Progress in the Synthesis and Properties of 2,5-Furan Dicarboxylate based Polyesters

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Biomass is a class of abundant renewable resource. Its efficient use in the field of biobased materials is one of the important ways for implementation of sustainable development strategies. 2,5-Furandicarboxylic acid (FDCA) as a potential alternative of terephthalic acid (PTA) to make alipharomatic polyesters, can be obtained in mass amount from cellulose *via* bio- or chemical process. For this reason, FDCA-based polyesters have gained high interest recently. This review systematically summarizes recent progress in the making of FDCA-based polyesters (including poly(ethylene 2,5-furandicarboxylate) (PEF), poly(propylene 2,5-furandicarboxylate) (PPF), poly(butylene 2,5-furandicarboxylate) (PBF), poly(hexylene 2,5-furandicarboxylate) (PHF), and their copolyesters), especially highlighting the progress and fundamental aspects for their synthesis and properties. Significant advantages (and also disadvantages) of the FDCA-based polyesters are clearly indicated relative to price, performance, and sustainable development, in reference to traditional petroleum-based polyesters in industrial application. The goal of this review is to provide useful information regarding the synthesis and properties of FDCA-based polyesters.

Keywords: FDCA; FDCA-based polyesters; Copolyesters; Synthesis; Polycondensation

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INTRODUCTION

Plastics are closely related to the development of human society. Terephthalic acid (PTA) based polyester, as one of the most important plastics, has been widely used in food packaging, plastic toys, plastic furniture, and engineering plastics. In recent years, due to the excessive consumption of fossil resources and environmental problems, the search for new materials with environment friendly and unique properties to synthesize biobased polymers has attracted extensive attention. Simultaneously, European countries and the United States have begun to support the development and use of biomass-based products to reduce the excessive reliance on oil-based products. Against this background, a large number of monomers derived from renewable resources, such as dodecanedioic acid (Green *et al.* 2000; Zou *et al.* 2018; Firoozi and Kang 2019; Zhang *et al.* 2019a;), lactic acid (Duo *et al.* 2016; Herran *et al.* 2019; Montava-Jorda *et al.* 2019; Wu *et al.* 2019), levulinic acid (Hartweg and Becer 2016; Pileidis and Titirici 2016; Amarasekara *et al.* 2018; Sinisi *et al.* 2019), isosorbide (Sousa *et al.* 2016a; Chebbi *et al.* 2019; Hu *et al.* 2019a; Kieber *et al.* 2019), ethylene diol (Haernvall *et al.* 2017; Li *et al.* 2017; Lu *et al.* 2017; Sukhawipat *et al.* 2018), and succinic acid (Rizescu *et al.* 2017; Landim *et al.* 2018; Garcia-Campo *et al.* 2019; Hu *et al.* 2019b; Pasma *et al.* 2019) have been continuously developed and promoted the synthesis and widespread use of a large number of new biobased polymers products.

Among them, 2,5-furandicarboxylic acid (FDCA) is deemed as a promising platform chemical to prepare biobased polyesters.

FDCA has two carboxylic acid groups, and this implies that there is good potential as a replacement for PTA due to similarities between PTA and FDCA (Moreau *et al.* 2004). This aromatic diacid has been considered as a potential replacement and also as a renewable resource-based equivalent of PTA, which is a monomer in poly(ethylene terephthalate) (PET) plastics. The market for PTA exceeds 50,000 kt per year, demonstrating the large potential of FDCA for the preparation of polyethylene furanoate (PEF) as a replacement for PET (Eerhart *et al.* 2012; Amarasekara *et al.* 2017). For this reason, the biobased FDCA has attracted extensive attention from academy and industry, including the preparation of FDCA and its precursor, 5-hydroxymethylfurfural (HMF), together with varieties of FDCA-based materials that can be used in the domain of packaging, textile and coating. There have some related publications reviewing the progress and critical aspects in the synthesis and properties of FDCA-based polyesters a few years ago (van Es 2013; Sousa *et al.* 2015; Papageorgiou *et al.* 2016). Now, ongoing research and industrial production of FDCA-based polyesters, especially for poly(ethylene 2,5-furandicarboxylate) (PEF), poly(propylene 2,5-furandicarboxylate) (PPF), poly(butylene 2,5-furandicarboxylate) (PBF), poly(hexylene 2,5-furandicarboxylate) (PHF) and their copolyesters, has progressed in a new stage due to the increasing attention paid by researchers in recent years. In order to gain a deeper understanding of the current status of the synthesis and properties of FDCA-based polyesters, this mini review paper summarizes and discusses the recent progress, hoping to help readers to have a deeper understanding and cognition in this field, and to make a greater breakthroughs in this exciting research area.

SYNTHESIS OF POLY(ETHYLENE 2,5-FURANDICARBOXYLATE) (PEF)

Poly(ethylene 2,5-furandicarboxylate) (PEF) is the most eye-catching member of the FDCA-based polyesters family, which is considered a furan counterpart of the engineering polyester, PET (Gandini *et al.* 2009b; Sousa *et al.* 2015; Banella *et al.* 2019). Although fully renewable-based PET has been foreseen, and several routes are under development today, attempts to amplify the process have been limited due to the low yields (Tavener *et al.* 2003; Collias *et al.* 2014; Jerpdal *et al.* 2019). By contrast, PEF is totally based on renewable resources, as its two monomers, ethylene glycol (EG) and FDCA can be obtained from cellulose (Zhang *et al.* 2015; Zhou *et al.* 2019). It is expected that PEF will create its own market niche toward its full penetration in existing polyester market and be widely used in all works of life due to its high performance in high barrier, thermal, and mechanical properties (Sousa *et al.* 2015).

The synthesis of PEF dates back to the middle of the previous century; however, the literature on PEF is scanty after the research about the X-ray study of the FDCA-based polyester’s structure in 1968 (Sousa *et al.* 2015). Until the last decade, as people have been paying more and more attention to building a sustainable society, a revival of interest in the synthesis and characterization of PEF and related polyesters can be observed (Ji *et al.* 2008; Gandini *et al.* 2009a,b; Gomes *et al.* 2011). For example, Ji *et al.* (2008) developed a two-stage method for the preparation of PEF from cellulose (Fig. 1). In the first stage, dihydroxyethyl furanate monomers or oligomers can be obtained through the esterification or reverse transesterification between FDCA and EG. Next, the polycondensation reaction allows the polymerization product to reach the corresponding molecular weight. In the process of polycondensation, the excessive and generated EG is removed by raising the temperature and vacuum degree to promote the polycondensation reaction in the direction of PEF formation.

