



Bio-based polyesters for Ecofriendly packaging materials

Mona H. Abdel Rehim

Packaging Materials Department, National Research Centre, Elbehoth Street 12622, Dokki, Cairo, Egypt



Abstract

The rapid depletion of fossil resources and rising environmental concerns are recent challenges facing polymer industry which rely on petroleum. Therefore, seeking an unconventional solution to these problems is crucial. Recently, the synthesis of polymers from renewable resources has become a serious solicitude of researchers. The utilization of green polymers provides a suitable solution for fossil fuel consumption and the consequent rising environmental menace.

Polyesters, one of the foremost versatile polymers, have been widely used in fibers, plasticizers, plastics, and coatings. The majority of these materials are produced from petrochemical resources. However, many researchers are specializing in developing and industrializing polyesters derived from bio-based monomers. Moreover, bio-based polyesters are closely related to monomers renewable resources. However, these monomers are favorable for synthesizing polyesters cover most of monomers with new structures and characteristics. This review deals with different synthetic approaches for bio-based monomers to polyester and its application in environmentally friendly packaging materials.

Keywords: Polyester; Biodegradability; Enzymatic polymerization; Packaging.

1. Introduction

The recent environmental concerns and climate changes motivated the scientific community to find suitable and cost-effective alternatives to petroleum-based polymeric materials. Over the past five decades, millions of tons of plastic products were manufactured. In 2008, the global plastic production worldwide was around 260 million tons, which has dramatically increased within the last ten years to reach almost a 350million tons in 2017. Indeed, only about 10 percent of that is recycled and of the plastic that is simply trashed, about 7 million tons end up in oceans each year. Polymers are either synthetic or natural, the first type of polymer is commonly produced via polymerization of petrol-based chemicals having simple structures. Metal catalysts are normally utilized as chemical catalysts in the polymers' assembly. Numerous synthetic polymers are developed because of the profitable petrochemical industry and therefore the accompanying availability of cheap petroleum oils, as well as, the well the establishment and advancement of polymerization techniques. For instance, phenol-formaldehyde resins, polyolefins, PVC, polystyrene, polyesters, and polyamides. Synthetic polymers which include the massive group referred to as plastics became prominent in the first 20th century; and plastics are

widely used as bottles, bags, boxes, textile fibers, films, and so on. In contrast with natural polymers, synthetic polymers usually possess far more simple and random structures. [1] On the other hand, natural polymers occur in nature, they are water-based and can be extracted. Examples of natural polymers are wool, silk, protein, DNA, and cellulose.

Polyester polymers have crucial functions in many applications such as fabrics, coatings, and packaging materials. They can be aliphatic polyester, semi-aromatic, or fully aromatic polyester. (Scheme 1) Bio-based polymers are the main source for most known aliphatic polyesters because the majority of their building blocks may be derived from biomass feedstock. Aliphatic polyesters also are (bio) degradable materials that might be recycled and have an occasional environmental impact upon disposal, compost and incineration. Aliphatic polyesters are widely used as thermoplastics and thermoset resins, with many products and specialty applications. [2] Poly(lactic acid) (PLA) is the most well-known aliphatic polyester, which might be used as fibers, food packaging materials, and robust goods, with a worldwide demand of around 360-kilo tons in 2013.[2] Poly(butylene succinate) (PBS) is another important commodity polyester that might be applied as packaging films and disposable cutlery, with a

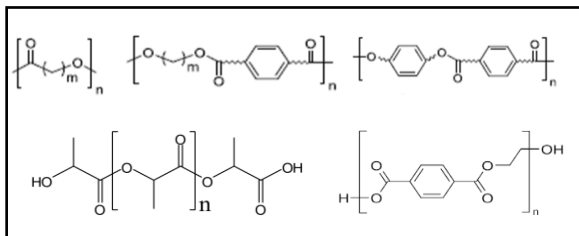
*Corresponding author e-mail: monaabdrehim23@gmail.com; (Mona H. Abdel Rehim).

Receive Date: 15 August 2022, Revise Date: 29 August 2022, Accept Date: 12 September 2022

DOI: 10.21608/EJCHEM.2022.156185.6768

©2022 National Information and Documentation Center (NIDOC)

worldwide market of around 10 -15 kilo tons. [3] Additionally, aliphatic polyesters have found potential applications in biomedical and pharmaceutical fields due to their biocompatibility and biodegradability. [4-6]



Scheme 1: a) aliphatic polyester, b) semi-aromatic polyester, c) aromatic polyester. Examples for aliphatic and semi-aromatic polyesters are: d) polylactic acid and e) polyethylene terephthalate, respectively.

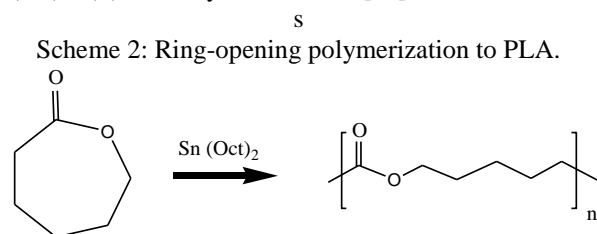
Biodegradability is a term used for materials that degrade naturally with time regardless of the origin of these materials. Among various biodegradable polymers, aliphatic polyester occupies a leading position due to the ease of hydrolytic or enzymatic chain cleavage to hydroxy-carboxylic acids that are eventually metabolized. [7] Nature produces an enormous amount of biomass by photosynthesis every year 75% of it can be included in the class of carbohydrates. However, 3.5 % of these compounds are used by mankind. [8-10] Many of these renewable resource polymers are biodegradable under suitable conditions. [11] However, aside from polylactide, their high cost restrains their widespread use as bulk polymeric materials, relative to conventional petroleum-based plastics. More economically viable processes and also the synthesis of the latest forms of biodegradable polymers would increase the applications for these polymers and additionally lower their cost. For this reason, several research groups have directed investigative efforts toward the synthesis of the latest renewable monomers and therefore the conversion of these monomers into their corresponding polymers. The present review is concerned with different synthetic approaches for bio-based polyesters by chemical method or inhomogeneous processes involving catalysts such as enzymes. A combination of chemical and enzymatic methods will also be described. It summarizes the application of biodegradable polyester in eco-friendly packaging materials.

