

Perspective

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ACS Sustainable Chem. Eng., **Just Accepted Manuscript** • DOI: 10.1021/
acssuschemeng.0c01862 • Publication Date (Web): 19 May 2020

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Bio-based Poly(ethylene 2,5-furancoate): No Longer an Alternative, But an Irreplaceable One in Polymer Industry

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ABSTRACT: Recently, studies on the synthesis, modification and functionalization of polyesters derived from 2,5-furandicarboxylic acid (2,5-FDCA) have attracted widespread attention. Among them, poly(ethylene 2,5-furanoate) (PEF) is the center of spotlight due to its greener production process, higher glass transition temperature (T_g), good mechanical performance and excellent barrier properties, which has been considered as the new generation of packaging material to replace polyethylene terephthalate (PET). Being a promising rising star in the field of bio-based polymers, yet there is no review entirely focused on it. This article focused on the research of PEF, discussing its mainstream synthetic methods including optimization of catalysts with solutions of coloration and side reactions, comprehensive properties as thermal, crystallization, mechanical and barrier performances. Other aspects concerned are modifications for the better properties and introducing biodegradability as well as the construction of composites materials. This article aims to reveal the development path of PEF and help us to understand it more deeply and widely in a short time.

KEYWORDS: poly(ethylene 2,5-furanoate); synthetic methodology; barrier properties; modification; biodegradability

INTRODUCTION

If holding the current growth rate, by 2050, the global production of plastics will reach 1124 million metric tons per year¹. For now, almost all the synthesized plastics are sourced from petroleum, which consumed much petrochemical resources and their non-degradability would result in the so-called "white pollution", which in turn drive concerns to develop bio-based or biodegradable plastics. Currently, the bio-resourced polymer production capacity is reaching 12 million metric tons per year¹. However, if we have a look at the popular bio-based polymers, such as polylactic acid, polybutylene succinate, polyhydroxybutyrate and polyglutamic acid, you will find that all of them are aliphatic polyesters. Compared to the well-known petroleum-based engineering plastics, including poly (butylene terephthalate) (PBT) and bisphenol A-based

polycarbonates (PC), *etc.* the comprehensive performance of these mainstream bio-based polymers is weaker and the reason should be ascribed to the lack of aromatic structures (Figure 1).

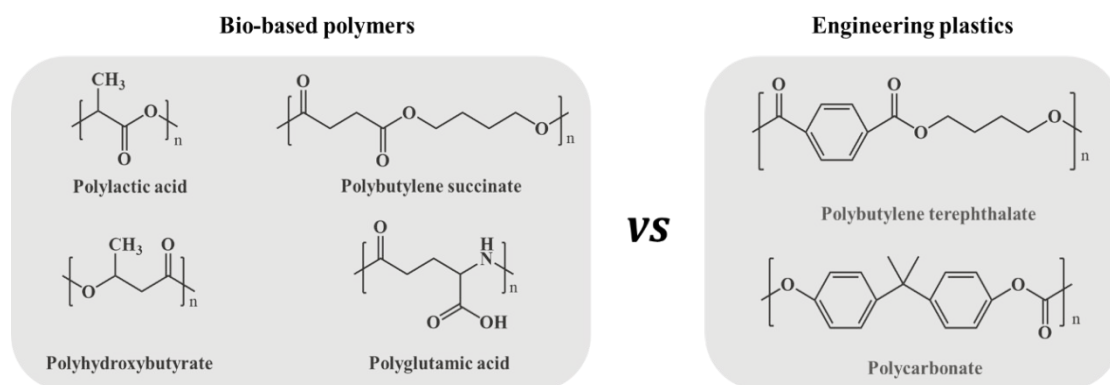


Figure 1. Structural comparison between well-known bio-based polymers and petroleum-based engineering plastics.

In 2004, the US Department of Energy published a list of “twelve platform bio-based chemicals”, and 2,5-FDCA is the only aromatic compound among them ². Generally, 2,5-FDCA can be prepared via five strategies illustrated in the following Figure 2: (1) Oxidation of aldehyde and methylol group of 5-hydroxymethylfurfural (HMF) to carboxyl groups by chemical or biological method ³; (2) Conversion of 2-furoic acid into 2,5-FDCA via the well-known Henkel Reaction ⁴; (3) Cyclodehydration of hexaric acid ⁵; (4) Cyclodehydration of xylose ⁶. Among these strategies, the HMF route is still a promising way for the industrialization of 2,5-FDCA, although HMF is unstable as an intermediate product under acidic conditions and a variety of by-products are currently inevitable. Many improved methods based on HMF routes have been reported in the recent literature ⁶⁻⁸. Up to now, several chemical corporations including ADM, DuPont, and BASF, have involved in the industrial production of 2,5-FDCA along with FDCA-based polyesters and claimed 2,5-FDCA “a sleeping giant” due to its structural similarity to that of terephthalate (TA) ⁹, which has been widely applied in various polyesters such as PET and poly(butylene terephthalate) (PBT).

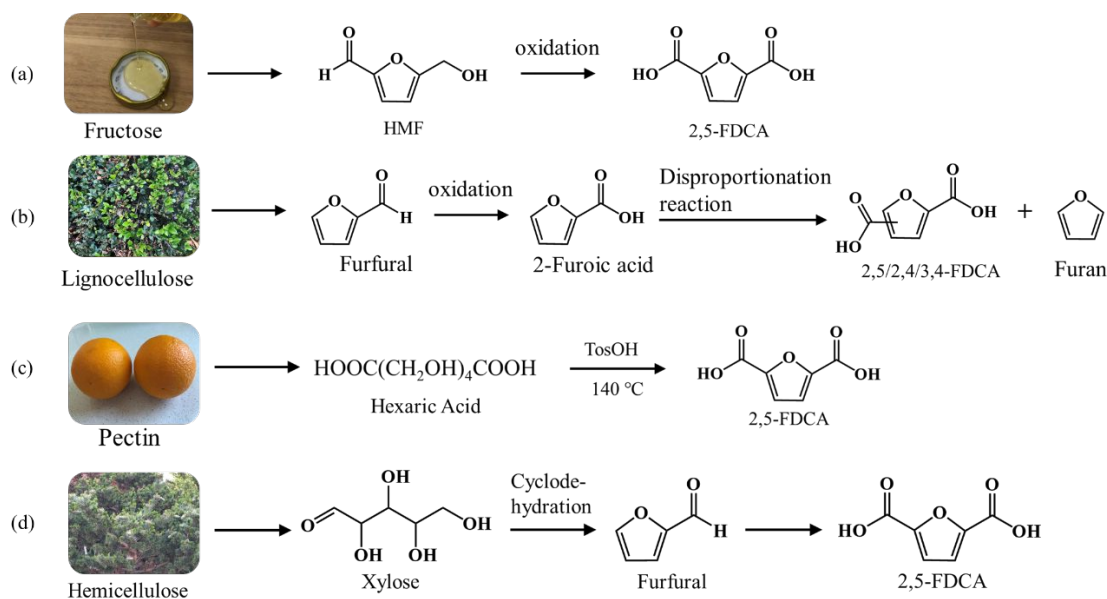


Figure 2. Strategies for 2,5-FDCA synthesis: (a) HMF route; (b) Henkel reaction; (c) hexose diacids Cyclodehydration; (d) Cyclodehydration of xylose.

