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The development and challenges of poly (lactic acid) and poly (glycolic acid)

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ABSTRACT

Bio-plastics have gained tremendous attention, due to the increasing environmental pressure on global warming and plastic pollution. Among them, poly (lactic acid) (PLA) is both bio-based and bio-degradable, which has been widely used in many disposable packaging applications. The global market for PLA demand doubles every 3–4 years, as estimated by Jem's law.

Compared to traditional petroleum-based plastics, PLA is more expensive and usually has less mechanical and physical properties. The recent compounding efforts and the commercialization of D(−) lactic acid and its polymer PDLA have the potential to improve the mechanical and thermal characteristics of PLA (e.g. by forming stereocomplex PLA) for applications in high-end markets. However, the usage of PLA in some other applications is still limited.

With a structure similar to PLA, poly (glycolic acid) (PGA) has promising characteristics such as good biodegradability and barrier properties, which is potentially a beneficial supplement to PLA. The modification of PLA with PGA can be achieved via co-polymerization, physical blending and multilayer lamination. PGA and its combination with PLA have been widely studied in bio-medical applications, but not been well developed at large scales due to its relatively high production cost. In this case, the development of novel production technology and the advent of government regulations are the key drivers for the global transition towards bioplastics. Recently, multiple governmental regulations have been released that restrict the use of traditional plastics and facilitate bio-degradable plastic applications. PGA can be derived from industrial waste gases using an innovative production technology, which reduces carbon emissions and its production cost. By developing the production and compounding technology, PGA can be combined with PLA to play an essential role for a sustainable and environmental friendly plastic industry, especially for single-used products requiring fast degradation at room temperature or in the nature environment.

1. Introduction

Over the past decades, the development of synthetic petroleum-based plastics has contributed to economic development and brought great benefits to human life. The annual production of plastics has been increasing worldwide, which was only 1.5 million tons dating back to 1950s and was dramatically increased to approaching 400 million tons in 2018. It is projected that global plastic production will reach 1800 million tons per year by 2050 [1].

Synthetic plastics have been extensively used due to their low cost, light weight, good durability and processability. However, the majority of plastic products are packaging and single used items with very short service life before disposal. Only 18% of overall plastic wastes have been recycled, and less have been incinerated. Around 70 million tons of the 90 million tons of plastic produced by human beings are accumulated in the environment and eventually

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break down into microplastics causing serious health concerns [2]. There are around 8 million tons of plastic wastes entering into the oceans annually and the accumulated amount of plastic wastes in the oceans is estimated to be around 100 to 200 million tons, which have caused catastrophic damage and deaths of marine animals. At this rate, the mass of plastics in the ocean will exceed the mass of fish by 2050 [1]. Microplastic contamination has reached an alarming level in the air, water, seafood and salts. Recent research has shown overwhelming evidence that microplastics can absorb chemicals and metals in the environment which then be enriched in the food chain to endanger not only marine lives but also human beings. Plastic wastes on the sea shore and ocean surface may be removed, but debris and microplastics suspended in the ocean or at the bottom of sea floor can hardly be cleaned up [2].

Another problem is the global warming caused by the excessive emission of greenhouse gases such as CO_2. In the past 800 thousand years, the average CO_2 concentration in the atmosphere was around 280 ppm. Due to the industrial revolution in the late 18th century, the CO_2 concentration had increased to over 390 ppm and the global temperature had increased by 0.9 °C, as reported in the Copenhagen COP 15 conference in 2009 [3,4]. In 2019, the former has increased to over 400 ppm and the latter rises by 1.0 °C [5]. United Nations have adjusted the critical limit of global warming from 2.0 °C to 1.5 °C to avoid dramatic (and irreversible) weather changes. Based on the current rate, we most likely will go over the 450 ppm and 1.5 °C limit in 20–40 years [6].

The above mentioned environmental issues of global warming and plastic pollution have contributed to an increase in demand for alternative materials. Bio-based plastics are being developed to replace traditional petroleum-based plastics to reduce carbon emissions (because the bio-based raw materials absorbed CO_2 from atmosphere) while bio-degradable plastics are developed to reduce plastic pollution (because they degrade much faster than traditional plastics). Poly (lactic acid) (PLA) is one of the most commercially successful bio-plastics (at least among the rigid ones) due to its good processability and mechanical properties. Its monomer, lactic acid, is derived from renewable sources, such as starch or sugar, through fermentation. The global production volume of PLA is around 190,000 tons in 2019 (estimated by the authors). It has better mechanical strength, durability and transparency compared with most other bio-degradable plastics. PLA has been widely used for short life-time packaging products, such as food packaging and single used items. However, PLA can only degrade promptly in months at a high temperature (around 58 °C) typically under the industrial composting conditions. Moreover, PLA has a low heat distortion temperature and poor water barrier properties compared with conventional thermoplastics.

Poly (glycolic acid) (PGA) has a similar chemical structure with PLA, but exhibits very different characteristics. As a bio-degradable polymer, PGA can degrade quickly in the natural environment. It also has a high heat distortion temperature, good mechanical properties and gas barrier properties due to high stereoregularity. PGA may be a beneficial supplement to PLA in certain single-use or relatively short-term applications, i.e. high gas barrier packaging. The combination of PGA and PLA can be achieved via co-polymerization, physical blending and/or multilayer lamination. Previous researches have shown that the degradability and the mechanical properties of PLA were significantly improved by combining PGA [7,8]. However, PGA has been mainly used in bio-medical applications and not been well produced at large scales for industrial (non-medical) applications due to its relatively higher cost compared with other bio-degradable polymers. Traditionally, PGA is produced from petroleum resources and the production cost is prone to be varied by the supply and the price of crude oil. The development of new technology of PGA production is of vital importance for industrial scaling-up. For example, PGA can be made from the waste gases of coal chemical plants, which can dramatically reduce its production cost and carbon emissions.

The growth of PGA and PLA industry may be strongly affected by government regulations and public awareness. A number of regulations have been installed by many governments to restrict the usage of traditional plastics and promote the bio-degradable plastic industry. For example, EU parliament has voted to ban many single-used plastics by 2021 [9]. Hainan province in China also plans to ban all the single-used non-biodegradable plastics by 2020 [10]. According to a new report from the U.N. Environment and the World Resources Institute, at least 127 countries have made regulations to against plastic bags by 2018 [11]. Therefore, it is imperative to raise the global awareness of environmental pollution, implement economically competitive technology for producing bioplastics and facilitate the widespread commercialization of bioplastics such as PLA and PGA in various industrial applications.

This paper reviews the current status, challenges and future applications for the use of PLA and PGA in industrial (non-medical) applications. Various production routes of PLA, PGA and their monomers are reviewed. The characteristics of PLA and PGA are compared and previous research on the combination of PLA and PGA is thoroughly reviewed. The future applications and the challenges of PLA/PGA combination in non-medical industry are also discussed.

