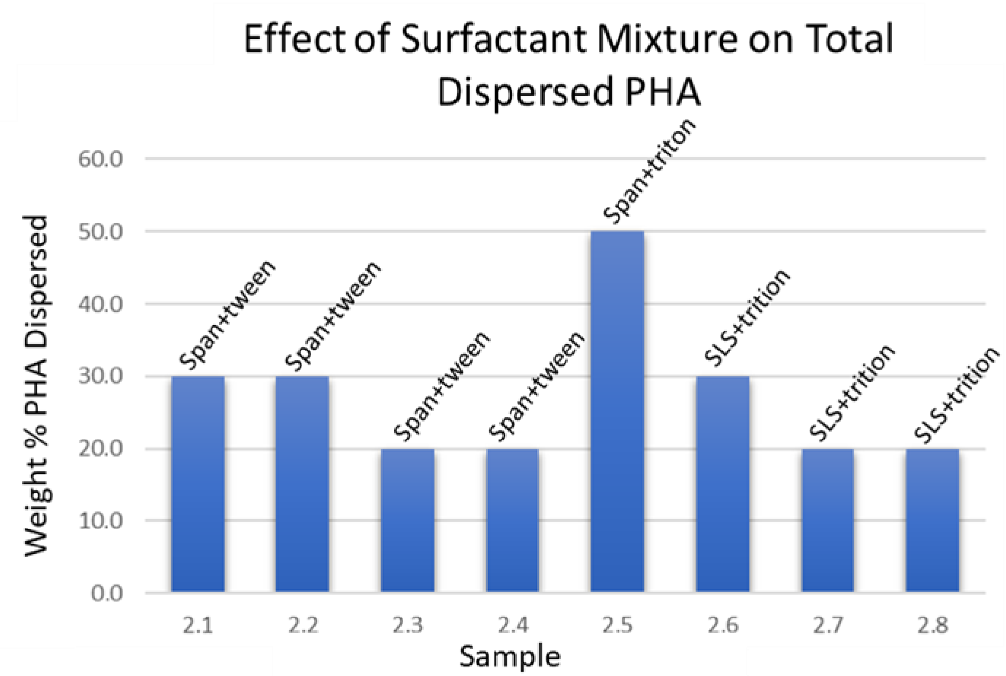
For the next experiment, a much higher loading of PHA was necessary to test the effectiveness of surfactant mixtures in dispersing hydrophobic PHA particles. This experiment targeted HLB between 13-16 based on the success of higher HLB surfactant blends in previous work. But this experiment utilized 4 different surfactants: span 80 (HLB = 4.3), tween 20 (HLB = 16.7), triton x-100 (HLB = 13.5), and sodium dodecyl sulfate (HLB = 40.) Span 80, tween 20, and triton x-100 are all food contact approved nonionic surfactants, while sodium dodecyl sulfate (SDS) an ionic surfactant was chosen to compare to nonionic surfactants.

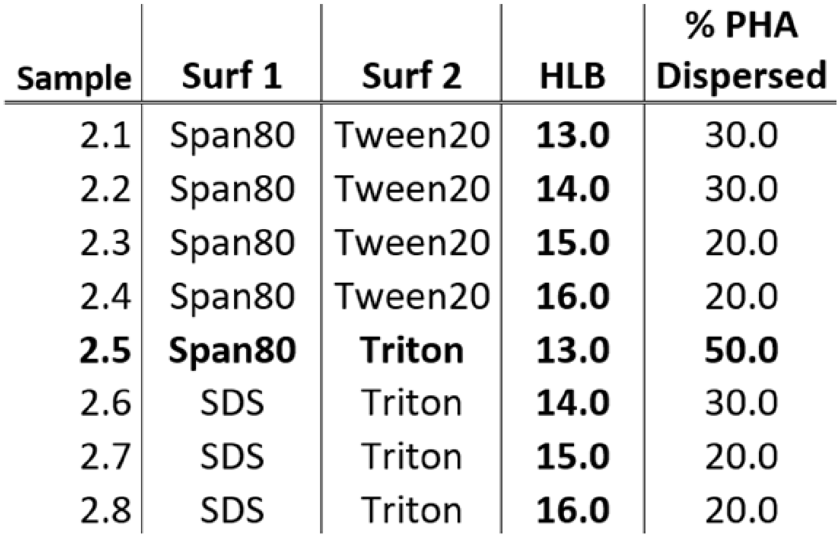
Contrary to the previous experiment, PHA was added gradually to the dispersant mixture in increments of 10% weight until either 50% weight of PHA was dispersed into stable suspension with no agglomerates, or not all of the PHA added was able to be dispersed through sonication in the allotted time. By adding the PHA over time it was noticeable which surfactant blends performed the best at dispersing hydrophobic particles. The results of this are shown in figure 3-3.

While tween 20 – span 80 blends were capable of suspending lower weight suspensions, when adding up to 30% weight of PHA it was no longer able disperse PHA and reach waterlike viscosity in the time of sonication. As seen in the previous experiment, as HLB increased past 14 and up to HLBs of 15 or 16, the dispersibility of PHA decreased and only up to 20% total weight PHA was possible. Surprisingly, when trition X-100 is used in place of tween the effectiveness of dispersant to suspend PHA was greatly improved. While the tween 20 surfactant blend of HLB 13 was having trouble suspending up to 30% weight of PHA, trition X-100 HLB of 13 suspended 50% weight of PHA and seemed like it could continue to disperse more. The difference in ability of trition

X-100 and tween 20 to disperse hydrophobic PHA is likely related to surfactant chemistry. Trition X-100 is less polar, having an HLB of 13.5 with a shorter hydrophobic tail made up of aromatic and t-butyl groups, while tween 20 is more polar having a linear aliphatic hydrophobic tail. Since PHA is an aliphatic polymer particle there is likely a limit to the level a highly polar surfactant can stabilize it, and so a more balanced slightly more nonpolar surfactant is key.

Since SLS is an ionic surfactant (HLB = 40) it's difficult to compare HLB blends of SLS and trition to blends of trition and other nonionic surfactants. When SLS and trition were combined to disperse PHA, dispersant effectiveness decreased as SLS concentration increased. Additionally, the level of foam produced as SLS was increased was greatly inhibitive of the dispersing process. Combination of cavitation and ionic surfactant SLS caused bubbles to spray and foam out of the sample vial. When the samples of experiment 2 were left to sediment 24 hours a contrast was noted in that while trition x-100 and span 80 blends were capable of dispersing the most amount of PHA, sample 2.5 was fully sedimented. Most all other samples were also fully sedimented, except samples 2.3 and 2.4 which contained less % weight PHA. These results show that while a dispersant blend of surfactants may be effective at producing PHA suspensions, another additive is necessary to assist with long term stability.





Sample	Surf 1	Surf 2	HLB	% PHA Dispersed
2.1	Span80	Tween20	**13.0**	30.0
2.2	Span80	Tween20	**14.0**	30.0
2.3	Span80	Tween20	**15.0**	20.0
2.4	Span80	Tween20	**16.0**	20.0
2.5	**Span80**	**Triton**	**13.0**	**50.0**
2.6	SDS	Triton	**14.0**	30.0
2.7	SDS	Triton	**15.0**	20.0
2.8	SDS	Triton	**16.0**	20.0

Figure 3-3. Capability of different surfactant blends to disperse PHA particles.

3.4.2 Surfactant Concentration Necessary to Stabilize PHA Suspension:

While surfactant usage is necessary for the dispersion and stabilization of suspension, not all effects of surfactant addition are positive. Since most dispersing surfactants are water soluble, the inclusion of surfactants in a barrier coating will reduce the water resistance of that coating[8]. Additionally, surfactants that fall into the functional group of oil in water dispersants all act to produce foam. Air inclusions are a constant battle when producing waterborne coatings since water surface tension allows bubbles to persist and if an air bubble is placed on a coating it will produce an imperfection in that otherwise perfect coating. Because of this it is important to minimize the amount of foam and formulate to use as little surfactant as is necessary to the application.

A method of observing the concentration necessary to stabilize PHA particles in suspension was devised comparing rheology results of the surfactant-water-PHA particle compositions. PHA wt.% was chosen and kept constant at 45% while varying concentration of surfactant mixture. The surfactant mixture used was triton X-100 (HLB = 13.5) and span 80 (HLB = 4.3) for a combined of HLB 12.9, and 4 different percent weight of surfactants were used: 0.33, 0.66, 0.98, and 1.31% weight of the total suspension. All mixtures were easily suspended, though a distinct difference was noted in the 0.33% weight surfactant system, which seemed thicker to a trained eye.

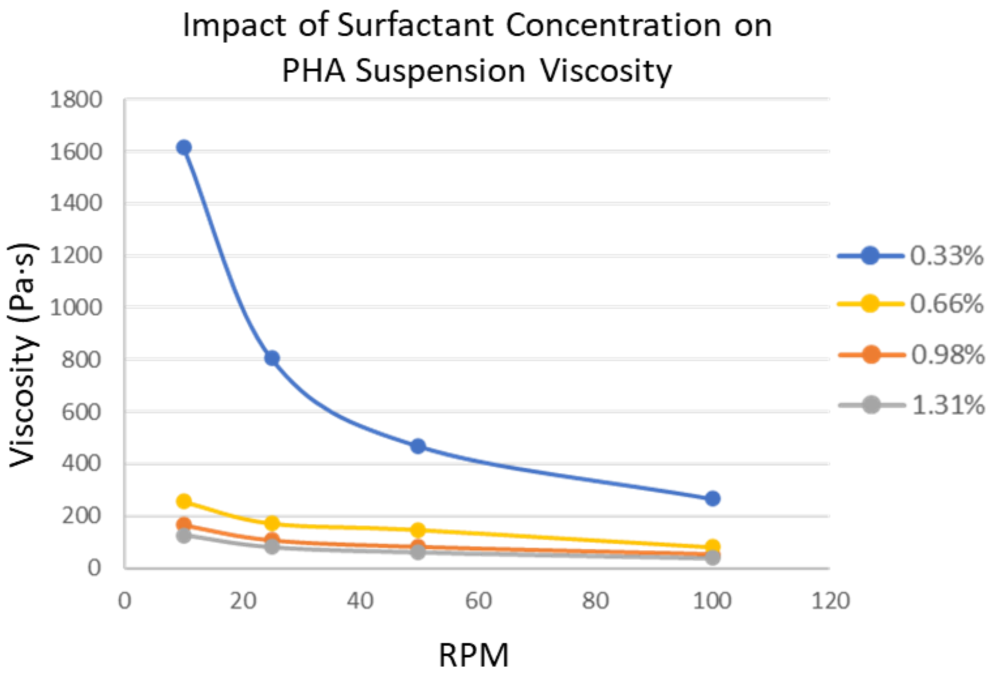


Figure 3-4: Effect of surfactant on viscosity for suspensions of PHA containing varied weight percent of surfactant.

When performing rotation flow sweeps for each suspension all suspensions exhibited non-Newtonian shear thinning, as their viscosity decreased under shear strain. After plotting the results in an overlay, it was noted that the three surfactant concentrations higher than 0.33% weight surfactant appeared identical in viscosity. Based on these results it was determined that 0.66% surfactant was necessary to fully solubilize 45% weight of PHA in water, simply put, the amount of surfactant is decreased until a noticeable thickening is apparent. When the suspensions were left to sit on the bench overnight it was again noted that they fully sedimented.

3.4.3 Reversible Thickening of PHA Suspensions

While producing a PHA suspension a great deal of shear is necessary to separate particle agglomerates, wet particles, and removed adsorbed air. During this high shear process heat is generated as friction or energy from cavitation. During the time of mixing PHA begins to wet and disperse into suspension, thereby reducing viscosity, but as shown in figure 3-5 at 45°C a noticeable thickening is experienced and PHA falls out of suspension. After waiting for the mixture to cool and beginning shear again, the suspension reaches its original waterlike viscosity.