- Chemical polymerization to polyesters

1) Ring-opening polymerization (ROP)

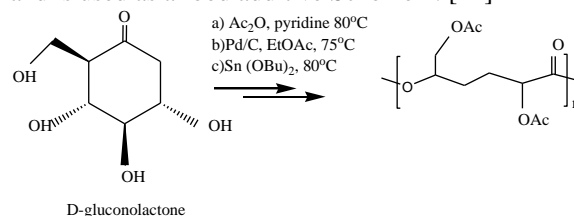
Poly(lactic acid) (PLA) is biodegradable, biocompatible polyester that can be considered a promising alternative to polyethylene terephthalate and polystyrene in packaging application that meets

environmental regulation. [12] The most economical method used for industrial production of PLA is the ring-opening polymerization of lactone monomer in presence of stannous bis(2-ethylhexanoate) ($\text{Sn}(\text{Oct})_2$) as catalyst Scheme 2. [13]



Scheme 3: Conventional ROP of ϵ -Caprolactone to polycaprolactone (PCL).

Polycaprolactone (PCL) is mostly prepared from petroleum-based monomers. However, Tang et al. described the ROP of a carbohydrate lactone, the yield was 90% from the commercially available D-gluconolactone which is derived from gluconic acid and is used as a food additive Scheme 4. [14]



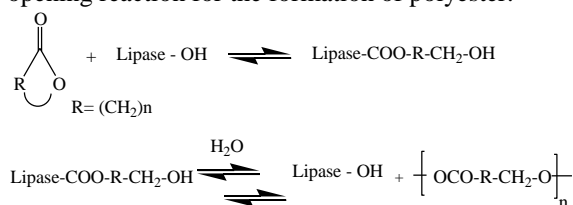
Scheme 4: Synthesis of PCL from the sugar-based monomer.

A new synthetic route for the preparation of caprolactone from 5-hydroxymethyl furfural is reported that opens the way for bio-based PCL. [15] Recently, a review describing synthesis of renewable carboxylic acid using metal catalysts is published. It covered the bio-based polyesters from cellulosic sugars but also includes hemicellulosic sugars and lignin. [16]

- Enzymatic polymerization of non-petrochemical monomers to polyesters

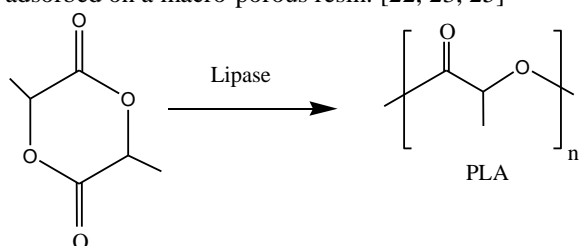
Enzymes are protein in nature that catalyzes biological reactions in vivo and also can catalyze in vitro unnatural substrates. Enzyme catalysis is characterized by high yield, mild reaction conditions, a high reaction rate with no formation of byproducts, and high selectivity. The enzymatic polymerization technique is an appealing approach for synthesis that can be considered an alternating technique for the production of polymeric materials. [17-21] Moreover, it can reduce dependence on non-renewable resources and address the pollution effects of the polymer industry. Scopus database showed more than 4000 articles is published in the period 2008-2021 covering enzymatic polymerization method, from these 110 documents dealing with bio-based and biodegradable

polymers. Scheme (4) shows the enzymatic ring opening reaction for the formation of polyester.



Scheme 4: Reaction mechanism of eROP to produce polyester.

Enzymatic polymerization is the most preferable technique synthesis of PLA by ring opening polymerization due to the wider range of molecular weight that can be produced (Scheme 5). [22, 23] Lipases are effective catalysts in the enzymatic production of aliphatic polyester. [24] The most widely used catalyst for the formation of PLA is Novozym 435 (N435) which consists of immobilized *Candida Antarctica* lipase B (CALB) physically adsorbed on a macro-porous resin. [22, 23, 25]



Scheme 5: Enzymatic ring opening polymerization of lactide to produce PLA.

Commercially available such as *Candida rugosa* lipase (LCR), [26] *Burkholderia cepacia* (LBC), and the lipase from *P. fluorescens* (lipase AK), lipases that have been used for the production of PLA. [27-29] In another approach, isolation of the enzyme from a strain of microorganism is described by Panyachanakul et al. [30] The new thermally stable enzyme identified as *Streptomyces* sp. Showed tolerance toward 10-20% (v/v) hexane and toluene. However, the kinetics of ring open polymerization of lactone is slow and the type of enzyme affects the polymerization rate. [28] Moreover, Duda et al. studied the thermodynamics of polylactone production by chemical and enzymatic ring open polymerization (eROP) and found that the rate of enzymatic reaction increases with the ring size of the used monomer. [31]

The rate-determining step in eROP comprises a lactone-lipase complex that promotes hydrophobicity of the monomer and it increases with larger lactone rings. Concerning lactone polymerization, N435 is the most effective enzyme of high reactivity as concluded by reactivity comparison experiments conducted by Duchiron et al. [28,32] In most eROP

