Production of polyhydroxyalkanoates (PHA)-based renewable packaging materials using photonic energy: A bench and pilot-scale study

MICHAEL JOYCE, LOKENDRA PAL, AND TOM TRAN

ABSTRACT: This work describes the utilization of a new photonic heat treatment technology in combination with polyhydroxyalkanoates (PHA) materials for the development of biofriendly packaging and coated substrate materials. This technology advances the use of aqueous PHA coatings as a replacement for less environmentally friendly extruded plastic and fluorotreated packaging papers and boards. The new technology utilizes short burst photonic energy to heat PHA latex coatings. Utilizing a rapid pulse of photonic energy enables PHA particles to melt and form a film within milliseconds, as compared to conventional equilibrium drying that takes several minutes.

Coatings were applied to commercially produced papers in order to validate the combined use of photonic treatment technology with PHA materials for commercial applications. Photonic treatment for both bench-top and roll-to-roll pilot-scale studies resulted in kit values of 12, and 2 min Cobb values of <2 g/m^2. Repulpability studies showed the material to be completely repulpable, having 100% accepts after screening. The results demonstrate that the photonic treatment of PHA polymers could be used in current commercial settings to produce environmentally friendly packaging and coated products.

Application: By combining aqueous based PHA coating with photonic drying technology, it is now possible to implement PHA in commercial applications pertaining to environmentally friendly barrier coatings for the manufacture of functional paper and paperboard products, specifically for moisture vapor, moisture, and grease resistance. It presents an alternative to conventional non-renewable extruded polyethylene, petroleum-based latex coatings, and fluorochemical and chromium-containing coatings. Industry impacts for the introduction of this technology include: introduction of green chemistry formulations into coating processes, reduction of plastic waste in the recycle stream, increased utilization of renewable and sustainable product lines, and decreased carbon footprints.

Petroleum-based plastics present a major environmental and societal challenge. In 2015, approximately 34.5 million tons of plastic waste was generated in the United States, which accounted for approximately 13.1 percent of total municipal solid waste that same year [1]. Along with negative environmental impacts, conventional plastics are known to contain various additives that impact human health. These additives include bisphenol A (BPA), Di(2-ethylhexyl) phthalate (DEHP), and polyfluorinated compounds [2]. The substitution of plastics with biobased alternatives can help mitigate, if not eliminate, the negative consequences of petroleum-based plastic use. The use of polyhydroxyalkanoate (PHA) as a biodegradable plastic has been extensively studied and has shown great promise as a replacement for conventional plastics, including polyethylene (PE) and polypropylene (PP) [3-8]. It has also been shown that PHA improves the moisture resistance of paper [7] and its modification or blending of PHA with other natural materials provides similar barrier properties as plastic, such as water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) [8].

In addition to the use of PHAs as a renewable and compostable barrier material, starch as a low-cost filler for bioplastic and petroleum-based polymers to improve the mechanical and thermal properties of films have been well studied. As a filler, it tends to reduce the tensile strength, elongation to break, and toughness of a blend, and tends to increase the blend's modulus. Starch has been blended with biodegradable polymers, such as aliphatic polyesters, to lower the cost and to enhance the biodegradability of the blends. For example, starch has been blended with polymers such as polycaprolactone (PCL) and poly-(hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). Ramsay et al. [4] blended granular starch with PHBV. As the starch content increased from 0 to 50% (w/w), tensile strength decreased from 18 to 8 MPa, and Young's modulus increased from 1525 to 2498 MPa. The biodegradation rate was faster when starch was present in PHBV. Park et al. [9] blended granular cornstarch with poly(lactic acid) (PLA) and star-shaped PLA. Sun and Ke [10] blended PLA with granular cornstarch and talc to find starch effectively increased the crystallization rate of PLA. Reis et al. [11] found blends of

polyhydroxybutyrate-hydroxyvalerate (PHB-HV) with increasing waxy maize corn starch contents of 0%, 20%, 30%, 40%, and 50% to decrease the Young's modulus, strain to break, and puncture force. A lack of interfacial adhesion between starch and PHB-HV was also reported.