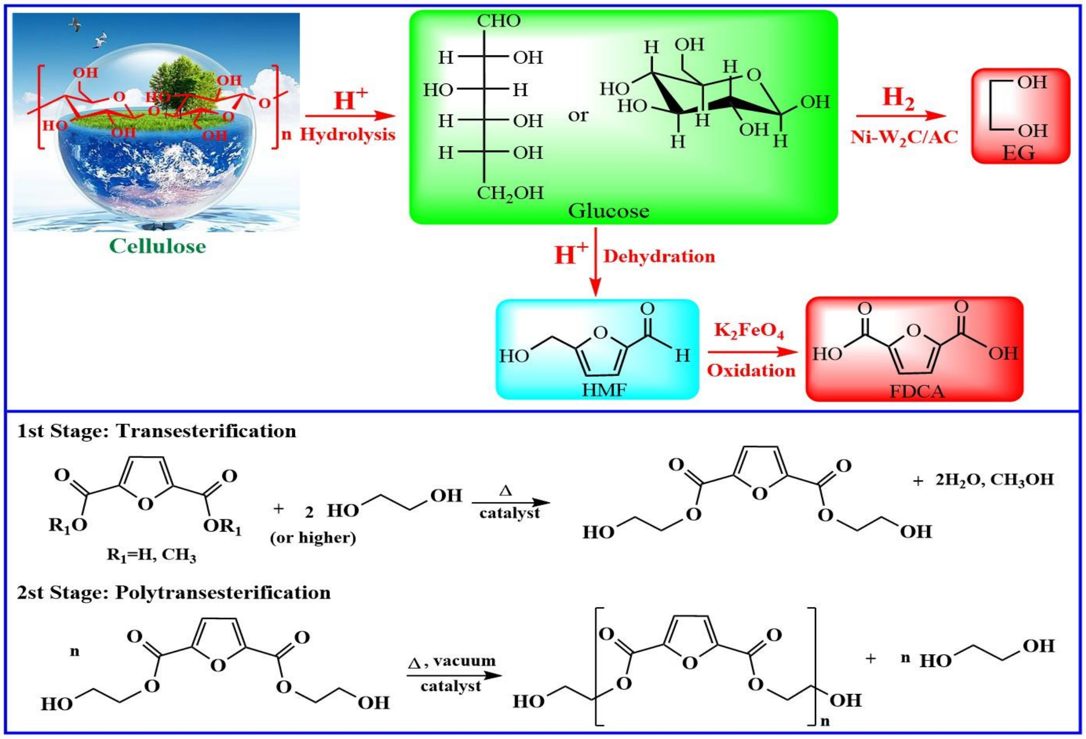

Fig. 1. Typical route for the synthesis of EG and FDCA from cellulose and the two-stage approach for the synthesis of PEF

Gandini *et al*. (2009a,b) developed two methods for the synthesis of PEF from FDCA and EG. They used a small amount of hydrochloric acid to catalyze the esterification of FDCA with EG, then antimony trioxide (Sb_2O_3) was used as the catalyst for condensation polymerization to obtain some white PEFs with DP_n values of 250 to 300. It was determined that the PEFs exhibited good chemical stability, which was only soluble in strong acid (trifluoroacetic acid, TFA) and strong polar organic solvents (hot tetrachloroethane, TCE), and was thermally stable (around 300°C) by TGA analysis. Further analysis of the differential scanning calorimetry (DSC) and X-ray diffraction (XRD) showed that the PEFs exhibited a high degree of crystallinity, and the melting temperature (T_m) was 210 to 215 °C. Furthermore, the glass transition temperature (T_g) was 75 to 80 °C (Gandini *et al.* 2009b). In the same year, they developed another method to obtain PEF, which had similar properties to their prepared PEFs. The product was soluble in TFA and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) but insoluble in TCE; however, the difference was that the DP_n was very low (about 70) (Gandini *et al.* 2009a).

Gomes *et al.* (2011) used a similar method to get PEF with a number-average molecular weight (M_n) of 22400, weight-average molecular weight (M_w) of 44500 and polydispersity index (PDI) of 1.99. The peak value of X-ray diffraction was obtained at 2θ=16.0, 20.1, and 27.8°. In addition, the thermogravimetric analysis (TGA) and DSC measurements revealed that the thermal decomposition (T_{di}), maximum decomposition temperature (T_d), T_g, crystallization temperature (T_c), and T_m was 300, 398, 80, 165, and 215

°C. The T_g as well as the T_c only appeared on the second DSC scan trace after quenching the melted polymer, indicating that the obtained PEF had a high degree of crystallinity.

In addition to the two-step method, direct esterification is also an important method to prepare PEF. For example, Jiang *et al.* (2012) prepared the PEF *via* direct esterification method. The obtained PEF had a specific viscosity (η_{sp}) of 1.20 dL/g, and its M_n, M_w, and PDI values were 105300, 252000, and 2.39. In addition, the tensile test of PEF samples showed that PEF was a thermoplastic polyester material. Its tensile modulus, tensile strength, and elongation at break of PEF were 2070 MPa. 66.7 MPa, and 4.2%, respectively. Codou *et al.* (2014) also obtained some melt-crystallized and glass-crystallized PEF samples *via* the direct esterification method. The products exhibited similar crystallinities and unit cell structures with those reported for PEF obtained by transesterification (Gandini *et al.* 2009b; Papageorgiou *et al.* 2014). In addition, the non-isothermal data analysis of PEF was carried out by DSC, and a new calculation method was used to evaluate the Hoffman-Lauritzen theory. The evaluation equation of the method showed that the effective activation energy of the growth rate depended on the melting temperature (T_m) and the assumed temperature (T_∞), and results showed the growth kinetics of the crystals were different during the two crystallization processes. Nevertheless, PEF crystals from the glass temperature and melting temperature had a similar structure. Furthermore, compared with melt crystallization rate of PEF, the experimental data of glass crystallization was in good agreement with the predicted value of Hoffman-Lauritzen rate equation (Codou *et al.* 2014). The main reason for the de*via*tion of melt crystallization was that the secondary nucleation limited the transverse growth rate (Codou *et al.* 2014).

In order to further understand the unique characteristics of the PEF, its crystal structure, dynamics, structure-property correlations, and penetrant transport have attracted much attention (Burgess *et al.* 2014, 2015; Tsanaktsis *et al.* 2015a; Mao *et al.* 2016; Burgess *et al.* 2016; Araujo *et al.* 2018; Rosenboom *et al.* 2018). For example, Mao *et al.* (2016) determined the crystal structure of PEF with X-ray fiber diffraction (XRFD) and molecular model, which was composed of monoclinic unit cell with a space group of $P2_1$, whose cell parameter was a=5.784 Å, b=6.780 Å, **c**=20.296 Å, and γ=103.3º, and the density of this crystalline structure was 1.562 g/cm^3. Araujo *et al.* (2018) revealed that the PEF presented strained syn^{FDCA}-trans^{EG} extended zigzag conformation in the crystalline region, which was favorable in the crystal but was not feasible for single chain due to the formation of a large array of C−H···O bonds. In the amorphous regions, PEF chains tended to the anti^{FDCA}-gauche^{EG} helical conformation. Compared with PET, PEF with a high energy difference among the amorphous and crystalline chains resulted in a higher crystallization temperature, while strain-induced crystallization required a higher tensile ratio. The use of novel inelastic neutron scattering (INS) spectroscopy further indicated that the PEF chains of several low frequency vibration modes was less flexible than that of PET, so that the gas barrier properties were higher.