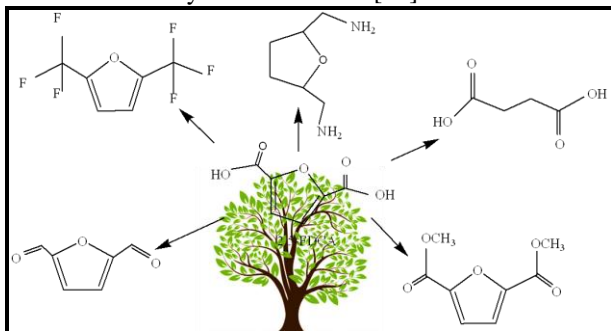
of PLA, the enzyme was not dried and the presence of water is crucial in the polymerization reaction. There are two types of water associated with enzymes, free water present on the surface of the enzyme and structural water embedded inside the enzyme molecules. [33] The measured free water content of N435 was found to be 0.77–1.97 wt%. [33] Synthesis of PLA with different patches of N435 yielded polymers of decreasing molecular weights with increasing free water in the enzyme. Conduction eROP by freeze-dried enzyme led to an increase of polymer molecular weight by nearly 17%. [28] Immobilization of the enzyme is carried out to control and improve the kinetics of the polymerization reaction. Immobilization of the enzyme allows its recyclability and reduces processing costs. It also prevents aggregation and enhances enzyme reactivity by increasing enzyme rigidity and solvent tolerance. [34,35] Moreover, non-immobilized enzymes are susceptible to deactivation by raising temperature due to protein unfolding and enzyme aggregation. [36] clay- and acrylic resin-immobilized *Candida antarctica* lipase B (CALB) and its free form were used in the synthesis of D,L-lactide isomers and it was found the immobilized enzyme converted 70% of the monomer and small amounts of oligomers. [37] The slower polymerization reaction proceed for 4 days and these slow kinetics compared to the free enzyme could be attributed to the hydroxyl groups at the clay surface that can act as co-initiator in the polymerization reaction. Employing N435 in the eROP to produce PCL and poly (δ -valerolactone) in a flow tubular reactor was reported. [38] The enzyme was used to produce PCL in toluene at 70°C 10 times with proven high efficiency. Several parameters confirm the success of the polymerization process such as polymer molecular weight, glass transition temperature, polymer crystallinity, and yield. Lassalle et al. utilized immobilized CALB in isopropyl ether to prepare PLA for four days. [25] The range of polymer molecular weight of the obtained solid was between 400-244 g/mol and LA conversion between 22-96%. Production of PLA of Mw 20000g/mol and polydispersity (PDI) around has been achieved by eROP with the use of IL [BMIM][PF6] at 130°C. [33] The formed polymer can find application as a carrier for drug delivery and release or as a soft block of thermoplastic elastomers. It is worth mentioning that the highest reported molecular weight for PLA was $M_n = 78,100$ g/mol using *Burkholderia cepacia* for seven days at 125 C. [27] It should be pointed out that large-scale polyester production can be attained by lipase-catalyzed polymerization as described by Binns et al. [39] In this work, 1,6-hexanediol and adipic acid are reacted in presence of N435 using two stage approach. The researchers claimed that pilot

production of up to 2 tons can be scaled up and the achieved molecular weight of the formed polymer was M_n of 16400 g/mol. Combination of enzymatic and chemical catalysis for the synthesis of biopolyester in the so-called chemo-enzymatic reaction is described for the enantioselective synthesis of β -amino acid ester in free- solvent process. [40] Pellis et al. investigated chain-length selectivity of *Candida antarctica* lipase B during the preparation of polyester from various C4-C10 diesters acids and C4-C8 diols. [41] The polymerization reaction was carried out in solventless media for 24 hours which led to monomer conversions up to 90% and polymers of molecular weights (M_w) of nearly 13KDa.

Poly(octamethylene suberate) is a biodegradable polyester that belongs to poly(alkylene dicarboxylate)s that found enhanced interest lately. [42,43] The synthesis of poly(octamethylene suberate) (POS) using miniemulsion polymerization in water allowed the reuse of the enzyme several times. [44,45] Pfluck et.al. used immobilized *Pseudozyma antarctica* lipase B (IMM-PBLI) in a two-step polymerization method to obtain poly(octamethylene suberate). [46] Prepolymers were obtained after 8 hours of reaction time with molecular weights of (M_w s) of 2800, 3400, and 4900 g/mol. In the second step, the prepolymers were incubated with IMM-PBLI, at temperatures 68-80°C to obtain final polymers with increased molecular weights of 5000, 5800, and 19,800 g/mol. This method opens the way to a greener and industrially applicable method to prepare bio-based polyester.

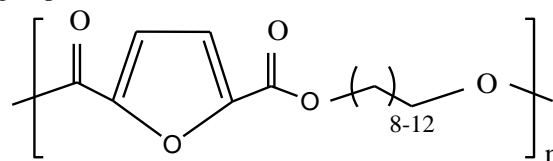
Furan-Based Polyesters

Dehydration of hexose derivatives yields 2,5-Furandicarboxylic acid (FDCA) which is considered a "sleeping giant" for its chemical similarity with terephthalic acid utilized in the production of various thermoplastic polyesters such as polyethylene terephthalate (PET). [47] Consequently, in the last three decades, The researchers showed enhanced interest in polyesters prepared from diols and 2,5-Furandicarboxylic. [48-68] In the late seventies, Moore et al. synthesized various polyesters from 2,5-furandicarbonyl chloride which suffered from strong thermal instability and coloration. [69]



Scheme 6: Some derivatives of 2,5-FDCA.

The importance of 2,5-FDCA represents the most important member in the furane-based polyesters. It produces polyethylene furanoate (PEF) which has superior mechanical and barrier properties compared to PET [70-73] according to the extensive studies for the crystallization kinetics, [74,75] mechanical properties (68,76) and enzymatic degradation of PEF. [77] Semi-crystalline polyesters based on 2,5-FDCA and diols containing 8,9,10 and 12 methylene groups were synthesized using a facial approach. In the three stages method, bis-hydroxy-alkylene furan dicarboxylates (BHFD) is produced by reacting bis-hydroxy-alkylene furan dicarboxylates in the first transesterification stage with the corresponding diols. Then the BHFD reacted with dimethyl ester (DMFD) again at temperatures of 150–170 °C for 4-5 h. Finally, the temperature was raised to 210–230 °C and a vacuum was applied for 2–3 h. [78] The polymers produced have the chemical structure shown in scheme 7 of low coloration and molecular weight (M_n) ranging from 34,500 to 39,900 g/mol. The obtained polyesters have crystallization transition, melting and glass transition temperatures of values depending on the number of methylene groups of the used diol.