The use of PHA and its family of co-polymers with the addition of other natural materials for use in packaging has also been well studied. Shawaphun and Manangan [12] studied the possible use of PHA and PLA paper coatings for food packaging by dip coating papers with PHA and PLA resins dissolved in different solvents. The results showed PHB coated papers to have higher water resistance, but lower oil resistance in comparison to the PLA coated papers. Arrieta et al. [13] studied blends of PHB and PLA by preparing compression molded films from resin blends. Films were prepared with and without plasticizer and their properties compared. The addition of PHB greatly increased the film's oxygen barrier while decreasing wettability. The addition of poly(ethylene glycol) (PEG) and acetyl(tributyl citrate) (ATBC) showed the ATBC to be more effective than PEG in plasticizing the films. Modi et al. [14] used PHB with different polyhydroxyvalerate (PHV) contents (5%, 12%, and 20%) and varying molecular weights to obtain polymers with glass transition temperatures between 10°C and 20°C. The addition of PHBV enabled films with high elastic modulus, as well as flexural strength with low tensile strength and elongation at break, to be obtained. The WVTR of the films showed the PHBV polymers to be very hydrophilic. As a result, their WVTR in comparison to other thermoplastic polymers used for packaging were high. Bucci et al. [15] compared the dimensional and mechanical properties of PHB and polypropylene (PP). It was found that PHB packages had a different resistance to dynamic compression when compared to PP. The deformation value was about 50% lower than PP, due to the increased rigidity and lower flexibility of the PHB material. For freezing and refrigeration conditions, the PHB's performance was lower than that of PP. However, at higher temperatures, the PHB performed better than PP. Follain et al. [16] studied the structure and barrier properties of PHA films prepared by solvent cast and compression molding methods. It was found that the film-forming process used had a negligible influence on the thermal features displayed in the PHA films.

Much of the work that has been completed using PHA has focused on its use in thermoforming or hot melt extrusion applications; however; there is little research that has been done pertaining to its use in aqueous coatings. Since PHA particles are highly hydrophobic, additional steps are required to stabilize them in aqueous media. The ability to stabilize PHA particles in aqueous media was first reported by Showa in 2004 [17]. This work was furthered by Whitehouse in 2015, where a method for producing aqueous PHA emulsions with polymer dispersants was described [18]. Whitehouse's work was utilized by Metabolix (Cambridge, MA, USA) for the creation of barrier coatings.

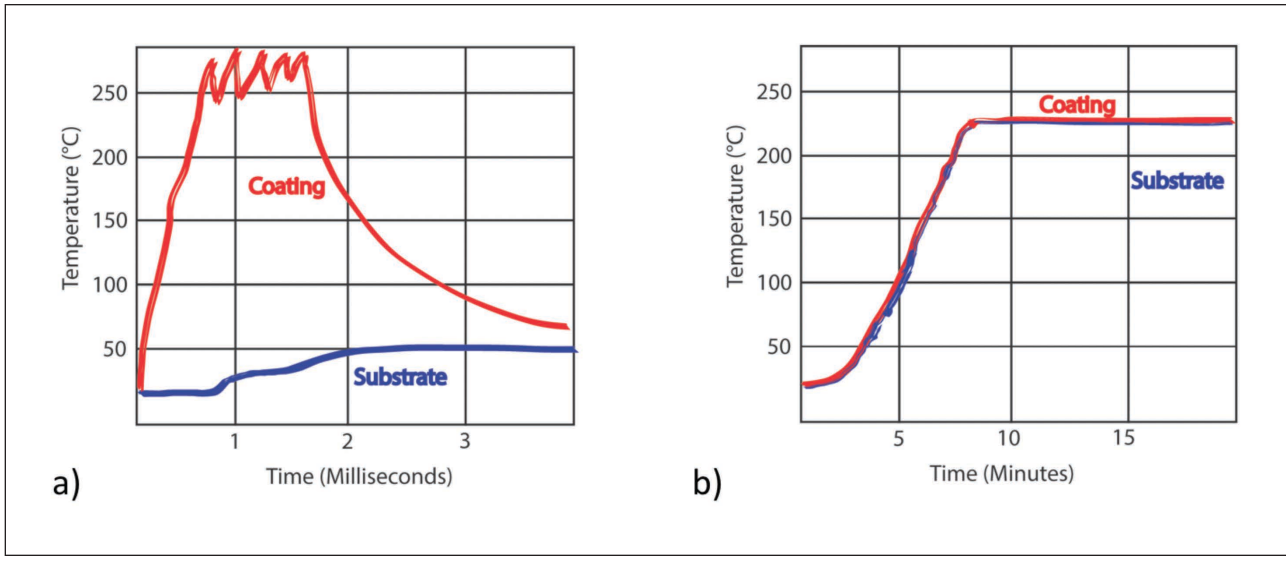
The ability of aqueous PHA latex to provide barrier properties makes it a viable candidate to replace holt melt extruded or fluoro treated papers and paperboards in applications such as food packaging. However, limiting factors such as high raw material costs [9] and loss in processing speed due to long dry time requirements still exist. Even if drying PHA materials using conventional techniques was not an issue, there would still be the issue of base substrate degradation due to the longer dwell time at high temperatures. As a result, the utilization of PHA materials for packaging has not been commercially adopted. Instead, extrusion or thermoforming processing methods that enable the high temperatures required to melt and form films from low cost petroleum-based plastics without detrimentally impacting the base substrate is practiced. However, as an off-machine process, its processing costs are higher than inline aqueous coating application methods.