A large quantity of polyesters synthesized from 2,5-FDCA and different aliphatic diols has received extensive attention. Among them, PEF is the optimal and closest polyester to PET, in both thermal and mechanical properties (Table 1). The glass transition temperature (T_g) of PEF is between $82\text{--}87^\circ\text{C}$, higher than that of $71\text{--}75^\circ\text{C}$ for PET, which is beneficial for the packaging material when high heat resistance is required. While its melting temperature (T_m) is about 40°C lower than that of PET, enhancing the convenience for blow molding and extrusion process. Besides, the higher strength and modulus of PEF allow the thinner walls in finished bottle products. And the most shining part is the surprising good gas barrier properties of PEF, demonstrating a reduction in carbon dioxide (CO_2) and oxygen (O_2) permeability of several times compared with that of PET. This is amazing, especially for the packaging of CO_2 or O_2 -sensitive beverages, such as beer. In 2019, the flexible packaging market was valued at more than 250 billion, and is expected to reach about 315 billion by 2025. The focus on sustainability is increasing which promoted the flexible packaging in the fields of food, beverages and tobacco products ¹⁰. Furthermore, Flexible Packaging Europe reported that when flexible packaging dominated the market, the waste would decrease

26 million tons every year and a reduction of 77% of the total amount of waste (recycled and landfilled) ¹¹.

Table 1. Thermal and mechanical properties of FDCA- or TA-based polyesters.

Polyester	T_g /°C	T_m /°C	Tensile Modulus (GPa)	Tensile Strength (MPa)	M_n (10 ³ g/mol)	Ref.
Poly(ethylene furandicarboxylate) (PEF)	82-89	210-215	2.5-2.8	67-85	83-105	12-16
Poly(propylene furandicarboxylate) (PPF)	51-58	172-176	1.6-2.7	53-68	10.1-30	12-15
Poly(butylene furandicarboxylate) (PBF)	36-44	169-172	1.8-2.0	55-62	11.8-17.8	12-15
Poly(trimethylene terephthalate) (PTT)	45	228	-	67.6	20	17
poly(neopenthyl glycol 2,5-furanoate) (PNF)	70	197	1.6	45	34	18
poly(pentamethylene 2,5-furanoate) (PPeF)	13	-	0.009	6	29.6	19
poly(hexamethylene-b-triethylene furanoate) (PHFTEF-CE)	18	141	0.7	34	---	20
Poly(ethylene terephthalate) (PET)	71-75	246-260	2.0-2.5	65-72	6.4	12
Poly(butylene terephthalate) (PBT)	24-30	220-227	1.4-1.6	51-56	17.7-44	12, 21

In terms of environmental impact, the energy and greenhouse gas (GHG) balance study of PEF in comparison to PET was performed via ASPEN Plus modeling simulation by application of the life cycle assessment (LCA) ²². Compared to PET, the production of PEF can reduce non-renewable energy use by approximately 40% to 50%, while the greenhouse gas emission dropped by approximately 45% to 55%. Besides, the GHG results could be further cut down if the lignocellulosic was employed as the feedstock. With the global market of approximately 15 million metric tons of PET bottles per year, the complete replacement of PET by PEF bottles will save us 440 to 520 PJ of non-renewable energy and reduce the greenhouse gas emissions by 20-35 Mt of CO₂ equivalent at the same time, which should be a great progress towards the

sustainable development of polymer industry. Two LCA reports of carbonated beverage packaging concluded that 2 liter PET bottles have a smaller environmental impact than the other options, and involving recycling would further reduce its impact^{23,24}. The report showed²⁵ that FDCA showed no significant effect on gene expression of soil invertebrates while HMF exhibited genotoxicity, which indicated that the environmental risk of FDCA production from biomass is relatively low, yet may be slightly affected by the release of HMF compounds.²⁶ In addition, the European Food Safety Authority (EFSA) has showed positive testing results when PEF is used for food container. They reported that FDCA does not raise a safety concern for the consumer when it was used as a starting monomer for PEF production and the migration of the substance does not exceed 5 mg/kg, which meets the current requirement.

The recycling of plastic is a significant but challenging issue which is facing the problems of contaminations, multilayered structures, etc. In fact, the new high barrier multilayered films trending these days are being the main obstacle in recycling compared to the simple packaging materials like paper or glass. Fortunately, it was shown that for PEF the mechanical recycling (re-extrusion) and chemical recycling (hydrolysis and methanolysis) were possible. Also, the report showed that no negative influence was observed on the mechanical and physical properties of PEF/PET blends where 5% (w/w) of PEF was added²⁷. Bioplastics as PEF which showed benefits for the environment and economy, also owned great potential for the development of a circular economy which is developing by the European Parliament that waste prevention and recycling are strongly supported. For example, more plastic waste had been recycled than landfilled (41%) in 2016. These all make PEF a promising bio-based polymer for packaging material¹⁹. The leading company in the bioplastic industry, Avantium, owns the most advanced technology YXY® plant-to-plastics-process that catalytically converts biochemicals into plastics like PEF and has successfully build the pilot plant in Geleen, the Netherlands. In 2023, the flagship plant will be started up with a designed annual capacity of 5 kilotons of FDCA and PEF²⁸. Mitsui (Japan) also made a partnership with Synvina, a joint venture of Avantium and BASF, to commercialize PEF in Asia. Due to the present difficulty in PEF synthesis, the high cost of FDCA and

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4 patent protection, the price of PEF is much high and it's costly to replace PET with PEF
5 products. However, the progress on PEF commercialization is rapid and the direction
6 is very clear.
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9 In this work, the synthetic routes and variable effects on the coloration, molecular
10 weight and properties of PEF were involved in the first part. The statement of
11 performance was followed where emphasis placed on the crystallization and barrier
12 properties. Other aspects pursued lied on the modifications whether to enhance its
13 intrinsic advantages (excellent barrier property) or to make up for shortcomings (poor
14 crystallinity and low elongation at break). The objective of this article is devoted to
15 offer a complete description of PEF, covering merits and challenges from synthesis to
16 functionalization, then promote its faster development.
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27 **SYNTHESIS OF PEF**

28 **Synthetic Routes**

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30 In fact, the first work involving synthesis of PEF was reported more than 70 years ago
31 ²⁹, right after the first PET patent in 1941. In 1978, Moore and his coworkers ³⁰ prepared
32 a series of polyesters from 2,5-furandicarboxyl chloride. Unfortunately, the products
33 suffered from severe thermal degradation and coloration. From then on, due to the
34 difficulty of obtaining 2,5-FDCA with high purity and its unacceptable price, few works
35 about the synthesis of FDCA-based polymers has been reported since. In the last decade,
36 with the rapid development of biotechnology and chemical industry, the
37 industrialization of 2,5-FDCA is being realized, and increasing attention has been paid
38 on 2,5-FDCA-based polyesters again. In 2009, a variety of methods for PEF preparation
39 were reported by Gandini *et al* ³¹. And then, the excellent properties of PEF were well
40 recognized ¹². Summarily, the reported synthesis of 2,5-FDCA-based polyesters can be
41 divided into four categories, including transesterification^{32, 33}, direct esterification^{13, 34}
42 and solution polymerization^{31, 35}, along with other synthetic methods.
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56 Transesterification is a traditional way for polyesters synthesis starting from
57 dimethyl ester of 2,5-FDCA (DMFD). This reaction requires high temperature and
58 vacuum which is like the direct esterification yet demands a huge, excessive number of
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diols³⁶. For the industrial production of PEF, the direct esterification is preferred. Joshi *et al*³⁷ investigated the effect of temperature on solubility of 2,5-FDCA in EG and esterification kinetics. Results showed that the esterification temperatures of 180-190 °C led to a complete DMFD conversion within four hours. Codou³⁴ also utilized direct esterification to prepare PEF and found that the obtained PEF exhibited a fast crystallization rate from the glass state, which was favorable for solid-state post-condensation (SSP) to further increase the final molecular weight (83,000 g/mol). SSP in PEF production is analogous to the industrial processing of PET that applied after melt polymerization and has already been applied to the pilot production of PEF. In this process, the pellets are isothermally treated in a reactor at the set temperature (between T_g and T_m), and after which, the M_n , mechanical and rheological properties would be enhanced. Usually, high temperature and vacuum are conducive to the removal of small molecules generated in this process. If the T_m of polyester is low, the SSP temperature may be limited and the crystallinity may be not up to the standard, thus making the SSP process inefficient. During SSP, the balance between cost and efficiency is a significant issue.