Scheme7: polyester based on the reaction of bis-hydroxy-alkylene furan dicarboxylate with different diols.

Qu et al. described the synthesis of poly(ethylene 2,5-furandicarboxylate) by polycondensation reaction of ethylene glycol and FDCA in presence of acidic ionic liquid as a catalyst. [79] They demonstrated that the solubility of the monomers in the ionic liquid is the main factor affecting the canalization of the reaction. A biocatalyst is used in solvent-free polycondensation reaction of dimethyl furan-2,5-dicarboxylate and 1,4-cyclohexanedimethanol. The immobilized enzyme was reused but the yield of the produced oligomers is reduced with each reuse. [80] Maniar et al. studied the copolymerization reaction of dimethyl 2,5-furandicarboxylate (DMFDCA) and 2,5-bis(hydroxymethyl)furan (BHMF)—with linear aliphatic monomers using Novozyme 435 as biocatalyst. [81] High molecular weight polymers were produced but a notable decrease in the molecular weight by replacing diol monomers with diacid ethyl esters. It should be pointed out that metallic catalysts such as dibutyltin (IV) oxide are also used for the synthesis of FDCA-based polyester. [82] The yellow discoloration of the polymer occurred by increasing the reaction temperature to

280°C. However, it was observed that using metal catalysts (Ti, Sb, Sn) caused polymer coloration and decreased thermal stability beside environmental and health concerns. [83, 84] Researchers' attempts to overcome these problems by ring-opening polymerization technique of cyclic FDCA oligomers, have been reported. [85] These cyclic oligomers are formed in the first step through polycondensation of esterified FDCA and ethylene glycol. The obtained uncolored polymer number-average molecular weight higher than 3000g/mol showed high thermal stability and lower melting point which facilitate the processing step. Utilization of non-metallic catalysts in the ring-opening polymerization of the oligomers was described by Carlos-Molares -Huerta et al. [86] Among the interesting and appealing properties of polymerized FDCA is the barrier property which is much related to food and beverages packaging. The detailed investigation of water and gas barrier properties of the polymer compared with PET demonstrated that CO₂ permeability is reduced 19 times and O₂ is reduced by 11 times. [70,71] The reason for that was attributed to the restricted flipping of the furan ring and carbonyl rotation which hinder the diffusion of gases or water molecules. [87] Additionally, by comparing the thermal stability of PET and PEF (poly(ethylene 2,5-furandicarboxylate)) synthesized from 2,5-furandicarboxylic acid, it was found the thermal behavior of PEF is similar to that of PET and its thermally stable at temperature up to 350°C. [88] Also, for PEF of molecular weight ≈45000g/mol, a melting point of 210-215°C and glass transition temperature of 75-80, were measured. [52]

- **Industrialization of bio-based polyesters for packaging application**

Fast-growing packaging materials in the area of plastic industry led to the evolution of serious environmental problems due to their harmful effect on marine life. Lately, serious environmental concerns were raised with the increasing demand for single-use plastic items and packaging during the COVID-19 pandemic. [89] Due to the excessive utilization of plastic –single-use items such as hand gloves and face masks, these wastes have found their way to the environment and threatened marine life. (90-94) It must be admitted that mismanagement and treatment of plastic wastes do not match with the increasing production of plastic based on fossil fuels. However, the action plan released by European Commission in 2020 to tackle the growing climate change challenges targets the transformation of "the EU into a fair and prosperous society, with a modern, resource-efficient and competitive economy where there are no net emissions of greenhouse gases in 2050 and where economic growth is decoupled from resource use". (95-p.2) Before this, the global concerns of climate change and sustainable

developments are discussed in international conferences that issued developed visions for dealing with the implementation of integrated efforts for sustainable development. [96-98] However, the development of bio-plastics for packaging applications is strongly considered lately. [99] In the area of food packaging, accumulative research from academia and industry for searching for new bio-based packaging materials results in high barrier biopolyesters even those containing heterocyclic structures such as furan or pyridine units. [100-102] Furthermore, oil-based derivatives such as 1,4-cyclohexanedicarboxylic acid is used for the synthesis of polyester characterized by their high photo-oxidative stability, good melt viscosity, better humidity, and impact resistance compared to PET. [103] However, the problem of rigidity of the films due to high crystallinity has been reduced by their reaction with suitable counter monomer. [104,105] Lately, copolymerization of poly(butylene trans-1,4-cyclohexanedicarboxylate) with camphoric acid was described by Guidotti et al. to improve unsatisfying properties of the polyester such as opacity and fragility without sacrificing the good ones already exists. [106] Moreover, the aliphatic moiety in the camphoric acid increased the thermal stability of the formed modified polyester. Other biodegradable polyesters belonging to the family of Poly(hydroxyalkanoates) (PHAs) are commercially synthesized by microorganisms. [107, 108] Poly(hydroxybutyrate) (PHB) is formed of a short chain carbon atoms monomer and a member of PHAs and commercialized in the late 1980's Imperial Chemical Industries (ICI) under the trade name of Biopol®. [109] Later, It was produced and registered under the name Biomer in 1994. [110] Another commercially available polyester is PLA which can be manufactured via ring-opening polymerization in presence of stannous chloride as a catalyst. The polymer can be obtained in high molecular weight and its film is a thermoplastic of good water barrier properties and it can withstand several manufacturing techniques such as injection molding, blow molding or vacuum thermoforming process. [111] A list of commercially available products based on PLA can be found in a recent review. [112] The successful manufacture of PLA fibers that can be used in non-woven articles such as teabags is reported. [113] Consumption of PLA in the world market is about 0.2 million tons (10 % of total production) and in 2020 the world production increased to 18.7 % of total biobased plastics. [114] Coating is considered a good tool for improving the properties of packaging material. The notation "coating" is used to describe the layer covering the surface of another material called a substrate. [115] In the packaging field, coatings are covering the surface