Although advances in technology have improved the production yields of PHAs, at current manufacturing volumes the cost of PHA is not competitive with petroleum-based plastics. However, it is predicted that PHAs will be able to compete if manufacturing volumes increase. In order for manufacturing volumes to increase, a large-scale application is needed. Paper and paperboard coating applications could serve this need, if the process limitations noted previously could be overcome with the exposure of PHA latex coated papers to photonic energy.

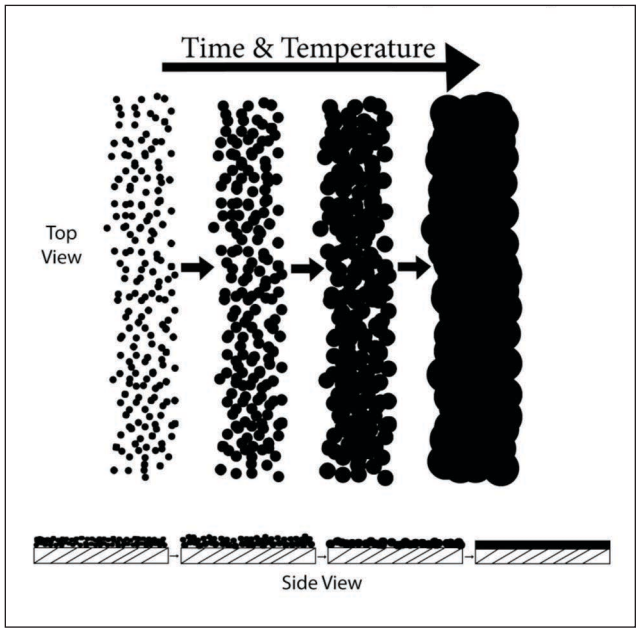
In this work, a high energy photonic surface treatment is explored due to its very specific advantage of rapidly heating a coated or printed surface to a high temperature without degrading the substrate. This is achieved by emitting a pulse of high intensity light from a xenon bulb. With this system, heat is transferred to the coating within milliseconds. The change-point for photonic vs. conventional drying is that photonic technology emits a light energy that is just intense enough to ensure thermal equilibrium between the particles and the substrate is never achieved (**Fig. 1**). The particles are treated and cooled before any substantial heat transfer to the base substrate occurs [19].

This drying technology differs from conventional equilibrium (oven) drying techniques where both the base substrate and coating material reach the ambient temperature within the drying system. The application of photonic energy enables the high-throughput film formation of (PHA) particles without damage to the base substrate. Melting of the PHA particles is required to create a continuous polymer film to achieve the desired barrier properties for packaging (**Fig. 2**).

The use of non-equilibrium drying methods will result in differences in the heating and cooling rates of the polymer throughout the coalescing and interdiffusion processes. Heating and cooling rates are known to impact the crystallinity of a polymer, which will subsequently impact functional barrier properties. The ability to tailor these heating and cooling rates may lead to the ability to further optimize functional coatings for application specific purposes. In this work, the main focus was on the feasibility of commercial implantation of this technology for drying of PHA materials. Future work could focus more on the optimization of barrier properties through a manipulation of heating and cooling rates via changes in photonic energy and/or pulse conditions.



1. Temperature of coating and substrate vs. time for a) equilibrium drying, and b) photonic drying.



2. Coalescing and interdiffusion of polyhydroxyalkanoates (PHA) particles with time and temperature.

EXPERIMENTAL

Materials

The PHA coating used was the trademarked Mirel 8000 latex supplied by Metabolix. Paper samples were supplied by two commercial paper manufacturers. The grade and basis weights of the substrates used are shown in **Table I**.

These basis weights are similar to the basis weights of products used in baking release and lightweight packaging applications. Having bleached and non-bleached samples was important to study the influence of color on photonic energy requirements.