2. Production of lactic acid and poly (lactic acid)

Lactic acid (2-hydroxy propionic acid) is perhaps the most widely occurring carboxylic acid in nature. The Swedish chemist Scheele first discovered it in 1780. It exists in two different isomers (Fig. 1): the *dextrorotatory* form called L(+) or S lactic acid, vs. the *levorotatory* form called D(−) or R lactic acid. The sign of (+) and (−) indicates the direction of rotation of plane-polarized light given by a chemical. They are produced by different enzymes (lactate dehydrogenases) present in living organisms. In this paper, they will be referred to as D-lactic acid (D-LA) and L-lactic acid (L-LA). Naturally formed lactic acid is usually in L-form, but D-LA may co-exist with L-LA in some cases especially if secreted by non-specific microbes [12].

L-LA and D-LA are the mirror images of each other. In their pure forms, they have identical physical and chemical properties except that they rotate plane-polarized light equally in opposite directions, and they may react differently to other asymmetric (chiral) reagents such as most enzymes in biological systems.

Lactic acid can be manufactured by chemical synthesis or microbial fermentation processes. The Chemical Synthesis process uses petroleum-based chemicals which may subject to the potential supply problem of crude oil and its dramatic price variation. A disadvantage of the Chemical Synthesis process is that it produces

(S)-lactic acid
L(+)-lactic acid

(R)-lactic acid
D(-)-lactic acid

Fig. 1. Two stereo-isomers of lactic acid. The dot lines from the asymmetric center carbon atom project behind the plane of paper [12].

only the racemic (50:50) mixture of D-LA and L-LA (i.e. D/L-LA), which is not desirable for the food, drink, and pharmaceutical industry due to the metabolic problems that D-LA may cause, and is not appropriate for the PLA industry typically requiring lactic acid with a high optical purity (e.g. ~99% L-LA and ~1% D-LA) [12].

The first commercial operation of Microbial Fermentation process for lactic acid production was set up by Avery Ltd. in USA in 1881. Microbes contain enzyme(s) called Lactate Dehydrogenase (LDH) which can convert pyruvic acid to lactic acid. Depending on the particular microbe and the specificity of its LDH, the lactic acid fermentation process can produce rather pure D-LA or L-LA with high optical purity, or a mixture of them with low optical purity. Many microbes can produce lactic acid but a competitive commercial process requires a robust, fast-growing, low-pH, and high-yield strain with low-cost nutrient requirements. Typical *Lactobacillus* fermentation is anaerobic requiring minimal energy for operation, with the most significant cost typically coming from medium components such as carbohydrate. When a fungus such as *Rhizopus oryzae* is used, the aerobic fermentation requires significant agitation and aeration with high energy cost and long fermentation time due to its slow growth and production rates [12]. Recently, genetically engineered *E. coli* strains have been used to produce optically pure lactic acid with fast growth, high yield and conversion rates using defined media to further reduce the costs.

During fermentation, alkalis such as lime (calcium hydroxide solution) must be added to neutralize the lactic acid produced by microbes and control the pH of fermentation broth at an optimal level for the microbes. Consequently, calcium lactate salt will be formed which must be acidified later by strong acids such as sulfuric acid to release lactic acid from the salt for further recovery. However, this process typically generates gypsum (calcium sulfate) as a by-product and must be disposed as a solid waste with limited usage.

After fermentation, lactic acid must be recovered from the broth and purified to meet its final specifications. Depending on the raw materials, microbes, and media used, the recovering steps and conditions may need to be adjusted. A typical downstream process includes: 1) removal of production microbes (biomass), 2) the above mentioned sulfuric acid treatment, 3) removal of gypsum to recover crude lactic acid, and 4) purification of lactic acid by ion exchange chromatographic resins to produce food-grade lactic acid containing some impurities, and/or by distillation to produce polymer (or heat-stable) grade lactic acid free of any protein, sugar and most other impurities [12]. The largest industrial-scale LA producer in the world is Corbion Purac, with the 140,000 tons LA plant in Thailand (next to the PLA plant under Total Corbion joint venture) plus multiple plants around the world with a total of over 200,000 metric ton LA capacities. The second largest LA plant is Cargill's in the USA (next to the NatureWorks PLA plant under the joint venture between PTT Public Company Limited and Cargill). Jindan in China owns a ~100,000 ton LA plant since 2000. Galactic owns a LA plant in Belgium and is converting its 40,000 ton LA plant in China to 80,000 tons with BBCA (by 2020). Several other companies such as Baisheng and Golden Corn are building new LA plants using genetically engineered strains. The current key industrial LA projects are listed in Table 1 with the total production capacity over 600,000 tons globally, including the captive usage for PLA [12]. Many new ambitious LA projects were announced in China recently for PLA but may not actually be installed.

The polymerization processes and characteristics of PLA have been thoroughly reviewed in literature [13–15]. Polymerization of PLA has been conducted since 1932 by either a Direct Poly-Condensation of lactic acid, or by a Ring-Opening reaction of lactide, a cyclic dimer of lactic acid (Fig. 2). Both methods rely on highly purified polymer-grade lactic acid or lactide to produce PLA with good quality, high molecular weight, and a high yield. Crude lactic acid with impurities would strongly impact the production process, the yield, and the characteristics of PLA. Therefore, purification of lactic acid from the industrial fermentation process is of decisive importance. The optical purity (in addition to the chemical purity) of lactic acid or lactide also strongly affects the characteristics of PLA [12].

The Direct Poly-Condensation (DPC) process dehydrates lactic acid into oligomers then further polymerized to PLA with simultaneous dehydration to avoid the degradation of polymer molecules by moisture. However, removal of water generated from the condensation of lactic acid is very difficult during the final stage of polymerization because the diffusion of moisture in the highly viscous polymeric melt is very slow. The residual water trapped in the PLA melt may limit the achievable molecular weight and the characteristics of PLA. Consequently, DCP process is rarely used except reported by Tongjieliang and Mitsui Chemical [16].

Most PLA production processes utilize the more efficient conversion of lactide (the cyclic dimer of lactic acid) to PLA via the Ring-Opening Polymerization (ROP) catalyzed by organometal catalysts [15]. Lactic acid is dehydrated and poly-condensed into its oligomers at high temperature and under vacuum to remove moisture. Then lactide is obtained from catalytic depolymerization of these short poly lactic acid chains under reduced pressure. Residual moisture, lactic acid and the meso-lactide may be removed from the optically pure D or L form lactide by various means such as distillation or crystallization. The purified lactide is polymerized by a Ring-Opening reaction into PLA at temperatures above the melting point of lactide and below the degradation temperatures of PLA. The un-reacted lactide (around 5%) must be removed from PLA and the resulting PLA resin is solidified and/or crystallized into pellets. During the ROP of lactide, there is no/little moisture to be removed from the molten PLA resin [12].