of the packaging material or are sandwiched between two layers. The thickness of the coating ranges from a few microns to a few tenths of nanometers. Coatings add many benefits to the packaging material of food and beverages such as increasing water vapor and gas barrier properties, optical properties including UV and transparency, mechanical properties, and antibacterial or antioxidant activity through using definite active coatings. However, the application of the coating layers can be achieved by different techniques such as spraying, spinning, chemical vapor deposition, or dipping. The most common technique is roll to roll e.g. curtain coating and gravure coating. [116] Researchers developed anti-fog coating to inhibit fog formation inside the packaging material to get clear flexible films for fresh food. The coat contained plasma-treated polyester to obtain a super hydrophilic surface. [117] However, the inclusion of biobased multifunctional polyester has been proposed by Nuraje et al. [118]

Utilization of bio-based polyester as coating film for metal cans that act as a resisting layer against solvents was described. [119] Self-esterification of the naturally occurring 9,10,16-trihydroxyhexadecanoic (aleuritic) acid yielded polyaleuritate. The physical properties of 2-3 thick coating layers on three different metal cans, namely Aluminum (Al), electrochemically tin-plated steel (ETP), and chromium-coated tin-free steel (TFS) were evaluated. The coating film showed acceptable adherence to the substrate, wettability, and gloss appearance.

Conclusion and prospects

Large abundance and inducement of ecological concerns are pushing toward expanding the use of bio-based materials in the food packaging sector. Nevertheless, much effort is required to find solutions for sustainability and higher performance of the bio-based packaging material. These solutions should be novel, feasible, and compatible with present technology and take advantage of the distinguished properties of bio-based materials. In the review, different synthetic approaches to bio-based polyester are demonstrated. However, despite the large steps that have been taken in this field some major points should be thoroughly researched. Among them, the preparation of high molecular weights of polyester remains challenging due to side reactions. Therefore, developing suitable catalysts or tailoring ligands, or stable initiators is required. For the coating technology, bio-based polymers suffer from poor mechanical properties and sensitivity to moisture, these drawbacks can be overcome by using suitable nanofillers. Nevertheless, other strategies have been suggested such as grafting and chemical functionalization, formation of interpenetrating

networks, and layer-by-layer precipitation, which need to be thoroughly studied.

Acknowledgment

The author acknowledges the support of National Research Centre through the in-house project number E120104.

References:

1. J. Mathieu.-L. Tschan, Emilie Brule, Pierre Haquette and Christophe M. Thomas. *Polym. Chem.*, 2012, 3, 836
2. Lactic Acid and Poly Lactic Acid (Pla) Market Analysis by Application (Packaging, Agriculture, Transport, Electronics, Textiles) and Segment Forecasts to 2020; Grand View Research, Inc.: San Francisco, USA, 2014.
3. J. Lunt, Marketplace Opportunities for Integration of Biobased and Conventional Plastics; Agricultural Utilization Research Institute, Minnesota Corn Research & Promotion Council, and Minnesota Soybean, Research & Promotion Council: **2014**, 1.
4. M. A. Hillmyer, W. B. Tolman, *Acc. Chem. Res.* **2014**, 47, (8), 2390.
5. H. Seyednejad, A. H. Ghassemi, C. F. van Nostrum, T. Vermonden, W. E. J. Hennink, *Control. Release* **2011**, 152, (1), 168.
6. M. Vert, S. M. Li, G. Spenlehauer, P. J. Guerin, *Mater. Sci. Mater. Med.* **1992**, 3, (6), 432.
7. C. M. Thomas and J. -F. Lutz, *Angew. Chem., Int. Ed.*, **2011**, 50, 9244.
8. M. Poliakoff and P. Licence, *Science*, **2006**, 211, 810.
9. A. J. Ragauskas, *Science*, 2006, 311, 484–489.
10. A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, 107, 2411–2502;
11. C. K. Williams and M. A. Hillmyer, *Polym. Rev.*, 2008, 48, 1–10.
12. R. Auras, B. Harte, S. Selke, *Macromol. Biosci.* **2004**, 4, 835.
13. T. Narancic, S. Verstichel, S. Reddy Chaganti, L. Morales-Gamez, S.T. Kenny, B. de Wilde, R. Babu Padamati, K. E. O'Connor, *Environ. Sci. Technol.* **2018**, 52, 10441.
14. M. Tang, Andrew J. P. White, Molly M. Stevens, Charlotte K. Williams. *Chem. Commun.*, 2009, 941.
15. T. Buntara, S. Noel, P.H. Phua, I. Melián-Cabrera, J. G. de Vries, H. J. Heeres. *Angew Chem Int Ed* **2011**, 50, 7083.
16. J. Iglesias, I. Martínez-Salazar, P. Maireles-Torres, D. Martin Alonso, R. Mariscal and M. López Granados, *Chem. Soc. Rev.*, 2020,49, 5704-5771
17. A. Singh, D. L. Kaplan, In Vitro Enzyme-Induced Vinyl Polymerization. In Enzyme-Catalyzed

