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A study on the synthesis, modification and current market status of PBAT

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Abstract. With the increasing awareness of environmental protection, the problem of "white pollution" caused by waste plastics has become more and more important to all countries, and the restriction of plastic and plastic ban has become a global consensus, which has ushered in a good opportunity for the biodegradable plastic industry. Polybutylene adipate-butylene terephthalate (PBAT) is one of the most widely used biodegradable plastics at present. This paper mainly introduces the synthesis, modification and current market status of PBAT. At present, the synthesis process of PBAT mainly adopts direct esterification method, often blended with other resins for modification, and the prepared products are used in the field of film bags. In recent years, the production capacity of PBAT has grown significantly, mainly in China.

1. Introduction

With the rapid improvement of science and technology, human living standards have also been improving. While technology brings convenience to human beings, disposable tableware, plastic bags and other plastic products have also caused serious white pollution to the ecological environment. According to Our World in Data, humans produce nearly 6 billion tons of waste plastic, of which only less than 2% is recycled. According to Science, China, a global manufacturing base, accounts for 28% of the global waste plastic volume. [1] The growing environmental problems not only take up valuable land resources, but also destroy the ecological balance, while posing a threat to human health.

In this context, China's plastic restriction order has been increased to a plastic ban order. Biodegradable plastics are safe, economical and environmentally friendly, and can be degraded by microorganisms or under certain conditions, so they have received a lot of attention for their great advantages. According to the different ways of degradation, biodegradable plastics are divided into four categories: biodegradable plastics, photodegradable plastics, light and biodegradable, and water-degradable plastics. Among them, biodegradable plastics can retain the use function of plastic products and be completely degraded into harmless substances by microorganisms under certain bioactive environment, so they are the mainstream products of degradable plastics.

As one of the biodegradable plastics, polybutylene adipate-butylene terephthalate (PBAT) is the most promising and popular petroleum-based biodegradable plastic because of its higher elongation at break than other biodegradable plastics, good flexibility and easy production on a large scale. The performance of PBAT is comparable to that of low density polyethylene， therefore, it is widely used in the fields of agricultural films and packaging, and has been extensively studied. The synthesis methods of PBAT can be divided into two types: direct esterification and ester exchange method. The research on PBAT is mainly focused on the direct esterification method.

This paper presents the research on the synthesis process and modification of PBAT, as well as its current market status in China.

2. Synthesis process

Currently available methods for the synthesis of PBAT are mainly direct esterification and ester exchange methods.

The direct esterification method uses terephthalic acid (PTA) or diol terephthalate (DMT), adipic acid (AA) and 1,4-butanediol (BDO) as raw materials and performs the esterification and polycondensation reactions directly under the action of a catalyst. The esterification reaction is carried out at a relatively low temperature, while the polycondensation reaction requires high temperature vacuum conditions. The ester exchange method is based on polybutylene adipate (PBA), PTA (or DMT) and BDO as raw materials, and the esterification or ester exchange reaction is carried out under the action of catalyst to produce butylene terephthalate (BT) prepolymer, which is further subjected to ester exchange melt polycondensation with PBA to obtain PBAT.

Ester exchange process equipment is simple, the reaction system has fewer intermediate substances, the relative molecular mass distribution is narrower, the viscosity of the product is easy to adjust and the waste can be reused, but the product quality may vary from batch to batch [2], and the small molecule produced is methanol. The reaction system of direct esterification is more complex, the relative molecular mass distribution is wide and not easy to control, the reaction conditions are harsher,

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and some BDO is prone to cyclization and dehydration to form tetrahydrofuran (THF), which affects the quality of the product, but its small molecule product is H2O, so compared with the ester exchange method, the direct esterification method has the characteristics of environmental friendliness. Moreover, direct esterification is the mainstream synthesis method for PBAT because of its shorter production process, higher raw material utilization and higher production efficiency, and lower cost.

The PBAT synthesis process is shown in Figure 1.