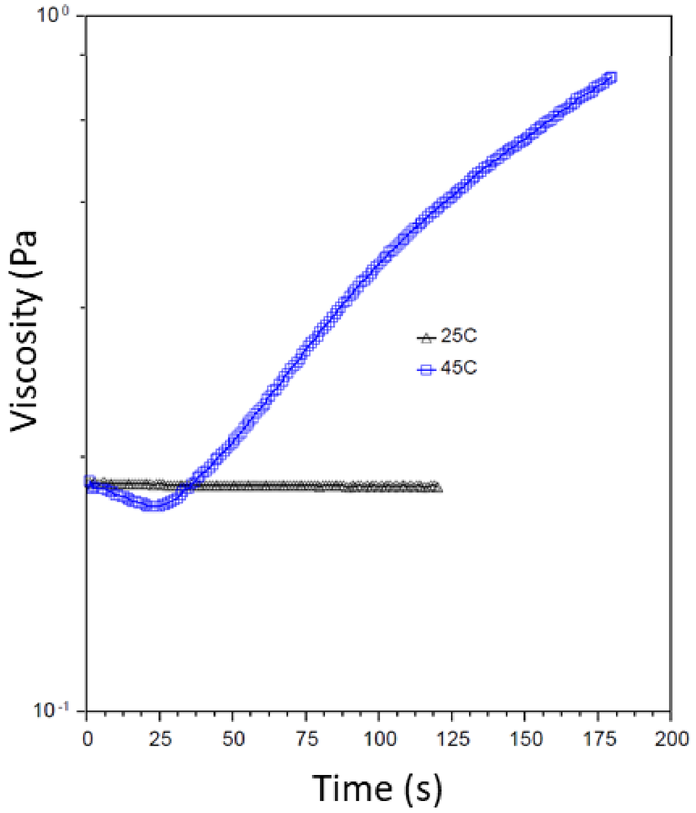


Figure 3-5 Thermally induced thickening event of nonionic surfactant suspended PHA.

Most water soluble nonionic surfactants change in turbidity as fluid temperature is increased, a phenomena known as the surfactant's cloud point[9]. At the cloud point of a surfactant a previously homogenous amphiphilic solution undergoes phase separation into both surfactant rich and surfactant poor phases[10]. This phase separation at the cloud point drives PHA previously in suspension out and into agglomerates, which is unsurprising considering cloud point phenomena is utilized to concentrate and extract organic compounds, inorganic compounds, and heavy metals[11-13].

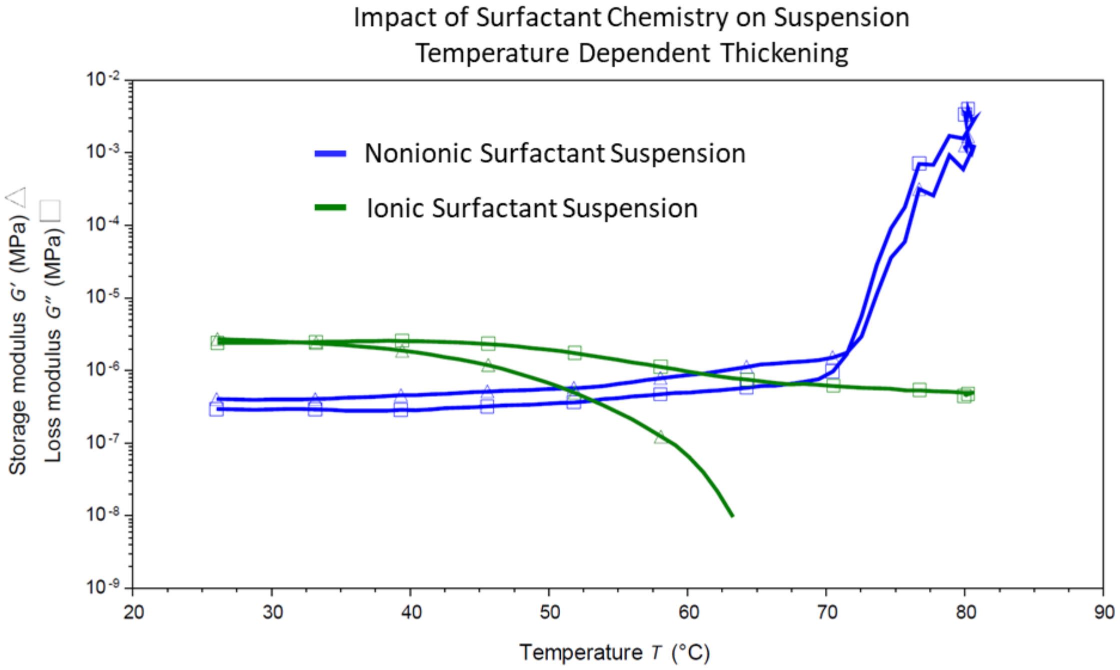


Figure 3-6. Impact of surfactant charge on suspension temperature dependent thickening.

To determine the dependance of this thermal thickening event on the presence of nonionic surfactant, two PHA suspensions were created, one containing only nonionic surfactant, and the other containing only ionic surfactant. A 45 percent weight suspension was produced and then run on the rheometer under oscillatory experiments using 40mm parallel plates. Isothermal amplitude and frequency sweeps were performed to determine optimum conditions for running the following tests. Once the frequency and amplitude of shear in the linear viscoelastic region were known a temperature sweep was performed on each of the two suspensions.

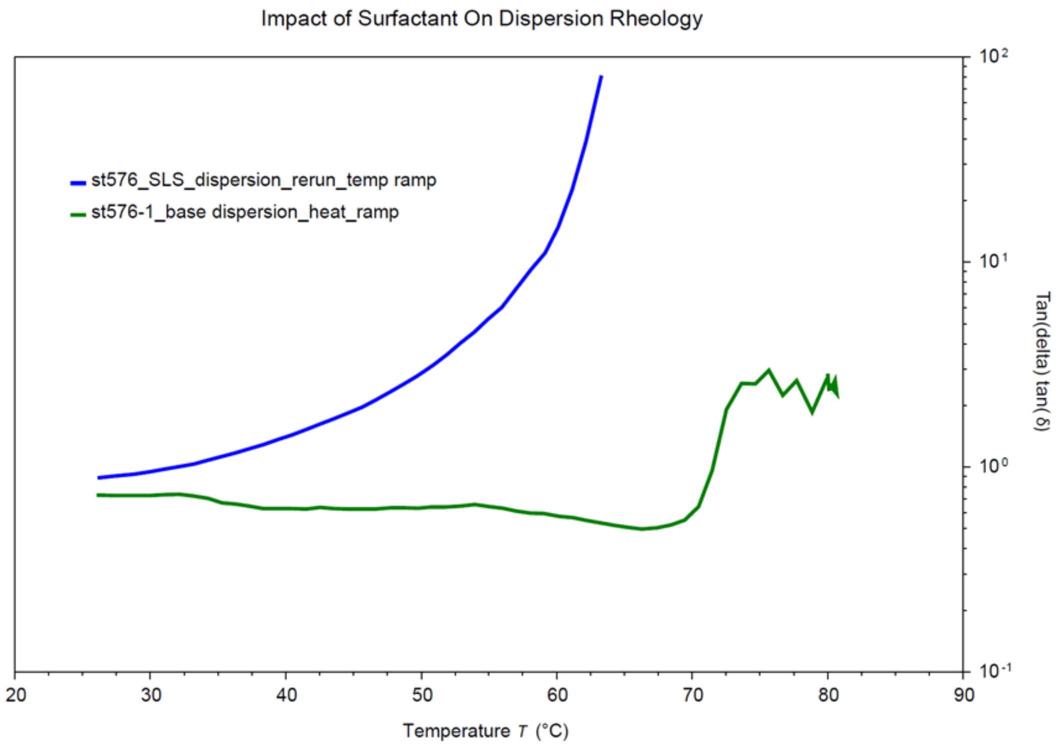


Figure 3-7. Impact of surfactant charge on tan(δ) of suspension rheology

As shown in figure 3-6 the ionic surfactant suspension of PHA exhibits a normal decrease in storage modulus as temperature increases, but the nonionic surfactant suspension increases in storage and loss modulus together as temperature increase. This is further shown by figure 3-7, where a large increase in tan(δ) for the ionic suspension of PHA shows this material acts increasingly as a viscous liquid as its viscosity decreases at higher temperature. The tan(δ) of nonionic PHA suspension slightly decreases as temperature rises, becoming more elastic and unable to dissipate the energy of shear until the onset of a peak at 70°C. This peak at 70°C is the cloud point of Trition X-100 surfactant[14-16].

While the cloud point phenomena can have an impact on PHA suspensions, the effects have not been problematic except at low volumes of prepared suspension. This is because larger volumes of water buffer the mixing/friction temperature increase through the high specific heat of water. But if the cloud point phenomena is an issue during suspension production, then ionic surfactants can be used to overcome the thickening event.

3.5 Conclusions

The hydrophilic lipophilic balance is used to formulate a dispersant system for PHA using a mixture of polar and nonpolar nonionic surfactant. Surfactant chemistry and HLB were found to be important in suspending hydrophobic PHA particles to high % weight loadings, such that a balance in surfactant polarity is necessary to achieve high suspension weight percent. Specifically, a mixture of triton x-100 and span 80 with HLB of 13 was found to be the most effective. Though a surfactant system can accomplish weight percent loading of PHA greater than 50%, the suspension produced is still susceptible to flocculation. This shows that gravity and other particle-particle interactions greatly overpower Brownian motion stabilizing forces, likely because the PHA particles stabilized are outside of the colloid range of 1nm - 1µm. Based on this an important next direction is to include in the formulation a rheology modifier to further stabilize the suspension.

In order to minimize problematic increase in water permeability and foaming related to high surfactant concentrations, the lowest necessary concentration of that surfactant system to disperse 45% wt. PHA was determined to be 0.66%. Lastly, a thermally induced repeatable thickening phenomenon encountered is shown to be the cloud point of triton X-100. If the thermal thickening event is troubling for small scale production of PHA suspensions due to heat buildup, a solution is shown to be a swap from nonionic to ionic dispersing surfactant.

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CHAPTER 4

COATING APPLICATION AND STABILITY OF A RHEOLOGY MODIFIED AQUEOUS POLYHYDROXYALKANOATE SUSPENSION[3].

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[3] Tull, Scott. “Coating Application and Stability of a Rheology Modified Aqueous Polyhydroxyalkanoate Suspension.” To be submitted to the Journal of Applied Polymer Science

Abstract

Improvement of waterborne coating films requires reduction in coating film defects such as pinholes, streaking, cracking, sagging, and leveling. Many waterborne coating formulation additives such as surfactants are intended to cope with surface tension and the variety of problems surface tension causes. Another functional tool that must be added to help rectify the problems encountered in waterborne coating is a rheology modifier, which changes the viscosity of the aqueous suspension. Xanthan gum is shown to be an advantageous rheology modifier of polyhydroxyalkanoate (PHA) suspensions due to its pH, ionic strength, temperature, and ability to biologically degrade. A method of xanthan gum thickening of PHA suspensions is shown to provide linearly predicted and repeatable thickening viscosities compared to alternatives. Addition of xanthan gum advantageously stabilize PHA suspensions from sedimentation, showing less than 1% loss in suspended PHA weight over time. which is capable of less than 1% weight sedimentation over time. The amount of xanthan gum required to limit coating defects for a coating application is shown to be determined based on the 3-interval thixotropy test, in which is an oscillatory rheology experiment simulates the coating process and film formation previous to drying.

4.1 Introduction

Surface tension has a tendency to stabilize coating defects occurring during application such as leveling, and sagging, and craters/pinholes. When adding surfactant to a waterborne suspension the interfacial tension between liquid and air or solid are in fact reduced, though the problems caused by surface tension are not fully alleviated. Additionally, while surfactant enables hydrophobic PHA particles to be suspended in water to weight percentage of PHA greater than 50 %, the suspension is not stable over time. Once a suspension of particles having diameter outside the colloid range (1nm - 1 µm) is created it immediately begins to fall out of suspension due to gravity and particle-particle interactions[1]. To further improve PHA suspension stability and reduce defects encountered during coating application a rheology modifier, also referred to as a thickener, is necessary[2].

