Application and Development Prospect of Degradable Biomaterials in Fruit and Vegetable Packaging

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Keywords: Polylactic Acid (PLA), Polyvinyl Alcohol (PVA), Poly(3-Hydroxybutyrate) (PHB), Whey Protein, Carboxymethyl Cellulose, Chitosan.

Abstract: In this paper the biodegradable packaging materials newly developed in the international food industry in recent years were summarized, and the food development field was sorted out and the international development direction was speculated. Besides, the materials of polylactic acid, polyvinyl alcohol, poly (3-hydroxybutyrate), protein and coating materials were treated respectively.

1 INTRODUCTION

In the past half century, plastic has been widely used in manufacturing packaging materials because of its excellent performance and convenient production. The food industry has a huge demand for packaging materials based on petroleum derivatives. However, due to the excellent stability of plastics, it is difficult or takes a long time for traditional plastics to be degraded except incineration. With the development of technology and abundant food, many biodegradable materials have come out one after another. In this paper, new biodegradable materials which can be used in food packaging in recent years are collected and sorted out. Biodegradation will eventually degrade organic materials into carbon dioxide and water, or anaerobic state containing methane, but no toxic residues remain. This article will focus on polylactic acid (PLA), polyvinyl alcohol (PVA), polyhydroxybutyrate (PHB), protein and plant starch.

2 POLYLACTIC ACID (PLA) MATERIAL

Polylactic acid is a transparent hydrophobic material with good mechanical properties, which is produced by polymerization of lactic acid. Lactic acid is a renewable carbohydrate produced by fermentation of bacteria (Lactobacillus) (Garlotta, 2009); (Shirai, 2013). Its moisture resistance and gas resistance are slightly worse than PET material (Huneault, 2007). Polylactic acid monomer is nontoxic and can be safely used as food packaging material, However, due to its high cost, high brittleness (Shirai, 2013); (Lu, 2009); (Koh, 2018) and poor heat resistance and impact resistance (Sun, 2018), it is best to blend with other polymers or nanoparticles to overcome its shortcomings. Starch, nano-cellulose and chitosan are also renewable resources, which can be blended with polylactic acid to reduce costs, improve its mechanical properties and barrier properties, and produce environment-friendly food packaging materials. However, because starch, cellulose and chitosan are hydrophilic materials, the interfacial tension between incompatible polymers will greatly affect the mechanical properties. Therefore, blending polylactic acid with hydrophilic polymers will lead to the decrease of tensile strength and elongation. (Huneault, 2007)

Dan, L., Chunhong, Z., Zihui, W., Zhonghua, L., Lin, L. and Fuli, Z.
Application and Development Prospect of Degradable Biomaterials in Fruit and Vegetable Packaging.
DOI: 10.5220/0011206400003443
In *Proceedings of the 4th International Conference on Biomedical Engineering and Bioinformatics (ICBEB 2022)*, pages 331-341
ISBN: 978-989-758-595-1

The solution is to chemically modify the surface of incompatible polymer blends (such as branching and cross-linking, etc.), which will significantly improve the mechanical, thermal and barrier properties of PLA blends. Different methods will be described below.

2.1 Chemical Modification and Blending of Polylactic Acid and Starch

Table 1 lists the methods and effects of preparing polylactic acid blends in recent years from starch branching method, polylactic acid branching method, crosslinking modification method, esterification modification method and plasticizer Faroe.

Table 1: Modification Methods of Polylactic Acid and Starch.