- Synthesis of Polymers, Kobayashi, S.; Ritter, H.; Kaplan, D., Eds. Springer-Verlag: Berlin Heidelberg, **2006**, Vol. *194*, 211.
18. H. Uyama, S. Kobayashi, Enzymatic Synthesis of Polyesters Via Polycondensation. In Enzyme-Catalyzed Synthesis of Polymers, Kobayashi, S.; Ritter, H.; Kaplan, D., Eds. Springer-Verlag: Berlin Heidelberg, **2006**; Vol. *194*, pp 133.
19. S. Kobayashi, A. Makino, Chem. Rev. **2009**, *109*, (11), 5288.
20. R. A. Gross, M. Ganesh, W. Lu, Trends Biotechnol. **2010**, *28*, (8), 435.
21. N. Miletić, K. Loos, R. A. Gross, Enzymatic Polymerization of Polyester. Biocatalysis in Polymer Chemistry, Loos, K., Ed. Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, **2010**; pp 83-129.
22. M. Hans, H. Keul, M. Moeller. Macromol. Biosci. **2009**, *9*, 239.
23. R. García-Arrazola, D. A. López-Guerrero, M. Gimeno, E. Bárzana, Polym. Adv. Technol. **2008**, *19*, 1396.
24. C. Gkoutela, M. Rigopoulou, E. M. Barampouti, S. Vouyiouka, Eur. Polym. J. **2021**, *143*, 110197.
25. V. Lassalle, M. Ferreira, J. Chem. Technol. Biotechnol. **2008**, *83*, 1493.
26. R. Rahmayetty D.R. Barleany, E. Suhendi, B. Prasetya, T. Andiyani, World Chem. Eng. J. **2017**, *1*, 70.
27. S. Målberg, A. Finne-Wistrand, A. C. Albertsson, Polymer **2010**, *51*, 5318.
28. S.W. Duchiron, E. Pollet, S. Givry, L. Avérous, RSC Adv. **2015**, *5*, 84627.
29. F. Guzmán-Lagunes, A. López-Luna, M. Gimeno, E. Bárzana, Fluids **2012**, *72*, 186.
30. T. Panyachanakul, T. Lomthong, W. Lorliam, J. Prajanbarn, S. Tokuyama, V. Kitpreechavanich, S. Krajangsang, Polymer **2020**, *204*, 122812.
31. A. Duda, A. Kowalski, S. Penczek, H. Uyama and S. Kobayashi, Macromolecules, **2002**, *35*, 4266.
32. Christina I. Gkoutela and Stamatina N. Vouyiouka, Macromol **2022**, *2*, 30.
33. H. Zhao, G.A. Nathaniel, P.C. Merenini, RSC Adv. **2017**, *7*, 48639.
34. A. Pellis, E. Herrero Acero, V. Ferrario, D. Ribitsch, G.M. Guebitz, L. Gardossi, Trends Biotechnol. **2016**, *34*, 316.
35. D.G. Filho, A.G. Silva, C.Z. Guidini, Appl. Microbiol. Biotechnol. **2019**, *103*, 7399.
36. M. Noel, D. Combes, J. Biotechnol. **2003**, *102*, 23.
37. H.Ö. Düsünkörur, A. Bégué, E. Pollet, V. Phalip, Y. Güvenilir, L. Avérous, J. Mol. Catal. B Enzym. **2015**, *115*, 20.
38. W. Adhami, Y. Bakkour, C. Rolando, Polymer **2021**, *230*, 124040.
39. F. Binns, P. Harffey, S. M. Roberts, A. Taylor, J. Chem. Soc., Perkin Trans. 1, **1999**, (19), 2671.
40. S. Strompen, M. Weiß, H. Gröger, L. Hilterhaus, A. Liese, Adv. Synth. Catal. **2013**, *355*, 2391.
41. Alessandro Pellis, James W. Comerford, Andrew J. Maneffa, Mika H. Sipponen, James H. Clark, Thomas J. Farmer, Eur. Polym. J. **2018**, *106*, 79.
42. S. Gestí, M.T. Casas, J. Puiggali, Eur. Polym. J. **2008**, *44*, 2295.
43. S. Gestí, M. Zanetti, M. Lazzari, L. Franco, J. Puiggali, Eur. Polym. J. **2009**, *45*, 398.
44. A.C.D. Pfluck, D.P.C. De Barros, L.P. Fonseca, Technology. Processes **2021**, *9*, 365.
45. L.P. Fonseca, A.C.D. Pfluck, D.P.C. De Barros, English Title—Synthesis of Polyesters in Aqueous Polymerization Media “from de Solid to Solid” via Biocatalysis. Notif International Application Number PCT/PT2020/050051 and published as WO 2021/137711 A1. Portuguese Patent PT 116045, 31 December 2019.
46. Ana C. D. Pfluck, Dragana P. C. de Barros, Abel Oliva, and Luis P. Fonseca. Technology. Processes **2022**, *10*, 221.
47. J. J. Bozell, G. R. Petersen, Green Chem. **2010**, *12*, 539.
48. R. Storbeck, M. Ballauff, Polymer **1993**, *34*, 5003.
49. A. Khrouf, S. Boufi, R. El Gharbi, N. M. Belgacem, A. Gandini, Polym. Bull. **1996**, *37*, 589.
50. M. Okada, K. Tachikawa, K. Aoi, J. Polym. Sci., Part A: Polym. Chem. **1997**, *35*, 2729–2737.
51. S. Gharbi, J. P. Andreolety, A. Gandini, Eur. Polym. J. **2000**, *36*, 463.
52. A. Gandini, A. J. D. Silvestre, C. P. Neto, A. F. Sousa, M. Gomes, J. Polym. Sci., Part A: Polym. Chem. **2009**, *47*, 295.
53. E. De Jong, M. A. Dam, L. Sipos, G. J. M. Gruter, In Smith, P. B.; Gross, R. A., Eds.; Biobased Monomers, Polymers and Materials; ACS Symposium Series, 2012; Vol 1105, DOI: 10.1021/bk-2012-1105.ch001.
54. Y. Jiang, A. J. J. Woortman, G. O. R. Alberda van Ekensteina, K. Loos, Polym. Chem. **2015**, *6*, 5198.
55. A. F. Sousa, C. Vilela, A. C. Fonseca, M. Matos, C. S. R. Freire, G. J. M. Gruter, J. F. J. Coelho, A. J. D. Silvestre, Polym. Chem. **2015**, *6*, 5961.
56. J. C. Morales Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra, Polymer **2016**, *87*, 148–158.
57. G. Z. Papageorgiou, D. G. Papageorgiou, Z. Terzopoulou, D. N. Bikiaris, Eur. Polym. J. **2016**, *83*, 202.
58. Z. Terzopoulou, V. Tsanaktsis, M. Nerantzaki, G. Z. Papageorgiou, D. N. Bikiaris, Polym. Degrad. Stab. **2016**, *132*, 127.