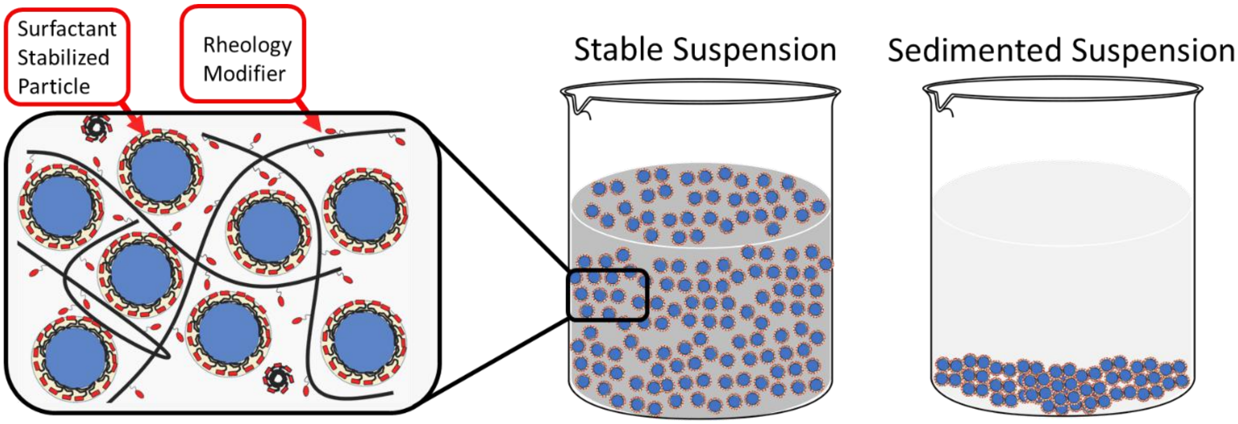


Figure 4-1: Impact of a rheology modifier on stability of suspended hydrophobic particles where only the stable suspension did not sediment.

A conventional rheology modifier is a water-soluble polymer having molecular weight higher than 10^5 g/mol. Conventional rheology modifiers use their high molecular weight and water solubility to hydrodynamically “tie” up a significant portion of previously free water[3]. Conventional rheology modifiers also thicken suspensions through depletion flocculation. Depletion flocculation occurs when surfactant coated particles come into close contact and displace conventional thickener chains, resulting in water moving away from the suspended particles to keep the displaced thickener chains solvated and consequently driving suspended particles closer and closer[4, 5].

A conventional rheology modifier for PHA suspensions intended to coat paperboard in food contact applications must contain only food contact additives such as those on the generally regarded list (GRAS) [6]. Additionally, since PHA suspensions provide an advantageous end of life alternative to currently utilized commodity plastics, all formulation additives such as a rheology modifier should also be biologically degradable in the environment. Since the target viscosity of a PHA suspension can have an important impact on the final properties of the coating, it is important for the thickener to provide expected and repeatable thickening viscosities. A rheology modifier that accomplishes all of this, while also being edible is the now ubiquitous xanthan gum. Xanthan gum is now found in many different food products to provide stability to drinks and products where settling or phase separation is undesirable, such as in a well-known coffee beverage containing milk, coffee, and ice, where the xanthan gum provides a smooth texture and provides stability from separating proteins and sugars.

Xanthomonas campestris polysaccharide, also known as xanthan gum was discovered in 1959 by USDA labs as being produced by Xanthomonas campestris, which is found on the leaves of common grocery vegetables[7]. Xanthan gum is made up of a cellulose identical backbone of β-1,4-linked D-glucose residues having trisaccharide branches with one glucuronic acid unit between two mannose units, which are linked to every other glucose unit in the main chain[8]. Advantageously, xanthan is insensitive to the effects of pH, temperature, ionic strength, and is readily biodegradable[9]. Xanthan gum possesses a rigid helical structure when solvated which dissociates upon shear and rapidly reassociates when recovering[10]. This ability to quickly regain structure drastically improves the sag resistance in coatings and filler suspensions.

Since xanthan gum is of extraordinarily high molecular weight, it is intensely difficult to disperse in high solids loading. The solvation of xanthan gum is typically met with “fish-eyes” or agglomerated clumps of un-solvated xanthan gum which must be filtered out as they may persist in the final product, or worse continue to change the rheology of the coating to unexpected results[11]. In the laboratory, it is possible to produce high solids xanthan solutions through high shear and menially slow additions of xanthan powder. To scale up production the addition rate of thickener powder must be greatly increased, which then requires much higher shear than what is currently achievable in the laboratory. A potential solution to this is the use of high shear cavitation or rotor stator design mixers. Additionally, this is important for repeatability since the viscosity of xanthan solutions is dependent on the temperature and preparation method of the solutions[12].

4.2 Materials

Span 80, triton X-100, xanthan gum, and guar gum were acquired from VWR chemical. 18.2mΩ deionized water is produced in lab and is used for all experiments. A polyhydroxyalkanoate copolymers poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) containing 6.33 % 3-hydroxyhexanoate comonomer was produced at the New Materials Institute of the University of Georgia.

4.3 Experimental

4.3.1 Brookfield Viscosity Determination

Brookfield viscosity is determined using a DV2T model viscometer. All measurements of viscosity were performed in the same 250mL beaker using the RV spindle set and temperature is maintained at 25°C. For suspensions of PHA with viscosities between 50 and 1000 cP an RV-3 spindle was used to measure viscosities. Spindle rotation per minute is adjusted to maintain viscosity measurements of 30-70% torque but is typically used at a rate of 100 RPM for suspensions of viscosities between 50 and 500cP.

4.3.2 Quantification of Suspension Settling Over Time

To determine how much weight percent of PHA is still in suspension after a known time has passed, a simple gravimetric evaporation % volatiles test is performed. This is performed using a moisture balance, which evaporated all volatiles (water) by heating the suspension to 150°C and gives a sample weight loss due to evaporated volatiles. The weight percent of PHA still in suspension is then calculated using equation 4-1.

$$\% \boldsymbol{Solids} = \mathbf{100} - \left(\frac{\boldsymbol{Weight\ Loss}}{\boldsymbol{Starting\ Weight}} \times \mathbf{100}\right) \qquad \textbf{Eq 4-1}$$

Where the weight loss is the weight lost due to evaporation, starting weight is the initial sample weight, the fraction is converted into percentage by multiplying by 100, and is subtracted from 100 to convert to a weight percent.

4.3.3 Xanthan Thickening Method

Two different methods of dispersing xanthan gum were investigated in order to determine the method of xanthan addition that provides repeatable thickening viscosity increases. The first method involved simply adding xanthan gum to the already dispersed PHA particles, while the second involved producing a separate solution of high loadings xanthan gum dissolved in water. The two methods are shown in figure 4.2.

In the xanthan powder addition method, surfactant additives are suspended in DI water. PHA is then added to water and fully dispersed to a weight percent of 45% before beginning xanthan addition. Once PHA is fully dispersed with no agglomerates, xanthan gum powder is added during high shear with care taken to avoid xanthan gum “fisheyes.” Cavitation from an ultrasonicator was used as high shear during xanthan gum addition. Once the target viscosity is reached, xanthan gum fisheyes are removed using a course filter. The suspension is then stirred lightly to allow air bubbles to bloom to the surface and viscosity is measured over time until reaching a stable number.

In the xanthan solution addition method, a 2.5 weight percent solution of xanthan gum is prepared by adding xanthan gum slowly to room temperature DI water while high shear agitation is maintained to minimize xanthan gum fisheyes. A suspension of PHA is then produced by first dispersing surfactant additives in DI water before shearing PHA into suspension. The PHA weight percentage of the suspension should be greater than 50%. Once PHA is fully dispersed with no agglomerates, the prepared xanthan gum solution is added with care taken not to create bubbles. Viscosity is then checked and monitored while adding a mixture of xanthan gum solution and pure DI water until the desired viscosity is reached. The suspension is then stirred lightly to allow air bubbles to bloom to the surface and viscosity is measured over time until reaching a stable number.

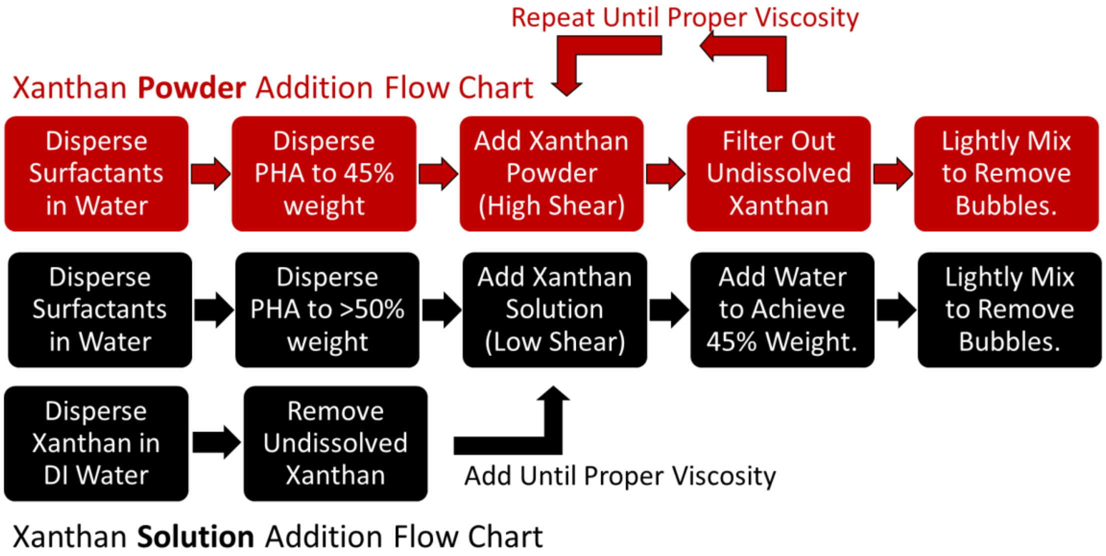


Figure 4-2. Flow chart describing two different methods of dispersing xanthan gum in PHA suspensions.

4.3.4 Impact of Xanthan Gum on PHA Suspension Stability

Suspensions of 50 percent weight PHA were dispersed with components as shown in table 4-1. A PHA having particle size distribution (D90 = 5.2 micron) was dispersed with 0.66% weight surfactant mixture of HLB 12.9 using ultrasonication. The suspension was filtered through a 300micron sieve and then either deionized water or 0.45 total weight percent of xanthan was added as a solvated thickener. The suspensions were mixed on a stir plate with stir bar to remove bubbles overnight then placed into 50mL centrifuge tubes. 24 hours after the suspensions were produced testing of percent solids began as follows: using a plastic pipette, the disperse phase of the suspension was sampled from the mid-bottle, mid-top, and top of the test tube before performing a moisture balance test of total % solids. This was repeated over several weeks to collect data on rate of sedimentation of PHA suspensions thickened by xanthan gum.

Table 4-1. Formulation of pha suspensions thickened with xanthan gum to reduce sedimentation.

Sample	Water (g)	PHA (g)	Triton X-100 (g)	Span 80 (g)	Xanthan Gum (g)
St475-1	49.05	50.00	0.86	0.09	0.00
St475-2	48.71	50.00	0.86	0.09	0.34
St475-3	48.26	50.00	0.86	0.09	0.79
St475-4	47.68	50.00	0.86	0.09	1.37
St475-5	44.54	50.00	0.86	0.09	4.51

4.3.5 Three Point Thixotropy Test

Three PHA samples were produced using the xanthan powder addition method using either, 0.18, 0.45, or 0.54 weight percent xanthan gum added to the PHA suspension as shown in table 4-1. Once all three suspensions were produced, they were stirred overnight to remove any bubbles caused during suspension production. After 24 hours the suspensions were retested for Brookfield viscosity before beginning testing on a TA discovery hybrid rheometer. The rheometer was equipped with 40mm parallel plates geometry with solvent trap to retain humidity and limit evaporation from PHA suspension samples. Amplitude and frequency sweeps were performed to determine linear viscoelastic range for each sample while maintaining 25°C.

Table 4-2: Additives used to produce rheology modified suspensions of PHA in preparation of performing 3-interval thixotropy testing.

Additive	% Weight of Additive		
	Test 1	Test 2	Test 3
Water	54.02%	54.11	54.38%
PHA	45.00%	45.00	45.00
Tween 20	0.44%	0.44%	0.44%
Span 80	0.22%	0.22%	0.22%
Xanthan Gum	0.54%	0.45%	0.18%

Once the linear viscoelastic region for a sample was determined, the three-interval thixotropy test was performed as follows:

1. 100 seconds of low oscillatory shear to simulate behavior at rest.