Grade	Basis Weight, g/m²	Sample, #
Unbleached kraft	23	A
Bleached kraft	22	B
Bleached kraft	38	C
Unbleached kraft	90	D
Bleached kraft	95	E

I. Paper substrates.

Methods

Mirel 8000 latex was applied on selected papers using Meyer rods. Three different Meyer rods (#0, #10, and #22) were used to vary the coat weight applied. Sheeted samples were then treated using a photonic energy treatment system from Novacentrix (Austin, TX, USA). As a control, a set of samples was also dried using a hot air convection oven at 155°C for 10 min. The oven drying condition was selected based on the recommendation of the PHA latex supplier. After the initial lab screening to determine the photonic energy required to form a PHA film, studies were moved to pilot trials on a roll-to-roll coater equipped with a rod and gravure coating station, as well as photonic heat treatment units. For the application of PHA coating, an anilox roll with 9 billion cubic microns (bcm)/200 lines per inch (lpi) cells and Meyer rod #10 were used. **Table II** shows the pulse conditions used during the trial.

The determination of coat weight was completed using the ASTM F2217/F2217M-13 Standard Test Method "Standard practice for coating/adhesive weight determination." Coated samples were treated by one of two methods: infrared (IR) dried, and photonic energy treated. The pulse conditions varied based upon the coating application method used and the color of the substrate (white for bleached or brown for unbleached).

Condition #	Unbleached (Brown) Papers		Bleached (White) Papers
	1	2	3
Coating method	9 bcm Anilox	#10 Meyer rod	9 bcm Anilox and #10 Meyer rod
Power, V	275	320	400
Pulse length, us	5000	5600	5000
Number of pulses	1	1	1
Coating speed, ft/min	10 ft/min	10 ft/min	10 ft/min
Energy per unit area	3.35 J/cm^2	6.21 J/cm^2	10.38 J/cm^2

II. Pulse conditions used during pilot trial (bcm = billion cubic microns).

Name of Test	TAPPI Standard Test Method
Basis weight	T 410 "Grammage of paper and paperboard (weight per unit area)"
2-minute Cobb	T 441 "Water absorptiveness of sized (non-bibulous) paper, paperboard, and corrugated fiberboard (Cobb test)"
3M kit test	T 538 om-01 "Roughness of paper and paperboard (Sheffield method)"
Gurley porosity, HS, 10 mL/min	T 460 om-02 "Air resistance of paper (Gurley method)". T 536 om-96 "Resistance of paper to passage of air (high pressure Gurley method)"
Water vapor transmission rate	TAPPI T 448 "Water vapor transmission rate of paper and paperboard at 23°C (73°F) and 50% RH". ASTM E96/E96M Wet Cup Method "Standard Test Methods for Water Vapor Transmission of Materials"
Surface energy	T 558 "Surface wettability and absorbency of sheeted materials using an automated contact angle tester"

III. Standard TAPPI Methods for paper testing.

For unbleached papers, it was found that two different pulse conditions could be used: one for anilox coated samples and another for Meyer rod coated samples. The bleached substrates all utilized the same pulse condition regardless of the coating method utilized. The need for two different pulse conditions when using unbleached substrates is attributed to differences in coat weights obtained by both application methods. Less coating was transferred by the 9 bcm anilox. A larger anilox was not available. The higher energy required for bleached papers in comparison to the unbleached papers is attributed to the higher absorption of energy by the darker substrate. Also, because the color of the applied coating was white, differences in coat weight did not reduce the amount of energy absorbed. As a result, the pulse conditions required were the same regardless of the application method for the bleached papers.

When the #2 pulse condition was used for unbleached anilox coated samples, the substrate ashed. This problem did not occur with the bleached substrates as they absorbed much less energy. Higher energies were not used for the bleached substrates when using the Meyer rod due to lamp limits nearly being reached.

The particle size of PHA dispersion was measured with Malvern Panalytical 3600 Zetasizer particle size analyzer (Malvern Panalytical; Malvern, UK). Along with particle size, the viscosity of the coating at different shear rates was measured using a Brookfield DV-III Ultra viscometer (Ametek Brookfield; Middleboro, MA, USA) with a #3 spindle at 21°C. The thermal properties of the PHA coating were measured by thermal gravimetric analysis (TGA) with a TA Instruments Q500 TGA (New Castle, DE, USA), and differential scanning calorimetry (DSC) was used to purge the system using a TA Instruments Q2000 DSC (utilizing nitrogen gas). The TGA procedure was set to equilibrate at 30°C prior to ramping to 475°C at 10°C/min. TGA experiments were also run using air as a comparison to the nitrogen gas to determine if any oxidation reactions could be occurring that may affect the coating material structures. DSC measurements were run using a 10°C/min ramp to 100°C, where they were held for 10 min. They were then ramped to 190°C at 10°C/min. A purge gas flow rate to 20 psi was used for both TGA and DSC experiments.