What's more, a preliminary experiment and analysis of uniaxial stretching of PEF were carried out by Menager *et al.* (2018). It turned out that strain-induced crystallization (SIC) can develop under appropriate stretching conditions with PEF and controlled in a manner comparable to that of PET to promote strain hardening. According to the tensile conditions of PEF, the crystals with different morphologies were formed. On the other hand, the three-phase models can be well applied to the stretched PEF. The mobile amorphous content was between 0.50 and 0.65, and the rigid amorphous content was between 0.15 and 0.30. In addition, when the tensile condition was at the most rubbery state of polyester, the mobile amorphous content in the polymer was much higher, reaching 0.70.

In addition, correlations between molecular weight and solution viscosity for PEF in comparison to PET were studied by van Berkel *et al.* (2018). Their research revealed that the melt viscosity of PEF was a function of molecular weight, and the temperature-dependence of the melt viscosity showed a higher activation energy for PEF, and the shear rate dependence indicated a lower reputation time. They found that the PEF with sufficient molecular weight displayed ductility but overall a higher tendency to brittleness than PET in the glassy state, which resulted in a significantly higher yield stress combined with a higher strain rate dependence.

However, PEF has some inherent shortcomings in thermomechanical properties, such as slow melt crystallization and brittleness, which may limit the application of PEF. In order to strengthen PEF, some PEF blends or copolymers have been developed. (Sousa *et al.* 2013; Yu *et al.* 2013; Matos *et al.* 2014; Sousa *et al.* 2016a; Wang *et al.* 2017a; Poulopoulou *et al.* 2019b; Xie *et al.* 2019). For example, Yu *et al.* (2013) prepared some poly(ethylene 2,5-furandicarboxylate-co-ethylene succinate) (PEFS) copolymers with FDCA and succinic acid *via* melt polycondensation in the presence EG. Random copolymers with number-average molecular weights exceeding 25600 and thermal stability exceeding 300°C were obtained.

Sousa *et al.* (2013) prepared a straightforward partial substitution of non-renewable PET by renewable homologous PEF through random copolymerisation of bis(2-hydroxyethyl) terephthalate (BHETP) and bis(hydroxyethyl)-2,5-furandicarboxylate (BHEFDC) (Fig. 2). They found that the isolation yields of all copolyesters were around 80%, quite independent of the stoichiometric ratio of BHETP/BHEFDC used. This was an indication of the successful incorporation of both aromatic and furanic units into the copolyesters backbone.

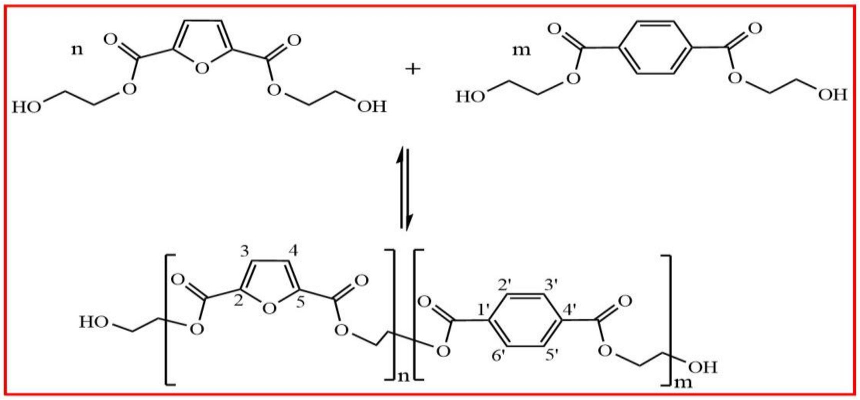

Fig. 2. Polytransesterification reaction of BHEFC with BHETP

The M_w of these polyesters ranged between 13000 and 47000, and the polydispersity index (M_w/M_n) was close to 2. They found that the most relevant copolyesters corresponded to PET-ran-PEF 4/1, whose chemical structure contained 20% of aromatic and furanic units. Its T_g, T_c and T_m were 62.4, 125.2, and 220.1 °C, respectively, which were very similar to the properties of commercial PET. Furthermore, the thermal stability of the PET-ran-PEF 4/1 was as high as 260°C and the operating temperature determined by dynamic mechanical analyses ranged from -40.9 to 67.5 °C, which were very close to those of PET.

Matos *et al.* (2014) developed some poly(ethylene 2,5-furandicarboxylate)-co-poly(lactic acid) copolyesters based on both PEF and poly(lactic acid) (PLA) to enhance their degradability. They found that the obtained copolyesters were amorphous polymers with high glass transition temperatures and had improved degradability with compared with PEF homopolyester counterpart.

In addition, Sousa *et al.* (2016a) reported the synthesis of fully renewable-based poly((ether)ester)s (PEEs) from FDCA, poly(ethylene glycol) (PEG), and isosorbide by polycondensation reactions (Fig. 3). Poly((poly(ethylene glycol)) 2,5-furandicarboxylate) (PEGF) polymers were obtained by polycondensation of FDCA with PEG or a mixture of PEG and isosorbide, and the isolation yield was about 65%. Furthermore, the PEGF polymers had a number-average molecular weight (M_n) in the range of 3300 to 17300, and the polydispersity values were close to 1.4, which was determined by size-exclusion chromatography in $CH_2Cl_2/CHCl_3$/HFP. The properties of PEGF material could be easily adjusted by changing the chain length of PEG and adding isosorbide or not. The product had comparable or better thermal properties than that of the fossil-PEE, and the diluted PEGISF200 chloroform solution can be cast directly on the surface of a Teflon plate to form a film. PEGF series polyesters was found to be a single T_g and below room temperature by DSC thermograms analysis. The crystallization domains were formed by a sufficiently long chain (soft PEG segments) modification so that the T_m of the PEGF200 was about 49 °C. However, due to the enrichment of the second amorphous phase in the stiff isosorbide-furandicarboxylate segments, the existence of PEG2000 and the amorphous domains of PEG soft segments, poly((poly(ethylene glycol) 2,5-furandicarboxylate)-co-poly(isosorbide 2,5-furandicarboxylate) (PEGISF2000) exhibited different thermal properties, resulting in a T_g value of 168 °C, while T_m and T_g were about 40 °C and -26°C. In addition, the XRD results revealed that the semicrystalline character of PEGF2000 and PEGISF2000 has two sharp signals at $2\theta \approx 19$ and 23°, which was similar to that of PEG2000 polyester. Additionally, XRD analysis of PEGF2000 and PEGISF2000 revealed an amorphous center at about 20°, whereas the more crystalline PEG precursor did not appear.