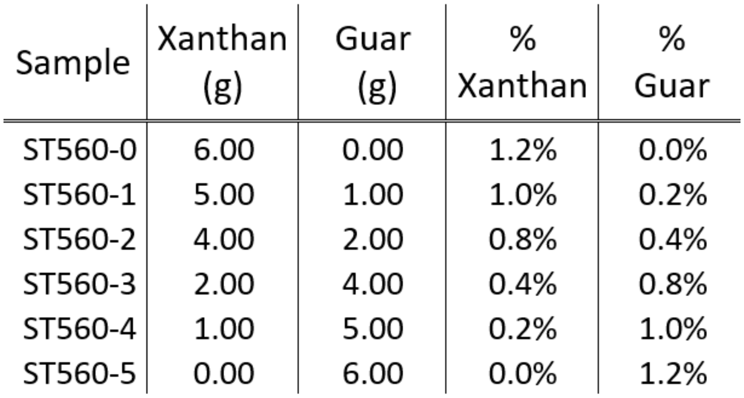
2. 5 seconds of high intensity rotational shear to simulate application.
3. >500 seconds of low oscillatory shear to simulate structure regeneration after application.

The results of the test were then plotted and the recovery of storage modulus over time was determined.

4.3.6 Guar + Xanthan Gum Blends

To evaluate the influence of a blend of guar and xanthan gum as a viscosity modifier for PHA suspensions, several samples of PHA suspensions were prepared using mixtures of xanthan and guar gum. First, solutions of each binary thickener blend were prepared as shown in table 4-2. Xanthan and guar gum were weighed out in the amounts specified and then added to a high shear mixer containing 500g of DI water. The thickener powders were added over 30 seconds, and addition rate of each blend to the high shear mixer was kept as consistent as possible between samples.

Table 4-3. Amounts of xanthan and guar gums used to prepare binary thickener blends.



Sample	Xanthan (g)	Guar (g)	% Xanthan	% Guar
ST560-0	6.00	0.00	1.2%	0.0%
ST560-1	5.00	1.00	1.0%	0.2%
ST560-2	4.00	2.00	0.8%	0.4%
ST560-3	2.00	4.00	0.4%	0.8%
ST560-4	1.00	5.00	0.2%	1.0%
ST560-5	0.00	6.00	0.0%	1.2%

4.4 Results and Discussion

Since the viscosity of a coating impacts the final properties of the coating, it is important for the thickener to provide expected and repeatable thickening viscosities. When using xanthan gum, it is apparent that while the material is soluble in water, it is difficult to dissolve and tends to form clumps of xanthan wet agglomerates, also known as fisheyes. Once fisheyes are produced it is difficult to shear the high molecular weight polymer agglomerates back apart and into solution. Because of this there are two cases: remove fisheyes formed during xanthan gum thickening, or never produce them through methods of efficient particle wetting.

Two methods of thickening PHA suspensions using xanthan were devised, the first by adding xanthan powder directly to the suspension once PHA is properly dispersed, and the second involves producing a xanthan thickened solution separately from the final PHA suspension. In order to accomplish the first method, more xanthan must be used than is necessary to thicken, since some of it will be filtered out as fisheye agglomerates at the end. While, in the second method a PHA suspension must be capable of being created higher than the final PHA weight percent loading. This is because the thickened and fisheye free xanthan solution must be added post PHA suspension to avoid PHA-xanthan agglomerates and reduce bubble formation. Once the PHA solids desired are properly suspended, the suspension is then thickened using the fisheye free xanthan solution until reaching the application specific viscosity, thereby diluting the percent weight PHA in suspension.

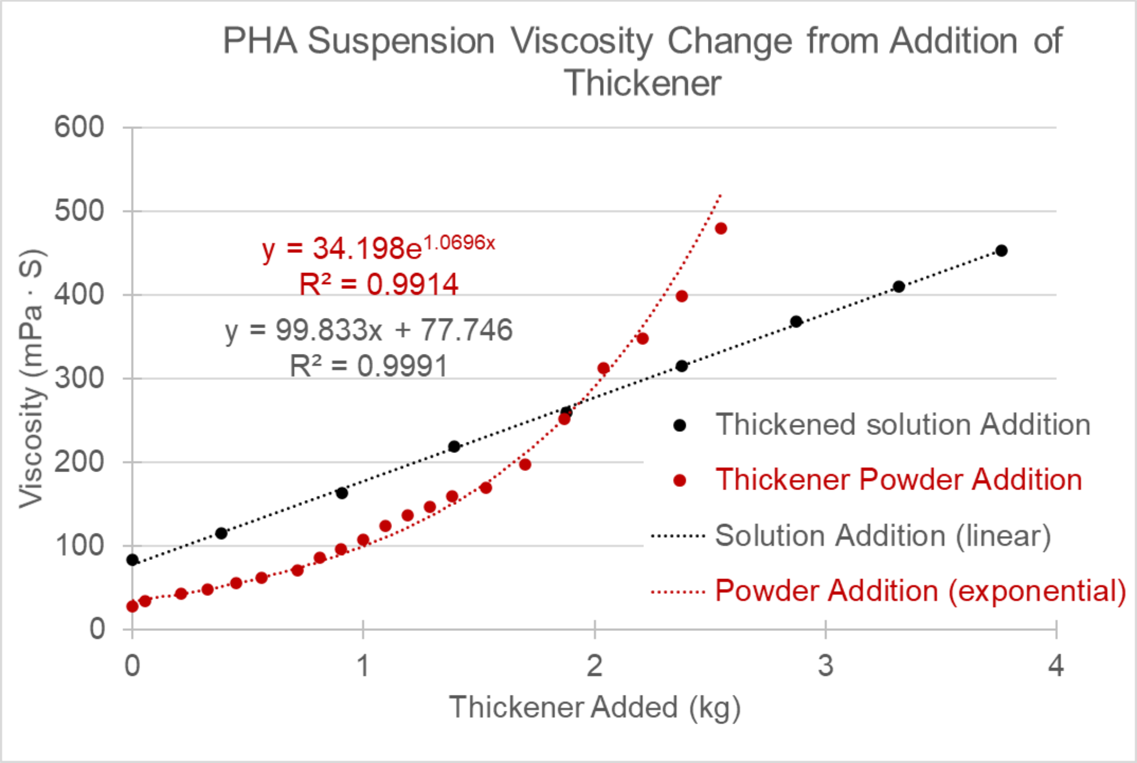


Figure 4-3 Additions of this thickener to an aqueous suspension of PHA gave linearly scalable viscosities and was found to be reproducible.

Once the two methods of xanthan addition were used to prepare PHA suspensions, the impact of thickener added to final viscosity was related to the total amount of xanthan added. A plot of this is shown in figure 4-3. A drastic difference is noted in the slope of viscosity change with xanthan gum added, such that xanthan added as powder follows a near exponential increase in viscosity with thickener added, while thickener solution added is perfectly linear. This can be explained by the addition of xanthan fisheyes due to improper shear, since the fisheyes of xanthan produced continue to solvate and increase viscosity, thereby contributing to a delayed increase in viscosity. This is why the fisheyes produced must always be removed or else the viscosity will continue to climb and reach an unexpected value of viscosity. Based on these results the most effective and repeatable method of thickening PHA suspensions with xanthan gum is to follow the solution thickening method.

4.4.1 Impact of Xanthan Gum on PHA Suspension Stability

Additions of xanthan gum as a rheology modifier were found to greatly improve the stability of a PHA suspension. Of the 5 suspensions thickened to varying degree using xanthan gum shown in figure 4-4, all suspensions thickened sedimented slower than the control having no rheology modifier added. The non-thickened control contained close to 0 weight percent PHA still in suspension after 30 hours, which is likely due to a small fraction of the PHA that was dispersed having a particle size in the colloid range of 0.5nm to 1 μm, which would make those particles stable to sedimentation due to Brownian motion.

While thickening did decrease the rate of PHA suspension sedimentation, it was found that samples below 125 mPa·s viscosity sedimented rapidly, while 125 mPa·s thickened slowly, and samples 250 mPa·s and above did not sediment due to gravity. This is due to the ability of xanthan gum, a conventional thickener of molecular weight greater than 10^6 to provide a superstructure capable of reducing the chance of particles to encounter one. Xanthan gum also acts as a web keeping particles from falling to the bottom of a container due to gravity. This shows by adding xanthan gum to thicken a PHA suspension to at least 248 mPa·s the suspension will be stable long term and will potentially allow time to sit on shelves for industries to coat products destined for consumer usage.

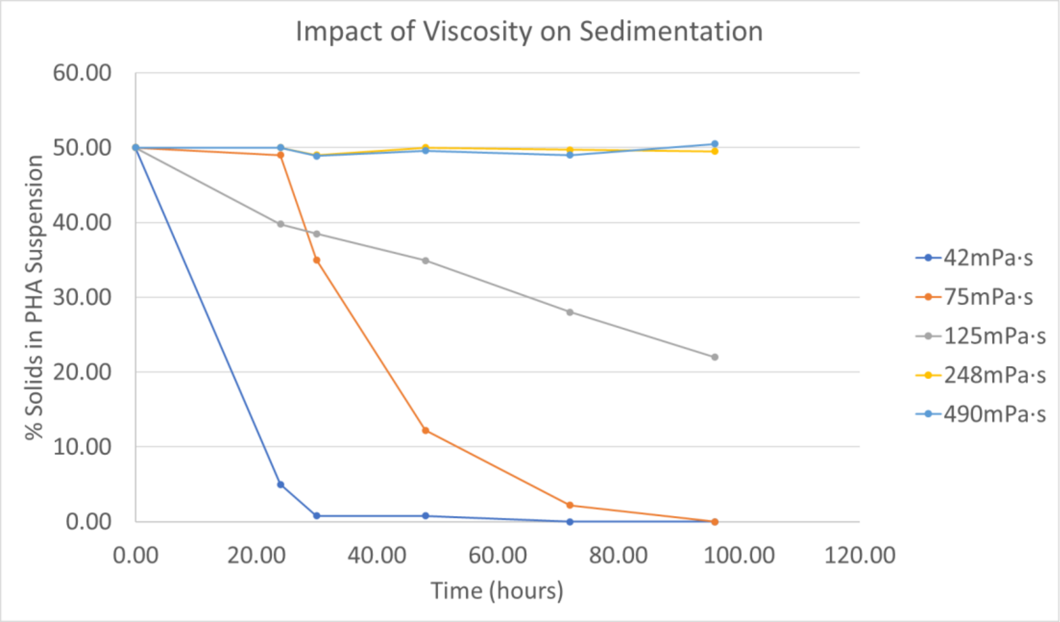


Figure 4-4. Impact of viscosity on sedimentation of xanthan gum thickened PHA suspensions over time.

4.5 Sagging and Leveling Balancing

Rheological properties greatly influence a coating's ability to effectively form a film without defects, and the optimum waterborne coatings on paperboard are coating method dependent [13, 14]. Because of this it is important to be able to target the viscosity required by the intended application and coating method. Many of the defects created during the coating application such as sagging, leveling, and cratering must be resolved or reduced before the coating is dried [15].

Through properties such as sagging and leveling the waterborne coating experiences gravity and surface tension forces differently once coated on a substrate. At the point of application an aqueous coating should shear thin and wet out over the substrate, but after post application and previous to drying the coating must continue to change in order to alleviate film imperfections[16]. The coating should recover modulus fast enough that it does not encounter running too thin and sagging due to gravity. Also, the coating should not recover so fast as to not allow the surface to flow and level out its pits, peaks, and general inconsistencies[17].

To develop a procedure of evaluating PHA suspension coatings viscosity and intended end application, a method of simulating the coating process of structure devolvement followed by gradual recovery was developed using the 3-interval thixotropy test[18]. As the name suggests this rheology test utilizes three steps. The first step simply finds the baseline structure modulus under the proscribed shear rate and amplitude, the second step is designed to simulate coating application of high-rate intense shear to destroy coating structure and modulus, while the third step returns to the same conditions as step 1 of constant rate and amplitude. During step 3 the structure modulus builds back up over time. Based on the rate of modulus recovery a viscosity can be chosen that promotes leveling by not recovering too quickly, while recovering fast enough to limit sagging[19].

To test this method the three coatings of different viscosities were first mapped to determine their linear viscoelastic range. Then the 3-interval thixotropy test was performed and the rate of structure recovery was evaluated as shown in figure 4-5. As shown the time required for the coating to cover 90% of its storage modulus is dependent on the amount of xanthan added, and consequently the viscosity of the thickened coating. The time required to recover 90% of storage modulus G’ was fastest for the coating of viscosity 1250 mPa·s, which is likely because of xanthan gums ability to rapidly recover structure compared to other rheology modifiers[20].