The properties of uncoated and coated substrates measured and the test method used are shown in **Table III**. The 2-min Cobb test is a measure of water resistance, the 3M Kit test is a measure of oil and grease resistance. Gurley porosity is a measure of air permeability. Surface energy is a measure of printability (potential for anilox coating transfer), and level of internal sizing. The surface energy of the coated substrates was measured using an FDS OCA 15 EC goniometer (Future Digital Scientific; Garden City, NY, USA) with ultra-pure deion-

ized water and methylene iodide as the two testing fluids. Calculations were made using the Owens-Wendt method.

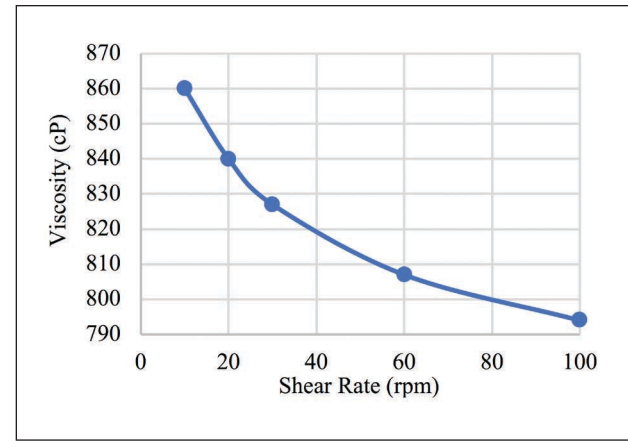
Scanning electron microscopy (SEM) images were obtained using a Hitachi S-3200N (Hitachi; Tokyo, Japan) variable pressure SEM system. Samples were sputter coated with 15 nm of Au/Pd (60/40) using a Hummer II sputter coating system (Anatech USA; Hayward, CA, USA) prior to imaging.

Repulpability testing was accomplished using the repulpability protocol established by the Fiber Box Association (Itasca, IL, USA). The two substrates tested were the #10 rod coated photonic treated and oven dried high basis weight unbleached paper, and the lowest basis weight bleached paper. These samples were tested because they represent the two different ends of the spectrum in regards to their properties and fiber types, with one being very bulky and porous (high basis weight unbleached grade) and the other having a very low grammage and low porosity (lowest basis weight bleached grade).