The ROP process is sometimes referred to as a “Two-Step” process due to its clear intermediate lactide step, while the DPC process without a lactide step is referred to as “One-Step”. But both polymerization processes actually go through multiple processing steps to produce PLA from lactic acid. The typical ROP process presented by NatureWorks is demonstrated in Fig. 3 [12,17]. Lactic acid is converted into low molecular weight PLA pre-polymers continuously. The oligomers are then catalytically converted into lactide by cyclization depolymerization in another reactor. Residual lactic acid is removed from the molten lactide in the vacuum distillation column. Purified lactide in a polymer reactor goes through the Ring-Opening Polymerization by an organic tin-catalyst without expensive solvents. Un-reacted lactic acid and/or lactide are removed by vacuum for recycling. Purified PLA polymer is compounded with additives, and extruded to form resin pellets for crystallization and packaging [12].

Typically, polymer-grade L-LA with high chemical purity and optical purity is used for commercial PLA production. When L-LA is dehydrated at high temperature into L-lactide, some L-LA may be converted into D-LA. D-LA mixed in L-LA contributes to meso-lactide (the cyclic dimer of one D-LA and one L-LA) and hetero-polymer PLA (with both D-LA and L-LA units). Hetero-PLA exhibit slower crystallization kinetics and lower melting points than their homo-PLA (of pure L-LA units or pure D-LA units) [12].

The largest industrial-scale PLA production plant in the world is operated by NatureWorks in the USA with a 70,000 metric ton PLA line built in 2002, which was then expanded to a total of 150,000 tons capacity in 2015. The second largest one is the 75,000 tons PLA plant in Thailand under the Total and Corbion's joint venture company. Hisun built a 5000 ton PLA line in China then added a 10,000 ton line in 2017. Hengtian built multiple lactide-to-PLA fiber lines with a total capacity of 10,000 tons while COFCO installed a

Table 1
Key LA Projects with estimated capacities in 2019–2020 [12].

Key Lactic Acid Producers in 2018–2020	Location of Production Plants	KT
Corbion Purac	Netherlands, Spain, USA, Brazil, Thailand	240
Cargill (for NatureWorks' PLA)	USA	180
Jindan	China	100
BBCA & Galactic	China	80
Xinghan	China	30
Baisheng	China	20
Galactic	Belgium	18
Musashino	Japan, China	10
ADM	USA	10
Huakang	China	10
Golden Corn	China	4
Other newly announced projects (e.g. Tongbang, Youcheng)	China	N/A

10,000 tons lactide-to-PLA plant, both in China in 2018. Synbra built a 5000 line to produce Expandable PLA (BioFoam™) to replace EPS-based foamed products [18]. Other PLA facilities installed to date are smaller pilot plants for testing the process technology and feasibility. Multiple new projects have been announced, such as BBCA-Galactic's ~40,000 tons line and Hisun's new 30,000 tons line (on the top of its 15,000 ton plant) to be completed in 2020. Corbion Purac has also been producing pharmaceutical grade PLA and PGLA for medical applications during the last 30 years. These medical applications (e.g. sutures, bone screws) are not the focus of this article which covers only the large-scale industrial applications of PLA. The current key industrial PLA projects are listed in Table 2 with the total production capacity over 300,000 tons by 2020 as estimated by the author (but not all of them are fully functioning yet partially since they start with lactide which is short of supply).

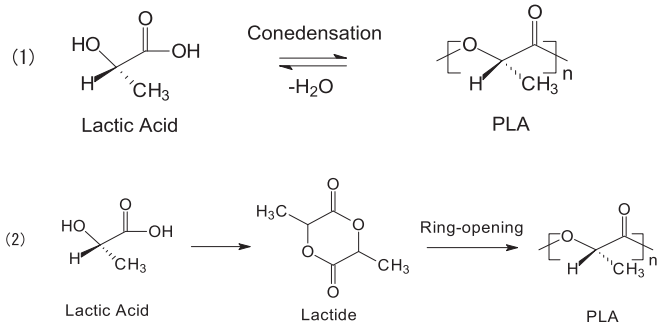

Fig. 2. PLA production processes, (1) direct poly-condensation of lactic acid and (2) ring-opening polymerization of lactide [12].

3. Production of glycolic acid and poly (glycolic acid)

The monomer of PGA, i.e. glycolic acid, is the smallest alpha-hydroxy acid that contains both alcohol and carboxyl groups. Glycolic acid can be obtained from either petroleum or renewable resources (e.g. sugarcane, sugar beets, pineapple). At industrial scales, glycolic acid is mainly produced from petrochemical resources. The predominant approach is to prepare glycolic acid from formaldehyde and carbon monoxide using acidic catalyst, for its low cost [19,20]. Glycolic acid has also been produced from glycolonitrile in aqueous condition using an enzyme catalyst (scheme of this reaction is shown in Fig. 4) [21]. VTT Technical Research Center of Finland has recently prepared bio-based glycolic acid from nature resources (sugar or sugar containing hydrolysates) by constructing engineered yeast strains and fermentation reactions [22]. The global market of glycolic acid in 2015 was USD 160 million and is estimated to reach USD 415 million in 2030 driven by the growing demand of GA in cosmetic products and household cleaning agents [23].

Being the simplest aliphatic polyester PGA was firstly synthesized from petrochemical resources in 1940s. Basically, PGA can be synthesized by two polymerization methods: Poly-Condensation of glycolic acid and Ring-Opening Polymerization of glycolide (see Fig. 5) [24,25].

Poly-Condensation of glycolic acid is a simple process but not very efficient in producing high molecular weight PGA. This is because condensation polymerization of PGA forms water as a by-product, which limits the molecular weight of the final product. In addition, the reaction temperature of Poly-Condensation of PGA is very close to the melting point. Since PGA has poor thermal stability above its melting temperature, it can be easily degraded during Poly-Condensation process [25]. It is reported that PGA started to be thermal degraded at 240 °C and 50% weight loss was carried out in unstabilized PGA when the temperature increased to

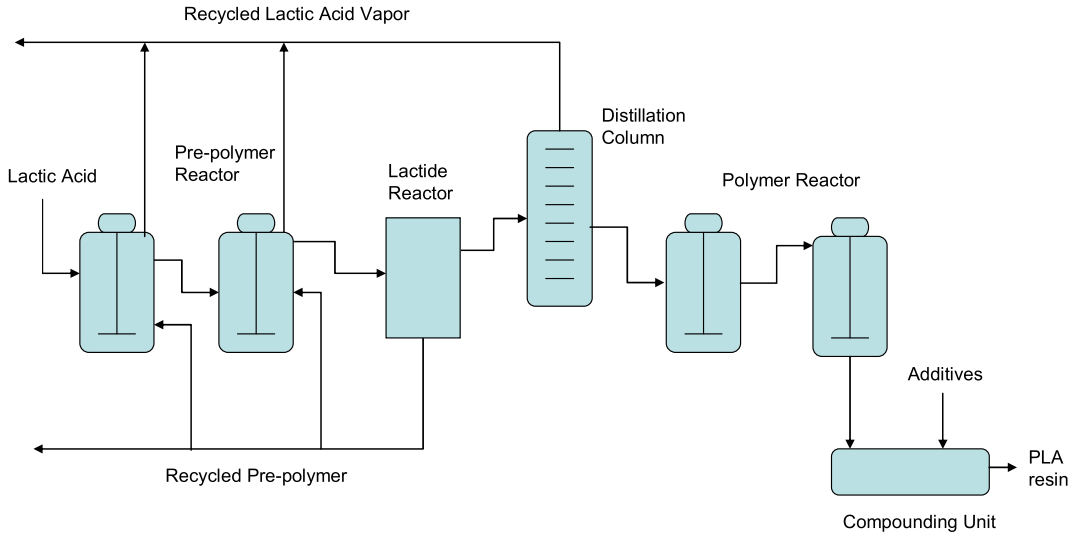

Fig. 3. Schematic diagram of a typical Ring-Opening Polymerization process [12].