The tin-based catalyst was preferred than titanium catalysts since the higher molecular weight can be reached.²⁷ Papageorgiou³⁸⁻⁴⁰ conducted many investigations on SSP during the PEF synthesis. They obtained PEF with M_n of 33900 g/mol after SSP at 205 °C for 5 h, which was applicable in packaging material. They also studied the effect of catalysts on SSP kinetics, and reported that titanium (IV) isopropoxide (TIS) showed the highest reaction rates, while dibutyltin (IV) oxide DBTO led to higher crystallinity. More catalysts including antimony acetate (III) (Sb Ac), zirconium (IV) isopropoxide isopropanol (Zr Is Ip), antimony (III) oxide (Sb Ox), zirconium (IV) 2,4-pentanedionate (Zr Pe) and germanium (IV) oxide (Ge Ox) were also studied in the SSP process. Zr Is Ip yielded the lower activation energies, while Ge Ox resulted in the highest one. It has been proved that using SSP method, the molecular weight of PEF could be enhanced to reach the standard of special applications, such as bottle and tire-cord manufacturing⁴¹.

Although the reaction time of the above-mentioned esterification methods is short, it

must be carried out under high temperature and vacuum conditions. Relatively speaking, solution polycondensation has the advantages of mild conditions without obvious decomposition and coloration. However, products obtained from this method often suffer from low molecular weight and high price. Gomes ³⁵ employed 1,1,2,2-tetrachloroethane as solvent, then 2,5-furandicarbonyl chloride was condensed with EG. And the M_n of obtained PEF was rather low, about only 2,000 g/mol. Up to now, there is little literature on solution polycondensation due to the shortcomings of low molecular weight, long reaction time, complicated processing and a large amount of solvent employment.

Enzymatic polymerization for furan-based polyesters aroused some interests due to its sustainable characteristics. Maniar *et al* ⁴² synthesized a range of polyesters using *Candida Antarctica* lipase B (CALB) as a biocatalyst. The CALB preferred longer aliphatic diols where higher DP_n (degree of polymerization) of 122 had achieved. Poly(caprolactone-co-butylene 2,5-furandicarboxylate) was prepared using supported CALB *via* enzymatic ring-opening polymerization ⁴³. The cyclic oligomers c(BF)_n were made by high-dilution condensation, and finally, the enzyme was removed by filtration. The ordinary ROP is another strategy for PEF synthesis to further minimize the side reactions, which means the molecular weight and polydispersity can be controlled more precisely. For instance, Morales-Huerta *et al* ⁴⁴ obtained the cyclic oligomers by high dilution condensation and thermal cyclodepolymerization, then take Sn(Oct)₂ as a catalyst to conduct the ring opening polymerization (ROP). The weight-average molecular weights of synthesized PEF were in the range of 50,000 and 60,000 g/mol. However, more investigation is needed concerning the properties of obtained PEF from ROP.

Generally, the DMFD transesterification strategy is preferred in the laboratory since it can prevent the decarboxylation of 2, 5-FDCA during polycondensation and lighten the coloration. In addition, DMFD is easier to be purified than 2,5-FDCA, which is comparable to the situation for TA in the 1960-1970s. As for the industrial scale, direct esterification would be the first choice. If starting from 2, 5-FDCA, only H₂O is generated in the transesterification process, rather than the volatile CH₃OH.

Furthermore, PET is currently produced from TA, so the existing production equipment and procedure can be reserved for the direct esterification route. Although it did mention that the mild reaction conditions for solution polymerization can alleviate the decomposition of 2,5-FDCA and coloration of PEF, the Achilles' heel of low-molecular-weight problem is still unsolved. The advantages of ROP are the absence of by-products, low viscosity and minimized coloration. The emergence of bio-enzyme catalysts overcame some of the shortcomings of novel metal catalysts, with unique advantages such as mild synthetic conditions and economic efficiency. In 2018, scientists in ETH Zürich reported a rapid synthesis method for the synthesis of bottle-grade PEF via ring-opening polymerization and they are working with Sulzer to make the new process to be applied in industrial mass production.^{45,46} The characteristics of different strategies were summarized in the following Table 2.

Table 2. Comparison of different strategies for PEF synthesis.

Synthetic methods	Starting Material	Temperature/pressure	Coloration	Molecular Weight (M_n)	Polycon. Time	Environmental impact
Transesterification	DMFD	High	Light	High	Short	Yes
Direct esterification	2,5-FDCA	High	Dark	High	Short	Yes
Solution polymerization	dichloride of 2,5-FDCA	Mild	Light	Low	Long	High
Ring-opening polymerization	cyclic oligomers	Mild	Light	High	Long	Yes
Enzymatic polymerization	2,5-FDCA or DMFD	Mild	Light	High	Long	Low
Avantium's YXY technology	FDCA	High	Light	High	Long (days)	Yes
Sulzer process	cyclic oligomers	High	Very light	High	Very Short	Low

Diethylene Glycol Content, Molecular Weight, Decomposition and Catalysts

With the presence of acid catalysts, diethylene glycol (DEG) is usually formed from the dehydration of ethylene glycol, resulting severe decrease of T_g as well as T_m of

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4 resulted polyesters⁴⁷. Besides, DEG units also adversely affect their mechanical
5 behaviors and light stability^{48, 49}. Plus, the crystallinity and barrier property of
6 polyesters would also be damaged due to the mobility of the ether block. For the
7 synthesis of PET, DEG can be utilized as a processing agent to soften its relative rigid
8 chain, lower the crystallization accordingly.

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13 Research indicated that the DEG content in PEF decreased with the increasing usage
14 of 2, 5-FDCA, since DEG units come from excessive diols⁵⁰. In addition, the content
15 of DEG could be adjusted by different catalyst systems. As reported, when 1,8-
16 diazabicyclo[5.4.0]undec-7-ene (DBU) was employed as the catalyst, the obtained PEF
17 prepared by transesterification polycondensation method showed fast crystallization,
18 and which was attributed to the low content of DEG, about 1.7%³⁶. Banella *et al*⁵¹
19 once synthesized low DEG-content PEF using zinc acetate and aluminum
20 acetylacetonate as the catalysts. They stated that the esterification condition altering to
21 high vacuum and temperature (5 bar, T > 240 °C) may help reduce the DEG moieties.
22 Terzopoulou *et al*⁵² tried four catalysts, including TBT, TIS, tin(II) 2-ethylhexanoate
23 (TEH) and DBTO, for the synthesis of PEF. Results indicated that different types of
24 catalysts hold a negligible impact on thermal stability. While in other respects,
25 polyesters containing titanium showed the highest decomposition temperature and
26 titanate would promote the decomposition caused by DEG to a greater extent compared
27 to Sb catalysts. Therefore, the selection of proper catalyst is one of the most important
28 factors determining the content of DEG and thermal properties of polyesters, PEF is no
29 exception.