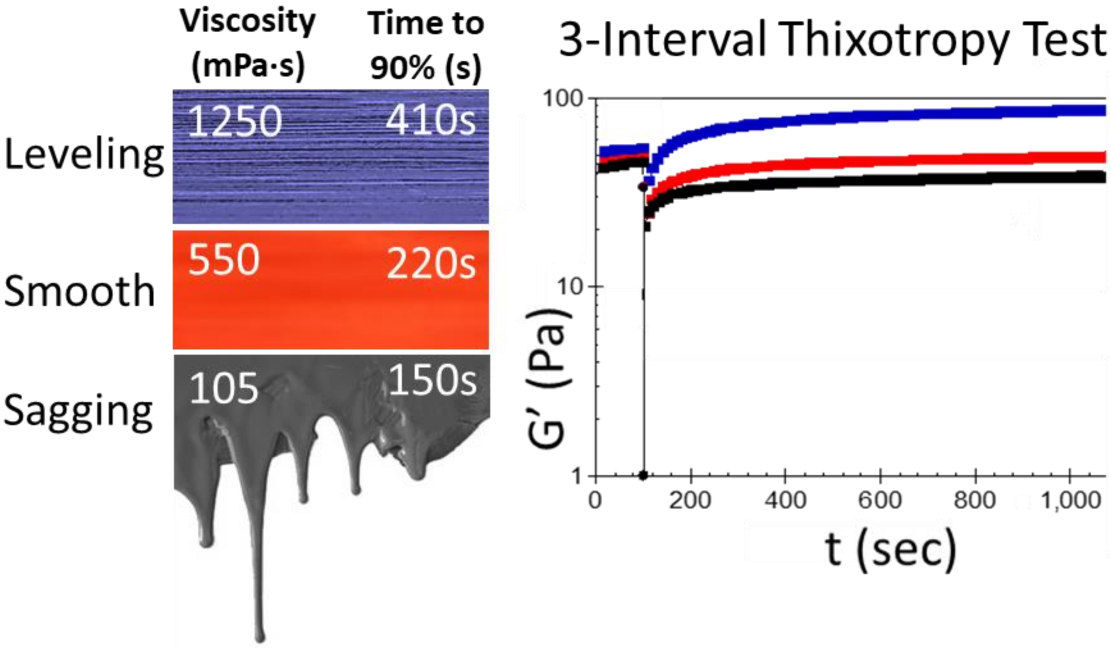


Figure 4-5: Impact of structure recovery rate on sagging and leveling of a PHA suspension coating as evaluated by the 3-interval thixotropy test.

Structure regeneration is shown in terms of storage modulus (G’), which can also be calculated as a % of original storage modulus from 3 interval thixotropy test step 1. As shown in the plot the blue curve regenerates structure the fastest and allows no sagging defects, but also allows no time to fill in coating leveling line defects. The black curve regenerates structure too slow and allows gravity to pull the coating down the page leaving sagging streaking defects. Finally, the red curve shows a balance between structure regeneration and time, producing the smoothest coating with minimal defects. Based on this, once shear rate is known for the coating application method such as gravure, rod, or blade then the viscosity of a PHA coating can be estimated and determined [21, 22].

4.6 Multi-Component Rheology Modifier

Xanthan gum provides a rheology modifier insensitive to the effects of temperature, pH, is readily biodegradable, and dissociates structure modulus upon shear. But upon structure dissociation xanthan gum rapidly reassociates when recovering, which improves sag resistance at the cost of limiting the coating's ability to fill in leveling defect lines. Advantageously, blending xanthan gum with other rheology thickener gums can provide reduced recovery rates and potentially reduce the total amount of thickener necessary to reach optimum viscosity[23].

To explore xanthan gum mixture with other biodegradable gums available, guar gum was selected based on its strong association with xanthan gum[24]. Xanthan gum was combined with guar gum in varying weight ratios of total weight percent, and the xanthan solution thickening method was utilized to thicken PHA suspension. Once these suspensions were created, they were tested for viscosity, as displayed in figure 4-6, which showed a noticeable difference in viscosity between pure guar and xanthan gum thickeners. When binary thickener blends were added to PHA suspensions the viscosity was also found to be increased with the weight fraction of guar gum added.

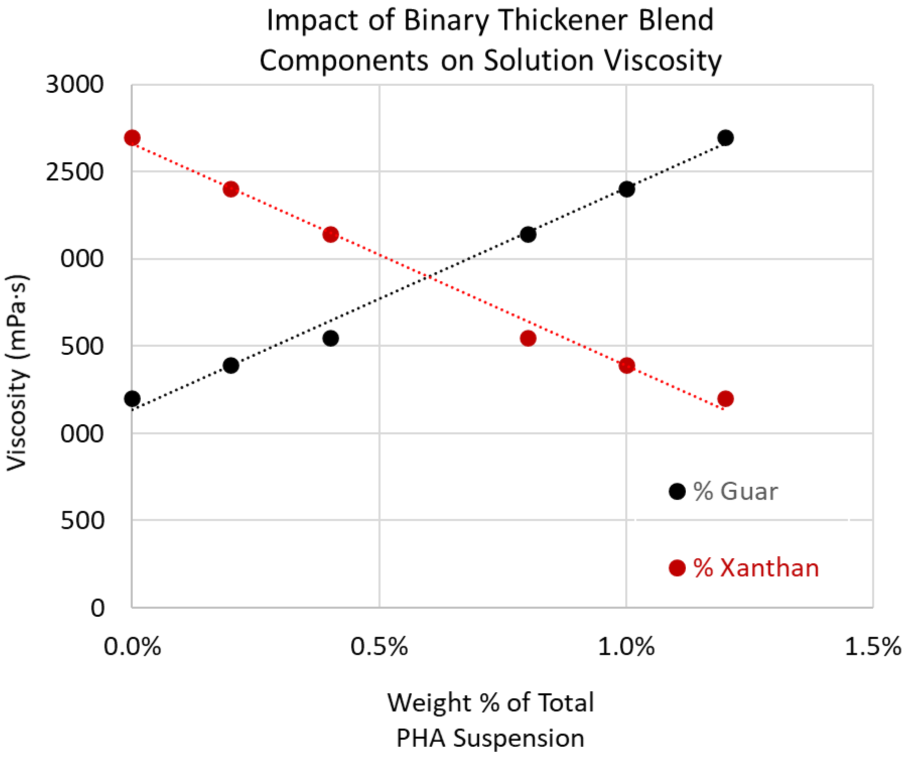


Figure 4-6 Impact of binary thickener blend components on PHA suspension viscosity.

By using a lower amount of xanthan/guar gum binary blend thickener the same viscosity can be reached requiring higher amount of xanthan gum for the intended PHA suspension optimum coating viscosity. This is especially advantageous in the scalability of PHA suspensions, since shearing high molecular weight gums into solution requires high shear and energy. Additionally, it may be possible that xanthan gum/guar gum thickeners provide lower structure recovery times than pure xanthan gum, which when dialed in effectively could reduce the number of leveling imperfections caused during coating application.

4.7 Conclusions:

To further protect a dispersion from flocculation and sedimentation it is imperative to include a conventional thickener in the formulation. A conventional thickener spreads itself throughout the dispersion, acting to shield each particle from flocculation due to van der Waals interactions of other particles. In this specific formulation that includes xanthan gum, a readily degradable high molecular weight water soluble polymer. Xanthan gum is chosen because of its low pH and temperature susceptibility, charge stabilization, and ability to efficiently thicken the at less than 0.5% weight of the total suspension.

Using xanthan gum a shelf stable PHA suspensions capable of less than 1% weight sedimentation over time was shown to be attainable. This allows the coating to be produced and shipped to industrial coating facilities before use without the worry of having to remix or produce the coating on site. Although xanthan gum is a difficult to disperse high molecular weight polymer, a method of xanthan thickening was shown to be advantageous using high shear. The xanthan thickener is dissolved in water previous to PHA suspension, which can then be added over time to the coating to obtain a linear change in viscosity based on amount of xanthan gum solution added.

Additionally, the formulation of PHA suspension coating viscosity using xanthan gum allows for a smoother more consistent and imperfection free coating due to improvement of sagging and leveling properties. This is due to the influence of xanthan gum on coating structure recovery post coating application. Coupling the knowledge of coating application shear rate and the 3-interval thixotropy rheology test, it is possible to target a xanthan modified coating of optimum viscosity.

Lastly, an advantageous binary thickener blend is shown to require less thickener added than a single xanthan thickener agent. In future work this coating will be tested to determine whether or not this is advantageous over pure xanthan or guar and compare the structure recovery rate of xanthan/guar mixtures to pure xanthan or guar gum thickened PHA suspensions.

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CHAPTER 5

HETEROGENOUS NUCLEATION OF POLY(3-HYDROXYBUTYRATE-CO-3-HYDROXYHEXANOATE) AQUEOUS SUSPENSIONS[4]

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[4] Tull, Scott. "Heterogenous Nucleation of Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) Aqueous Suspensions." To be submitted to the journal of Industrial & Engineering Chemistry Research

Abstract**:**

Aqueous suspensions of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) are a primary target for paperboard coating applications due to their advantageous biodegradability, barrier performance properties, and heat sealability. However, polyhydroxyalkanoates (PHAs) tend to have slow crystallization kinetics rate and poor performance when insufficiently nucleated. Aqueous suspensions of PHA are advantageous for coating on paperboard for their functional barrier properties, but the coating must nucleate rapidly as required by industrial application. Homopolymer polyhydroxybutyrate (PHB) is shown to be an additive that greatly increases nucleation rate and density, though its ability to nucleate is reduced when melted at above 190°C. This was remedied through the use of a binary nucleation blend of pentaerythritol and PHB. Addition of pentaerythritol was shown to worked synergistically with PHB to nucleate PHA. These results were investigated using differential scanning calorimetry (DSC) and polarized optical microscopy (POM), showing close agreement between methods. DSC was shown to be useful in determining the peak crystallization temperature and comparatively determining which nucleator worked best. Whereas POM allowed visible indication when nucleation occurred and inference into nucleation density based on spherulite size. The improvements in the nucleation rate and material properties of PHA allow for these materials to be a viable option for many industrial applications, including those requiring almost instantaneous nucleation.

5.1 Introduction:

Polyhydroxyalkanoate (PHA) polymers are an advantageous solution to end-of-life polymer mismanagement when used as a replacement for single use commodity plastic barrier coating. Stable suspensions of PHA are possible without the need for complicating milling or grinding since the polymer possesses preferable particle size distribution at the point of its production. Further, important properties required by single use applications such as substrate heat sealability barrier performance properties are achievable by PHA due to its thermoplastic nature. But one of the problems still holding PHA coatings back from replacing polyolefin and other commodity plastics and entering the markets of single use plastic coating is related to the crystallization kinetics of the polymer post melt.

In order to produce non-brittle PHA polymers capable of melt processing below the onset of rapid thermal degradation the material is copolymerized through bacterial fermentation. By copolymerizing 3-hydroxybutyrate (3HB) with 3-hydroxyhexanoate (3HH), the pendant 3HH defects created in the polymer backbone lead to reduction in total crystallinity and result in a preferable melting transition below the thermal degradation onset[1]. Because the total crystallinity of PHA copolymers is depressed the rate of crystallization of the raw polymer is reduced[2]. Molten uncrystallized PHA are tacky and stick to materials such as metal, paper, and itself. This creates a problem for applications where the coated substrate is wound up, such as textiles and industrial paper coatings, and so the molten polymer coating must solidify through crystallization fast enough to limit any unwanted adhesion[3].

The nature of paperboard coatings applications requires the thermoplastic coating to be crystallized when rolling up at the rewind or the tacky coating will adhere each layer of paper to each other, a phenomenon coined “blocking” since the coated roll effectively becomes an unrollable solid block [4]. A schematic diagram depicting the industrial coating of a PHA suspension on paperboard is shown in Figure 1. The substrate is unwound and then passes through the coating head where dispersion is added via gravure, rod, or other coating methods [5]. Coated substrate then passes through ovens to dry the coating before melting PHA granules into a molten film [6]. After ovening and melting of the coating, the use of temperature-controlled rollers allows for the coating to be held at the temperature of most rapid crystallization before rewind.