Type	Method	Effect	Literature
Preparation of polylactic acid blend from starch Zhilian	The starch surface was modified by grafting bio-based ester epoxidized itaconic acid (EIA) or bio-based ether epoxidized cardanol (Epicard) onto the starch surface by twin-screw extruder.	The hydrophilic starch changed into hydrophobic starch, and the angle increased from 44 degrees to 100 degrees. And the tensile strength is improved from 35mpa to over 50mpa.	7
	Maleic anhydride was grafted onto PLA and corn starch by one-step compatibilization process.	Chemical bonding exists between PLA grafted with maleic anhydride and starch, which increases the interfacial bonding force between PLA and starch and improves the compatibility between PLA and starch.	8
	Grafting 2- ethylhexyl acrylate onto the surface of cassava starch to improve the hydrophobicity of starch and the interfacial adhesion between PLA and starch, and then preparing films by solvent blending and casting.	Without reducing the thermal stability of PLA, the elongation and toughness of the coating prepared by grafting starch (90:10) and polylactic acid (PLA) were significantly improved.	9
Preparation of polylactic acid blend by branching polylactic acid	Maleic anhydride (MA) was grafted onto PLA with free radical initiator to improve interfacial adhesion. Firstly, polylactic acid was grafted with maleic anhydride, and then the grafted polylactic acid was blended with wheat, pea and rice starch.	The tensile strength of grafted PLA/ starch blend is twice as high as that of unmodified PLA/ starch blend. The elongation at break of grafted PLA/ starch blends is 100-200%, while that of unmodified PLA/ starch blends is 5-20%.	6
	Three-step synthesis. I: They salivate some hydroxyl groups of starch to protect them. II: They grafted the rest hydroxyl groups in amylose onto polylactic acid as initiator. III: They removed the protective effect of sialylated groups in amylose.	The article did not mention	10
Cross-linked modified starch	The hydroxyl groups of wheat starch were crosslinked with citric acid to form ester groups, which were then blended with polylactic acid by extruder.	Compared with unmodified polylactic acid/starch blend, adding acidic acid can reduce water vapor transmission rate by 80% and oxygen transmission rate by 90%.	11
	Acetic acid modified polylactic acid/starch blend	The film is softer and the tensile strength reaches 41mpa, which is the same as that of pure PLA	12

	The PLA/ tapioca starch blend was prepared by using methylene diphenyl diisocyanate (MDI) as crosslinking agent (interfacial compatilizer) to crosslink starch with PLA. The mixture was prepared by melt blending at 190°C.	With MDI added, the tensile strength of PLA/ starch /MDI blends increased from 25.1mpa of PLA/ starch blends without MDI to 42.6MPa.	13
Esterified modified starch	PLA/ starch blends were prepared by esterifying corn starch with maleic anhydride. PLA/ esterified starch blends were produced by twin-screw extruder, and then the subsequent films were prepared by extrusion molding.	After esterification, the hydrophobicity of PLA/ esterified starch was improved, and starch esterification treatment made PLA/ esterified starch have better fluidity and processability.	14
Use plasticizer to increase interfacial adhesion	Flexible film of PLA/ starch was produced by using plasticizer adipate or citrate.	The film containing adipate has better elongation (148%), lower Young's modulus (3.8MPa) and lower tensile strength (0.9Ma).	2

2.2 Polylactic Acid Packaging Material Reinforced by Nano Cellulose

Nanocellulose CNC, a low-cost, renewable, degradable, high-strength and rigid material, has been used to improve the mechanical and barrier properties of biodegradable food packaging materials. (Yu, 2014) It can be extracted from wood or non-wood materials by acid hydrolysis. (Mokhena, 2018) However, due to the incompatibility between the two materials due to their hydrophilicity, it is difficult to disperse them into PLA matrix. For this reason, scientists have tried many methods, which will be described in Table 2.

Table 2: Finishing table of polylactic acid reinforced by nano cellulose

Intensifier	Modifier/solubilizer	Proportion or dosage	Effect	Literature
CNC	Maleic anhydride grafted PLA(PLA-g-MA)	5%CNC and 5%PLA-g-MA	The tensile strength of PLA increased from 22.4MPa to 60.3MPa, and the tensile modulus increased by 40%	(Ghasemi, 2017)
CNC	Stearic acid	1% modified CNC	The tensile strength and elastic modulus of PLA/CNC film increased by 40.03% and 55.65%	(Lijie, 2018)
Cellulose nanofiber (CNF) and bacterial cellulose (BC)	Propyl 3-(trimethoxysilyl) methacrylate	1% and 10% of modified CNF were added to self-reinforced PLA to obtain SR-PLA/modified CNF hybrid membrane	Adding 1% modified CNF into PLA resulted in the tensile strength of the film being 4, 10 and 16 times higher than that of self-reinforced PLA/1% unmodified CNF blend, self-reinforced PLA and pure PLA, respectively	(Somord, 2018)
CNC	NCFHL with high lignin content	10%NCFHL	Tensile strength of PLA/NCFHL membrane increased by 111%, modulus of PLA/NCFHL membrane increased by 88%, and water vapor permeability decreased by 52% compared with pure PLA	(Nair, 2018)