- 59., D. G. Papageorgiou, N. Guigo, V. Tsanaktsis, S. Exarhopoulos, D. N. Bikiaris, N. Sbirrazzuoli, G. Z. Papageorgiou, *Ind. Eng. Chem. Res.* **2016**, *55*, 5315.
60. V. Tsanaktsis, Z. Terzopoulou, M. Nerantzaki, G. Z. Papageorgiou, D. N. Bikiaris, *Mater. Lett.* **2016**, *178*, 64.
61. L. Genovese, N. Lotti, V. Siracusa, A. Munari, *Materials* **2017**, *10*, 1028.
62. M. Soccio, D. E. Martínez-Tong, A. Alegría, A. Munari, N. Lotti, *Polymer* **2017**, *128*, 24.
63. G. Guidotti, M. Soccio, N. Lotti, M. Gazzano, V. Siracusa, A. Munari, *Polymers* **2018**, *10*, 785.
64. L. Genovese, M. Soccio, N. Lotti, A. Munari, A. Szymczyk, S. Paszkiewicz, A. Linares, A. Nogales, T. A. Ezquerro, *Phys. Chem. Chem. Phys.* **2018**, *20*, 15696.
65. D. Maniar, Y. Jiang, A. J. J. Woortman, J. van Dijken, K. Loos, *Chem. Sus. Chem* **2019**, *12*, 990.
66. G. Papamokos, T. Dimitriadis, D. N. Bikiaris, G. Z. Papageorgiou, G. Floudas, *Macromolecules* **2019**, *52*, 6533.
67. Lalanne L, Nyanhongo GS, Guebitz GM, Pellis A. *Biotechnol Adv.* 2021 May-Jun; 48:107707.
68. G. Guidotti, M. Soccio, M. C. García-Gutiérrez, E. Gutiérrez-Fernández, T. A. Ezquerro, V. Siracusa, A. Munari, N. Lotti, *ACS Sustainable Chem. Eng.* **2019**, *7*, 17863.
69. J. A. Moore, J. E. Kelly, *Macromolecules* **1978**, *11*, 568.
70. S. K. Burgess, J. E. Leisen, B. E. Kraftschik, C. R. Mubarak, R. M. Kriegel, W. J. Koros, *Macromolecules* **2014**, *47*, 1383.
71. S. K. Burgess, D. S. Mikkilineni, D. B. Yu, D. J. Kim, C. R. Mubarak, R. M. Kriegel, W. J. Koros, *Polymer* **2014**, *55*, 6870.
72. S. K. Burgess, R. M. Kriegel, W. J. Koros, *Macromolecules* **2015**, *48*, 2184.
73. J. Wang, X. Liu, Z. Jia, Y. Liu, L. Sun, J. Zhu, *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 3298.
74. V. Tsanaktsis, D. G. Papageorgiou, S. Exarhopoulos, D. N. Bikiaris, G. Papageorgiou, *Cryst. Growth Des.* **2015**, *15*, 5505.
75. C. F. Araujo, M. M. Nolasco, P. J. A. Ribeiro-Claro, S. Rudic, A. J. D. Silvestre, P. D. Vaz, A. F. Sousa, *Macromolecules* **2018**, *51*, 3515.
76. R. J. I. Knoop, W. Vogelzang, J. van Haveren, D. S. van Es, *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 4191.
77. S. Weinberger, J. Canadell, F. Quartinello, B. Yeniad, A. Arias, A. Pellis, G. M. Guebitz, *Catalysts* **2017**, *7*, 318.
78. Vasilios Tsanaktsis, G. Z. Papageorgiou, Dimitrios N. Bikiaris. *J of polym Sci: part A, polym chem* **2015**, *53* (22) 2617.
79. X. Qu, M. Jiang, B. Wang, J. Deng, R. Wang, Q. Zhang, et al. *ChemSusChem* **2019**, *12*, 1.
80. P. Skoczinski, M. K. Espinoza Cangahuala, D. Maniar, R. W. Albach, N. Bittner, K. Loos, *ACS Sustain. Chem. Eng.* **2020**, *8*, 1068.
81. Dina Maniar, Yi Jiang, Albert J. J. Woortman, Jur van Dijken, Katja Loos, *Cem. Sus. Chem* **2019**, *12*, 990.
82. M. Gruter, Gert-Jan; Sipos, Laszlo; Adrianus Dam, Matheus. *Combinatorial Chemistry & High Throughput Screening* **2012**, *15*, 180.
83. J. Wu, H. Xie, L. Wu, B.-G. Li, P. RSC Adv. **2016**, *6*, 101578.
84. G. Z. Papageorgiou, D. G. Papageorgiou, Z. Terzopoulou, D. N. Bikiaris, *Eur. Polym. J.* **2016**, *83*, 202.
85. J. G. Rosenboom, D. K. Hohl, P. Fleckenstein, G. Storti, M. Morbidelli, *Nat. Commun.* **2018**, *9*, 1–7.
86. J. Carlos Morales-Huerta, A. Martínez De Ilarduya, S. Muñoz-Guerra, *Polymer* **2016**, *87*, 148.
87. S. K. Burgess, D. S. Mikkilineni, D. B. Yu, D. J. Kim, C. R. Mubarak, R. M. Kriegel, et al. *Polymer* **2014**, *55*, 6861.
88. Z. Terzopoulou, V. Tsanaktsis, D. N. Bikiaris, S. Exarhopoulos, D. G. Papageorgiou, G. Z. Papageorgiou. *RSC Adv.* **2016**, *6*, 84003.
89. Yiming Peng, Peipei Wu, Amina T. Schartup, and Yanxu Zhang, Plastic waste release caused by COVID-19 and its fate in the global ocean. *PNAS* **2021**, *118* (47) e2111530118.
90. C. I. Fraser et al. *Nat. Clim. Chang.* **2018**, *8*, 704.
91. D. W. Laist, “Impacts of Marine Debris: Entanglement of Marine Life in Marine Debris Including a Comprehensive List of Species with Entanglement and Ingestion Records” in *Marine Debris, J. M. Coe, D. B. Rogers, Eds. (Springer Series on Environmental Management, 1997)*, pp. 99–139.
92. C. L. Waller et al., *Sci. Total Environ.* **2017**, *598*, 220.
93. J. A. Ivar do Sul, M. F. Costa, M. Barletta, F. J. A. Cysneiros, *Mar. Pollut. Bull.* **2013**, *75*, 305.
94. T. P. Bondaroff, S. Cooke, *Masks on the Beach: The Impact of COVID-19 on Marine Plastic Pollution (Oceans Asia, 2020)*.
95. European Commission. *A New Circular Economy Action Plan For a Cleaner and More Competitive Europe COM(2020) 98 Final; European Commission: Brussels, Belgium, 2020*
96. United Nations Conference on Sustainable Development, Rio+20: sustainable development knowledge platform, June 20–22, 2012, <https://sustainabledevelopment.un.org/rio20>.

