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Microbial polyhydroxyalkanoates from food and agricultural wastes: A biodegradable candidate for coating paper-based packaging

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ABSTRACT
The use of petroleum based plastics for coating poses the threat of non-biodegradability to the paper based packaging materials which are otherwise fully biodegradable. The microbial polyhydroxyalkanoates (PHA) which are biodegradable and biocompatible will help to improve the properties of paper in an eco-friendly manner. The problems with PHA production are less yield and high cost of substrate for the growth of microorganisms. This can be solved by the use of wastes as substrates including food waste, agricultural waste, sewage water etc. The studies on production of PHA from food and agricultural wastes and reports on the coating of paper using PHA are discussed in this article.

Keywords: Paper, Polyhydroxyalkanoate, Packaging, Coating

Paper-based packaging is an adaptable and cost-efficient method to preserve, protect and transport a variety of products including food, textiles and pharmaceuticals. It is light weight and the properties can be customised according to the customer needs. About 92% of paper is produced from wooden sources and 2% is from agricultural wastes, globally (Fahmy *et al.* 2017). Paper processing consists of two major steps, pulping and moulding/shaping pulp into sheets. It is composed of cellulose molecules with a crystalline structure. The crystalline structure is not continuous because of the presence of amorphous structures in between. Paper is a safe packaging material because of its biodegradable character. The porosity of paper and the hydroxyl groups of cellulose result in reduced water vapour barrier properties of paper which affects the mechanical properties also (Kwaldia *et al.* 2010). In order to increase the barrier properties, coatings with plastics can be given, but the biodegradability will be lost. So a potential alternative for plastics should have good biodegradable property along with barrier properties.

PHAs are produced by microbes as energy storage materials. They are polyester compounds synthesised as intracellular granules. More than 150 analogues of PHA are there and these structural variation depends on the microorganism and substrate used for the production of PHA. Two categories of PHAs are there. One is short chain length PHA where the β-hydroxy fatty acids having 4-5 carbon units are the repeating units. They are highly crystalline and are like thermoplastic materials. They exhibit properties comparable to polyethylene and polypropylene. The medium chain length PHA have repeating units with 6 or more carbon atoms and are more of amorphous nature. They have elastomeric or free flowing properties (Ashby and Solaiman, 2008).

A bioplastic is said to be fully biodegradable if it satisfies 5 criteria of marine biodegradability, soil biodegradability, industrial compostability, home compostability, and anaerobic digestibility. Thermoplastic starch and PHA are the only two bioplastics that satisfies these criteria. The biocompatibility and biodegradability of PHA makes it stand alone among other plastics. But the lower yield and cost of raw materials increase the cost of PHA which restricts its applicability and industrial production. Now a days researchers are focussed on utilising wastes for the culture and production of PHA which increase the scope of PHA as a potential bioplastic.

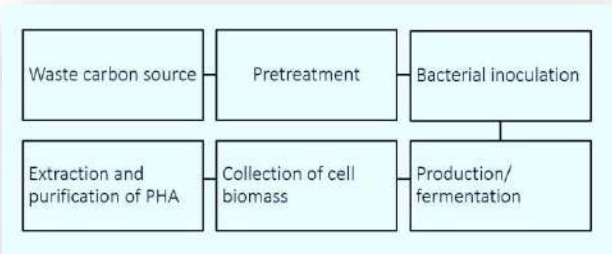

Fig 1. Steps in production of PHA using food and agricultural waste

The wastes used for PHA production (Figure 1.) includes municipal waste, sewage water, agricultural waste etc. Different agricultural and food wastes studied for the production of PHA is given in Table. 1.

Table. 1. Utilisation of food and agricultural waste for production of PHA (Nielsen *et al.* 2017)

Food waste source	Microorganisms(s)	PHA polymer type	Dry cell weight (dcw) (g/L)	Maximum PHA production reported (g PHA per g dcw)
Whey	Highly osmophilic organism	PHBV	NA	8–10%
Whey	*H. mediterranei*	PHBV	10.91	66%
Whey	*H. mediterranei*	PHBV	7.45	53%
Whey	*T. thermophiles*	PHV and mcl-PHAs	1.60	35.6%
Whey permeate	*C. necator*	PHB	8	25%
Cassava starch wastewater	*Cupriavidus* sp. KKU38	PHB	9.69	61.60%
Starch	*A. chroococcum*	PHB	54	46%
Soy bean and rapeseed oil	*C. necator*	PHB	6.1	57%
Soy bean, rapeseed and corn oil and lard	*C. necator*	PHB	6.5	79%
Palm oil and lard	*C. necator*	PHB	6.8	83%
Tallow	*C. necator*	PHBV	5.8	80%
Waste frying rapeseed oil	*C. necator*	PHB	10.8	67.9%
Waste frying palm oil	*C. necator*	PHB	11.9	58.0%
Waste frying sunflower oil	*C. necator*	PHB	10.812.53	52.4%
Corn oil	*Psuedomonas* species	mcl-PHA	12.53	35.63%
Spent coffee grounds oil	*C. necator*	PHB	16.7	78.40%
Spent coffee Grounds oil	*C. necator*	PHB	55.4	89.10%
Spent coffee grounds hydrolysate	*B. cepacia*	PHBV	4.91	54.79%