2.3 PLA Was Blended with Chitosan by Chemical Modification

Like nano-cellulose, chitosan is also a biodegradable material, which is produced by the deacetylation of chitin (CHOUWATAT, 2010), and has good mechanical properties and selective permeability to gases. However, its hydrophilicity makes its moisture resistance poor (Suyatma, 2010), and it is difficult to disperse into hydrophobic PLA matrix. At present, one research direction is to increase the hydrophobicity of chitosan, for example, chitosan reacts with sodium dioctyl sulfosuccinate (DSS) to increase its hydrophobicity, and the modified chitosan has good compatibility with PLA. (CHOUWATAT, 2010) Another direction is to graft PLA directly onto chitosan, and p-toluenesulfonic acid can be used as catalyst to graft PLA directly onto chitosan; PLA can also be grafted onto chitosan by open loop method with triethylamine as catalyst. Both methods can improve the flexibility of chitosan chain. (Suyatma, 2010) Another research direction is to directly prepare PLA/chitosan mixture, mix chitosan/PLA at a ratio of 10% without adding plasticizer, and then extrude them into particles in a twin-screw extruder. Then, the granules were pressed at 190℃ for 4 minutes at 7.5 tons to form a film. The mechanical properties (tensile strength and elongation at break) of PLA/chitosan film were improved. However, due to the interfacial tension between PLA and chitosan, this improvement is limited. (Claro, 2016)

3 POLYVINYL ALCOHOL MATERIAL (PVA)

Polyvinyl alcohol has a simple carbon chain and a series of hydroxyl groups. And its performance is mostly related to its structure. Polyvinyl alcohol (PVA) is one of the most common polymers, which is non-toxic, highly crystalline, hydrophilic, biodegradable, tasteless and has excellent film-forming ability. Although its structure brings good hydrogen bond formation ability, its defects are limited barrier property, thermal stability and relatively high cost. (Tânase, 2015) Because of its crystal structure and close connection between molecules (Rahman, 2010), the water permeability is relatively high, but the water resistance is poor. The experimental results show that the starch /PVA blend membrane has good water resistance, and the water retention rate is nearly 20% higher than that of pure PVA membrane. (Mathew S, 2018) Chitosan /PVA plays an obvious role in the preservation of apples, and there is no sign of degradation during storage. (Yun, 2017)

4 POLY (3-HYDROXYBUTYRATE) (PHB)

Polyhydroxyalkanoic acid (PHA) is a natural polyester produced by microorganisms, and poly (3-hydroxybutyrate) (PHBs) is the main representative of PHA family. PHB can accumulate in the cytoplasm of cells, and the size of PHB particles is about 0.5 microns. If the growth environment is suitable, cells can produce PHB up to 90% of their stem cell weight. (Coskun, 2019) Bacillus is the best flora for producing PHB by using cheap agricultural residues such as sugarcane bagasse, and the best pH value and temperature are 7 and 37℃, respectively, and incubation time is 48h at 150 rpm. (Getachew, 2016) This is conducive to reducing costs, reducing environmental pollution and solving the treatment of agricultural wastes. As a packaging material, PHB has excellent mechanical and physical properties due to its crystallinity, and also has good air permeability and plasticity. (Iopp.org. Bioplastics in Food Packaging, 2019) Haugaard et al. compared cups made of PHB and high density polyethylene (HDPE). PHB and HDPE have similar effects in preventing food quality changes. (Rydz, 2018) Table 3 lists a variety of exploration work on PHB modification at present.

Table 3: Synthetic application form of PHB.

Type	Material	Effect	Literature
It is synthesized from two completely degradable materials	PLA/PHB, 75: 25, not recommended	PHB can be used for crystallization of polylactic acid to obtain higher barrier performance and better mechanical resistance. However, for PLA/PHB film, it is necessary to add plasticizer, which will reduce the improvement effect of the film.	(Marina, 2017)
	PCL/PHB, 75: 25, not recommended	It can't be mixed by physical method, so free radical initiator DCP/BIB needs to be added. In addition, PHB degrades during processing and reacts with free radicals.	(Przybysz, 2018)
	CF/PHB	Melting samples show that high CF leads to lower melting point and lower melting point viscosity of PHB. The crystallinity and transmittance of all PCL/PHB samples are lower than those of pure PHB samples, but the transparency is high.	(Tănase, 2015)