Table 2
Key PLA Projects with estimated capacities in 2019–2020.

Key PLA Projects in 2018–2020	Location of Operation	KT
NatureWorks	USA	150
Total Corbion PLA JV	Thailand	75
Hisun	China	45
BBCA & Galactic	China	40
COFCO	China	10
Hengtian	China	10
SuPLA	China	10
TongJieLiang	China	10
Synbra	Netherlands	5
TianRen	China	3
Futerro (under Galactic)	Belgium	1
Jiangxi KeYuan	China	1
Sulzer	Switzerland	<1
Pyramid (under Udhe)	Germany	<1
Other announced projects (e.g. XinNing, HongDa, TongBang, YouCheng)	China	N/A

346 °C [26]. Thus, PGA produced from Poly-Condensation usually exhibits poor mechanical properties. However, this process has been widely used to produce PGA in drug delivery applications due to the final product being of highly amorphous and biocompatible [27].

To obtain high molecular weight PGA, Azeotropic Condensation Polymerization and Ring-Opening Polymerization could be applied. In the Azeotropic Condensation Polymerization process, the water removal problem has been solved, and hence high molecular weight PGA is produced. Water as a by-product of the condensation reaction is removed azeotropically, and the solvent is dried and recycled back during the reaction. The reaction temperature of this method is below the melting point of PGA, which can prevent depolymerization during the process. However, this method is in a solution environment using a low boiling point organic solvent and a high activity catalyst. Hence it is not suitable for industrial scale-up due to solvent disposal issues.

Some researchers synthesized high molecular weight PGA via solid-state Poly-Condensation [25,28]. For example, Takahashi et al. [28], used zinc acetate dehydrate as catalyst and obtained PGA with a molecular weight up to 90,000 g/mol via solid Poly-Condensation. In another case, Epple et al. [29,30] prepared PGA for bio-medical applications by thermally induced solid-state Poly-Condensation in sodium chloroacetate and obtained porous PGA with a small molecular weight of 2300 g/mol.

Among all the polymerization methods, Ring-Opening Polymerization yields PGA with the highest molecular weight and less residual monomer of about 1–3%, which leading to good processability and mechanical strength [24]. Glycolide is the cyclic dimer of glycolic acid that can be depolymerized from PGA oligomer [25]. The process of Ring-Opening Polymerization can be either in melt or solvent conditions. In bulk polymerization process, glycolic acid is dehydrated into a low molecular weight oligomer, which is then heated under high vacuum with a suitable catalyst to produce glycolide. Ring-Opening Polymerization of glycolide is a complex process that requires appropriate catalysts and high purification. Various catalysts have been investigated, for example, metal catalysts (e.g. potassium, tin, aluminum, zinc) and ligands (e.g. alkoxy, imidate, hexamethyldisilazide). It is reported that the most commonly used catalyst in PGA industrial production is $Sn(Oct)_2$ [31]. Gautier et al. [31] compared the effect of different initiators in Ring-Opening Polymerization of PGA in melt conditions. Lu et al. [32] synthesized high molecular weight PGA using diphenyl bismuth bromide as catalyst via Ring-Opening Polymerization. The advantage of bulk polymerization is that it yields high molecular weight PGA and less degradation products. A disadvantage is that the polymer crystallizes in the end of the process resulting the polymer forms the shape of the reactor which is difficult to take out.

Unlike PLA, PGA has not been well developed in scaling-up because its monomer, glycolic acid, is relatively more expensive than lactic acid. In 2011, Kureha opened the first plant in Belle, West Virginia, U.S. with a capacity of 4000 tons/year [33]. Other PGA producers (e.g., Polymtek, BMG, Foryou Medical Ltd.) only focus on the development of their products for medical applications at much smaller scales [34]. In recent years, some new industrial-scale PGA plants have been announced. In 2018, Jiangsu Golden Polyalloy Material Co., Ltd started to build a PGA plant in China with an annual capacity of 3000 tons. Pujing Chemical Industry Co., Ltd (PJCHEM) is planning to open a 1500 tons/year PGA plant in China by early 2020. PJCHEM uses an innovative technology to produce PGA from waste gases derived from coal chemical industry (as shown in Fig. 6). In this new method, carbon monoxide (CO) is extracted from the industrial waste gases, followed by a series of carbonization and esterification reaction, and then converted into dimethyl oxalate. The dimethyl oxalate is hydrogenated into methyl glycolate, then polymerized to form PGA. This technology uses industrial waste gases as raw material which extremely reduces the production cost of PGA and carbon dioxide emissions. The whole process is environmental friendly and will be further scaled-up.

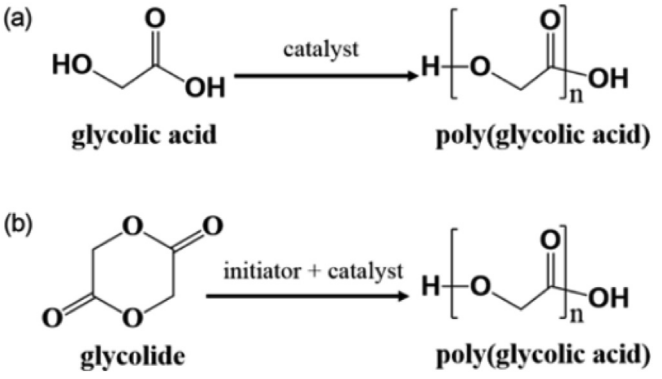

Fig. 5. PGA preparation routes: (a) by Poly-Condensation of glycolic acid, (b) by Ring-Opening Polymerization [25].

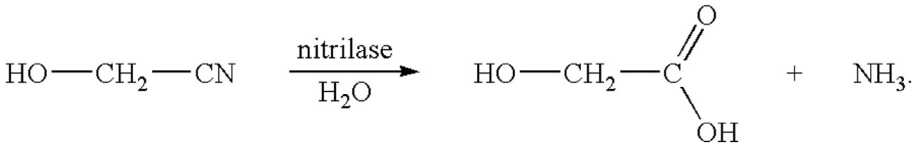

Fig. 4. Scheme of the reaction from glycolonitrile to glycolic acid [21].