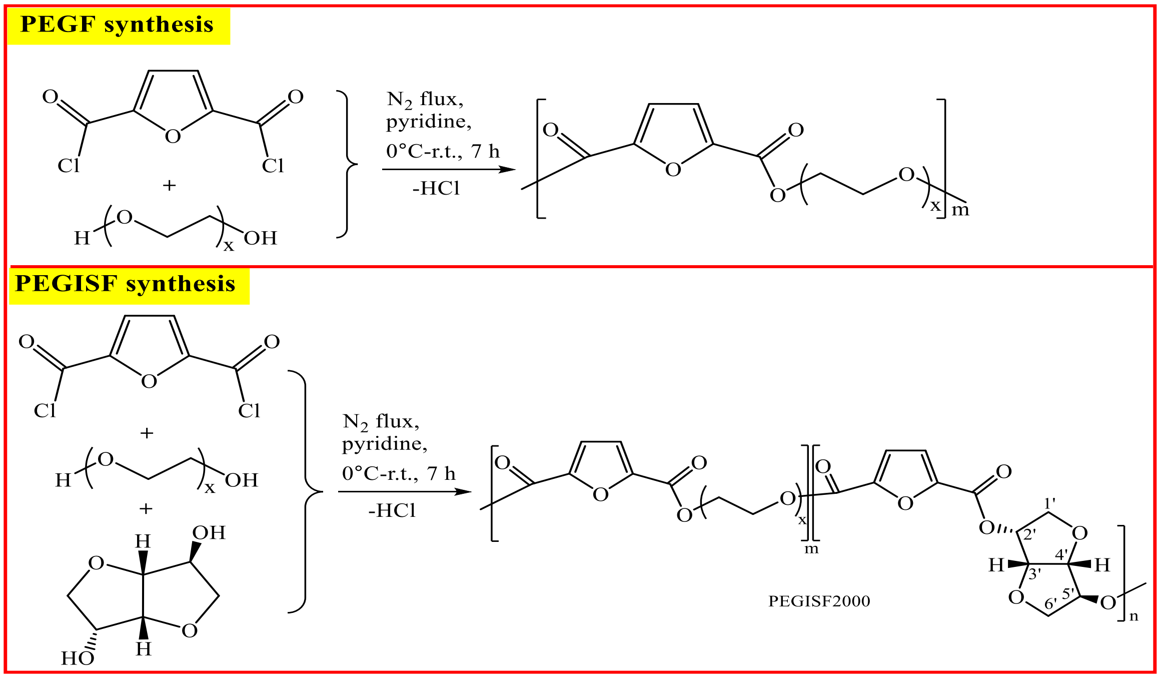

Fig. 3. Synthesis of two series of FDCA-based poly((ether)ester)s (PEGF and PEGISF2000) by polycondensation reaction

Wang *et al.* (2017a) prepared a series of multiblock copolymers poly(ethylene 2,5-furandicarboxylate)-poly(ethylene glycol) (PEFEGs) from FDCA, EG, and PEG through a two-step melt polycondensation method (Fig. 4). TGA analysis showed that PEFEGs had good thermal stability. Additionally, by changing the chain length and content of the PEG, the properties of PEFEGs, including melt crystallization peak, melt peak, and enthalpy of PEG block, were improved. It was also found that the elongation values at break of PEFEGs were significantly higher than PEF, such that they exhibited excellent shape memory properties.

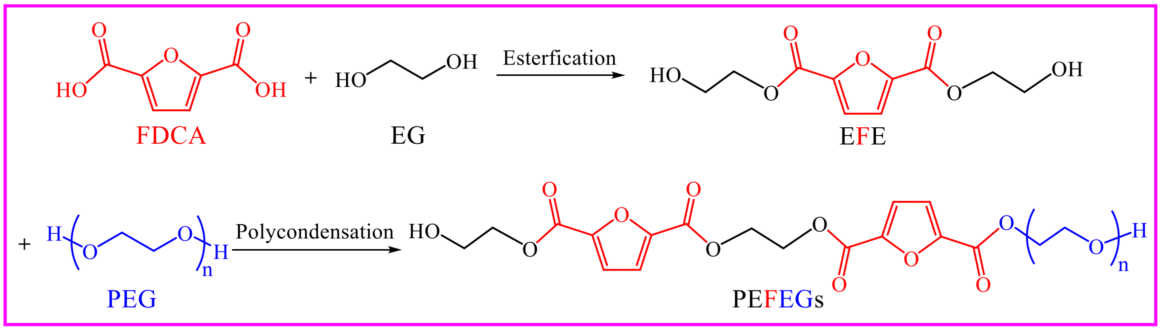

Fig. 4. Synthetic route to PEFEGs copolyesters

More recently, Xie *et al.* (2019) modified PEF with biobased 1,5-pentanediol *via* melt copolycondensation to improve its tensile strength and O_2 barrier property. The obtained poly(ethylene-co-1,5-pentylene 2,5-furandicarboxylate)s (PEPeFs) demonstrated that the amorphous copolyesters had excellent thermal stability. They found that the PEF-rich PEPeFs (ϕPeF 9-47%) showed greatly improved elongation at break, enhanced impact strength, improved O_2 gas barrier property, high Young's modulus and yielding strength in comparison with PEF. Poulopoulou *et al.* (2019b) revealed that the PEF-PPF copolyester with the belending of PEF and poly(propylene 2,5-furandicarboxylate) (PPF) showed a single composition-related T_g.

1,4-cyclohexanedimethanol (CHDM) and 1,4-cyclohexanedicarboxylic acid (CHDA) were also selected to be a copolyester monomer for the modification of PEF in recent years (Fig. 5) (Hong *et al.* 2016; Wang *et al.* 2016, 2018c). Wang *et al.* (2016) modified PEFs with CHDM to improve their mechanical and barrier properties. They found that the composition of the resulted poly(ethylene-co-1,4-cyclohexanedimethylene 2,5-furandicarboxylate)s (PECFs) had the characteristics of random polyester, and the composition of PECFs could be tunable by adjusting the molar amount of CHDM and dimethyl furan-2,5-dicarboxylate (DMFD). Also, the crystallinity, tensile modulus, and strength of the PECFs can be gradually reduced or increased by adjusting the amount of CHDM (0-59% or 76-100%), as revealed by DSC and tensile testing results. Furthermore, PECF-32 and PECF-76 exhibited better properties compared to PEN and PEI by barrier performance studies of O_2 and CO_2 permeability in PEF, which made PECFs more useful as a packaging material. Hong *et al.* (2016) also modified PEF with CHDM to obtain some copolyesters *via* esterification and polycondensation processes. They found that the CHDM had a positive effect on the previously seen drawbacks of furan-based polyesters, and the obtained co-polyester showed a dramatic increase in elongation at break (79±18%) and impact strength (4.0±0.1%). They thought that the cyclohexane ring conformational transition in the co-polyester chains containing CHDM improved the polyester's chain mobility and resulted in the ductility in the co-polyester. In addition, the results also revealed that the O_2 permeability and amounts of acetaldehyde (AA) content of the co-polyester-containing bottle was considerably lower than that of the PET-containing bottle. Therefore, they deemed that the obtained furan-based co-polyester was superior in both sustainability and performance and showed no limits in applicability for bottles and packaging. In addition, Wang *et al.* (2018c) synthesized a series of poly(ethylene 2,5-furandicarboxylate-co-ethylene 1,4-cyclohexanedicarboxylate)s (PEFCs) from FDCA, EG and CHDA through a two-melt polycondensation. Their results showed that all PEFCs displayed the properties of a random copolymer, and the composition of PECFs could be tunable by adjusting the molar amount of FDCA and CHDA. The obtained PEFCs were amorphous, and the T_g decreased with the increase of CHDA content, but its thermal stability did not change. Furthermore, it was found that the obtained PEFC-30 was a toughened plastic with tensile modulus and elongation of 801 MPa and 667%, respectively.