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46 In terms of molecular weight, Terzopoulou *et al*⁵³ discussed the effects of catalysts
47 in detail and found that TIS led to the highest M_n and reached about 5500 g/mol at the
48 end of melt polycondensation. TBT and DBTO made the molecular weight of PEF
49 successively decrease. While TEH resulted in polyesters with lowest M_n as well as low
50 yield which is in good agreement with the report by Jacquél *et al*⁵⁴ on the synthesis of
51 poly(butylene succinate). This result was ascribed to the generation of cyclic products.
52 Gruter *et al*³² compared the two most active catalysts, titanium(IV)isopropoxide and
53 butyltin(IV)tris(octoate) and found that when Ti concentration reached a certain point
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(0.04 mol% to DMF) the M_n did not increase while PDI increased. On another hand, the higher Tin catalyst concentration, the higher M_n was obtained. Gubbels *et al*⁵⁵ reported that TEH resulted in the high molecular weight polyester while titanium(IV)n-butoxide (TiBO) and zirconium(IV) butoxide (ZrBO) showed lower activities thus lower molecular weight polyesters were obtained. Furthermore, Yu *et al*⁵⁶ discussed TiBO, TEH, SnOBu, GeO₂ and Sb(Ac)₃ on the molecular weight of PEF. Among them, SnOBu was found to be the most effective one as M_n increased from 0.05% to 0.5%.

Terzopoulou⁵⁷⁻⁵⁹ reported that under 500 °C the β -hydrogen scission is the dominant degradation mechanism for furanic polyesters. When the temperature is higher than 500 °C, homolytic processes occur. The same team also found that polyesters degraded via β -hydrogen scission if titanium catalysts were employed in the synthesis stage. While in the case of TEH and DBTO, the homolytic scission would take place⁵². Then, they investigated the decomposition mechanism of PPF/graphene nanocomposites⁶⁰. The nanoplatelets showed no effect on the thermal stability and degradation mechanism of PPF as both -scission and homolysis took place but increased slightly the activation energy value with 2.5 wt% graphene added as well as the occurrence of homolytic degradation routes compared to neat PPF. In 2020⁶¹, they further discussed the effect of additives on the PEF degradation when antimony acetate catalyst was used. Results showed that all the selected thermal stabilizers, namely Irganox 1098, phosphoric acid and triphenyl phosphate, can slightly improve the thermal stability of PEF where P-containing stabilizers performed better. It's worth mentioning that the degradation mechanism was not changed by those additives but mostly the inhibition of heat transfer.

Coloration and Catalysts

Coloration is one of the major unsolved problems in the synthesis of furan-based polyesters. Unlike PET which can be directly produced with high transparency and low coloration from terephthalic acid and EG, the coloration of PEF is hard to be voided. The coloration of PEF was ascribed to three origins: 1) the incomplete purification of 2,5-FDCA; 2) the side reaction such as decarboxylation of 2, 5-FDCA under high temperature; and 3) the presence of catalysts and additives⁶². HMF is the intermediate

compound for 2, 5-FDCA production. During the conversion of HMF from lignocellulose or fructose, the remained impurities like formyl furoic acid (FFA) will cause coloration during the polycondensation. Wu⁶² observed that the coloration was 2,5-FDCA content-dependent in the preparation of poly(butylene succinate-co-butylene furandicarboxylate) using TBT as a catalyst. Jong²⁷ found that with the increasing content of 2,5-FDCA, the coloration also increased. This result may be due to the impurities in the 2,5-FDCA monomer. And also, the higher the temperature of polycondensation, the darker the coloration of the product. Moore *et al*³⁰ prepared PEF at 300 °C, then obtained a black, insoluble solid. Another report³² also confirmed that by elevating the temperature from 200 to 275 °C, the color of final polyesters deepened gradually. Gubbels *et al*⁶³ synthesized furan-based polyesters from DMFD and polyols via bulk polycondensation, and observed a colorless melt until the polycondensation step began at elevated temperature, which indicated that rather than the sugar-based impurities, high temperature should be responsible for the coloration. Plus, the catalysts such as manganese, cobalt and germanium were also found to deepen the coloration of the final products^{32, 53}. In fact, catalysts based on titanium, tin, antimony, and germanium have been proved to be suitable for the synthesis of PEF, but vital drawbacks still remained. For example, titanium-based catalysts always cause severe coloration which has been confirmed in the PET synthesis. While concerning environmental problems and food-contact safety, the use of organo-tin and antimony could be inconvenient¹. As for ruthenium-based catalysts, which were once very popular in PET manufacturing, has been limited due to the cost. So, some organic-based catalysts such as acidic surfactant and bismuth (III) trifluoromethanesulfonate were employed to synthesize polyesters⁶⁴⁻⁶⁷.

Liu *et al* tried to synthesize PEF from 2, 5-FDCA using the conventional direct esterification process in 2014 and the final product with dark color was obtained (Figure 3). In 2015, instead of 2,5-FDCA, DMFD was employed as the starting material and the yellow-brown PEF was obtained. Then the colorless PEF with high molecular weight was finally produced after the optimization of catalysts and polycondensation conditions, which confirmed the possibility of synthesizing high-quality PEF from

DMFD. Furthermore, the manufacture of bottles, fibers and films from colorless PEF has been demonstrated (Figure 4). In this vein, 2,5-FDCA was synthesized in his own laboratory, where furan and acetic anhydride were used as raw materials to synthesis 5-diacetylfuran *via* a two-step Friedel-Crafts reaction, then 2,5-FDCA was obtained through iodoform reaction⁶⁸. Other research teams, including Bikiaris, Daan S. van Es, Sousa, Soccio and Lotti *et al* also made great contributions to the synthesis of high-quality furan polyesters. And all of their work will be introduced in the following parts.

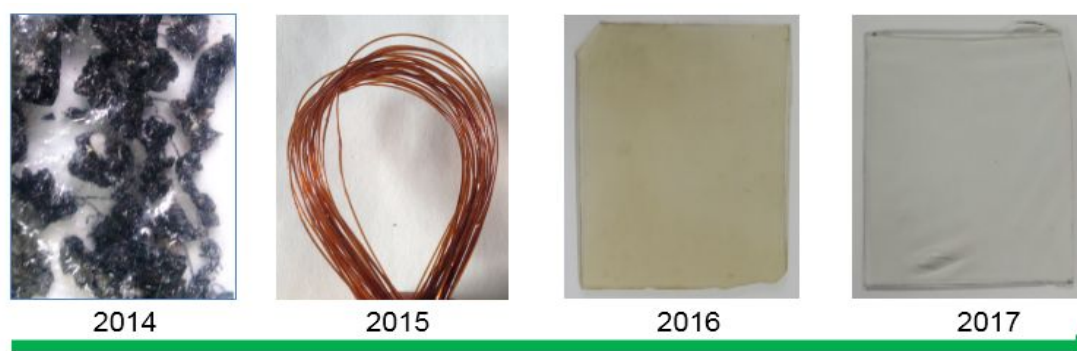


Figure 3 Synthesized PEF with different coloration from 2014 to 2017 in Liu's lab



Figure 4 Application demonstration of PEF in Liu's laboratory

MELT AND SOLID-STATE PROPERTIES OF PEF

Thermal properties

Papageorgiou *et al*⁶⁹ compared PEF with its terephthalate and naphthalate analogous with similar molecular weights in thermal analysis. The DSC traces of semi-crystalline PEF showed the heat fusion of 41 J/g and its T_g as well as T_m were 87 and 220.7 °C, respectively. Through Hoffman-Weeks extrapolation, the T_m^0 of PEF, PET and PEN were found to be 265, 294 and 337 °C, respectively. Fusion enthalpy of complete crystalline PEF was also estimated to be 137 J/g, close to that of PET (140 J/g) *via* the extrapolation method. To explain the complicated thermal behaviors of PEF, Stoclet *et al*⁷⁰ connected the microscopic structures to thermal properties. They suggested that the formation of a rigid amorphous phase facilitates the increase of crystallinity. Thus, the two-phase model, crystalline or amorphous fraction no longer applied for semi-crystalline PEF, so the three-phase model was introduced including a mobile amorphous phase, a crystalline phase and between them in the interface, a rigid amorphous phase where the motion of polymer chains is limited by the crystalline fraction. This model was proposed to explain the interaction between the crystalline and amorphous phase which also applied for various polyesters such as PET^{71, 72} and polylactic acid (PLA)⁷³. In general, the degree of orientation, amount of strain-induced crystallization, and the extent of amorphous chain confinement all relate to the thermomechanical and barrier property. For example, the rigid amorphous phase particularly led to an increase in the elastic modulus⁷⁴ and had a favorable influence on the barrier properties^{75, 76}.