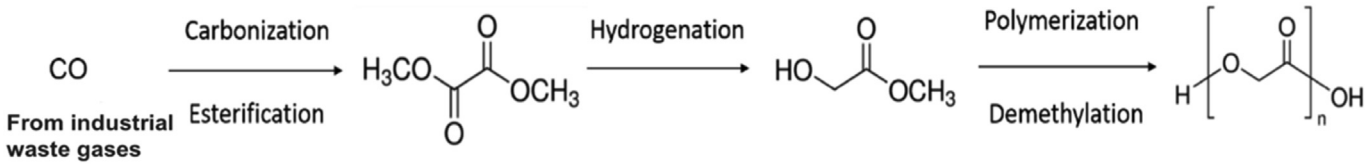

Fig. 6. PGA production route from waste gases.

4. Characteristics and modification of PLA with PGA for industrial applications

4.1. Characteristics of PLA and its current market applications

PLA is a thermoplastic polyester which can be spun to fibers, stretched to rigid films, extruded into sheets for thermoformed packaging, and injected into molds [35–37]. It has been used mainly in food packaging (e.g. salad containers, cups, candy wraps, bottles), textile (e.g. curtains, towels, apparels), non-woven (e.g. wet-wipes, non-woven bags), injection molded parts (e.g. mugs, toys). For flexible film applications such as shopping bags or mulch films, PLA needs to be blended with soft bio-degradable plastics such as poly (butylene adipate-co-terephthalate) (PBAT), typically in a 20:80 ratio to improve its flexibility. In other applications, PLA may require some modifications and improvements due to its unique performance profile. After compounding to improve its impact strength and heat stability, it may be used for engineering plastic applications such as the cases for computers, mobile phones, and radios.

The global PLA market demand in 2019 is estimated by the author to be around ~400,000 tons, up from the estimated 120,000 market volume in 2014 [12]. This dramatic growth of market demand was proposed by the Jem's Law in 2013, based on the author's market observation since 2004 (working for Cargill-Dow, NatureWorks, Corbion Purac, and Total Corbion PLA JV) [38–40].

Jem's Law states that the global PLA market demand doubles every 3–4 years. Fig. 7 plots the growth trend at an annual growth rate at 26% against the global PLA plants' capacities, and the available PLA production plants in the World. Since 2018, the market demand is clearly higher than the global PLA plant capacity, especially when some of these new plants (e.g. SuPLA, COFCO, Total-Corbion) are not fully operational to meet the market demand due to various reasons. This situation triggers a major PLA supply shortage and a dramatic PLA price increase of 20–50% (or even 100% in the second hand market) since early 2019. The PLA and related bio-plastic market and applications are damaged by that, and future market growth is and will be restricted or at least slowed down dramatically. Otherwise, the global PLA market could have grown to at least 250,000 tons in 2019, as estimated by the Jem's Law under the 4-year doubling mode. The above mentioned PLA supply shortage since 2018–2019 is mainly because NatureWorks did not expand its 150,000 ton plant, and other PLA plants are not fully operational due to their internal operation problem and/or the external monomer supply problem (e.g. the supply shortage of lactide to COFCO). Consequently, new PLA plants have been under construction to meet the market demand. For example, BBCA-Galactic's 80,000 tons LA plant and its ~40,000 tons PLA plant, and Hisun's new 30,000–50,000 tons PLA plant (on the top of existing 15,000 tons plant). Jindan is also building a 10,000 lactide plant (then its own PLA plant) to supply lactide to other PLA plants who can only use lactide instead of lactic acid as the raw material to polymerize PLA. If these projects work well, the global PLA supply capacity will go up from 275,000 tons to 375,000 tons by 2020. But there will be still around 100,000 tons of PLA supply shortage by 2020. Most likely NatureWorks will build another full-size

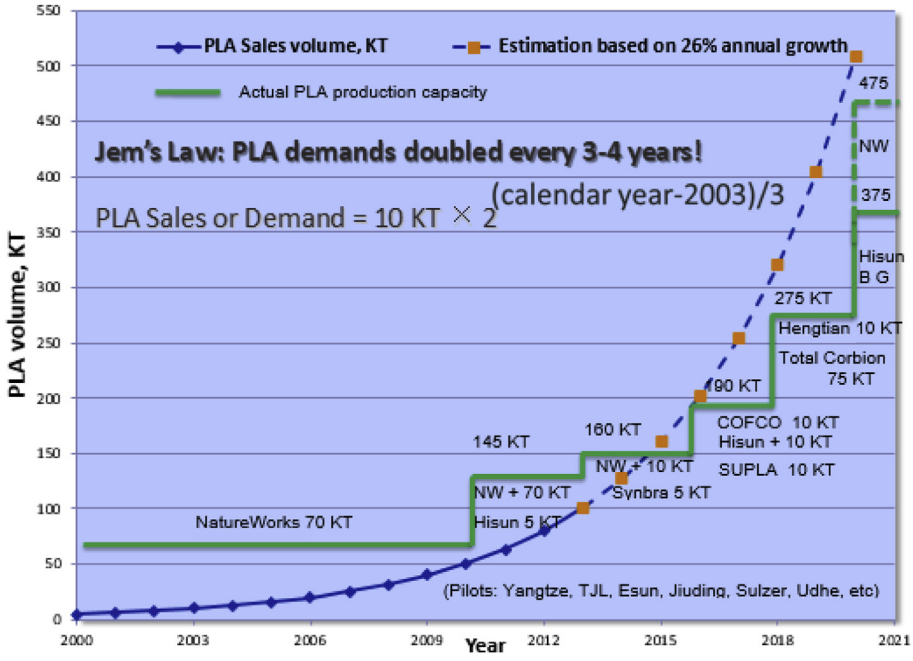

Fig. 7. The Global PLA Plant Capacity vs. the Market Demand Predicted by Jem's Law [38,40].

Table 3
Basic characteristics of PLA, PGA and other traditional plastics.

	Tg (°C)	Tm (°C)	Tensile strength (MPa)	Yong's modulus (GPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (GPa)
PLA [12]	57–58	140–180	53	2.4	5	92	3.4
PGA [41]	35–40	220–230	115	7	16.4	222	7.8
PBAT [42]	−30	110–120	20	0.08	> 900	3.1	0.08
PCL [43–45]	−60	60	14.6	0.4	600–900	23.4	0.6
PET [46–48]	69	255	47	3.5	2–83	118	4
PP [12,49]	−20	175	31	1.5–2	80–350	40	1.5
PS [12,50]	85	105–110	45	3–3.5	4	70	2.5
PA 6 [51]	60	220	56–90	2	70	77.2	1.3

Table 4
Beneficial characteristics of PLA for A) packaging and B) fiber applications [12].