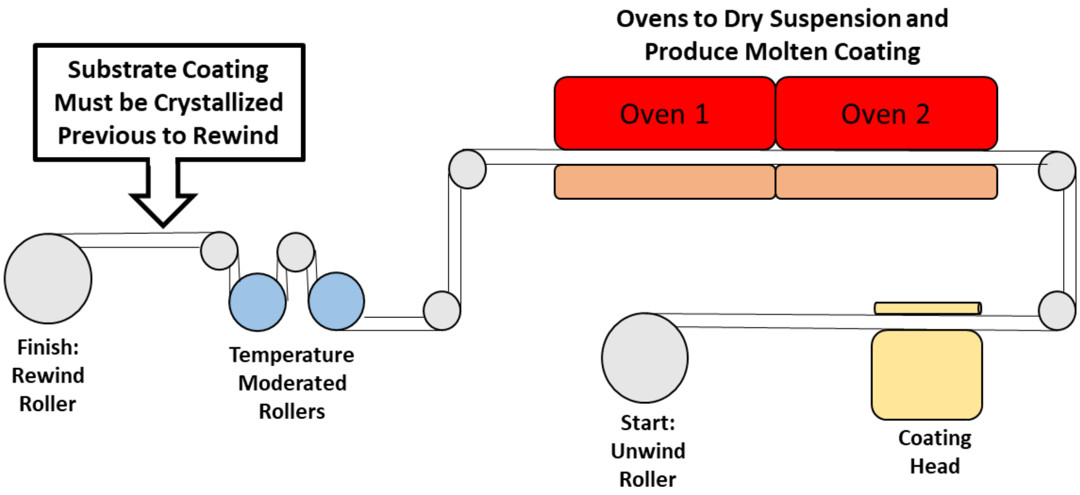


Figure 5-1 Schematic diagram example of a paper coating line where a PHA suspension coating can be applied to a paperboard substrate.

Though in the current state of PHA copolymer crystallization kinetics, PHA crystallization to a point where the coating is no longer tacky may require hours[7]. In order to produce PHA coated paperboard, after a molten film of PHA coating is produced the rate of substrate movement can be run very slowly to allow the coating necessary time to solidify and prevent adhesion to itself at rewind. This is not acceptable for mass production demanding greater than 1000m/min and so a solution to the nucleation problem must be formulated to improve PHA copolymer crystallization allowing for rapid kinetics.

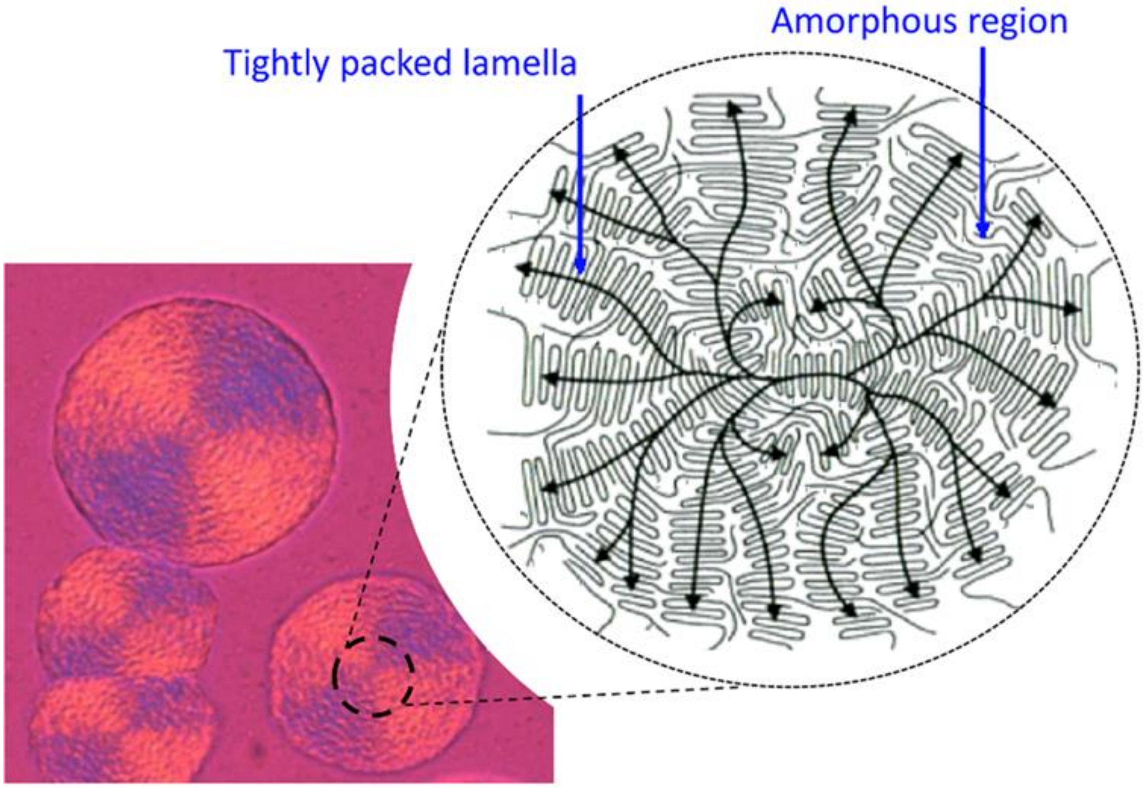


Figure 5-2 Spherulites of Polyhydroxyalkanoate (PHA) imaged using polarized optical microscopy and the spherulite structure. Arrows indicate packing molecular alignment growth of lamella.

Crystallization kinetics of polymers can be observed using polarized light microscopy where spherical regions of semicrystalline polymer (spherulites) can be viewed appearing and growing from a cooling film of molten polymer. Spherulites are visible in analyzed cross polarized light due to being birefringence, or having two refractive indexes[8]. Figure 5-2 shows large spherulites of pure PHA after being melted to 200C and an interpretation of the materials spherulites, where lamella pack tightly and copolymer defects are excluded via amorphous regions of the spherulite.

Luckily, slow crystallization kinetics is a common problem for extruded plastic applications such as injection molding where plastic is melted before addition to a mold of the desired article. Rapid crystallization is necessary since polymer must crystallize before exiting the mold or else the tacky polymer will simply stick to the metal mold and ruin its shape. A common method to accelerate crystallization rates of a polymer is to add a nucleating agent to the material, which can then lead to faster spherulite onset and crystallization. Nucleating agents can also improve mechanical and optical properties by increasing nucleation density which leads to production of smaller sized spherulite [9, 10].

Nucleation agents are dispersed before the bulk polymer is melted, and upon cooling facilitate nucleation of the amorphous polymer phase heterogeneously from the solid phase of a crystalline nucleating agent particle [11, 12]. Heterogenous nucleation is dependent on the surface area of the solid crystalline phase, and so a nucleating agent of smaller particle size produce higher nucleation densities[13]. Because of this, nucleating agents are chosen that remain crystalline throughout the entire processing window by having a melting point greater than 50 degrees higher than the polymer it is chosen to nucleate. Lastly, chemicals chosen as nucleating agents must be compatible with the application in which they are chosen.

5.2 Potential Nucleating Agent for PHA Coatings

The copolymer of PHA chosen for application as a paperboard coating is poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) containing 5-8% 3-hydroxyhexanoate (3HH) copolymer and experiences a melting peak at 140-143°C. This PHA copolymer has a melting transition advantageously above the consumer use temperature of hot serve beverage cups and food containers and its thermoplastic nature allows the PHA polymer to be the adhesive linking substrates called heat sealing. Prior to coating onto paperboard PHA copolymer particles are suspended in water using surfactants and other water-soluble additives, and so a nucleating agent should be chosen that satisfies the following:

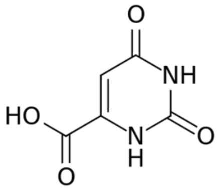
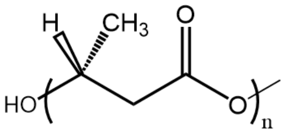
- Be readily suspended or dissolve in water.
- Should not drastically chemically alter formulation (pH, ionic strength, etc.)
- Should not require high % weight loadings that negatively affect PHA film.
- Melt above 200°C.
- Food contact approved.

Since effectiveness of a nucleating agent is based on its surface area with the polymer it nucleates the nucleating agent must be able to disperse homogenously within the suspension. The nucleating agent should also not chemically alter the suspension or interfere with the activity of surfactants and dispersants causing aggregation or flocculation of the suspended phase. Since the nucleating agent must be a crystalline solid to impart heterogeneous nucleation, it should not melt near the working conditions of the application. Lastly, because the intended application is a coated paperboard in contact with food, the nucleation agent should not be toxic or harmful in any way.

Many compounds display promise as nucleating agents for PHA, but the most effective found in literature to date that meet the criteria given are pentaerythritol [14], orotic acid [15], talc and boron nitride[16]. Pentaerythritol and orotic acid were chosen for investigation since talc requires greater than 10 percent loading to impart nucleation acceleration it was not chosen, and boron nitride is a toxic compound and is not approved for food contact.

One additional nucleator for PHA is PHA itself. Since PHA is a class of copolymer materials and the physical properties of a PHA copolymer are dependent on its polymeric makeup, it is possible to use homopolymer polyhydroxybutyrate (PHB) as a nucleating agent for copolymer PHA. This is possible because PHB melts at 174°C whereas a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) containing 6.33 % 3-hydroxyhexanoate (3HH) comonomer undergoes a melting transition at 140-143°C. The implication for PHB acting as a nucleating agent is that if it is melted it will have little impact as a nucleating agent since it is slow to nucleate. Information on the chosen nucleation agents is shown in table 5-1.

Table 5-1: Chemical structure and information on poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) nucleating agents.

	Pentaerythritol	**Orotic Acid**	**Polyhydroxybutyrate**
Melt Temp (°C)	260.5	345	174
Water Solubility	>6 g/100 mL at 20 °C	< 1 mg/mL at 20 °C	Hydrophobic
Nucleation	Known melt nucleator of PHA.	Known melt nucleator of PHA.	Unreported
Structure			

5.3 Materials Used:

Orotic acid, pentaerythritol, span 80, triton x-100, and xanthan gum was purchased from VWR. A polyhydroxyalkanoate copolymers poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) containing 6.33 % 3-hydroxyhexanoate comonomer was produced at the New Materials Institute of the University of Georgia. 18.2mΩ deionized water is produced in lab and is used for all experiments.

5.4 Experimental Setup:

5.4.1 Preparation of Aqueous Coatings:

Suspensions of PHA were produced at the scale of 250mL by first dispersing surfactants: 0.13 weight % span 80 and 0.79 weight % triton x-100 in water. PHA was then added in weight percent of 52.8 and mixed into suspension using high shear blender. If a nucleating agent was added it was mixed into the suspension while using high shear. Once a stable suspension was created, the mixture was stirred overnight to remove any air bubbles entrained during mixing. The next day the mixture was diluted with a 2% solution of xanthan until a viscosity of 400cP and 45% weight PHA. PHA suspensions were then dried 5 hours in a 50°C forced air oven before vacuum drying overnight.

5.4.2 Differential Scanning Calorimetry Measurement:

Thermal transitions, crystallization peaks, and glass transitions were determined through differential scanning calorimetry (DSC). All DSC experiments were performed on a TA instruments Discovery 250 DSC using T-zero pans. Samples were heated from 25°C to 180°C at a ramp rate of 10°C/min and were then cooled to -20°C at -10°C/min. A second heat up was performed on some samples to investigate crystallization behavior and whether a material experienced cold crystallization.

5.4.3 Polarized Optical Microscopy:

Polarized optical microscopy (also referred to as polarized light microscopy) was performed on a Nikon Eclipse LV100N POL Ci-POL microscope possessing cross polarizers and L-AN analyzer. The microscope was fitted with a Linkam THMS600 thermal stage. Experiments were performed in transmittance mode with 5x, 10x, or 20x optical magnitude.

Dried powder samples of aqueous coatings were sandwiched between glass cover slides and pressed carefully with a spatula. The slide sandwich was then placed onto the Linkam thermal stage, which heated at a rate of 10°C to 180°C, which was held until the sample fully melted, but no longer than 60 seconds. The temperature was then let free fall to 60°C, where the temperature was isothermally held. Images were taken every second and then referred to later.