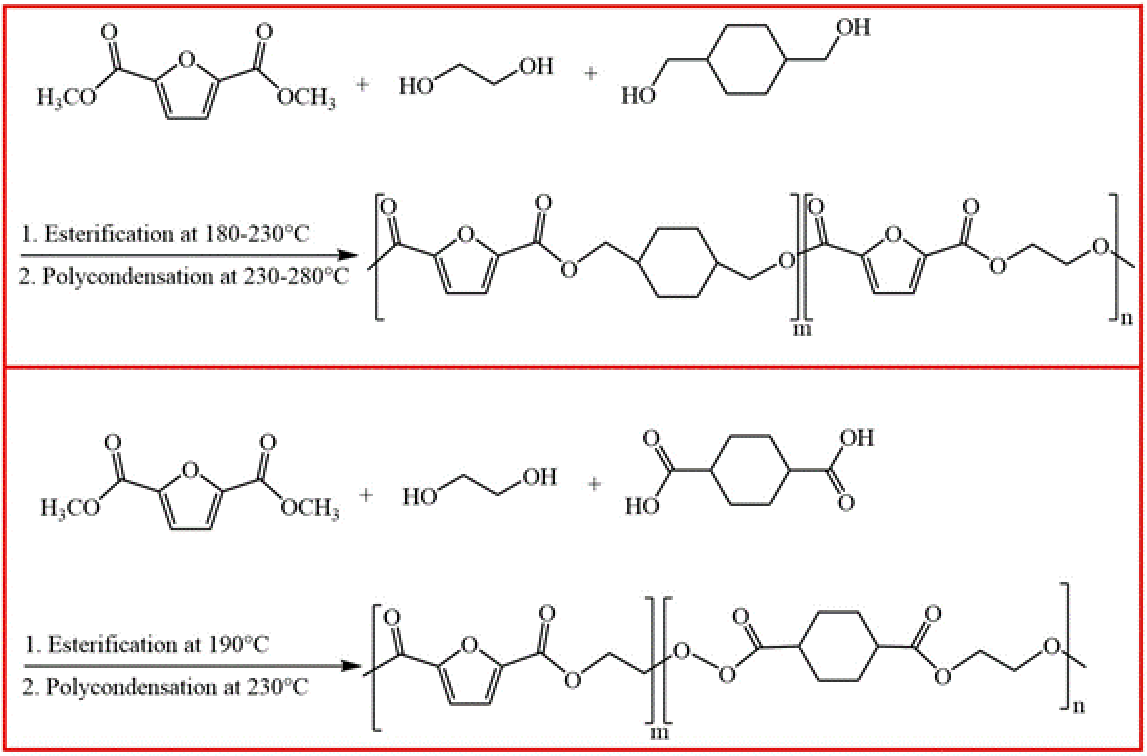

Fig. 5. Step-growth polycondensation of furan-based co-polyesters *via* melt transesterification and polycondensation processes

SYNTHESIS OF POLY(PROPYLENE 2,5-FURANDICARBOXYLATE) (PPF)

Polyesters derived from 1,3-propanediol (PD) were just reported in recent years due to the difficulties in the preparation of PD in sufficient quantities and purity (Bikiaris *et al.* 2008). However, the research of PD polymers has attracted wide attention in academic and industry, as the attractive process for producing PD from renewable resources has been developed (Haas *et al.* 2005; Papageorgiou and Bikiaris 2005; Tsanaktsis *et al.* 2015b; Poulopoulou *et al.* 2018). Poly(propylene 2,5-furan dicarboxylate) (PPF) is a thermoplastic polyester, and its synthesis and structural, thermal, and mechanical properties have been reported in recent years (Gandini *et al.* 2009a; Gomes *et al.* 2011; Jiang *et al.* 2012; Papageorgiou *et al.* 2015a; Vannini *et al.* 2015; Sousa *et al.* 2016b; Terzopoulou *et al.* 2017b; Guidotti *et al.* 2018; Papadopoulos *et al.* 2018; Wang *et al.* 2019).

Gandinii *et al.* (2009a) first reported the synthesis of PPF in 2009. They found that the prepared PPF had similar properties to PEF, except for the characteristic resonance related to the additional intermediate CH_2 groups, which can be obtained by FTIR and NMR spectra analysis of PPF. The T_m and T_g values of PPF were 174°C and 65°C, respectively, which were lower than their PEF homologues. This was attributed to the introduction of methylene groups in each polymer unit, resulting in higher macromolecular flexibility. Gomes *et al.* (2011) also synthesized some PPF polyesters with M_n and M_w values of 21600 and 27600. Analysis of the thermal properties revealed that PPF exhibited high crystallization ability, and its T_g as well as T_c appeared only on the second DSC scan trajectory after molten PPF quenching. In addition, Vannini *et al.* (2015) found that the PPF copolyester displayed excellent barrier properties due to their special crystal phase, which can be used as packaging material due to their properties of exceptionally low oxygen transmission rates and good impermeability to water vapors.

Papageorgiou *et al.* (2015a) reported the synthesis of PPF, and they compared their thermal behavior and solid-state structure with its terephthalate (PPT) and naphthalate (PPN) homologues. Through the structural analysis, they found that the final properties of the prepared samples were affected by different structural rings and ultimate chain stiffness. Compared with PPF and PPT, the PPN with higher rigidity showed higher T_g and thermal stability. The equilibrium melting point of PPF was obtained by the Hoffman-Weeks method at 199 ºC, and the heat of fusion of pure crystalline PPF polyester was calculated to be 141.8 J/g or 27.8 KJ/mol. In addition, the spherulites of PPFs at different temperatures were observed by polarized light microscopy (PLM), which revealed that PPF polyester formed small spherulites and had a slow growth rate. With the increase of temperature, the growth rate of PPN was faster and the spherulite was larger, and the band appeared in the spherulite grown above 160 °C. Then the PPT exhibited faster growth rates and banded spherulites, and as the crystallization temperature increased, the band spacing increased.

Recently, Wang *et al.* (2019) studied the effects of various PD on the properties of PPF. In this research, the FDCA polyester with different thermal properties was prepared by using FDCA and different substituent PD as the starting material, which had a similar skeleton structure to the PPF (Fig. 6). They found that the T_g and crystallinity of poly(neopentyl glycol furandicarboxylate) (PNF) was increased compared to PPF, whereas the T_g and crystallinity of poly(2-ethyl-2-butyl-1,3-propylene furandicarboxylate) (PEBF) with more -CH_3 substituted groups decreased compared with PNF. In this study, PNF exhibited high crystallinity with a ΔH_m value of 32.1 J/g, which had the highest T_g (70°C) and T_m (201°C). In contrast, PPF had a low ΔH_m value of 0.9 J/g and T_m of 173°C, while poly(2-methyl-1,3-propylene furandicarboxylate) (PMF) was a non-crystalline polyester. In addition, the gas barrier results revealed that PPF polyester had the best gas barrier property, followed by that of PMF and PNF, mainly due to the introduction of side chain -CH_3 substituents resulting in an increase in β relaxation and fractional free volume.