Crystallizing behavior and kinetics studies

Crystallization behaviors greatly affect the thermal-mechanical properties of PEF, and furthermore, the potential applications like packaging material, films and fibers, etc. The multiple melting peaks (MMP) behavior can also be observed in PEF as well as its terephthalate homologs. Knoop *et al*¹² investigated the isothermal crystallization of PEF in the temperature range of 110 to 200 °C, in which the highest crystallization rate temperature was around 155 °C, and the main melting temperature was always between 195-212 °C. They ascribed this MMP behavior to the melting of imperfect crystals with different sizes. They also reported the more imperfect the crystals, the more profound

the temperature dependence of the melting endotherms. PEF had the slowest crystallization rate while PET owned the fastest when the supercooling rate was fixed^{77, 78}. It is not surprising since symmetry is significant for crystallization and PET has the highest chain symmetry, while PEF has the lowest. This result was also proved in Pan's work⁷⁹. All those studies mentioned above showed the poor crystallinity of PEF.

Berkel *et al*⁸⁰ shed light on the stress-strain behavior of PEF during biaxial orientation. Typical rod-like or fibril-like crystallites had been generated under uniaxial stretching, while during symmetrical biaxial stretching, the crystals were uniform and highly oriented along both directions⁸¹⁻⁸³. The rigid amorphous fraction originated from their strong fixation to the surrounded crystal lamella enhanced crystallization of PEF⁷⁰. The molecular orientation and crystalline behavior of PEF during biaxial elongation have also been studied⁸³. Results showed that when the elongation ratio was above 2%, the strain hardening occurred and the crystallinity of PEF increased. When the elongation ratio was above 3%, the crystallinity increased with the increasing strain rate until the final upper bound. The chain was strongly oriented in the direction of stretching plane-strain area while by the relaxation above the critical strain ratio, the orientation of the chains seemed to be only slightly inclined which may be due to the obstruction of strain-induced crystallization of PEF.

Considering the crystalline morphology, the small spherulites of PEF were observed. The crystalline form called α grown at $T_c=170$ °C was more regular than α' appeared at lower temperature⁷⁰, and the β phase was observed after crystallization from solvent⁷⁶. The more detailed study of these three crystalline phases was conducted by Maini and his coworkers⁸⁴. In their work, α -PEF was obtained by annealing at 195 °C. α' -PEF was obtained through isothermal crystallization and β -PEF was obtained by dissolving-precipitating method (Figure 5). It was noticed that, all of them were different from PET lattice as well as unit cell dimensions, which was mainly due to the lower chain mobility and higher rigidity of the furan ring. For α -PEF, the chain stretched in the opposite direction of the furan ring owing to the orientation of the two ester groups. The monoclinic units of α' -PEF showed double volume than α -PEF. As for β -PEF, the

monoclinic volume which contained two plane molecules was slightly larger than that of α -PEF. However, Araujo *et al*⁸⁵. questioned the crystal structure proposed by Maini. They pointed out that the hypothetical α and β crystal forms were not reliable since they presented an unrealistic structure. Another self-contradictory evidence laid in vibrational spectra which demonstrated a different configuration from the proposed ones in crystal forms. They further demonstrated that PEF chains were in an extended zigzag arrangement if crystallized, while in the unoriented region where intermolecular interactions were weak and the main chain tend to coil in the statistical distribution of possible microstructures (Figure 6). Apparently, furthermore, investigation should be conducted to obtain the confirmed crystalline morphology of PEF.

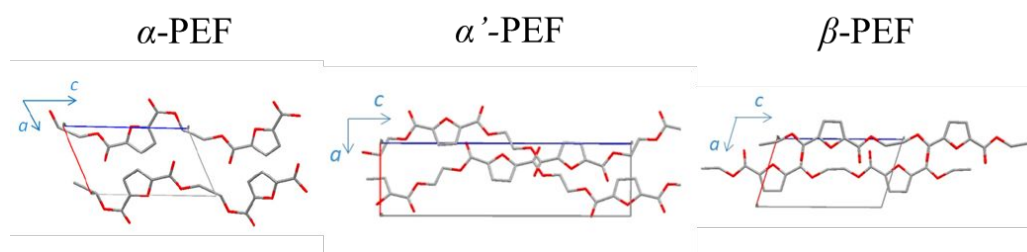


Figure 5 Views for chain packaging of different crystalline form of PEF. (adapted with permission from (Maini, L.; Gigli, M.; Gazzano, M.; Lotti, N.; Bikiaris, D. N.; Papageorgiou, G. Z. Structural investigation of poly(ethylene furanoate) polymorphs. *Polymers* 2018, 10, 296.). MDPI Open Access Policy.)

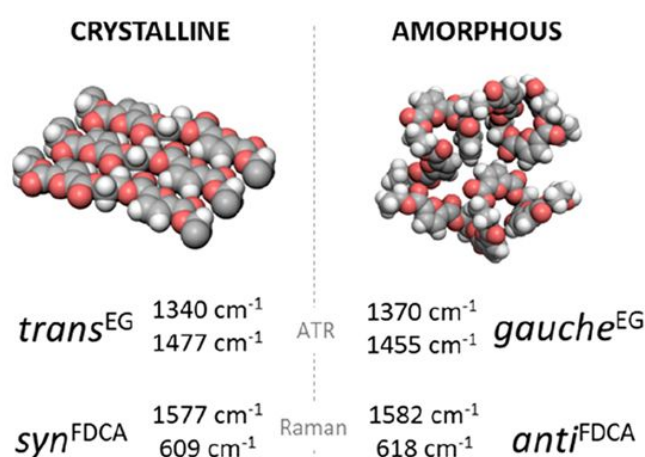


Figure 6 PEF's 3D models of the most representative molecular arrangement in crystalline and amorphous segments. (adapted with permission from (Araujo, C. F.; Nolasco, M. M.; Ribeiro-Claro, P. J. A.; Rudić, S.; Sousa, A. F. Inside PEF: Chain

conformation and dynamics in crystalline and amorphous domains. *Macromolecules* 2018, 51, 3515-3526). Copyright (2018) American Chemical Society.)

Mechanical and rheological response

PEF exhibits brittle fracture characteristic for lack of yielding in the stress-strain test, along with Young's modulus, the maximum stress and elongation at break determined to be about 2450 MPa, 35 MPa and 2.81%, respectively, with the M_n of 83000 g/mol after SSP¹². For PET, the Young's modulus and the maximum stress would be 2000 and 55-60 MPa, which are a little lower than those of PEF⁸⁶. The low elongation at break under 5% for PEF is absolutely known as a primary limitation for its practical applications, caused by the rigidity of furan ring. Thus, many reports have tried to improve its toughness. Up to now, many co-monomers, including 1,4-cyclohexanedimethylene (CHDM),⁸⁹ 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO),⁸⁷ poly(ethylene glycol) (PEG),⁸⁸ 1,4-cyclohexanedicarboxylic acid (CHDA),⁸⁹ ϵ -caprolactone (CL)⁹⁰ and 1,5-pentanediol⁷⁸ were employed to toughen PEF. The tensile properties of PEF and its co-polyesters were listed in Table 3. And more progresses on the copolymerization of PEF will be introduced in the following section.