5.5 Results and Discussion:

The pure polymer DSC results of the polyhydroxyalkanoate (PHA) copolymer dispersed in suspension as well as polyhydroxybutyrate (PHB) homopolymer used as a nucleating agent are shown in Figure 3. The melting peak of PHA copolymer in the first heat up was found to be 140.2°C while PHB homopolymer melting was determined to be 174°C. In order to determine the addition concentration of homopolymer PHB having greatest nucleation of PHA copolymer, PHB was added as a nucleation additive to PHA suspension by additions of 0.5, 1.0, 2.0 and 5% weight of the total aqueous PHA suspension. Once the suspension was dried it was then analyzed by DSC.

Evaluation by DSC crystallization peak showed addition of PHB nucleator increased nucleation onset and peak location until 1.0% loading, and upon higher weight loading addition of PHB nucleator no peak change or onset temperature was observed. Interestingly when 1% PHB was used to nucleate suspended PHA copolymer with a maximum temperature of 180°C, the peak crystallization

(98.9°C) temperature was observed to be directly between pure PHB homopolymer (124.7°C) and pure PHA (74.5°C) peak crystallizations.

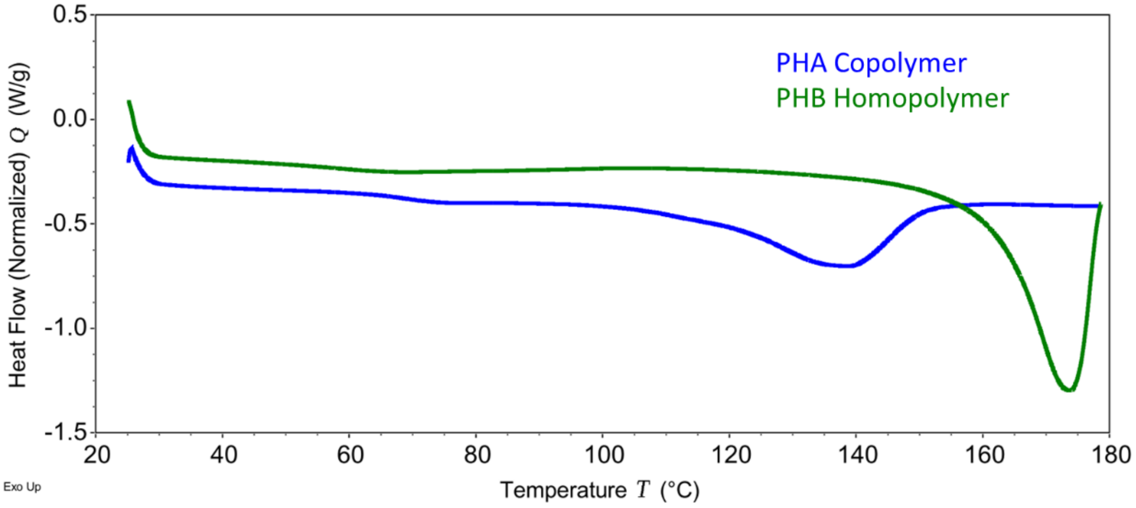


Figure 5-3 Figure 5-4: DSC plot showing the first heat up and melting transition of PHA copolymer and PHB homopolymer.

This was further evaluated using POM by imaging the dried mixture of suspended PHA copolymer with and without the PHB nucleating agent. The thermal stage was set to 180°C and after 10 seconds the dried suspension was fully molten. Shown in figure 6, when the sample was allowed to cool and held isothermally at 60°C, suspension without PHB did not begin to nucleate until after 30 seconds and was not fully nucleated by 180 seconds. The dried suspension containing 1.0% PHB was already crystallizing when the temperature reached 60°C (0 seconds), which showed full crystallization having no free area for crystals to form by 180 seconds.

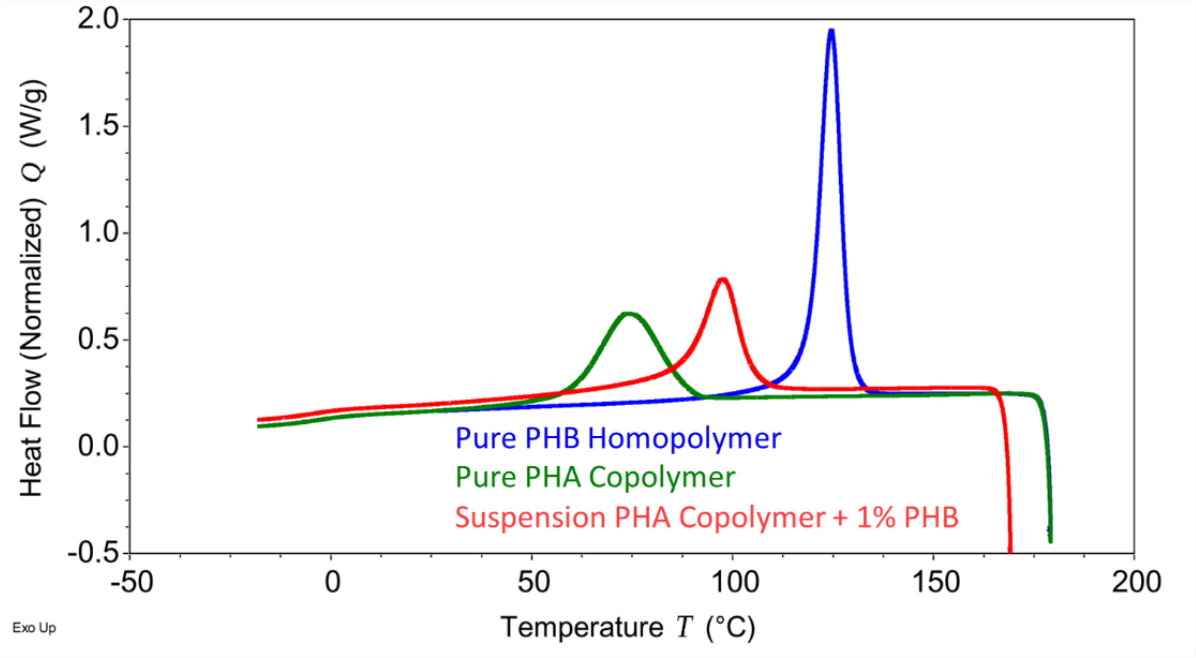


Figure 5-5: Figure 5-6 DSC plot showing the first cooldown from 180°C and impact of PHB nucleator on the nucleation of a PHA copolymer suspension.

A stark contrast was noted at the difference in spherulite size, where the no addition suspension produced large spherulites that were continuing to grow and would grow until impingement. Whereas, with the addition of 1.0% PHB the spherulites were too small to make out their shape. This shows the impact of nucleation density through the usage of a heterogeneous nucleator. When the experiment was repeated at the DSC peak crystallization temperature of suspension with 1.0% PHB a noticeable increase of nucleation rate was observed. The Pom results agree closely with results found from DSC analysis of PHB nucleation of the PHA copolymer suspension.

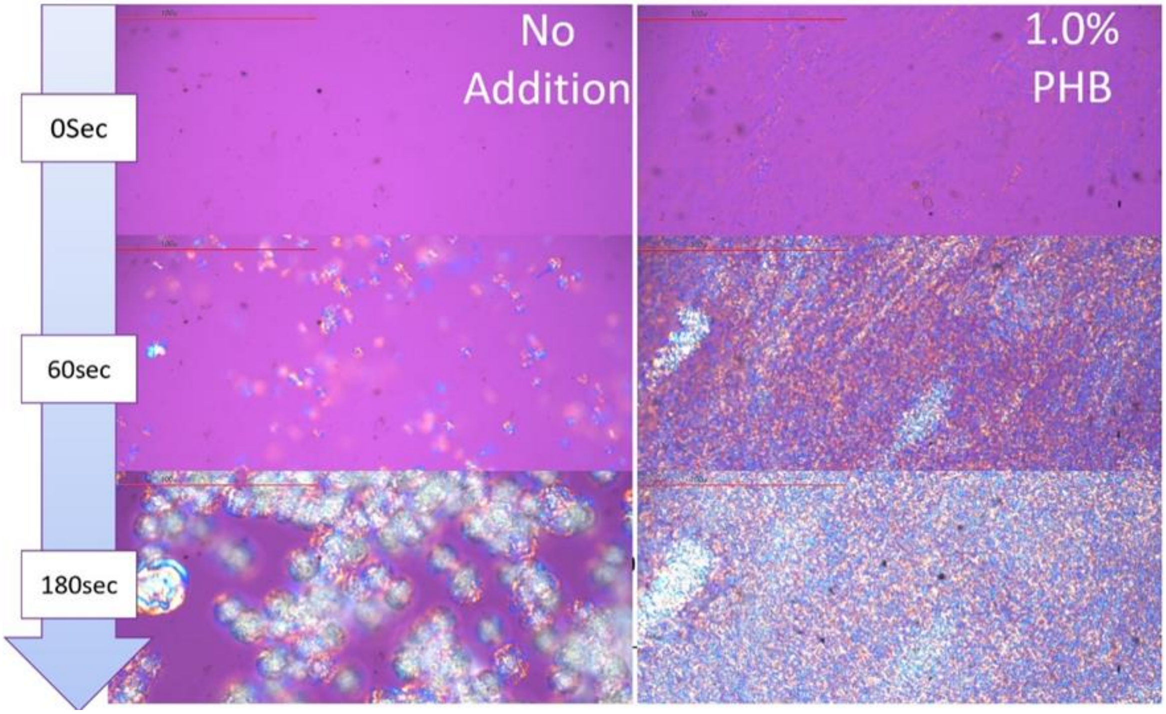


Figure 5-7: POM microscope images over time showing the nucleation of dried suspension of PHA with and without the addition of 1.0% PHB nucleation agent. The sample was melted at 180°C then held isothermally at 60°C.

The results of PHB homopolymer nucleating PHA show great promise in improving the nucleation rate and density of PHA films on paperboard, but in the case of industrial processing when PHA is applied to paperboard the coating is likely to encounter a wide range of conditions. To attain the fastest rate of nucleation for the PHB nucleated PHA copolymer currently the curing temperature must be kept beneath 180°C. When the temperature maximum was increased to 190°C, a greater enthalpy was found related to the melting of PHB, which led to a large reduction in crystallization. When PHB was melted by a temperature increase to 190°C none of the polymer blends were able to be nucleated in the time/temperature allowed and were found to exhibit cold crystallization. The limited processing window between the melting end set of PHA copolymer and PHB homopolymer onset and consequences due to processing outside that window show great limitation when utilizing the polymeric homopolymer nucleator.

Due to the constraints limiting PHB homopolymer nucleation of PHA, not all industrial manufacturing will be able to process without problem, since not every facility is able to precisely control temperature, and so the temperature of the coating may see time above 180°C. Because of this, it is important to formulate a more advantageous nucleating system such as blends of PHB with a second nucleating agent that melts far above the processing condition window. Two nucleating agents that fit this are orotic acid and pentaerythritol, which both have literature precedent, can be added in low weight loadings, and are not expected to inhibit biological degradation or food contact approval.

5.5.1 PHB + Orotic or PHB + Pentaerythritol Nucleating Agent Blends

To investigate the influence of an additional nucleating agent on the nucleation rate of PHA copolymers two new PHA suspensions were created containing binary nucleation packages of 1.0% PHB + 1.0% pentaerythritol or 1.0% PHB + 1.0% orotic acid. After drying these suspensions were characterized through thermal experiments similar to the previous work with PHB as a single nucleator. Surprisingly, when the maximum temperature does not exceed 180°C and the PHB is not fully melted, binary nucleation packages do not perform any better than PHB alone. This is shown in figure 5-8, where after heating to 180°C all first cooldown crystallization peaks overlay each other.