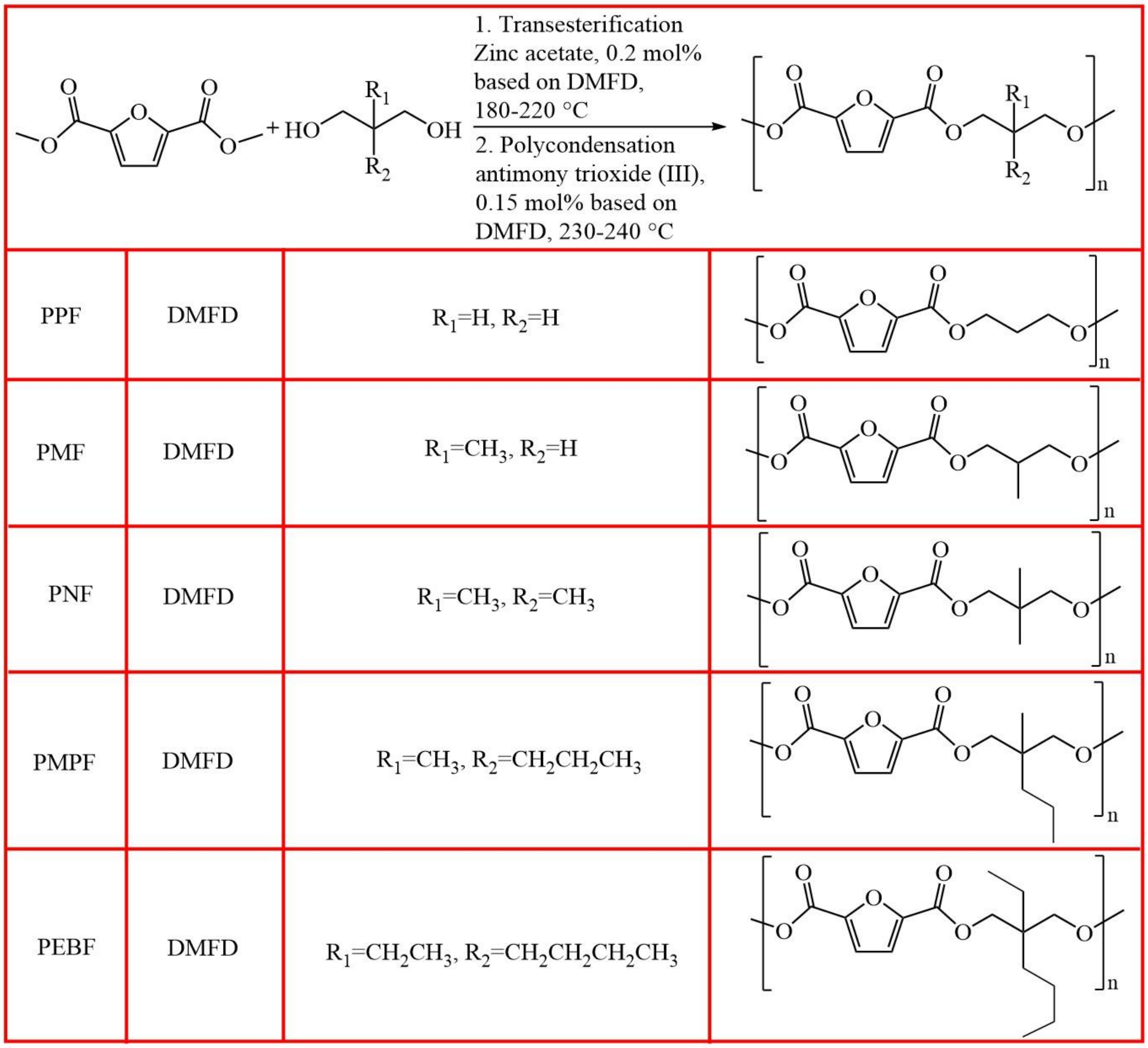

Fig. 6. Illustration for the synthesis of polyesters from FDCA and different diols (Reprinted with permission from Wang *et al*. 2019, American Chemical Society)

In addition, copolyesters based on FDCA and PD were also studied in recent years (Jiang *et al.* 2015; Lomeli-Rodriguez *et al.* 2016; Wang *et al.* 2017b; Jia *et al.* 2019; Righetti *et al.* 2019). For example, Jiang *et al.* (2015) studied the synthesis, structure, and properties of novel copolyesters from TPA, FDCA, and PD *via* direct esterification method by using tetrabutyl titanate (TBT) as catalyst. They found that the obtained copolyester was random copolymers with an average M_w more than 1×10^4 g/mol, which had similar thermal stabilities and higher elongation at break to corresponding homopolyesters. Wang *et al.* (2017b) used 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO) to modify PPF to get the copolyester of PPTF. They found that PPTF had the characteristics of random polyester. On the other hand, the semi-crystalline PPF can be made into a fully crystalline polyester by the addition of 10% CBDO, and it was easily to obtain higher transparency, and the T_g increased from 55.5 °C for PPF to 63.5 °C for PPTF. They also found that the O_2 and CO_2 barrier properties would decrease by the addition of CBDO units, but the modified copolyester still showed good barrier properties.

SYNTHESIS OF POLY(BUTYLENE 2,5-FURANDICARBOXYLATE) (PBF)

In earlier studies, it was found that poly(butylene terephthlate) (PBT) is an important semi-crystalline engineering thermoplastic with the advantages of high rigidity, low humidity, excellent properties, and favorable for processing and production (Tomar and Maiti 2010a; Sharma and Maiti 2013). Moreover, these characteristics were stable in a wide range of temperature and humidity. Compared with PET, PBT had more advantages, mainly depending on its facile crystallinity and easy dyeability, which made it the most commonly used durable product formed by inject molding (Tomar and Maiti 2010b; Sharma and Maiti 2013). However, in the current study, it can be found that the notched Izod impact strength of PBT was very low (Tomar and Maiti 2007, 2008). Therefore, the synthesis of poly(butylene 2,5-furandicarboxylate) (PBF) as PBT counterpart, from FDCA and 1,4-butanediol (BDO) has attracted much attention (Ma *et al.* 2012; Morales-Huerta *et al.* 2016a; Zhu *et al.* 2013).

Ma *et al.* (2012) successfully synthesized furan derivative polyester, PBF, and its crystallization properties was explored. The results of ^{1}H NMR at 750 MHz showed that chain-end groups were detected in different polymerization stages, which clearly revealed the process of polymerization. By further testing, it is revealed that the polymer had high tendency to form crystalline structured (T_m=130 °C and 169 °C; T_g=32°C), whose butylene segment is in a folded conformation, which was beneficial to the continuous fiber extraction from the melt of PBF.