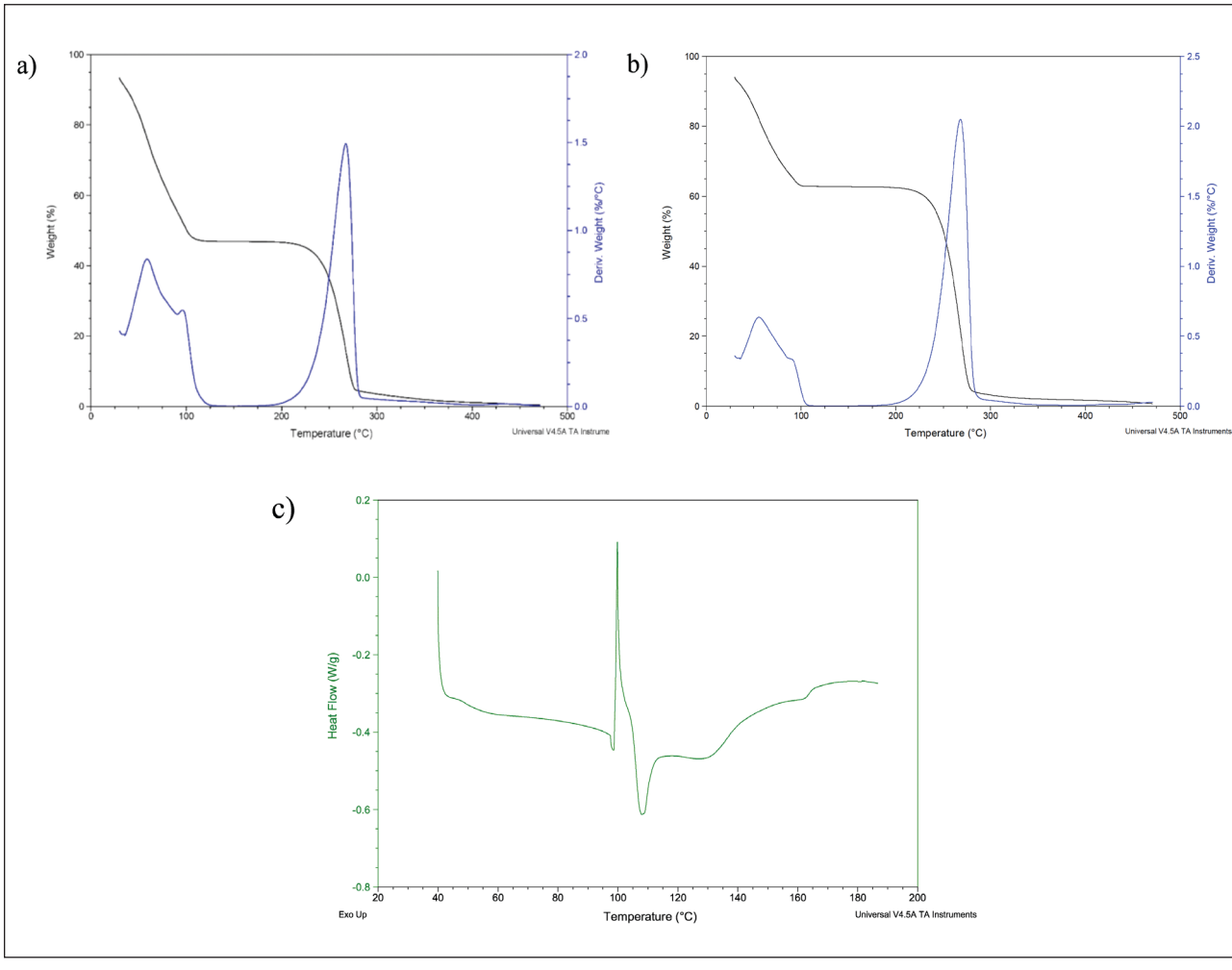
RESULTS

Aqueous PHA dispersion

The particle size was found to be 5 µm. The solids content and pH of the coating was measured and found to be 50.5% and 5.9, respectively. The Brookfield viscosities at different shear rates (rpm) is shown in **Fig. 3**. The density of the coating, measured using a pycnometer cup, was found to be 1.325 g/mL. The results of the TGA (left graph) and DSC (right graph) analysis are



3. PHA Brookfield viscosity as a function of shear rate.



4. PHA coating analysis using a) thermal gravimetric analysis (TGA; run with N_2), b) TGA (run with air), and c) differential scanning calorimetry (DSC).

Sample	Basis Weight, g/m²	2-min Cobb, g/m²	Porosity HP Gurley, s/10mL	Kit Value, #	Total Surface Energy, mN/m	Color
A	23	Fail	2.27	0	34.17	White (bleached)
B	23	15	0.84	0	41.03	Brown (unbleached)
C	36	18	4.08	0	17.33	White (bleached)
D	90	Fail	0.77	0	NA	Brown (unbleached)
E	97	30	0.96	0	35.33	White (bleached)

IV. Base sheet properties (HP = high pressure).

shown in **Fig. 4**. The results show the glass transition at 49.2°C, the crystallization at 99.8°C, and the product to have several melting points due to its multiple material constituents. Melting points are observed at 97°C, 108°C, 130°C, and 165°C.

From the TGA analysis seen in Fig. 4 (parts a and b), it can be seen that there are no oxidation reactions occurring that would impact the polymer performance. The relatively high T_g of this particular PHA material provides it with a unique plasticity that aids in film forming absent of excessive cracking. The ability to form a continuous film absent of cracking is necessary to provide optimal barrier performance, such as those of water vapor, oil, and grease. The melting temperature of this PHA is in line with previously published PHA/PHB materials [20,21].

Base substrate properties

The barrier properties of the uncoated substrates are shown in **Table IV**. Two of the base sheets failed the 2-min Cobb test. A failure of the Cobb test occurs when water penetrates through the test substrate and can be seen on the surface of the testing apparatus. The surface energy of one sample was unable to be obtained and is marked as ("NA") due to the test liquids penetrating into the substrate surface prior to the time to enable calculation of surface energetics.

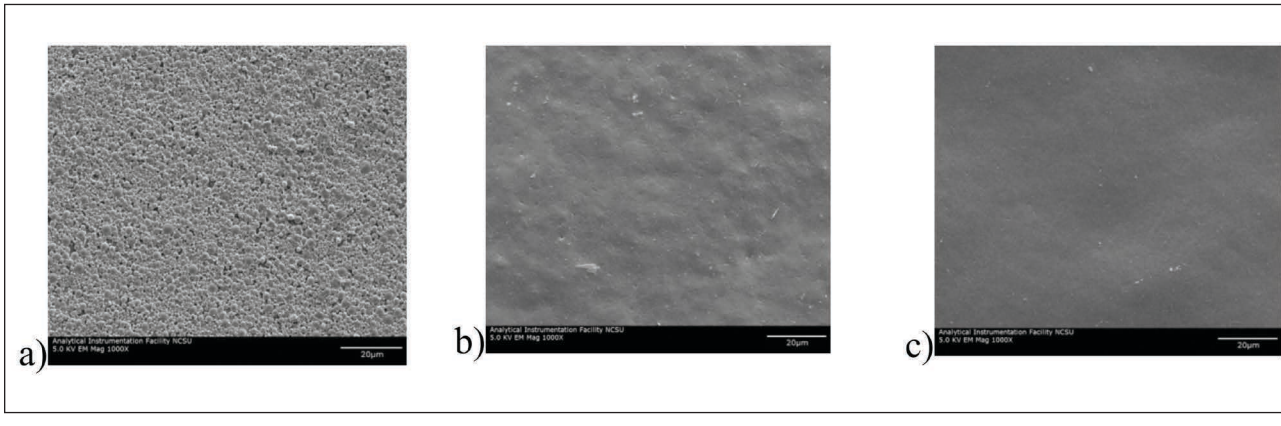
As expected, all samples showed little or no barrier to oil, grease, and water. Both Cobb and Gurley porosity are important because they influence coating holdout. Papers with greater coating holdout will tend to hold more coating on the surface (less coating penetration). Surface energy is a measure of surface wetting. The lower the surface energy, the less wetting on the surface.