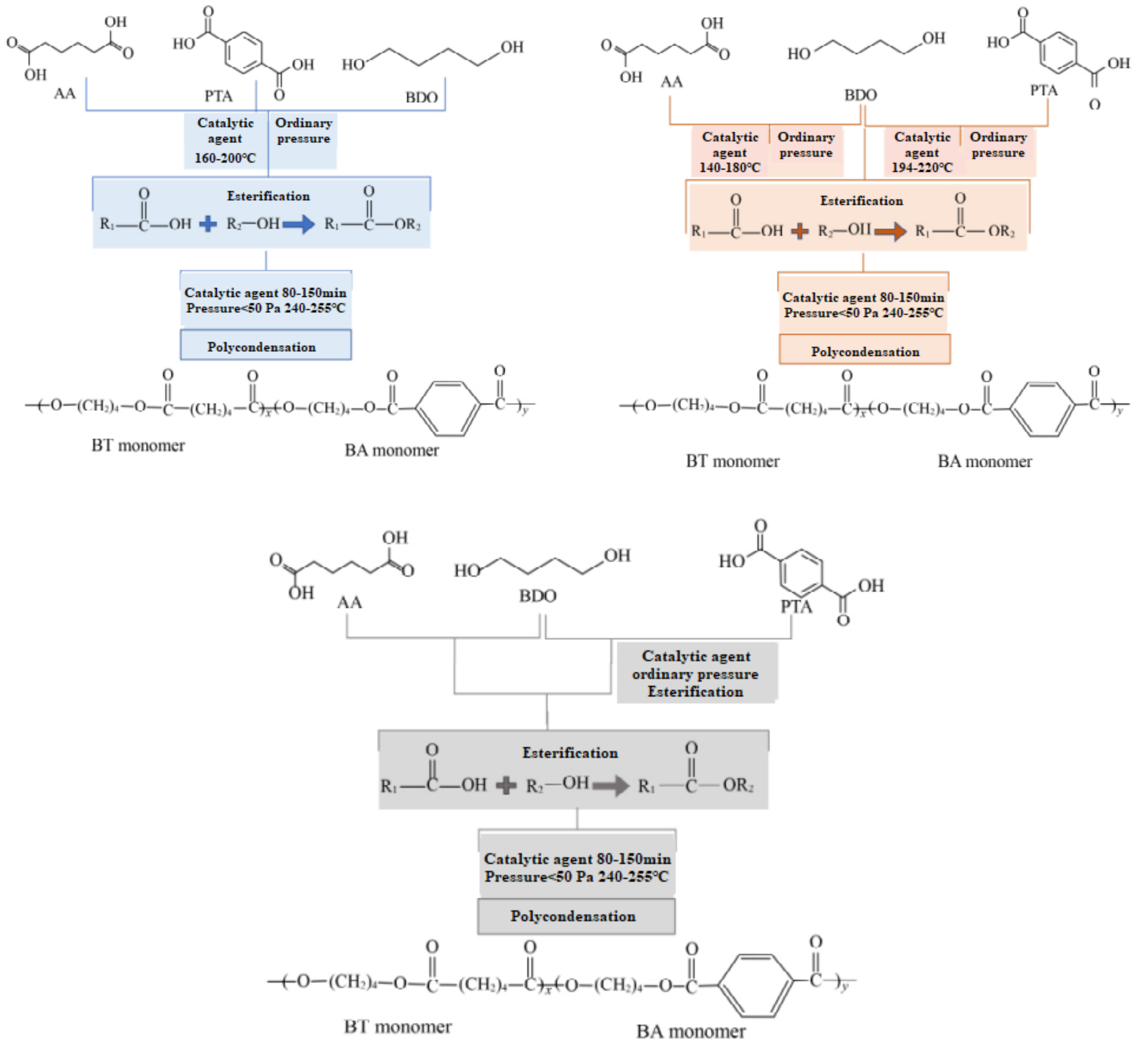

Figure 1. Schematic diagram of PBAT preparation process

3. Modified

PBAT combines the degradation properties of aliphatic polyesters and the mechanical properties of aromatic polyesters, with good ductility and elongation at break. However, compared with common plastics, PBAT suffers from lower melt strength, poor crystallinity and higher price, which limits its application in the field of fiber and membrane materials, and thus requires modification of PBAT. The current modification methods for PBAT can be divided into physical modification and chemical modification, among which physical modification is the main one. The commonly used physical modification method is blending modification, and the blended substances can be polylactic acid (PLA), polybutylene succinate (PBS), thermoplastic starch (TPS) and inorganic substances, etc.

3.1. Co-blended with PLA

PLA has the characteristics of high strength and high modulus, but low elongation at break, low impact strength, and very easy to bend and deform. The melt blending method is commonly used to prepare PBAT/PLA composites to improve the toughness of the material and ensure the degradation rate of the material while reducing the cost.