Table 3. Tensile properties of PEF and the co-polyesters.

Sample	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	M_n (10^3 g/mol)	Ref.
PEF	2070-2800	67-85	3-5	83-105	12, 13, 87
Poly(ethylene-co-2,2,4,4-tetramethyl-1,3-cyclobutanediol 2,5-furandicarboxylate) (PETF)	3100-3300	97-98	4-9	18-19	87
Poly(ethylene-co-1,4-cyclohexanedimethylene 2,5-furandicarboxylate) (PECF)	1740-2300	59-75	8-186	29-51	91
Poly(ethylene 2,5-furandicarboxylate)-poly(ethylene glycol) (PEFEG)	-	8-27	4-61	41-49	88
Poly(ethylene 2,5-furandicarboxylate-co-ethylene 1,4-cyclohexanedicarboxylate) (PEFC)	801-1880	18-49	16-667	18-22	89
Poly(ethylene 2,5-furandicarboxylate-co- ϵ -caprolactone) (PEFCL)	32-1632	2-116	32-2216	37-93	90
Poly(ethylene-co-1,5-pentylene 2,5-furandicarboxylate) (PEPeF)	0-3	12-83	29-315	--	78

Sun⁹² investigated the rheological properties of PEF. The zero-shear viscosity of PEF was about 18 Pa·s and its V_f was calculated to be 0.0073, which represents the free volume fraction (FFV) at polymer's T_g . The apparent activation energy for molecular chain cooperative motion (E_a) of PEF was determined to be 145 KJ·mol⁻¹. Generally, when the polyester contains rigid rings or groups, the E_a would be higher. The viscoelastic properties of PEF co-polyesters containing CHDM and isosorbide (ISB) units were also investigated⁹³. The zero shear viscosities of terpolyesters are much higher than that of PECF and although the M_w of the samples were similar, and the zero-shear viscosity increased with the increasing content of ISB moieties. Considering its bright future as an excellent packaging material, currently, the rheological investigation on PEF is far from enough, which should attract more attention.

Barrier Property

Generally, permeability is equal to the product of adsorption and diffusion contributions ($P=DS$), thus the gas permeability can be factored into sorption and diffusion contributions respectively. Although the static fractional free volume (FFV) of PEF (0.153) is higher than that of PET (0.130), PEF shows much higher gas barrier property⁹⁴. Research indicated that PEF and PET exhibited similar oxygen sorption in the given temperature, and the chemical structure differences between 2, 5-FDCA and TA explained the reduction of diffusion in PEF, which was related to the difficulty of furan-ring flipping caused by polarity and structural nonlinearity⁹⁵. As we know, the linearity of TA ring results in an angle of 180° between the two carboxylic acid carbons thus the phenyl ring-flipping is active in PET, while in 2,5-FDCA the angle is 129.4°⁹⁶. Due to the higher chain rigidity and difficulty of furan ring-flipping in PEF, in comparison with PET, the β transition peak of PEF was observed at higher temperature and its magnitude had been suppressed (Figure 7), which was related to various macroscopic properties, especially the gas diffusion in polymer matrix⁹⁷⁻¹⁰⁰. Generally speaking, the carbonyl groups in PEF is believed to have some kind of synergistic motion along with small scale EG unit oscillations, thereby further blocking the ring motion and consequently hindering the diffusion of gas molecules. Therefore, the ring-flipping

mechanism was proved to be significant in the process of diffusion¹⁰¹⁻¹⁰⁴.

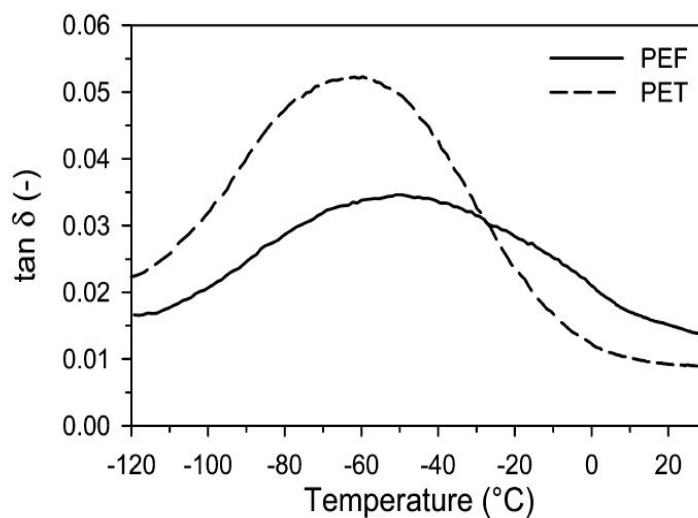


Figure 7. Tan δ curves for PEF and PET of the β relaxation. (adapted with permission from (S.K. Burgess, J.E. Leisen, B.E. Kraftschik, C.R. Mubarak, R.M. Kriegel, W.J. Koros, Chain Mobility, Thermal, and Mechanical Properties of Poly(ethylene furanoate) Compared to Poly(ethylene terephthalate), *Macromolecules* 47(4) (2014) 1383-1391). Copyright (2018) American Chemical Society.)

For packaging materials, it is also significant to understand the water sorption and transport behaviors under the humid or liquid contacting environment. Water exhibits more complex interactions with polyesters than oxygen. In PET, water is known to reduce T_g due to the plasticization effect. Results showed that PEF demonstrated about 1.8 times larger water sorption than that of PET¹⁰⁵. This growth in sorption once again confirmed the furan ring's polarity and a higher free volume in PEF. Obvious hysteresis was found both in PET and PEF between sorption and desorption circles due to the non-Fickian relaxations. Supplementary research about the dynamic water sorption showed a highly active penetrant plasticization presence in PEF and PET. In this vein, about 2.8 times reduction in permeability was observed in PEF compared to PET¹⁰⁶. It's noteworthy that PEN exhibits an analogous reduction of diffusion coefficient due to the similar ring-flipping hindrance caused by bulk naphthalene moiety¹⁰⁷.

As for the permeability of CO₂ in PEF, compared to PET, a 19 times reduction was observed¹⁰⁸. While the free volume and solubility were increased about 1.6 times due

to the enhancement of interaction between CO₂ and polar furan ring. It is also the hindered ring-flipping motions that impeded the gas diffusion process. However, Avantium reported a much lower reduction of CO₂ permeability of 4 times compared to the mentioned-before 19 times. The choice of PEF morphology might be the main cause for such a huge difference. Parallely, O₂ and CO₂ also exhibit large solubility and permeability reduction in semi-crystalline PEF. This improvement of gas barrier property is predictable since semi-crystalline samples contain a large amount of non-permeable microcrystals which can hinder the transport of gas molecular¹⁰⁹. Papamokos¹⁰³ discussed the conformational properties of poly(n-methylene 2,5-furanoate) polyesters. They found that PEF nonamer exhibited very compact helical structures that can be stabilized by π - π interactions of the furan rings, thus improved the barrier property compared to PET.