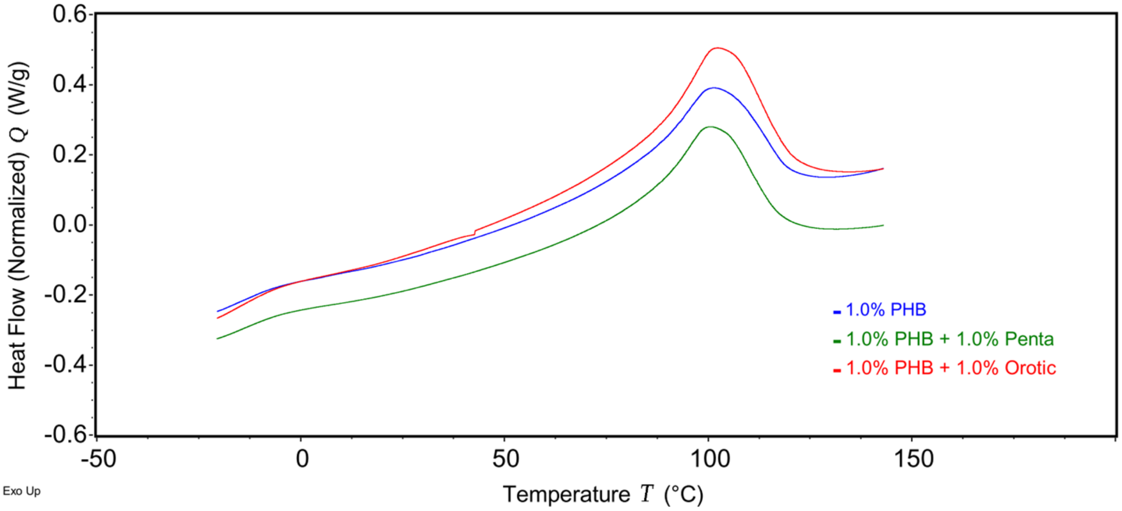


Figure 5-8. DSC plot showing cooldowns from 180°C for samples of dried PHA suspensions containing different nucleating agent mixtures.

Figure 5-8 shows PHB alone is a good single nucleator of PHA suspensions when 180°C is the maximum temperature. But after heating to 190°C a difference in the crystallization peak and rates of nucleation is noted. Figure 5-9 shows first cooldowns after heating to 190°C for PHB only, pentaerythritol + PHB, or orotic acid + PHB. A large impact is shown by the jump from 180°C to 190°C, which is due to the melting of PHB crystals in all samples, and then shows the difference orotic or pentaerythritol make upon the crystallization kinetics. Pentaerythritol was nucleated at a higher temperature and seemed to be the better nucleator.

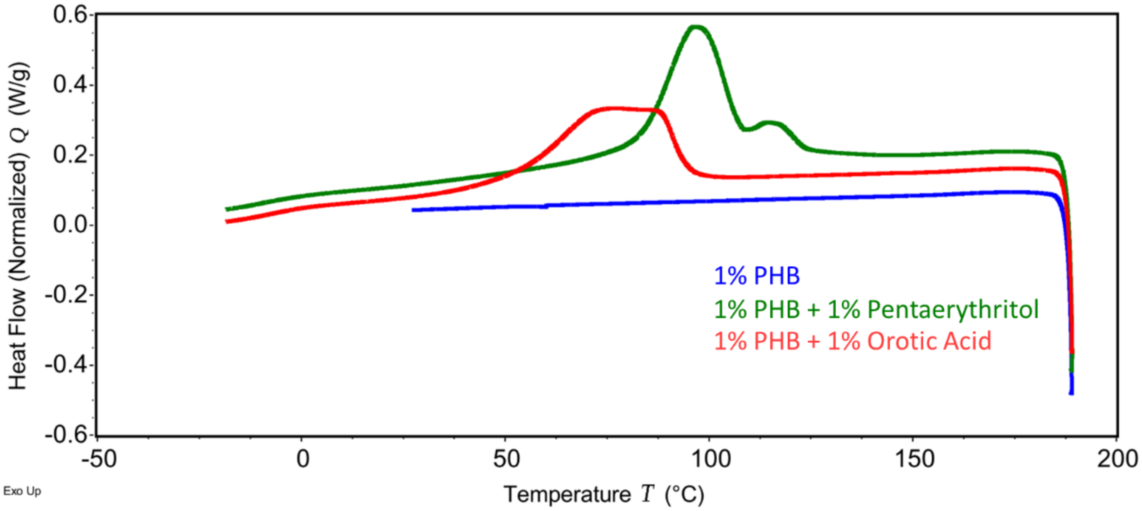


Figure 5-9. DSC plot showing cooldowns from 190°C for samples of dried PHA suspensions containing different nucleating agent mixtures.

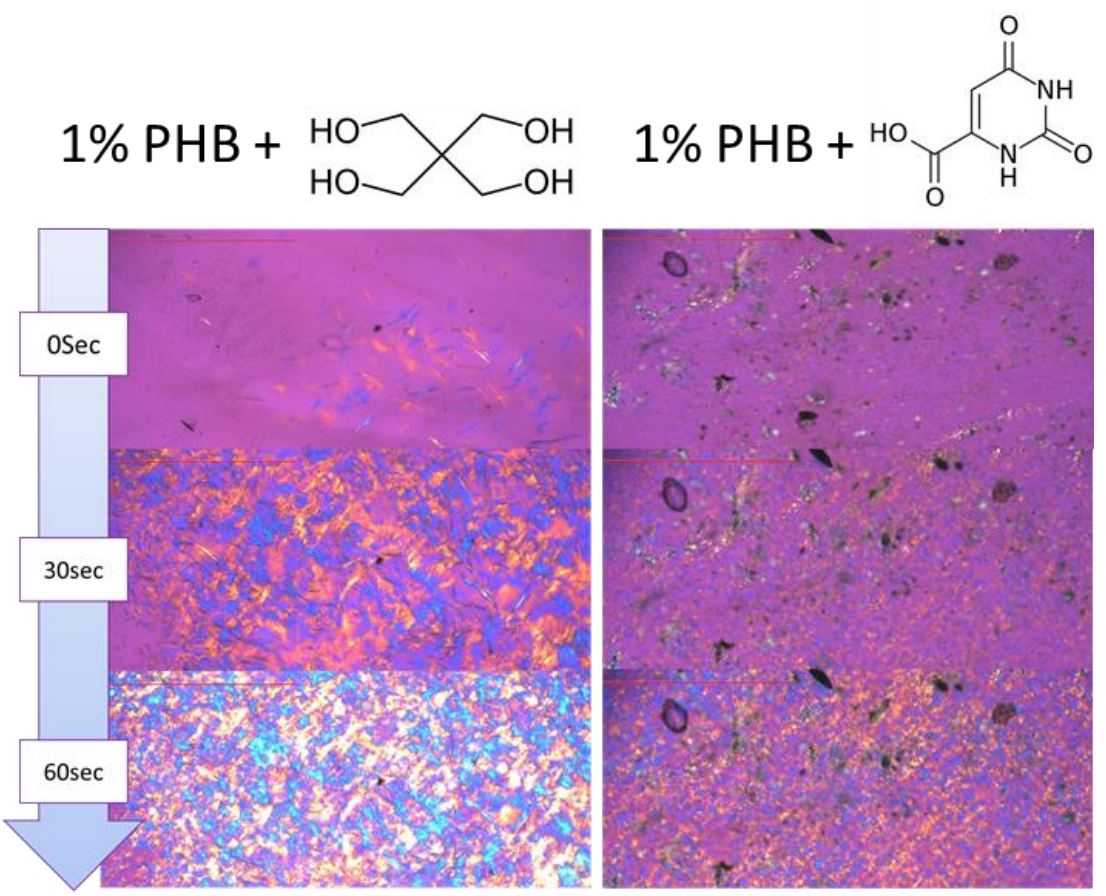


Figure 5-10 POM microscope showing nucleation over time of PHA suspensions with either PHB + pentaerythritol or PHB + orotic nucleation agent blends. The sample was melted at 180°C then held isothermally at 80°C.

As shown in figure 5-10, the suspension mixtures with PHB + pentaerythritol or PHB + orotic acid were evaluated by POM. The samples were fully melted at 190°C before cooling to hold isothermally at 90°C. 90°C was chosen as it is the peak for the highest peak temperature of the slower nucleating mixture (PHB + orotic) according to DSC results. The microscopy images show pentaerythritol nucleating with needle like crystals and fully impinging spherulites by 60 seconds, whereas orotic acid continued to nucleate past 60 seconds. When the peak temperature of PHB + pentaerythritol was chosen the nucleation, rate was increased for PHB + pentaerythritol, whereas PHB + orotic acid required more than 4 minutes to crystallize and formed larger spherulites.

5.6 Conclusions

The nucleation rate of PHA suspensions was greatly improved upon the addition of homopolymer polyhydroxybutyrate, though it was readily apparent that the benefits of PHB nucleation agent were lost upon heating to 190°C and melting the PHB. A second nucleation agent was used in conjunction with PHB, which was able to nucleate the faster than if the nucleation agent was added alone. Pentaerythritol/PHB nucleation conjunction was found to be the fastest. It should be noted that upon POM imaging it was noticed that adding orotic acid also added large crystals of material. Pure orotic acid was then analyzed through laser diffraction and found that it contained up to 300-micron particles. Since pentaerythritol is readily water soluble it is advantageous in the context of an aqueous coating.

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CHAPTER 6

CONCLUSIONS AND FUTURE DIRECTIONS

6.1 Conclusions

This dissertation is written to address the necessary components of an aqueous suspension of hydrophobic polyhydroxyalkanoate particles for use as a functional barrier coating of paperboard. This functional barrier coating imparts properties of barrier to water, water vapor, oil and grease, and function as a heat sealable adhesive. Chapter 1 provided an introduction and overview of current technology utilized in the single use plastic industry providing barrier properties to paperboard substrate. The definition of a suspension coating is given and necessary components to stably disperse hydrophobic PHA particles intended for coating on paperboard are discussed.

Chapter 2 discusses PHA as a polymer for a suspension coating and its advantages as a functional barrier coating of paperboard. A specific PHA copolymer, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) containing 5-8% comonomer is chosen due to its advantageous thermal properties. The dispersibility of hydrophobic PHA particle size is discussed as a function of the particle size by volume. The influence of dispersed PHA weight percent on film structure recovery was examined, and the best loading of PHA into suspension was determined. PHA is shown to improve both water vapor and liquid barrier through use of the Cobb value and water vapor transmission rate. Lastly, a method of determining PHA heat sealability is detailed and PHAs potential as a heat sealable coating is discussed.

Chapter 3 discusses the choice of a surfactants as a necessity for dispersing hydrophobic PHAs. Surfactant chemistry is considered, and nonionic surfactants are chosen to disperse PHA based upon their effectiveness as steric stabilizers and lower foamability than their ionic counterpart. The hydrophilic lipophilic balance is used to formulate a dispersant system for PHA utilizing mixtures of highly polar and nonpolar surfactants. The lowest necessary concentration of that surfactant system to disperse 45 weight percent PHA into stable suspension is determined using rheology. Lastly, a thermally induced repeatable thickening phenomenon is discussed, demonstrated as the result of polyethylene glycol surfactant cloud point, and a solution is given.

In Chapter 4 a rheology modifier xanthan gum is identified as suitable for application with PHA. The addition of this rheology modifier provides further stability to a PHA suspensions and greatly reduces sedimentation. Xanthan gum is used to thicken a PHA suspension to a preferable viscosity resulting in coatings having reduced defects due to the coatings ability to recover structure at an advantageous rate post coating, thereby limiting sagging and leveling. Additionally, a binary rheology modifier system is proposed with future outlooks.

In chapter 5 reduced nucleation kinetics of PHA copolymers is discussed as a dilemma. Polarized optical microscopy and analysis of DSC crystallization peaks are used to determine improvement in nucleation rates of dried PHA suspensions. Nucleation rates are greatly improved by using homopolymer polyhydroxybutyrate as a heterogenous nucleating agent. This system is revised by adding a second nucleating agent capable of increasing the temperature processing window.

6.2 Future Directions

This thesis has outlined how an aqueous suspension of polyhydroxyalkanoate was experimentally formulated as a functional barrier coating for paperboard. Although this coating is successful in improvement of the paper substrate, some work is still necessary before and is ongoing.

The following improvements need investigation:

- Add filler such as clay or calcium carbonate to formulation with the intention to reduce cost of coating and improve gas barrier properties such as WVTR.
- Add associative thickeners to improve high shear and zero shear viscosities to improve film formation and limit coating imperfections even further.
- Develop alternative surfactant packages capable of achieving lower surface tension for coating methods such as curtain coating.
- Further develop xanthan/guar gum binary rheology modifier.

6.3 Final Remarks:

As plastic production continues to increase and virgin plastic products continue to be more economical than recycled plastic, the necessity of improving end of life of plastic grows. Polyhydroxyalkanoate copolymers are the poster child of the second wave of sustainable materials promising to surpass PLA and other currently utilized “green” materials but requires progress and new innovation to even be considered for replacing petrol-based plastics. The research described in this dissertation has shown progress toward replacing unrecyclable “negative value” functional barrier coatings on paperboard and will continue to be optimized with the hopes of improving our environment, economy, and future.