Liu Haiyun et al. studied the structure, mechanical properties and viscoelasticity of PBAT/PLA composites and found that PBAT and PLA are thermodynamically incompatible; the phase morphology of the system undergoes a series of changes with the content of PBAT components, and the system reverses when the component content of PBAT is 59%; the blends can be reactively capacitated with tetrabutyl titanate (TBT). The phase domain of the disperse phase becomes smaller, the phase

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morphology is significantly improved, and the mechanical properties are enhanced after capacitating. Lin Qiang [4] et al. studied the effect of different levels of PBAT on the notched impact strength of composites and the properties of composites and found that the impact strength of PBAT on composites increased and then decreased with increasing PBAT content, and the maximum impact strength of composites was 5.33 kJ/m2 at 30% PBAT content. elongation at break increased and then decreased when PBAT content was At 10%, the elongation at break was the largest, increasing by 100.2% compared with pure PLA. However, its tensile strength showed a continuous decreasing trend. Meanwhile, the addition of PBAT decreases the crystallization temperature of the composites and inhibits the crystallization ability of PLA. Fu Li [5] analyzed PBAT/PLA composites with different PBAT contents and investigated the effect of PBAT content on the properties of the composites, and found that the toughness of the specimens was improved and the tensile strength decreased less when PBAT was added at 15%. Rongrong Hu [6] found that the addition of PBAT to PLA had basically no effect on the thermal stability of PLA; 5% was the optimal addition of PBAT for toughening PLA.

3.2. Co-mixing with PBS

PBS is the best available degradable plastic with excellent mechanical properties; however, the low viscosity leads to poor strength of the melt, which is unfavorable for processing by blow molding or cast, and the products have certain brittleness. Therefore, PBAT and PBS modified blends are used to make up for the defects by combining the advantages of both.

Lyu Huaixing et al. found that with the increase of PBAT content, the tensile strength of the composites tended to increase and then decrease, the elongation at break kept increasing, while the impact strength decreased and then increased. [7]When 20% PBAT was added, the elongation at break of the composites increased by a factor of 10, the tensile strength decreased by only 6%, and the impact strength increased by 82% compared to pure PBS. The composites crystallized slower and with less crystallinity compared to pure PBS.Raffaela [8] et al. found that high levels of PBAT inhibited the crystallization of PBS; gas permeability decreased with increasing PBS content; the composites with 25% PBS content were between the values of elastic modulus (135 MPa) and elongation at break (390%), so it was a better blending solution.

3.3. Co-mingled with TPS

Starch is composed of straight-chain starch (linear) and branched starch (highly branched), which is widely found in cereals, fruits, tubers and roots of jobs [9][10], and is abundant and renewable. Starch is also of interest because of its low price and ease of complete microbial degradation. However, in natural starch, the melting temperature is greater than the decomposition temperature due to the presence of crystalline structure of starch, so it cannot be processed thermoplastically and it easily absorbs water. When starch is subjected to high temperatures, shear forces and plasticizers, the starch granules with crystalline structure are destroyed, so they can be thermoplasticized [11-13], i.e., they are thermoplastic, and therefore are called thermoplastic starch (TPS). The incorporation of modified starch into PBAT matrix can significantly reduce the cost and accelerate the degradation rate of PBAT, thus reducing the cost and solving the problems of resource shortage and environmental pollution.

Ning Ping et al. studied the mechanical properties of PBAT/TPS composites and found that the overall properties of the blends tended to increase and then decrease as the TPS content increased.[14] The comprehensive mechanical properties of the material could be better improved at the additional amount of 5-10 parts. Tian Yincai et al. used corn plasticized starch as a filler to modify PBAT. the TPS/PBAT blends produced were studied and found that with the increase of TPS content, the crystalline perfection of PBAT gradually decreased and the crystallization temperature gradually rose, and when the TPS content was 50%, the tensile strength and elongation at break decreased by 38% and 70%, respectively, while the elastic modulus increased by 63% .

3.4. Inorganic filling

Activated calcium carbonate has a high reinforcement effect in PBAT modification due to its very small particle size and high activity. Xiao Yunhe et al. used different contents of ultrafine calcium carbonate filled with PBAT to obtain PBAT/CaCO3 composites with different ratios. Mechanical properties were tested by 100/0, 95/5, 90/10, 85/15, and 80/20 specimens, and the results showed that the tensile strength and tear strength of the blends increased with increasing CaCO3 content. However, when the CaCO3 content was higher than 10%, the tensile strength of the blends decreased significantly. The PBAT material modified by calcium carbonate is rapidly and completely biodegradable, which greatly reduces the product cost and improves the operability of PBAT in practical applications.