Zhu *et al.* (2013) also prepared bio-based polyester PBF with 2,5-furandicarboxylic acid (FDCA) and BDO as raw materials *via* a two-stage polymerization. The obtained PBF had good thermal stability, strength, and ductility. Its melting point was around 172 °C, and a maximum degradation rate occurred at 428 °C. In addition, it was found that the obtained PBF was triclinic (a= 4.78(3) Å, b= 6.03(5) Å, c= 12.3(1) Å, α=110.1(2)°, β= 121.1(3)°, γ= 100.6(2)°), which was very similar to the α- and β-forms of PBT.

In addition, Morales-Huerta *et al.* (2016a) prepared cyclic ethylene and butylene 2,5-furandicarboxylate oligoesters and then converted them to furan-based polyesters of PEF and PBF by ring opening polymerization (ROP). High yields of cyclic oligoesters were obtained by both high dilution condensation and thermal cyclodepolymerization methods, and they were found to be crystalline compounds melting within the 140 to 200 °C range. The obtained PEF and PBF by ROP had weight-average molecular weights between 50000 and 60000 g/mol.

The existing research shows that PBF is a semi-crystalline furanic polyester with T_g near 40 °C, with a high crystallization rate and a similar structure to PBT, which is a good production soft drink bottle or food packaging material. However, one of the main disadvantages of PBF is that the structure of the aliphatic chain of diol leads to its poor thermal performance, which is one of the main disadvantages of the most common aliphatic polyester. In order to extend the application market of polyester materials, the synthesis of a series of copolyesters has attracted the attention of researchers (Zhou *et al.* 2013; Wu *et al.* 2014; Diao *et al.* 2016; Morales-Huerta *et al.* 2016b; Kwiatkowska *et al.* 2017; Hu *et al.* 2018; Matos *et al.* 2018; Morales-Huerta *et al.* 2018; Sousa *et al.* 2018; Hu *et al.* 2019c; Poulopoulou *et al.* 2019a).

For example, some poly(butylene adipate-co-butylene furandicarboxylate) (PBAFs) copolymers with high molecular weight were synthesized (Zhou *et al.* 2013). They found that all PBAFs presented random structures, and their composition could be adjusted according to the feed molar ratio of the diacid monomers. The crystallization ability and melting temperature of PBAFs decreased firstly with the increasing of FDCA content, and the trend was reversed when the content of FDCA exceeded 70%. The semicrystalline copolyester with high FDCA content had higher T_g, good tensile modulus, and strength. It was worth noting that the obtained copolyesters with 0 to 50% of FDCA content were biodegradability.

Wu *et al.* (2014) obtained some high molecular weight biobased polyesters of PBF and aliphatic-aromatic copolyesters, including poly(butylene adipate-co-butylene 2,5-furandicarboxylate)s (PBAFs) with adipic acid, BDO and highly purified biobased monomer of 2,5-furandicarboxylic acid (FA) *via* a two-step melt polycondensation reaction. The solubility of PBAF in 5 mg/mL organic solvents was determined, and the results showed that the solubility was related to the composition. In the case where the ϕBF did not exceed 50%, the PBAFs had high elastic deformation and rebound resilience, and the tensile properties (E=18 to 160 MPa, σ_b=9 to 17 MPa, ε_b=370 to 910%) were comparable to those of poly(butylene adipate). When ϕ_{BF} was higher, stress hardening occurred in the tensile test, and PBAFs exhibited a low tensile modulus (42 to 110 MPa), a medium strength (30 to 42 MPa), and a high elongation at break (256%).

Along the same idea, some new PBF-based copolyesters had been synthesized, such as poly(butylene-*co*-1,4-cyclohexanedimethylene 2,5-furandicarboxylic acid) (PBCFs) and poly(butylene 2,5-furandicarboxylate-*co*-terephthalate) P(BF-*co*-BT) (Diao *et al.* 2016; Morales-Huerta *et al.* 2016b). For PECFs, which were synthesized from FDCA, BDO, and CHDM, displayed the characteristics of random polyester with a triad component, and by changing the molar content of BDO and CHDM, the structural properties of PECF will vary, such as the average sequence length and monomer percentage (Fig. 7). It was found that the BDO was easily removed in the process of polycondensation, which was beneficial to the formation of long chain containing CHDM unit. Compared with PBF, the PBCFs modified by CHDM had a significantly change in thermal performance and crystallinity. The DSC results revealed that the T_g, T_m, and decomposition temperature changed from 45.7 to 74.4°C, 140.1 to 251.9 °C, and 380.6 to 388 °C respectively with the molar percent of CHDM unit increased from 20% to 70%. The crystallizability and crystal structure was changed by CHDM incorporation. When the 1,4-cyclohexanedimethylene fragment (CF) unit increased to 31%, the copolyester was non-crystalline due to the difficulty in forming long regular segments, which had no cold crystallization and melting behavior. Nevertheless, the DSC analysis indicated that these copolyesters had multiple melting behavior with increase of CF content, and the shoulder peaks appeared on the main melting point side, mainly due to partial melt recrystallization and final melting (Diao *et al.* 2016). The copolymer P(BF-*co*-BT), which was prepared from cyclic oligomers of butylene 2,5-furandicarboxylate c(BF)$_n$ and bytylene terephthalate c(BT)$_n$ *via* ring opening polymerization (ROP), had an average molecular weight in the range of 55000 and 80000, displaying a good thermal stability (Fig. 8). Although the homopolymer PBF was highly crystalline, the crystallinity of the copolyesters was largely repressed due to the presence of furanoate units. It was found that both T_m and T_g of the copolyesters varied steadily according to the furanoate/terephthalate ratio and the values were comparable to those reported for similar copolyesters prepared by melt polycondensation by other authors (Morales-Huerta *et al.* 2016b).