UPGRADING AND FUNCTIONALIZATION OF PEF

Modification by Copolymerization

Although PEF is endowed with excellent barrier property, the poor crystalline and brittleness is limiting its further applications. Several studies have tried to enhance PEF's toughness and crystallization, without sacrificing its barrier property, T_g and mechanical strength. It's well-known that the long aliphatic diols can improve the crystallizability and toughness of polyesters. However, the problem remains that their thermal performance was inevitably weakened, indicating by a sharp drop of T_g ^{63, 110, 111}. For example, Xie *et al*⁷⁸ modified PEF with 1,5-Pentanediol (PeDO) and the results showed many advantageous properties such as high tensile strength, good thermal stability, increased elongation at break, as well as excellent O₂ barrier property. However, the highest T_g of poly(ethylene-co-1,5-pentylene 2,5-furandicarboxylate)s (PEPeFs) was only 24 °C. Poly (ethylene 2,5-furandicarboxylate-co-ethylene succinate) (PEFS) was also synthesized with the 2,5-FDCA units content of 11.98-91.32 mol %¹¹². From wide-angle X-ray diffraction (WAXD) patterns, when the EF content was 10 mol % and 70 mol %, the crystalline structure was similar to that of PES and PEF, respectively. While when the EF content was between 30-50 mol %, the co-polyesters

were completely amorphous.

The introduction of long aliphatic diols usually severely decreases the T_g of resulted co-polyesters. However, the employment of cyclic diols can enhance the toughness and crystallinity as well as T_g simultaneously. Several studies recently have focused CHDM and CHDA on improving properties of furan polyesters^{89, 91, 113-118}, which work well in the modification of PET¹¹⁹. Guidotti *et al*¹¹³ synthesized block co-polyesters from poly(propylene furanoate) (PPF) and poly(propylene cyclohexanedicarboxylate) (PPCE) via reactive blending. The cyclohexane unit improved the rigidity of PPF since elongation at break was high and elastic modulus was low and enhanced the good barrier property of PPF. Wang and his coworkers⁸⁹ once synthesized a series of poly(ethylene 2,5-furandicarboxylate-co-ethylene 1,4-cyclohexanedicarboxylate)s (PEFCs) from EG, 2, 5-FDCA and CHDA with M_n around 20000 g/mol. PEFCs all exhibited a single T_g that monotonically increased with the increasing content of 2, 5-FDCA. Compared to 2, 5-FDCA, the CHDA molecular was more flexible, therefore PEC showed much lower tensile modulus (76 MPa) and tensile strength (4 MPa) than those of PEF. As for PEFCs, from PEFC-90 to PEFC-30, the tensile modulus and strength were gradually decreased while elongations at break increased. Using CHDM, Liu *et al*⁹¹ prepared a series of PECFs with the characteristic of the random copolymer and the M_n range of which were between 29600-51600 g/mol (Figure 8). The T_g of PECFs were all above 80 °C with far more excellent gas barrier property. Meanwhile, the elongation at break was dramatically increased about 80% with the increasing CHDM content. Then, the influence of CHDM's configuration was further studied¹¹⁷. With the increase of *trans*-CHDM, PECFs changed from amorphous (PECF-*trans* 25) to highly crystalline polyester (PECF-*trans* 98). Different from the slowly crystallized polyesters like PEF and PPF, PECF-*trans* 98 showed a sharp cold crystallization peak at around 121 °C, indicating that its crystallizability was even better than PBF and PBT^{118, 120, 121}. These results confirmed that incorporation with CHDM cast a positive impact on the drawbacks of PEF.

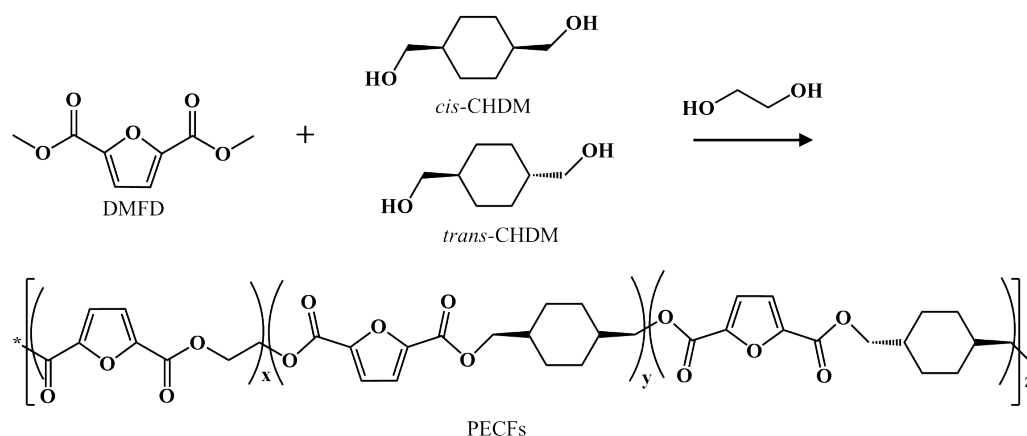


Figure 8. PECFs synthesized from EG, CHDM and DMFD

Besides the flexible CHDM, the more rigid cyclic diols, including isosorbide,¹²² isomannide,¹²³ 2,3:4,5-di-*O*-methylene-galactitol (Galx) and 2,4:3,5-di-*O*-methylene-*D*-mannitol (Manx),¹²⁴ 1,4-bis(hydroxymethyl)benzene,¹²⁵ and CBDO⁸⁷ were also taken to copolymerize with PEF to increase its chain stiffness and then improve their T_g . However, the high molecular weight is hard to be obtained. For instance, poly(ethylene-co-2,2,4,4-tetramethyl-1,3-cyclobutanediol 2,5-furandicarboxylate)s (PETFs) showed the advantages of high T_g and good transparency. However, when the content of the CBDO unit was more than 23 mol%, the molecular weight of PETFs was dramatically decreased due to the low reactivity of CBDO. In this vein, both the flexible CHDM and the rigid CBDO were both added into the backbone of PEF to synthesize the PECTFs. Results showed that the CBDO unit could increase the T_g of the copolyesters. While CHDM could compensate for the weakness of CBDO's low reactivity by contributing to the higher molecular weight¹²⁶. In this work, the trade-off between CBDO and CHDM was achieved, which resulted in the completely amorphous PECTF-45 showing T_g as high as 103.1°C and the M_n higher than 20000 g/mol.

PEF is a fully bio-based, but not a good biodegradable polyester. Studies involving enzymatic degradation of PEF have drawn much attention recently. Terzopoulou⁵⁸ investigated the decomposition mechanism of three different polyesters synthesizing from DMFD and varied diols. Results showed that β -hydrogen scission was the primary decomposition approach for furan-based polyesters since the after-reaction products

were mainly vinyl- and carboxyl-terminated molecules. Besides, homolytic and α -hydrogen bond scission was also taking place at the same time. Weinberger¹²⁷ studied the effects of molecular weight, particle size, and crystallinity on enzymatic hydrolysis of PEF. They found that the samples with lower molecular weight and crystallinity hydrolyzed much faster. Besides, the higher the molecular weight, the smaller the effect of particle size on hydrolysis. However, in another work, the molecular weight didn't show a clear tendency in degradation since both high and low molecular weight observed advantageous for degradation¹²⁸. This result may ascribe to other factors prevailed the minor impact by molecular weight. Yet further investigation should be conducted to get the confirmed conclusion.