A. Packaging Performance Benefits
Good clarity, gloss, and printability (similar to PET); Good surface adhesion
High stiffness (better than PET and PS) for down gauging of rigid packaging
Lower processing temperatures with energy savings; Sealable by heat, and ultrasonic
Excellent resistance to fat, oil, grease
Good twist and dead fold retention for candy wrap
Good breathability and moisture vapor permeability for vegetables, fruits, and bread
Natural resource-based; Food contact safety & compliance; Environmentally friendly
B. Fiber Performance Benefits
Melt-processable natural-based fiber
Staple fibers with good loft, bulk, resilience, insulative properties
Filament-based fabrics with great hand, drape and luster
Great comfort and wicking performance

70,000–150,000 ton plant to meet the market demand around 500,000 tons by 2021–2022. Multiple new projects have also been announced in China as reported in Table 2. Obviously, the actual market growth predicted by Jem's law will be restricted by the PLA supply capacity.

As a rigid thermoplastic, PLA has basic properties relatively comparable with some traditional plastics such as PET (polyethylene terephthalate) and PS (polystyrene), but rather different from polyethylene (PE) and polypropylene (PP). PLA has many unique characteristics (as shown in Tables 3 and 4) such as superb transparency, glossy appearance, high rigidity (which allows down-gauging of thermoforming parts), printing effects, twist retention. These special characters make PLA a perfect fit for some market sections such as fibers, disposable cups, salad boxes, and cold food packaging.

The characteristics of PLA can make it a good fit for some applications but also require modifications for some others. Table 5 compares the gas permeability and moisture permeability of PLA, PGA and other packaging plastics. PLA has an oxygen permeability of 38–42 cc mil/(100 in.^{2} day atm), CO_2 permeability of 183–200 cc mil/(100 in.^{2} day atm) and water vapor permeability of 18–22 g mil/(100 in.^{2} day). This high gas permeability corresponds to a poor barrier property, hence PLA is not good for some beverage bottle applications. Improvements are needed to enhance the barrier properties of PLA potentially by combining with high barrier plastics, for example PGA, through melt compounding or lamination.

4.2. Characteristics and applications of PGA

PGA is a bio-degradable polymer with good mechanical properties and biocompatibilities. It was firstly synthesized from petrochemical resources in 1940s and has been extensively studied in bio-medical applications. PGA was the first synthetic absorbable suture introduced in the early 1970s [53]. PGA also has been used in oil & gas industry and packaging applications owing to its good mechanical properties and barrier performance. In recent years, the shift in consumer preference towards bio-degradable polymers within packaging industry has increased the demand for PGA market. The global market of PGA was evaluated to be worth around USD 182 million in 2014, USD 240 million in 2017 and is estimated to be around USD 470 million by 2024, with an annual growth rate of 10% [54,55].

PGA has good solvent resistant to most common organic solvents. It is only soluble in hexafluoroisopropanol (HFIP) with a maximum molecular weight of 45,000 g/mol [31]. The glass transition temperature of PGA is between 35 and 40 °C and the melting temperature is in the range of 220–230 °C. Because of high stereoregularity, PGA can be quickly crystallized. The crystallization temperature of PGA is around 150–180 °C. The highest crystallinity of PGA was reported at up to 52% [27]. Amorphous PGA can be obtained by quenching its melt state in liquid nitrogen. The crystalline structure of PGA is reported to be planar zigzag conformation (similar to PE), which could be the reason for high mechanical property of PGA comparing with other biopolymers [56]. PGA also has a high heat distortion temperature at about 170 °C , allowing it to be suitable for high temperature uses. PGA can be degraded when exposed to oxygen at high temperature. The thermal degradation temperature of PGA is around 255 °C that is close to its melting point between 220 °C and 230 °C [31].

PGA has high mechanical properties comparing with other bio-degradable polymers. It has a tensile strength about 115 MPa and a Young's modulus about 7 GPa. The flexural strength and modulus of PGA are about 222 MPa and 7.8 GPa, respectively (as shown in Table 3). The mechanical properties of PGA are much higher than those of other bio-degradable plastics and most traditional plastics.

PGA possesses high barrier to gas molecules due to its high stereochemistry structure. Table 5 compares the oxygen permeability, CO_2 permeability and water vapor permeability of PLA, PGA and other common packaging polymers. The gas permeability of PGA at 0.036 cc mil/(100 in.^{2} day atm) for oxygen and 0.19 cc mil/(100 in.^{2} day atm) for CO_2 are about 1000 times lower than those of PLA. The moisture permeability of PGA is only 0.5 g mil/(100 in.^{2} day), about 40 times lower than PLA. The combination of PGA can help to improve the barrier performance of PLA in packaging applications. In addition, PGA exhibits a lower permeability compared with PA6 and EVOH that have been commonly used as high barrier layers in films and bottles. Such high barrier properties make PGA an ideal material for high barrier packaging applications.

As a bio-degradable polymer, PGA has a good hydrolytic degradation property owing to its extremely hydrolysable backbones. The degradation of PGA throughout the bulk of the material, starting with the hydrolysis reaction with water and followed by the random cleavage of the ester bonds in the polymer chain. The degradation rate is accelerated with a decrease of pH caused by the increase of carboxylic end groups during the reaction [57].

Table 5
Gas and moisture vapor permeability of PLA, PGA and other plastics [12,52].

	Oxygen/cc mil/ (100 in.^{2} day atm)	Moisture vapor/g mil/ (100 in.^{2} day)	CO_2/cc mil/ (100 in.^{2} day atm)
PLA	38–42	18–22	183–200
PGA	0.036	0.5	0.19
PET	3–6	1–2.8	15–25
HDPE	130–185	0.3–0.4	400–700
PP	150–800	0.5–0.7	150–650
PA6	2–3	16–23	10–12
EVOH	2–2.6	1.4–6.5	N/A
HIPS	300–400	10	N/A
PVC	4–30	1–5	4–50

Previous studies have reported the degradation time of various bio-degradable polymers in bio-medical applications (Table 6). Comparing with PLA, PGA has a relatively short degradation time, around 1.5–3 months on in-vitro degradation [58]. Hence, PGA has been extensively used to enhance the degradation rate of bio-medical products. The bio-degradation rates of PGA and cellulose in industrial composting condition and marine environment are shown in Figs. 8 and 9, respectively. The degradation time of PGA is very close to that of cellulose in marine environment at 30 °C (degraded in 1–2 months) and in industrial composting condition at 58 °C (both degraded in 2–3 months, much faster than PLA which degrades in 3–6 months) [41]. Therefore, PGA is a promising alternative to traditional plastics and even other compostable plastics in single-use applications with short self-life.