Oil palm empty fruit bunch	*B. megaterium*	PHB	24.29	51.60%
Wheat straw	*B.sacchari*	PHB PHB	146	72%
Rice straw	*B. firmus*	PHB	1.9	89%
Wheat bran	*H. boliviensis*	PHB	1.08	34%
Tequila bagasse	*S. degradans*	PHA	NA	> 0%
Molasses	*Psuedomonas* species	PHA	10.54	20.63%
Fermented mash	*Psuedomonas* species	PHA	7.02	23.56%
Spent wash	*Psuedomonas* species	PHA	8.56	25.46%
Sugarcane molasses	*B. megaterium*	PHB	72.2	42%
Sugar beet juice	*A. latus*	PHB	4.01	38.66%
Sugarcane bagasse	*Burkholderia* sp.	PHB	6.8	48%
Sugarcane bagasse	*C. necator*	PHB	NA	57%
Sugarcane vinasse	*H. marismortui*	PHB	12	23%
Sugarcane vinasse	*H. mediterrranei*	PHBV	28.1	70%
Rice-based ethanol stillage	*H. mediterrranei*	PHBV	23	71%
Malt waste	*A. eutrophus*	PHB	32.36	70%
Soy waste	*A. eutrophus*	PHB	18.42	32.57%
Bean curd waste	*A. latus*	PHB	3.73	66.56%

PHAs are resistant to hydrolytic degradation because of the hydrophobicity and have good barrier properties against water vapour and oxygen. They have poor resistance towards acids and bases and have good UV resistance. The physical properties of PHAs are compared with other plastics in Table 2.

Paper coatings with PHA

One of the major criteria for a packaging material is its barrier property for gases like oxygen, carbon dioxide, water vapour etc. In the case of food products, oxygen and water vapour barriers are necessary for maintaining the shelf life. The water activity of food products are to be maintained throughout storage especially for dried and intermediate moisture products. Because of the barrier properties, PHB, PHBV and PHBHHx films are promising materials for packaging food. The oxygen permeability of PHA is close to polyethylene and poly lactic acid and is higher than ethylene vinyl alcohol. But when compared to polypropylene, polyethylene and polystyrene, PHA have higher oxygen permeability and lower carbondioxide permeability. The temperature and relative humidity are important factors affecting the barrier properties (Ragaert *et al.*, 2019). Andersson *et al.* (2008) reported the use of PHB-coated paperboard packaging for ready meals and PHBV-coated packaging board for dairy products, dry products and beverages. In addition to the improvement in barrier properties, PHA also helps to functionalise sealability and grease resistance. At temperatures of 190-230°C, PHBV films can be sealed to the substrate or to itself and the sealing temperature increases with thickness of paper board. Low melt viscosity, low melting point, wide sealing temperature range and cohesiveness are the important properties governing heat sealability (Chandra and Rustgi, 1998).

Table 2. Physical properties of different bioplastics and petroleum based polymers (Anjum *et al*. 2016)

Polymer	Copolymer content	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Melting temperature (°C)	Glass transition temperature (°C)
P(3HB)		3.5-4	40	3-8	173-180	5-9
P(4HB)		149	104	1000	53	50
P(3HB-co-3HV)	3 mol% 3HV	2.9	38	na	170	na
	9 mol% 3HV	1.9	37	na	162	na
	14 mol% 3HV	1.5	35	na	150	na
	20 mol% 3HV	1.2	32	na	145	-1
	25 mol% 3HV	0.7	30	na	137	na
P(3HB-co-4HB)	3 mol% 4HB	na	28	45	166	na
	10 mol% 4HB	na	24	242	159	na
	16 mol% 4HB	na	26	444	130	-7
	64 mol% 4HB	30	17	591	50	-35
	90 mol% 4HB	100	65	1080	50	-42
P(3HHx-co-3HO)		na	10	300	61	na
P(3HB-co-3HA)	6 mol% 3HA	0.2	17	680	133	-8
P(3HB-co-HP)	67 mol% HP	na	na	na	44	-19
P(3HB-co-3HHx)		na	20	850	52	-4
P(3HO)		na	6-10	300-450	61	na
Isotactic PP		1-1.7	29.3-38.6	500-900	170-176	-10

HDPE		0.4-1	17.9-33.1	12-700	112-132	-80
LDPE		0.05-0.1	15.2-78.6	150-600	88-130	-36
PS		3.0–3.1	50	3-4	80-110	21
Nylon 6,6		2.8	83	60	265	50
PET		2.2	56	7300	262	69

For processing of PHA, different techniques can be used based on the average molar mass of the polymer and copolymer content. These techniques include extrusion, injection moulding, extrusion of bubbles into films and solvent casting. Besides these, melt extrusion processing and thermoforming are used to coat paperboard.