Convection oven treated and pilot photonically treated samples

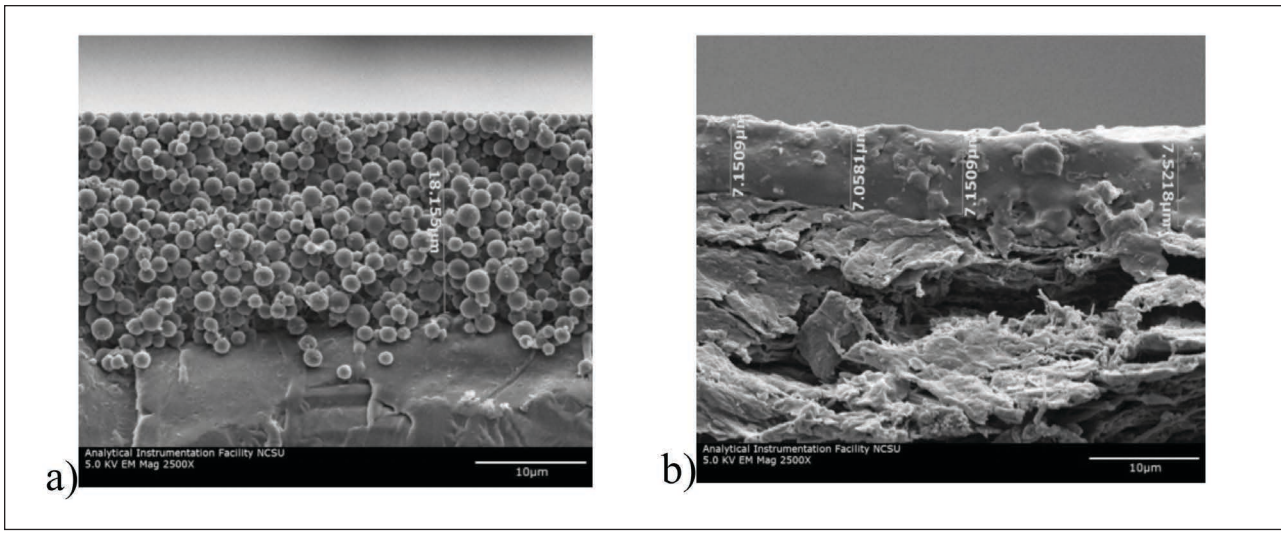
To determine the effect of photonic treatment on PHA film formation, SEM images were taken. **Figure 5a** shows the surface of the coating layer prior to heat treatment. Individual PHA particles are clearly present. Figures 5b and 5c show the surfaces after oven and photonic exposure. All images were taken at the same level of magnification. The differences show the effectiveness of heat treatment on film formation and that the two heat treatments are comparable.

It can be seen that the surfaces are significantly different, with discrete PHA particles clearly present on the surface of the uncured sample. The photonically cured surface shows a complete (continuous) film.

Cross-sectional images of the PHA coated samples both prior to and after curing (**Fig. 6**) were also taken. Prior to



5. Images of a) non-cured PHA coating, b) oven-cured PHA coating, and c) photonically treated PHA coating.



6. Cross section images of a) untreated, and b) treated PHA coating

Sample	Oven Treated			Photonic		
	2-min Cobb, g/m²	Kit, #	WVTR, g/m²/day	2-min Cobb, g/m²	Kit, #	WVTR, g/m²/day
A	2 (+/-) 1	8 (+/-) 1	70 (+/-) 8	3 (+/-) 1	9 (+/-) 1	84 (+/-) 7
B	2 (+/-) 1	8 (+/-) 1	102 (+/-) 20	5 (+/-) 1	8 (+/-) 1	115 (+/-) 35
C	2 (+/-) 1	9 (+/-) 1	70 (+/-) 6	10 (+/-) 1	10 (+/-) 2	90 (+/-) 7
D	Fail	2 (+/-) 2	70 (+/-) 4	Fail	3 (+/-) 1	95 (+/-) 4
E	4 (+/-) 1	6 (+/-) 1	86 (+/-) 9	7 (+/-) 1	6 (+/-) 1	81 (+/-) 5