Many researchers [60–66] have investigated the hydrolysis degradation of PGA. Shawe et al. [60] investigated the effect of surface-to-volume ratio of PGA samples on the degradation properties and found that the mass loss of the samples was related to sample thickness, whereas the melting point, molecular weight and crystallinity were independent of sample thickness. Chu [61] investigated the mechanism of hydrolytic degradation for semi-crystalline PGA in water and suggested that the degradation processes in two main stages: the first stage is degradation in the amorphous region that causes an increase in crystallinity; the second stage is degradation in the crystalline regions. Based on this assumption, Hurrell et al. [62] further investigated the mechanism of PGA's hydrolytic degradation and concluded that the degradation proceeds through four stages which are driven by both water diffusion and the hydrolysis rate of the process. In stage one, water quickly diffuses into the polymer and reaches its maximum concentration in the polymer within a few hours. In stage two, the diffusion of water becomes more slowly and the molecular weight decreases steadily as hydrolysis reaction begins. Similar to the observation by Chu [61], the decrease in molecular weight and the plasticizing effect of water lead to an increase of chain mobility in the amorphous phase, which results in an insertion of secondary crystallization. In stage three, the molecular weight reaches a critical value and the oligomers generated in stage two start to diffuse from the surface of the polymer into the solution. As more spaces are created in the polymer, more water can diffuse through the bulk of the polymer, and this in turn accelerates the reaction and creates sharp reaction–erosion fronts throughout the sample. It is hypothesized that as the fronts meet in the center of the sample, stage four starts and a further decomposition of the oligomers occurs [66].

4.3. Modification of PLA with PGA

Some high-end applications such as packaging for electronics require significant modification of PLA to improve its barrier property, mechanical strength, heat distortion temperature, durability. The most commonly used methods of polymer modification include chemical co-polymerization, polymer blending and nanocomposite technology. Tremendous efforts have been made to develop the performance of PLA via different modification methods [58,67–72]. PGA has a similar chemical structure with PLA, but possesses many unique properties such as high mechanical properties, high gases barrier and fast bio-degradation time. The combination of PGA with PLA has been studied to improve the performance of PLA. Most of these studies are through co-polymerization. Instead of polymerizing only lactic acid into PLA, it is possible to add other components to create the cross-linkage of PLA linear molecules, or to add other monomers (e.g. glycolic acid and ε-caprolactone) to form co-polymers such as PLGA and PCL/PLA/PCL block co-polymer with characteristics very different to PLA.

Co-polymerization of PLA and PGA has been investigated for many years. PLGA is a linear copolymer of lactic acid (LA) and glycolic acid (GA) that can be prepared at different ratios (Fig. 10). Low molecular weight PLGA can be prepared through solution Poly-Condensation of LA and GA at a temperature above 120 °C. Ajioka et al. [73] reported a one-step method of Poly-Condensation in an azeotropical solvent that demands a high process control and purification control, and thus its end product tends to be more expensive. To overcome this drawback, melt/solid Poly-Condensation method was used to prepare PLGA. High molecular weight PLGA can be produced by Ring-Opening Polymerization of lactide and glycolide with metal catalyst (e.g. stannous octoate). An alternative technique, enzymatic polymerization has been used to obtain PLGA with non-possible toxic metallic contaminations and is more favourable for bio-medical applications [58]. It is found that the sequence of PLGA affects the degradation rate dramatically, i.e. random PLGA degrades quicker than sequenced ones. Repeating-sequenced PLGA with high stereochemistry has been prepared using 1,3 diispropylcarbodiimide (DIC) and 4-(dimethylamino) pyridinium p-toluenesulfonate (DPTS) as catalysts [74].

Physical blending is an efficient method for developing new properties from two or more polymers with different properties. Tremendous efforts have been invested to compound PLA to raise its temperature tolerance and mechanical strength, and modify its performance to expand its applications into high-end markets. For durable high-end applications related to computer, electronics, and automobile, other characteristics such as flame resistance, good weatherability, and durability are required. As a bio-degradable plastic, PLA promptly degrades under the industrial compositing conditions (~58 °C and 80–90% humidity) and requires significant compounding efforts to alter its bio-degradability and to improve its durability. Consequently, PLA is commonly mixed with polycarbonate (PC) resulting in a phase-separated polymer blend, as widely done in Japan for electronics applications. But the PLA/PC compounded products are not fully bio-degradable. When the amount of PLA is over 50%, the compounded products are considered to be (partially) bio-based products and widely accepted in Japan. A drawback of such compositions is that typical PC properties like durability, impact and scratch resistance are increasingly lost as the PLA content is increased.

For disposable film products such as agricultural mulch film and trash bags, the bio-degradable and mechanical characteristics of PLA may need to be modified. Several 'soft' bio-degradable plastics such as PBAT can be used for blending with PLA to improve its flexibility. PLA has also been blended with other non-bio-degradable polymers such as poly (methyl methacrylate) (PMMA), acrylonitrile butadiene styrene (ABS), and Hytrel™ (by DuPont). Note that some polymers such as PE and PP are not very compatible with PLA and is hard to use for compounding, unless special compatibilizers are used. The key of polymer blending is to

Table 6
Degradation time of some bio-degradable polymers in bio-medical applications.

	Degradation time (months)
PGA	1.5–3 [58]
PLLA	6–24 [58,59]
PLGA (LA/GA = 50/50)	1–2 [59]
PLGA (LA/GA = 75/25)	4–5 [59]
PLGA (LA/GA = 85/15)	5–6 [59]
PCL	>24 [59]
Poly (dioxanone) (PDO)	6–12 [59]
Poly (glycolide-co-trimethylene carbonate) (PGA-TMC)	6–12 [44,59]

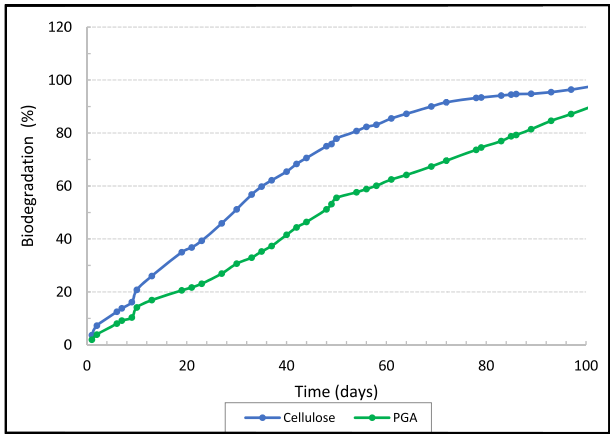

Fig. 8. Bio-degradation rate of PGA and cellulose in industrial composting condition at 58 °C (test standard: ISO 14855) [41].

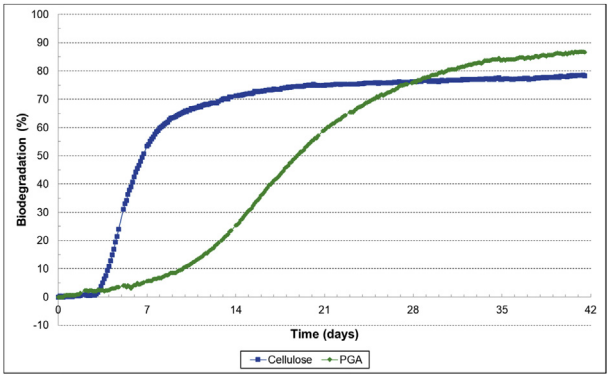

Fig. 9. Bio-degradation rate of PGA and cellulose in marine condition at 30 °C [41].

find the right compatibilizer to build a homogenous and miscible phase.