Other methods	Optimization of PHB electrospun fiber	If the sample is cooled slowly during isothermal annealing at 160℃, the morphology of the barrier will be denser and its performance will be improved. The optimized PHB electrospun fiber shows good self-adhesion performance, which is helpful to realize the whole bio-based multilayer film as a functional bio-based adhesive.	(Cherpinskia, 2017)
	PHB and Silver-based Nanocomposites	Oxygen permeability is reduced by about 56%	(Rydz, 2018)
	PLA and PHB/PBAT	The mechanical properties of the blends will increase the elongation at break and decrease the elastic modulus and tensile strength. At the same time, it is helpful to the compatibility between PLA and PHB.	(Ma, 2017); (Vinicius, 2018)
	Lactic acid oligomer (OLA)/ carvacrol and PLA/PHB blends	With the addition of OLA, the compatibility between OLA and PLA/PHB matrix is high, and the PLA/PHB film is easy to change from rigidity to toughness with high crystallinity.	(Armentano, 2015); (Burgos N, 2017)
	PHB/ rapeseed oil	It changes the thermal properties of the films, such as melt crystallization and delayed cold crystallization.	(Cláudia, 2017)

5 DEGRADABLE PLASTIC WRAP MADE OF PROTEIN

Protein is also a biodegradable biomaterial, which can not be used in practical production because of its high cost and low production efficiency. However, considering its potential value, it can be divided into plant protein and animal protein. Plant proteins include soybean protein, corn protein and wheat protein, which will be described in Table 3. Animal proteins are mainly casein, collagen and gelatin, which will be described in Table 4. (Sorrentino, 2007); (Zhao, 2008) protein from different sources have different structures, properties and film-forming conditions, so the films finally formed by them are quite different. Compared with the vegetable protein composite membrane, the animal protein composite membrane has stronger oxidation resistance and bacteriostasis.

Table 4: Arrangement table of plant protein materials.

Protein type	Advantages	Disadvantage	Available additives	Effect	Literature
Soybean protein	Strong adhesion, adhesion, film forming, water absorption and fat absorption; The content in plant mother is high	The mechanical properties and heat sealing properties are not ideal	Starch nanocrystals	To improve the physical and mechanical properties of the film	(González, 2015)
			Cloisite-Na+ suspension and glycerol	The tensile strength of nano-composite films without ultrasonic treatment and after ultrasonic treatment increased by 23% and 47%, respectively	(Dean, K, 2005)
Corn protein	High tensile strength, good water resistance and good heat sealing performance	Poor strength and high brittleness, and corn gluten powder is also the main source of animal feed	TiO2	The tensile strength of the composite membrane is the highest, reaching the maximum value of 14%, which has a certain antibacterial effect	(John, 2002); (Cuq, 1998); (Shukla, 2001); (Chen, 2011)

Wheat gluten protein	High tensile strength, good water resistance and good heat sealing performance	Poor solubility in water, the main food source	Water-ethanol solution	Poor water vapor barrier ability, but they are a very effective oxygen barrier.	(Zhang, 2010); (Mojumdar, 2011)
Wheat gluten protein	Homogeneity, transparency and strong mechanical strength	Anaphylactogen	Used in multi-layer packaging materials	\	(Krochta, 1994); (Gennadios, 1993)

Table 5: Arrangement table of actin materials.

	Mechanical properties	Oxygen resistance	Moisture resistance	Special performance	Optical property	Packaging applications	Literature
Lactalbumin	Good	Good	Good	Natural antibacterial property	Transparent	Coating of fresh cheese	(Erdohan, 2010); (Wagh, 2014); (Sabato, 2001); (Sullivan, 2011); (Di Pierro, 2011)
Casein	Good	Good	Good	Not mentioned	Colorable	Coating of fresh cheese	(Sullivan, 2011)
Collagen	General	Good	Good	Prevent oil migration and inhibit microbial reproduction	General	Suitable for food packaging with high fat content	(Iahnke, 2015)
Gelatin	It increased with the increase of protein content	General	It increased with the increase of protein content	Edible and hygroscopic	General	Food with low moisture content	(Karim, 2009); (Gómez-Guillén, 2011)

6 EXPERIMENTAL COATING OF PLANT EXTRACTS

Biodegradable packaging materials for fruits and vegetables can be simply divided into coating and laminating according to their functions. All the films mentioned above are covered with film, and the coating is a coat that comes into direct contact with products, and its application is mainly in fresh-cut fruits. This kind of film can not only be biodegradable, but also reach the level of direct consumption. Packaging of plant extracts has the characteristics of antibiosis, moisture resistance and gas insulation. This chapter describes CMC coating and chitosan coating.