3.5. Chemical modification

Chemical modification is reactive blending. Reactive blending is a simple and effective method to increase the capacity of polymer systems. By adding chain extender and cross-linker to PBAT and other substances in the blending process, the polymer molecular chains and functional groups react with each other, and the strong interaction forces (chemical bonds) generated at the interface of the two phases replace the weak intermolecular interactions (hydrogen bonds, van der Waals forces) formed by physical blending, further enhancing the interfacial adhesion of the two-phase system. Take the reactive blending of PBAT and PLA as an example, PLA and PBAT, as biodegradable polyester materials, contain terminal carboxyl groups, terminal hydroxyl groups, and a large number of ester groups in the molecular chain, which can react with epoxy groups, anhydride groups, isocyanate and other reactive groups at the interface of the two phases during melt blending and solution blending to generate new chemical bonds such as ester groups and ether bonds in situ, resulting in new chemical bonds similar to PLA-g PBAT macromolecular chains, thus improving the compatibility of both. The current PBAT/PLA composites can be capacitated by four different reactions: esterification reaction, cross-linking reaction, chain expansion reaction and inorganic particle synergy reaction.

PBAT composites have better physical properties. As can be seen from Figure 2, compared to pure PBAT, the tensile modulus of the composite material significantly increases, indicating that the tensile stiffness of the composite material is significantly higher than that of pure PBAT. The tensile stiffness of PBAT/ACN is greater than that of PBAT/CN. The presence of fibers increases the stiffness of the composite, improves the transfer of interfacial stress, and increases the tensile modulus. Therefore, when the amount of ACN added is 10%, the tensile properties of the composite are better.

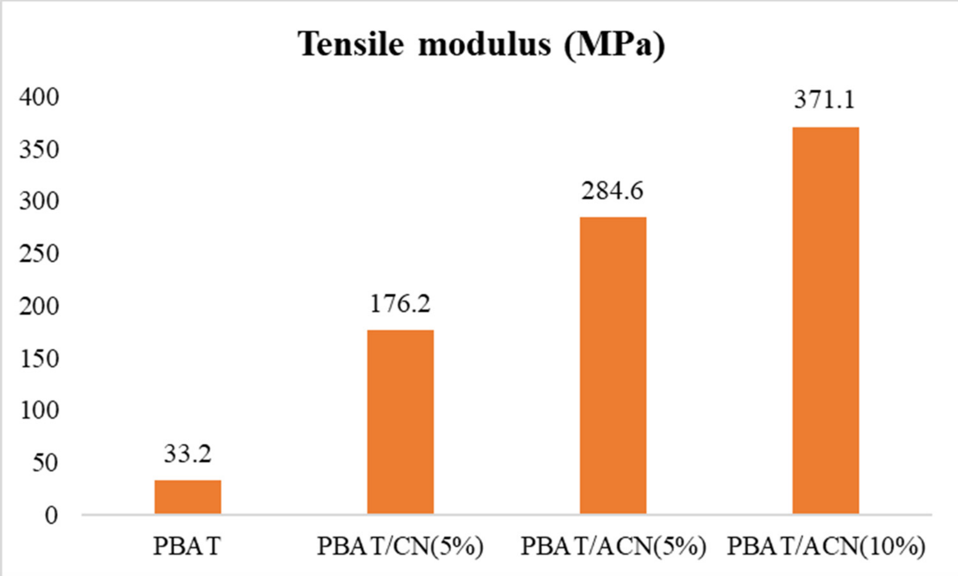

Figure 2. Tensile modulus of PBAT and PBAT composites

4. Current Market Conditions

4.1. Applications

Bio-based plastics cover a wide range of applications, including packaging, food and beverage products, consumer electronics, automotive, agriculture/horticulture and toys, textiles, etc. However, packaging is still the largest application area for bio-based plastics. PBAT is one of the most widely researched and best marketed degradable materials among biodegradable plastics, and the end products are usually modified by co-blending PBAT with other resins.

PBAT has similar properties to polyethylene (PE), and after modification, PBAT is more commonly used in film and bag products. The main application areas are as follows:

Table 1. Main application areas of modified PBAT

Applications	Specific Products
Plastic packaging film	Agricultural land film, shrink film, cling film
Plastic bags	Shopping bags, garbage collection bags
Paper lamination	Biodegradable coatings such as paper cup packaging
Disposable utensils	Disposable knives and forks, etc.