V. Comparison of oven and photonic curing (WVTR = water vapor transmission rate).

Coat Weight, g/m²	Oven		Photonic	
	20-min Cobb, g/m²	Kit, #	20-min Cobb, g/m²	Kit, #
2.1	19.6	12	19.3	9
4.7	17.2	12	10.9	9
10.2	17.9	12	5.6	12

VI. Improvement of barrier properties due to elimination of pinholes.

curing, the sample had a thickness of approximately 18 µm. After curing, the sample had an approximate thickness of 7 µm. This difference in thickness before and after curing results from the PHA particles coalescing and melting.

Table V compares high coat weight samples (16+1 g/m²) treated in an oven (control) to those treated using photonic treatment. The results of the low coat weight samples (<13 g/m²) resulted in the failure of barrier property tests due to incomplete coverage of the base sheet. Incomplete coverage was verified by spraying the surface with an isopropyl alcohol (IPA) solution containing a blue dye. The immediate penetration of IPA into the coated surface was observed, indicating incomplete coverage. This test is also used to detect the presence of pinholes.

The comparison of the oven to photonic results show the photonic heat treatment to be effective. The kit and WVTR values for the photonic treatment were similar to all oven dried results, while the 2-min Cobb values are all higher. The higher Cobb values are attributed to pinholes, indicating further refinement of photonic treatment settings is needed.

From the results, it is evident that the presence of pinholes prevents the full benefits of PHA coating to be realized, espe-

cially at lower coat weights. To determine if property improvements could be obtained if pinholes could be eliminated, one additional study was performed with application of PHA coating with different Meyer rods onto substrate C after applying a 10 gsm precoat. The Kit values of the precoated base paper were 4 min and 20 min Cobb 21.0 gsm prior to applying the PHA coating. The pulse conditions used for treating these samples were 400V, 5000 µs, and 8 ft/min with an overlap factor of 2. As shown in **Table VI**, barrier properties were significantly improved by sealing and smoothing the base paper with a precoating. The barrier properties of the precoating itself are not as significant as those found for the PHA coating. This finding indicates that additional substrate development may be needed to obtain the full benefit of this technology.

Results of repulpability tests performed on oven and photonic treated samples showed 100% repulpability, with no rejects present (100% accepts).

CONCLUSIONS

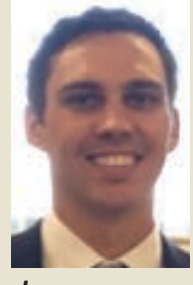
The results of the trial show that photonic treatment is a commercially viable option for the solution-based processing of aqueous PHA coatings. The application of photonic energy enabled the complete film formation of PHA particles within microseconds, without degradation to the base substrate. While the coating speeds utilized during this trial are low in comparison to commercial coater and press speeds, the results are scalable. For higher speeds, additional lamps and capacitors can be added.

The use of photonic energy provides papermakers with a new material tool box for developing new products by enabling use of higher melting polymers. The ability to utilize this technology inline with a paper machine or printing press offers economic benefits over offline operations. The use of PHAs as a barrier material for paper packaging will mitigate the environmental and health issues caused by conventionally generated plastics having bisphenol A, Di(2-ethylhexyl) phthalate, fluorochemicals, or any number of other additives that are known to cause health and environmental issues. **TJ**

ABOUT THE AUTHORS

We chose this topic to research because there is a very significant need for alternatives to conventional plastics. It was interesting to discover how well PHA can perform as compared to conventional plastics. The most difficult aspect of this work was the energy requirements, which we discussed with industry experts.

Mills may find benefit from this work from the standpoint of developing innovative products. The next step is to create a consumer product incorporating PHA.



Joyce

Pal

Joyce is a post-doctoral student, Pal is associate professor, and Tran is director, Product Innovation, at North Carolina State University, Raleigh, NC, USA. Email Joyce at Michael@snpinc.com. Email Pal at lokendra_pal@ncsu.edu.

ACKNOWLEDGEMENTS

This research was supported in part by grant funding from North Carolina Biotechnology Center (2016-CFG-8005) and Synthetic and Natural Polymers Inc. (SNP Inc.).

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