Only a few researchers studied the blending of PLA and PGA. Ma et al. [7] prepared PGA/PDLLA blend films by solution casting method, in which the copolymer of PGA and PDLLA was used as compatibilizer contributing to a homogenous morphology of the blend. After being blended with PDLLA and the copolymer, the crystallinity of the PGA decreased with the increase of PDLLA content. The degradation time of PGA/PDLLA blend was increased comparing with pure PGA samples, indicating that upon blending the degradation properties of the two polymers were compromised. Another study found that, the mechanical properties and degradation of PLA can be improved by mixing PGA fibers in PLA through melt blending. In this case, PGA fibers acted as reinforcement for PLA and increased the flexural strength and modulus. The

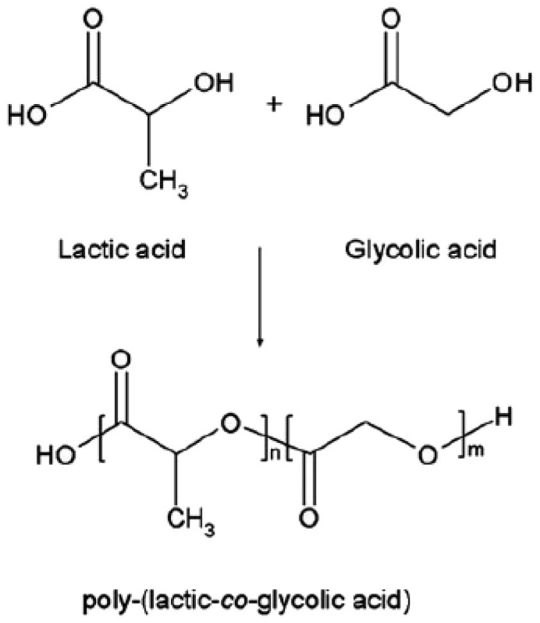

Fig. 10. Chemical structure of LA, LG and PLGA [58].

presence of PGA also increased the crystallinity and interfacial interaction of PLA, resulting in a further improvement in the modulus [8].

In film and packaging industries, the lamination of multilayered polymer has been widely used to improve the product function. PGA, as a biodegradable polymer with good barrier properties, has been reported to be made as a middle layer between two PET layers, which contributes to an improved barrier property of the multilayers [75]. Since PGA is biodegradable, the process of multilayer recycling is much simpler with limited effect on the environment compared with EVOH and MXD6 nylon that have been commonly used as high barrier layers in PET films and containers. The lamination of PGA and PLA on paper was also illustrated in a patent by using melt-extrusion lamination and heat-pressure methods. In the study, melt-extrusion lamination was conducted at 260 °C using three separate extruders and a feed block-type T-die for providing a lamination of three layers. Heat-pressure bonding process was used to produce four-layered biodegradable sheets at a temperature of 240 °C and heating roller pressure of 0.6 MPa. In both lamination methods, the layer thickness of PGA was controlled in the range of 20–60 μm. It was reported that, with the addition layer of PGA, the oxygen and moisture permeability of the multilayers were improved by about 100 times [76]. Although the multilayer application of PGA has been well investigated in several studies, this process has not been widely developed at industrial scales probably due to the high production cost of PGA restricting the scaling-up and the development in multilayer films.

Although the investigations into the combination of PLA and PGA are limited in the field of bio-medical applications, there are many potential opportunities in commodity and other high-end applications such as packaging, electronics and automobile. PGA possesses many advantages and can improve the performance of PLA in mechanical, barrier and bio-degradation properties via either chemical or physical modifications. The main challenge of this approach is that PGA has not been well established at industrial scales due to its high production cost. The production cost of PGA can be significantly decreased with the development of novel manufacturing approaches, for example, the preparation of GA from renewable resources and industrial waste gases. The market

demand of PGA increased with the development of bio-degradable polymers due to the awareness of plastic pollution that has caused serious environmental issues. With the development of production technology and government regulations on plastics, the combination of PGA and PLA may be extensively developed for non-medical applications.

5. Conclusion

In the last two decades, PLA has attracted tremendous attention and interests. The major reasons are probably the concerns on resource sustainability, global warming and environment pollution caused by plastic wastes. Currently, crude oil has been served as not only the energy source for transportation, but also the material source for chemical and plastic industries. However, the development of the petroleum industry has caused serious issues, e.g. greenhouse gas emissions and global warming [12]. To solve these issues, bio-based and bio-degradable plastics have been developed as a promising alternative to petroleum based plastics.

Compared to most other bio-degradable and bio-based plastics, PLA is by far the most important and promising one for rigid applications. The leading position of PLA is demonstrated by the current scale of the PLA industry, the number of pilot projects announced or under construction, the numerous products and applications of PLA in bio-degradable and/or bio-based polymer markets, the number of polymer companies and converters involved in PLA. However, PLA exhibits poor heat stability and water barrier properties compared with some conventional thermoplastics. Tremendous efforts have been made to improve the performance of PLA via different modification methods.

PGA has a high heat distortion temperature, good mechanical properties, high degradability, and good gas barrier properties, which makes it a beneficial supplement to PLA in certain applications. The combination of PGA with PLA can be achieved via co-polymerization, physical blending and/or multilayer lamination. Previous research has reported that the degradability and the mechanical properties of PLA were significantly improved by combining PGA [7,8]. The incorporation of PGA into PLA has been extensively studied, but mainly in bio-medical applications. The main challenge that hinders the large-scale production of PGA is its relatively higher cost compared with other bio-degradable polymers.

Many factors can affect the production cost and scale of PGA such as the development of polymerization and processing technologies, variation of raw material supply, and government regulations and public awareness. For example, with the development of synthesis and processing technology, PGA can be made from the waste gases of coal chemical plants, which can highly reduce its production cost and carbon emissions. A number of countries have restricted the usage of traditional plastics and promote bio-degradable plastics [11]. Basically, this banning approach can be considered to be a 4's "R", i.e. Rejection, on the top of the traditional 3 R's: Reduce, Reuse, and Recycle. The authors propose to replace this "Rejection" by 3 other R's: Replacement of traditional plastics by bio-plastics when possible especially for single-use applications, Research to further develop bio-plastics, and Regulation by governments to promote bio-plastic and restrict the use of traditional plastics in certain applications to protect the environment. It is imperative that more infrastructures such as garbage collection, composting and recycling systems are built and public awareness is raised so as to facilitate the development and wide use of environmentally friendly plastics.

With the development of production technology, the production scale, and the global awareness of environmental pollution, the production cost of PGA will be significantly reduced at industrial scales and the combination of PGA and PLA will be very promising in the future plastic industry.

Declaration of Competing Interest

The authors declare no conflict of interest.

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