6.1 Coating Film based on CMC

Carboxymethyl cellulose (CMC) is a natural cellulose, which is widely distributed in nature and has abundant sources. For example, rice stubble, an agricultural waste, has a high content of carboxymethyl cellulose, which can be combined with rice straw microcapsule powder to make a film (CMC-MP film), which can effectively maintain the quality of oily food such as green tea. (Rodsamran, 2018) In addition, it is a good trend to convert some wastes into useful packaging materials, and the specific application of CMC is described in Table 6. The evaluation of fruit CMC packaging is mainly based on the following factors.

First of all, the easiest way to measure the water barrier function is to find out the weight change of the control group, because the water activity of fruits is really high, and compared with metabolism, oxidation and browning, water transfer plays the most important role in the weight change. However, for some foods with low moisture content, such as green tea, packaging is to prevent moisture from entering, and color is a better way to show moisture. The increase of water content in green tea may be related to non-enzymatic browning reaction and higher degree of lipid oxidation

The second factor is antioxidation, that is, the function of gas barrier. Odor score can be used as a measurement method, and the increase of lipid oxidation will increase the odor score. (Rodsamran, 2018) Many fruits contain various natural antioxidants, such as CMC-Ag film protecting ascorbic acid in kinnor fruit (Shah, 2015), and total phenol content (TPC) of green tea packaged with CMC-MP film (Rodsamran, 2018). SOD, CAT and POD are antioxidant enzymes, and their activities in packaging products are directly related to oxidation. (Chen, 2017)

Another factor is tensile strength, which is completed by Design Expert (version 10.0.3.1). (Belan, 2018)

Table 6: Coating research table of CMC.

Types of food	Packaging type	Material characteristics	Measurement items	Result	Literature
Citrus fruit (Kinnor fruit)	CMC and guargum-based coating of carboxymethyl cellulose containing nano silver	Antioxidant activity	Total soluble solids (TSS), total sugar, reducing sugar, fruit weight, acid and total phenol	After applying the coating, the fruit of Kinnor can be preserved for 4 months at 4℃ and 2 months at 10℃	(Shah, 2015)
Green tea	CMC and straw extract film	Anti-lipid oxidation	Total phenol content	Based on the total phenol content, the shelf life of green tea with CMC-MP film at 25°C is 110 days	(Rodsamran, 2018)
Xinyu orange	CMC membrane (containing impatiens balsamina extract, 0.07% citric acid, 0.5% sucrose ester, 1.0% calcium propionate and 0.5% glycerol)	Antioxidant activity; Bacteriostasis (fungi, mold)	Sense organ	Delaying maturity and prolonging postharvest life; Store at 5℃ for 100 days	(Chen, 2017)
Strawberry	Garlic essential oil - CMC film	Antibacterial and antioxidant	Weight loss rate; Rot index; Breathing intensity; Soluble solids; Anthocyanin content; Titrable acid; Vitamin C content; Malondialdehyde content	Significantly reduce the weight loss rate ($P<0.05$), respiratory intensity, decay index, the increase of malondialdehyde and the decrease of soluble solids, anthocyanins, titratable acid and vitamin C of strawberry during storage	(Kang, 2016)

The last factor is antibacterial and antifungal effects. Traditional coating methods are useful but time consuming. Phenylalanine ammonia lyase (PAL) is the key enzyme of phenylpropanoid metabolism, which is involved in enhancing disease resistance. CHI and GLU are called pathogenic related proteins, which have been proved to play an important role in plant resistance to fungal diseases. (Chen, 2017)

6.2 Coating Film based on Chitosan

Besides carboxymethyl cellulose, chitosan is also an important material for biodegradable packaging. Studies have shown that chitosan has the ability to inhibit the growth of various microorganisms. Chitosan contains positively charged amino groups, which interact with negatively charged microbial cell membranes, resulting in leakage of microbial protein and other intracellular components. (Tian, 2019) The evaluation of chitosan packaging is mainly based on the tensile strength of antifungal function of moisture-proof, antioxidant, antibacterial, antibacterial and other factors. The specific application is described in Table 7.