Copolymerization is a promising strategy to endow polyesters with better biodegradability. For furan-based polyesters, CL,¹²⁹ adipic acid (AA),^{130, 131} isosorbide,¹³² and succinate acid^{62, 133} are common-used comonomers to enhance their degradability. The degradation of poly(pentylene 2,5-furandicarboxylate-co-caprolactone) (PPeCFs) and poly(hexamethylene 2,5-furandicarboxylate-co-caprolactone) (PHeCs) appeared to be a combination of various degradation mechanisms¹²⁹. The introduction of CL units into the polyesters chain resulted in lower crystallinity, T_m and T_g , so the PHeCF 50/50 and PPeCF 50/50 exhibited the highest decomposition rate which showed the weight loss of 32% and 15% under the same enzymatic treatment time, respectively. This result was converse to a recent report on poly(ethylene 2,5-furandicarboxylate)-co-poly(lactic acid), whose enzymatic hydrolysis was decreased after the chain length of alkyl diol units in co-polyesters was increased¹³⁴. The co-polyester containing 93 mol% lactic acid (LA) exhibited the highest weight loss of around 60% after 12 weeks, while for pure PEF and PLA, the weight loss was only about 2% and 7%, respectively. This result was consistent with the higher crystalline of PEF and PLA, which made their ester bonds inaccessible to hydrolysis. Haernvall¹³⁵ synthesized a series of furan-based co-polyesters with different polyols. Very interestingly, they found that when replaced the linear diols with branched ones or incorporated ethoxy units into the polymer chain, the enzyme activity was doubled. Papadopoulos¹³⁰ synthesized a full series of poly (ethylene furanoate-co-

ethylene adipate) and found that the introduction of ethylene adipate units into the chain can impart the polyesters with biodegradability. The rate of enzymatic hydrolysis depends on the content of the ethylene adipate unit. For example, with 90 mol% and more ethylene adipate units, the co-polyester could be completely degraded after 20 days. Guidotti ²⁰ synthesized multi-block co-polyester poly(hexamethylene-b-triethylene furanoate) (PHFTEF-CE) which can be a compostable, sustainable packaging material. In the composting study, the gravimetric weight loss reached 40% after 105 days. Soccio ¹³⁶ prepared poly(butylene 2,5-furanoate/diglycolate) random copolyesters, in which the butylene diglycolate moiety increased hydrophilicity thus presented higher biodegradability compared to PBF. Further, Gigli ¹³⁷ reported two different enzymatic hydrolysis mechanisms of poly(1,4-butylene 2,5-thiophenedicarboxylate) (PBTF) and PBF for *endo-wise* scission and *exo-wise* cleavage, respectively.

PEF Composites

In addition to 2, 5-FDCA-based polyesters, the burgeoning research of PEF composites has also attracted more and more attention. For inorganic fillers, SiO₂ and TiO₂ were usually added during SSP in PEF synthesis. The presence of these nano-additives results in higher transesterification kinetic rate constants, leading to the higher molecular weight of obtained PEF hybrid ¹³⁸. PEF nanocomposites containing multi-walled carbon nanotubes (MWCNTs) or graphene oxide (GO) were synthesized, which showed increased nucleation density and crystallization rate ¹³⁹. The nanocomposites based on PEF and modified Montmorillonite were prepared via solvent casting method ¹⁴⁰. Both the exfoliated and intercalated clay served as heterogeneous sites for PEF nucleation, thus promoted crystallization of PEF. Besides, the clay nanocomposite prepared by melt extrusion and compression molding showed molecular weight stabilizing effect ¹⁴¹. Papadopoulos ^{142, 143} prepared a series of PPF based nanocomposites. Among them, the sample with nanoclays Cloisite-Na improved the slow crystallization rate of PPF homo-polyester in all temperature ranges. Besides, the Halloysite and Montmorillonite CloisiteNa-based polymer nanocomposites exhibit

the highest elastic modulus while samples with Halloysite and carbon nanotubes demonstrate the highest hardness. Then, Papadopoulos¹⁴⁴ investigated the effect of graphene nanoplatelets of PPF that the crystallization times reduced, elastic modulus and hardness increased in the nanocomposites.

Codou *et al*¹⁴⁵ prepared PEF-cellulose composite films *via* extrusion and the nanocellulose exhibited high crystallinity as well as a large scale of intramolecular and intermolecular hydrogen bonds, which made it appropriate for gas barrier applications. Pouloupoulou *et al*^{146,147} observed that PBF could accelerate the crystallization of PEF in the blends. When the backbones differ by a single methylene unit, like PEF-PPF and PBF-PPF systems, the blends are dynamically homogeneous. In the case of two methylene units, for example PEF-PBF, the blends exhibit two distinct T_g thus resulted in the dynamically heterogeneous mixture. However, the dual T_g will eventually merge into a single one via reactive blending thereby changing the partially miscible PEF-PBF into a copolymer. As a comparison, terephthalate-based blends were also prepared which all showed single T_g probably because of enhancement in mobility. The temperature and time interval chosen for reactive blending were proved to be the crucial parameters that control the miscibility of furan-based polyesters¹⁴⁷. Furthermore, they suggested that poly(alkylene furanoate)/poly(alkylene terephthalate) (PAF/PAT) blends can be the next-generation engineering bioplastics¹⁴⁸.

Considering the rapid development of PEF and its enhanced performance with the introduction of fillers or blends, the research on PEF composites is about to break out.

CONCLUSIONS

PEF has been no longer an “alternative” of petroleum resources, but an irreplaceable polyester in the polymer industry, due to its excellent barrier property, environment-friendly origin and potential for molecular designing which will lead to further property enhancement. Over the past decade, the number of patents and papers about the PEF investigation has grown exponentially. As for the industrial production of PEF, the conventional direct-esterification followed by polycondensation would be the first choice, and the possibility of synthesizing high-quality PEF through catalyst selection

and processing optimization has been demonstrated. However, there is still a long way to go for PEF to grow into a commodity which requires cheaper and faster production. Compared with the well-recognized mechanism for its excellent gas barrier properties, the investigation on crystallization behaviors of PEF should be strengthened. With the rapid development of PEF production and continuously decreasing cost, its copolymerization modification and composites fabrication are in the right direction. Although some shortcomings are waiting to be overcome, the bright future of PEF is undoubted.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support from National Key Research and Development Program of China (2018YFD0400700), Zhejiang Provincial Natural Science Foundation of China under Grant No LR20E030001, “Science and Technology Innovation 2025” Major Project of Ningbo (2018B10015), National Natural Science Foundation of China (NSFC 21975270), National Ten Thousand Talent Program for Young Top-notch Talents, Ten Thousand Talent Program for Young Top-notch Talents of Zhejiang Province.

NOTES

The authors declare no competing financial interest.

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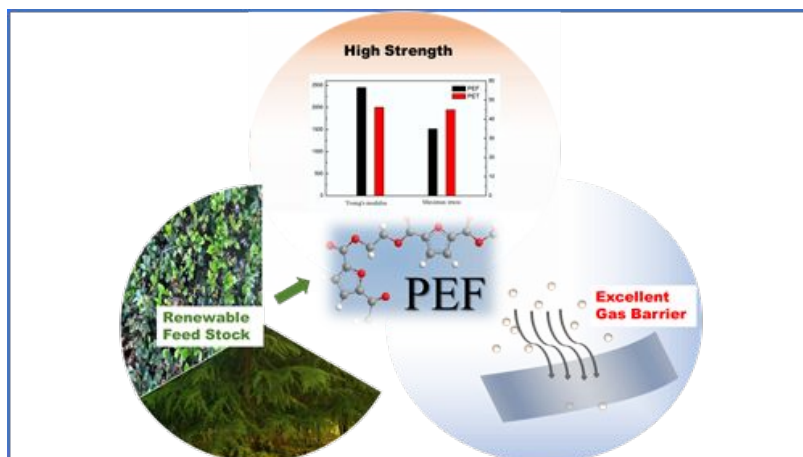
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High mechanical property, excellent gas barrier property together with fully biobased origins make PEF an irreplaceable one in polyester industry



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