97. Sustainable Development in the 21st century (SD21): sustainable development knowledge platform.
<https://sustainabledevelopment.un.org/resources/d21>.
98. COP21 - Paris Climate Conference.
<https://www.gouvernement.fr/en/cop21>, 2015. (Accessed 12 December 2015).
99. H.T.H. Nguyen, P. Qi, M. Rostagno, A. Feteha, S.A. Miller, The quest for high glass transition temperature bioplastics, *J. Mater. Chem. A*. **2018**, *6*, 9298.
100. G. Guidotti, M. Soccio, M.C. García-Gutiérrez, T. Ezquerro, V. Siracusa, E. Gutiérrez-Fernández, A. Munari, N. Lotti, *ACS Sustain. Chem. Eng.* **2020**, *8*, 9558.
101. G. Guidotti, L. Genovese, M. Soccio, M. Gigli, A. Munari, V. Siracusa, N. Lotti, Block copolymers containing 2,5-furan and trans-1,4-cyclohexane subunits with outstanding gas barrier properties, *Int. J. Mol. Sci.* **2019**, *20*, 2187.
102. X. Liu, N. Desilles, Bo Jiang, C. Chappey, L. Lebrun, *Polymer* **2022**, *247*, 124790
103. M. Gigli, N. Lotti, M. Gazzano, V. Siracusa, L. Finelli, A. Munari, M. Dalla Rosa, *Ind. Eng. Chem. Res.* **2013**, *52*, 12876.
104. V. Siracusa, L. Genovese, C. Ingraio, A. Munari, N. Lotti, *Polymers* **2018**, *10*, 502.
105. G. Guidotti, M. Soccio, V. Siracusa, M. Gazzano, A. Munari, N. Lotti, *Polymers* **2018**, *10*, 866.
106. G. Guidotti, G. Burzotta, M. Soccio, M. Gazzano, V. Siracusa, A. Munari, Naia Lotti, *Polymers* **2021**, *13*(16), 2707
107. E. Bugnicourt, P. Cinelli, A. Lazzeri, V. Alvarez, *Express Polym. Lett.* **2014**, *8*, 791.
108. T. Keshavarz, I. Roy, *Curr. Opin. Microbiol.* **2010**, *13*, 321.
109. G. L. Robertson, *Food packaging-principles and practice*, 3rd ed., Taylor & Francis, **2013**.
110. Biomer Biopolyesters.
<http://www.biomer.de>
111. M. Jamshidian, E.A. Tehrany, M. Imran, M. Jacquot, S. Desobry, *Comprehensive Reviews in Food Science and Food Safety* **2010**, *9* (5), 552.
112. Saurabh Sid, Rahul S Mor, Anand Kishore, Vijay Singh Sharanagat, *Trends in Food Science & Technology*. **2021**, *115*, 87.
113. V. Katiyar, *Bio-based plastics for food packaging applications*, (1st ed.), Smithers Pira, UK (2017)
114. European Bio-plastics Bioplastics market data (2020) Retrieved from <https://www.european-bioplastics.org/market/>, Accessed 3rd May 2021
115. Luciano Piergiovanni, Fei Li, Stefano Farris, *Packaging: Opportunities for Problem Solving and Innovations, Advances in Industrial Biotechnology* Ram Sarup Singh, Ashok Pandey & Christian Larroche (Eds.) IK International Publishing House Pvt. Ltd., India, (2014) Chapter 13. pp 233-251
116. S. Farris & L. Piergiovanni (2012) Emerging coating technologies for food and beverage packaging materials, In – *Emerging Food Packaging Technologies*, KL Yam & DS Lee (eds.), Woodhead Publishing Ltd, England.
117. P. Patel, C. K. Choi & D. D. Meng, *Journal of the Association for Laboratory Automation*, **2010**, *15*, 114.
118. N. Nuraje, R. Asmatulu, R. E. Cohen & M. F. Rubner, *Langmuir* **2011**, *27*, 782.
119. José J. Benítez, Sonja Osbild, Susana Guzman-Puyol, Antonio Heredia and José A. Heredia-Guerrero, *Polymers* **2020**, *12*, 942