According to Kuusipalo (2000), both Polyhydroxy butyrate and Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) can be used to improve the water vapour permeability and reduce moisture absorption. The solvent casting method can be used to deveop a double layered film of PHA and paper. The infusion of PHB enhances the barrier properties, tensile strength and modulus of paper because of its hydrophobicity (Cyras *et al*., 2007). Cyras *et al*. (2009) reported that the paper boards are to be acetylated before compression moulding for the preparation of bilayer films using PHB and cellulose paper. The barrier properties and mechanical properties including tensile strength, elastic modulus, and strain at break increased with increase in concentration of PHB used for moulding. But the use of 15% PHB cause an increase in uniaxial tensile strength and decrease in barrier properties.

A comparison of PHA and PLA was given by Shawaphun and Manangan (2010) when applied as a dip coat. PHB gave increased barrier property but the oil resistance decreased on comparison with PLA. The stable latex formed by PHB was reported by Bourbonnais and Marchessault (2010). Texture of polymer, temperature of drying, pressure and time of drying are the factors that affects paper sizing using PHB. At 160^{o}C, the pressing and heating of impregnated papers will cause formation of thin layers of PHB and thus improve paper sizing. Other important factors include the texture of the polymer and temperature, time, and pressure of paper drying. The PHB-coated paper using dip coating demonstrated better water barrier properties and lower oil resistance than the PLA ones. Obesoa *et al*. (2013) developed a biodegradable, cheap, flexible and hydrophobic material using a phase separation process after precipitation of PHB on the surface of cellulose fibres of papers.

Conclusion

The scope of utilising PHA for packaging especially paper based packaging is promisable. Hence, further studies are to be conducted on cost effective PHA production and its application for packaging.

References

Andersson, C. (2008). New ways to enhance the functionality of paperboard by surface treatment–a review. *Packaging Technology and Science: An International Journal*, *21*(6), 339-373.

Anjum, A., Zuber, M., Zia, K. M., Noreen, A., Anjum, M. N., & Tabasum, S. (2016). Microbial production of polyhydroxyalkanoates (PHAs) and its copolymers: a review of recent advancements. *International journal of biological macromolecules*, *89*, 161-174.

Ashby, R. D., & Solaiman, D. K. (2008). Poly (hydroxyalkanoate) biosynthesis from crude Alaskan pollock (*Theragra chalcogramma*) oil. *Journal of Polymers and the Environment*, *16*(4), 221-229.

Bourbonnais, R., & Marchessault, R. H. (2010). Application of polyhydroxyalkanoate granules for sizing of paper. *Biomacromolecules*, *11*(4), 989-993.

Chandra, R. U. S. T. G. I., & Rustgi, R. (1998). Biodegradable polymers. *Progress in polymer science*, *23*(7), 1273-1335.

Cyras, V. P., Commisso, M. S., Mauri, A. N., & Vázquez, A. (2007). Biodegradable double-layer films based on biological resources: Polyhydroxybutyrate and cellulose. *Journal of Applied Polymer Science*, *106*(2), 749-756.

Cyras, V. P., Soledad, C. M., & Analía, V. (2009). Biocomposites based on renewable resource: Acetylated and non acetylated cellulose cardboard coated with polyhydroxybutyrate. *Polymer*, *50*(26), 6274-6280.

Fahmy Y, Fahmy TYA, Mobarak F, El-Sakhawy M, Fadl MH (2017) Agricultural Residues (Wastes) for Manufacture of Paper, Board, and Miscellaneous Products: Background Overview and Future Prospects. International Journal of ChemTech Research, 10(2), 424-448.

Kuusipalo, J. (2000). PHB/V in extrusion coating of paper and paperboard: Part I: Study of functional properties. *Journal of Polymers and the Environment*, *8*(1), 39-47.

Khwaldia, K., Arab-Tehrany, E., & Desobry, S. (2010). Biopolymer coatings on paper packaging materials. *Comprehensive reviews in food science and food safety*, *9*(1), 82-91.

Masood, F. (2017). Polyhydroxyalkanoates in the food packaging industry. In *Nanotechnology Applications in Food* (pp. 153-177). Academic Press.

Nielsen, C., Rahman, A., Rehman, A. U., Walsh, M. K., & Miller, C. D. (2017). Food waste conversion to microbial polyhydroxyalkanoates. *Microbial biotechnology*, *10*(6), 1338-1352.

Obeso, C. G., Sousa, M. P., Song, W., Rodriguez-Pérez, M. A., Bhushan, B., & Mano, J. F. (2013). Modification of paper using polyhydroxybutyrate to obtain biomimetic superhydrophobic substrates. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *416*, 51-55.

Ragaert, P., Buntinx, M., Maes, C., Vanheusden, C., Peeters, R., Wang, S., ... & Cardon, L. (2019). Polyhydroxyalkanoates for food packaging applications. In *Reference Module in Food Science*. Elsevier.

Rastogi, V. K., & Samyn, P. (2015). Bio-based coatings for paper applications. *Coatings*, *5*(4), 887-930.

Shawaphun, S., & Manangan, T. (2010). Paper coating with biodegradable polymer for food packaging. *Science Journal Ubon Ratchathani University*, *1*(1), 51-57.