4.2. Capacity, Production and Price of PBAT

China has introduced a series of policies to encourage the application and promotion of PBAT in recent years, and on January 16, 2020, the National Development and Reform Commission (NDRC) and the Ministry of Ecology and Environment (MOE) issued the "Plastic Ban and Plastic Restriction Order", which requires that by 2025, the management system for the production, distribution, consumption and recycling and disposal of plastic products will be improved to gradually ban and restrict the use of non-degradable plastics. As a result, China's PBAT program has emerged. At present, China has become a major producer of PBAT in the world, with Europe and North America as the main export destinations for overseas sales. As the global PBAT market demand continues to grow, China's PBAT exports and the size of the Chinese market continue to rise.

According to the research results, the current global PBAT production capacity is about more than 500,000 tons. 2020 China's effective PBAT production capacity is

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at 280,000 tons, while the current PBAT production capacity in China is about 370,000 tons, of which the largest capacity manufacturer is Lanshan Tunhe (120,000 tons).

By July 30, 2021, China's PBAT production capacity under construction was nearly 1.5 million tons/year. Among them, Ningbo Changhong Polymer Technology Co., Ltd. has a capacity under construction of about 600,000 tons/year, Jinhui Zhaolong High-Tech Co., Ltd. and Henan Lianchuang Chemical Co., Ltd. have a capacity under construction of about 120,000 tons/year, and Zhongke Qicheng (Hainan) Biotechnology Co., Ltd. have a capacity under construction of about 100,000 tons/year.

According to incomplete statistics, as of July 30, 2021, the proposed production capacity of PBAT in China has reached 12.464 million tons (net of Phase I capacity under construction). Among them, the proposed production capacity of Xinjiang Wangjinglong New Material Co., Ltd. reached about 2.6 million tons/year. Compared with the beginning of 2021, more than 25 proposed PBAT industries were added in the second half of 2021.

In early 2021, the price of PBAT was as high as 33,000 yuan / ton, and then PBAT prices experienced a high level of decline, after PBAT companies have been overhauled to reduce production PBAT prices stopped falling back up. 2021 October 11 Ruifeng high material in the investor interaction platform, said the current PBAT market price of about 22000 yuan / ton. However, with the rise of the PBAT industry, while the epidemic caused some foreign manufacturers to be forced to shut down, the price of BDO, the main raw material for synthesizing PBAT, the lifeblood of the PBAT industry, steeply increased from the second half of 2020, reaching a new high in the past decade or so, and the downstream market demand for PBAT was therefore affected to some extent.

The production and market size of PBAT resin in China has also been rising in recent years.

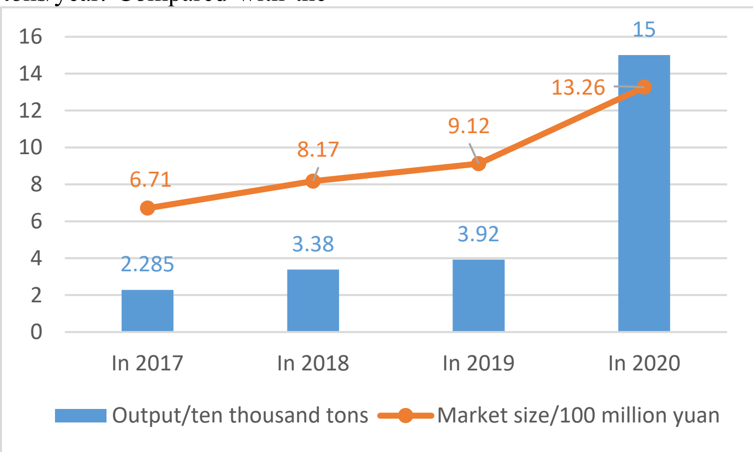

Figure 1. China PBAT output change chart from 2018 to 2020

4.3. Future projections for PBAT

At present, the consumption of biodegradable plastics in China is about 550,000 tons/year, and the market size is about 11 billion yuan, and the replacement rate for traditional plastics is only 1.2%. With the continuous progress of technology and further strict enforcement of the plastic ban, the public's awareness of environmental protection will gradually increase, and the demand for PBAT will be further enhanced, and the PBAT market has a wide space. As the number of PBAT projects under construction and proposed in China continues to increase, the production capacity of PBAT materials in China is expected to gradually increase in the coming years, and the possibility of PBAT becoming a mainstream plastic product or even replacing traditional plastics to achieve sustainable development will further increase.

5. Conclusion

Currently, the mainstream synthesis process of PBAT is direct esterification with PTA or DMT, AA and BDO as raw materials, which is environmentally friendly, low cost and high production efficiency compared with the ester exchange method. The common modification methods for PBAT are blending with PLA, PBS, TPS and inorganic substances, or chemical modification. At present, PBAT is mainly used in the field of film bags, and the production capacity, output and market size are on a continuous upward trend.

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