Chitosan packed with plant extracts has a good inhibitory effect on microbial growth, such as the inhibitory effect of chitosan and grapefruit seed extract on Salmonella in cherry tomatoes (Won, 2018), and the compound of chitosan and laurel extract can reduce the growth of mold, yeast and mesophilic bacteria in cashew nuts. (Azimzadeh,

2018) Plant extracts are usually rich in flavonoids, organic acids, polyphenols and antibiotics, which help to kill many fungi and bacteria. (Tian, 2019)

Chitosan packed with plant extracts also has good antioxidant function. Chitosan and ginkgo seed explorer extract kept the high level of antioxidant enzymes in ginkgo seeds. (Tian, 2019) The pomegranate peel extract coating keeps high content of ascorbic acid, total phenol and total flavonoids. (Nair, 2018).

Chitosan packed with plant extracts has no prominent moisture-proof function, and its tensile strength needs further study.

Table 7: Research progress table of chitosan coating.

Types of food	Packaging type	Material characteristics	Measurement items	Result	Literature
Mature ginkgo	Ginkgo exocarp extract/chitosan coating	Fresh	Antioxidant enzyme activities of peroxidase and superoxide dismutase	Coating group was significantly better than control group	(Tian, 2019)
Green pepper	Chitosan/Bamboo Leaf Extract Coating	Fresh keeping, antibacterial	1) Quality and color; 2) Phenolic substance content, carotenoid and reducing ability; 3) Microbial activity	1) After 21 days of storage, the fruit lost 30% weight and changed color by 15%. 2) The content of phenols, carotenoids and reducing ability increased by 18%; 3) The microbial activity decreased by 85%.	(González-Saucedo, 2019)
Cucumber seedlings	Chitosan/Osmanthus fragrans extract	Antibacterial	Microbes and Senses	There is a significant difference in 30 days at 27 degrees	(Azimzadeh, 2018)
Tomato cherry	Chitosan/grapefruit seed extract coating	Antimycotic	Microbes	28 days at 10℃ is significantly different from unpackaged, but there is no significant difference between single chitosan and added extract	(Won, 2018)
Strawberry	Chitosan/Natamycin Coating	Antibacterial	Microbes and Senses	40 days at 4 degrees	(Duran, 2016)
Strawberry	Chitosan/peony extract coating	Antibacterial	Microbes and Senses	16 days at 4 degrees	(Pagliarulo, 2016)
Guava	Chitosan/pomegranate peel	Fresh	Keywords Vc, total phenol, total flavonoids, antioxidant activity,	The above indexes decreased by 29%, 8%, 12%, 12%(DPPH) and 9%(FRAP) in 20 days at 10℃	(Nair, 2018)
Blueberries	Chitosan coating with blueberry leaf extract	Bacteriostasis	Fruit weight; Ph; Total soluble solids of titratable acid; Rate of decay; Total phenol content; Free radical activity	The higher the addition amount of blueberry leaf extract, the better the anti-rot effect of blueberry. During the 35-day observation period, 8% and 12% addition amount had certain inhibition effect on fruit rot.	(Yang, 2014)
Papaya fruit	Chitosan propolis	Antibacterial	Colony diameter	It was significantly smaller than the control group on the 8 th day	(Barrera, 2015)

7 CONCLUSIONS

At present, the biodegradable materials that can be popularized are PLA and PHB, both of which can use microorganisms as production raw materials. It is estimated that many scientists are trying to find the most efficient production strains and breeding environment. At present, there are strains that can store 90% of the autogenous dry weight of master batch. If they are continuously popularized, it is likely to reduce their production costs. After many years, when petrochemical resources are exhausted, it is likely to be the main source of plastics. However, PVA material is too expensive and not suitable for packaging. The coating material is still in the laboratory stage, which needs to coat the products one by one, and its long drying time makes it difficult to mass produce, while the plastic source based on protein will greatly reduce the existing grain reserves. To sum up, PLA and PHB materials may have a breakthrough one after another due to the focus of the scientific community.

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