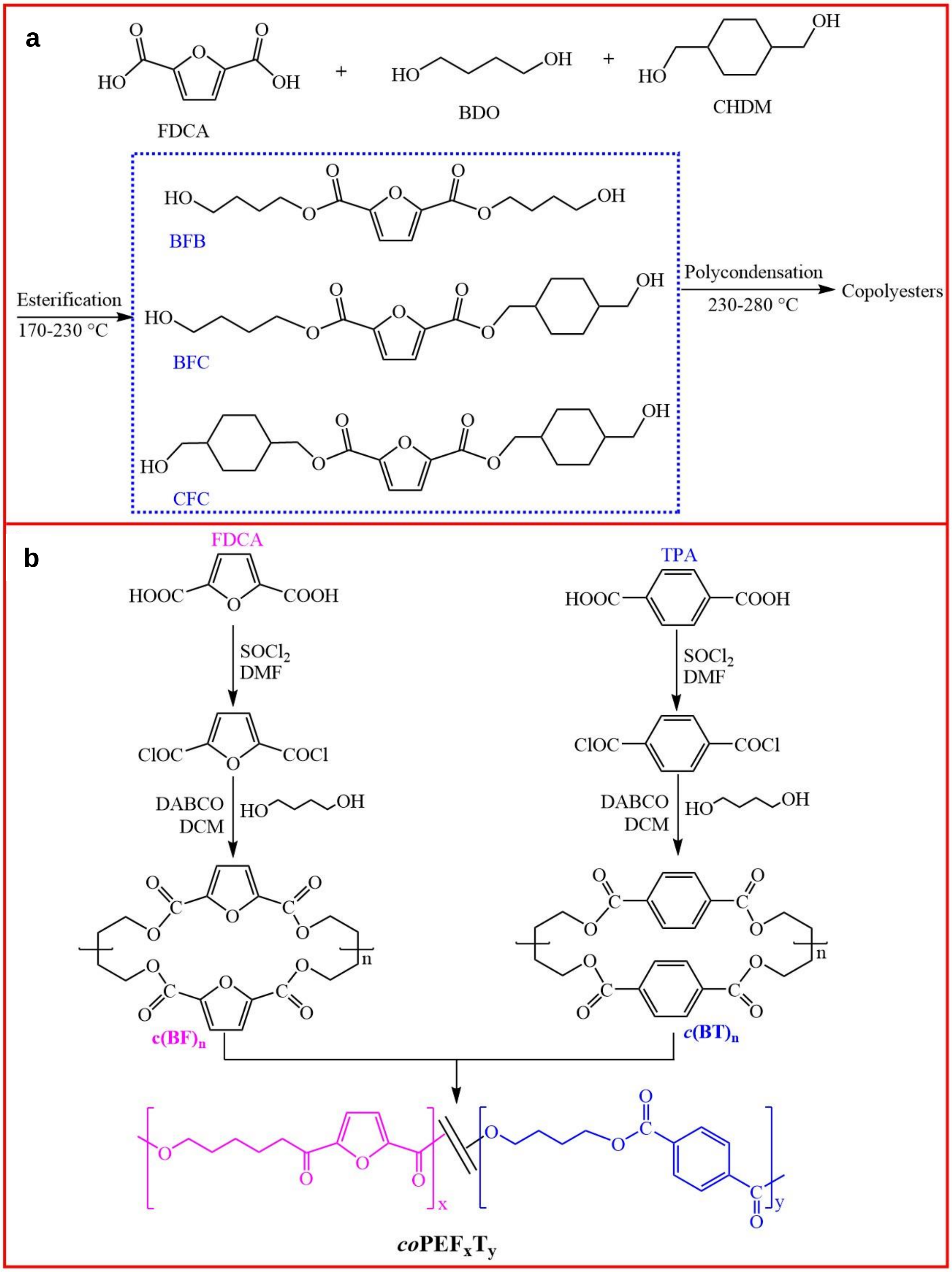

Fig. 7. (a) Polymer synthesis from FDCA, CHDM and BDO; (b) Synthetic route *via* ROP toward aromatic copolyesters containing butylene 2,5-furandicarboxylate and butylene terephthalate units (Reprinted with permission from Diao *et al*. 2016; Morales-Huerta *et al*. 2016b, American Chemical Society)

In a similar vein, Morales-Huerta *et al.* (2018) prepared the cyclic oligo(butylene 2,5-furandicarboxylate) and ε-caprolactone copolyester (PCL-PBF) *via* enzymatic ring-opening polymerization without using organic solvents and mental catalysts, making the polymer greener than conventional polycondensation methods. They found that the PCL-PBF copolyesters with wide and high yield molecular weight were obtained. The copolyesters were semi-crystalline, their monomers were distributed in blocks on the polymer chain, and their T_m and T_g values were between the PCL and PBF polyesters. More importantly, when an appropriate amount of furanoate was added to the chain, the T_g of PCL was significantly increased, which was related to the physical behavior of the polyester. They deemed that the obtained copolyester had the potential use in packaging and biomedicine due to their excellent properties.

Kwiatkowska *et al.* (2017) prepared poly(butylene 2,5-furanoate)-block-(dimerized fatty acid) (PBF-b-FAD) polymers with different properties by polycondensation of FDCA, 1,4-butanediol (1,4-BD), and dimerized fatty acid diol (FAD) under relatively mild and excessive diol conditions. A multi-block structure with ester groups was formed between the PBF blocks by the introduction of FAD and had a randomly distributed crystallizable rigid and non-crystalline flexible segment. It was found that the thermal performance of the PBF-b-FAD polymers was related not only to the molar amount of introduced FAD, but it also was affected by the thermal treatment of material. In addition, the mechanical properties of the macromolecular structure PBF-b-FAD polyesters varied with the molar ratio of PBF to FAD, which had a medium tensile strength and a relatively high deformation and damping at room temperature.

Matos *et al.* (2018), based on the synthesis of polyesters from FDCA, prepared a series of novel nanocomposite materials by introducing bacterial cellulose, such as acetylated bacterial cellulose/poly(butylene 2,5-furandicarboxylate) (Ac-BC/PBF) and acetylated bacterial cellulose/poly(butylene 2,5-furandicarboxylate)-co-(butylene diglycolate)s (Ac-BC/PBF-co-PBDG). The obtained copolyesters had high strength due to the adding of bacterial cellulose fibers. The T_g and T_m of the copolyesters were -25 to 46 °C and 61 to 174 °C, respectively. Furthermore, the nanocomposite copolyesters had better thermal stability (239 to 324 °C), and compared with pure copolyesters, the Young's modulus of nanocomposite copolyesters were as high as 1239 MPa.

In addition, Hu *et al.* (2018) prepared the poly(butylene furandicarboxylate)-b-poly(ethylene glycol), poly(butylene furandicarboxylate-co-glycolate) (PBFGA), and poly(butylene furandicarboxylate)-b-poly(glycolic acid) (PBF-b-GA) copolyesters (Hu *et al.* 2019c), which displayed good thermal, mechanical, barrier and degradable properties.

More recently, the PBF blends were also reported by Sousa *et al.* (2018) and Poulopoulou *et al.* (2019a), which showed some advantageous processing features as revealed by the lower melting temperature and higher thermal stability as compared with PBF.

SYNTHESIS OF POLY(HEXYLENE 2,5-FURANDICARBOXYLATE) (PHF)

Poly(hexylene 2,5-furandicarboxylate) (PHF) is a furan-type polyester that is synthesized by monomers of renewable resources and has a similar structure to poly(hexamethylene terephthalate) (PHT). PHF was first synthesized as reported by Moore and Kelly (1978), but in recent years, a series of poly(alkylene 2,5-fruandicarboxylate)s including PHF have been synthesized and characterized (Jiang *et al.* 2012; Papageorgiou *et al.* 2015b; Terzopoulou *et al.* 2016b; Haernvall *et al.* 2017; Zhang *et al.* 2019b).

For example, Jiang *et al.* (2012) reported the synthesis and characterization of some poly(alkylene 2,5-fruandicarboxylate)s including PHF. The obtained PHF with a M_w of 66700 had a tensile modulus, tensile strength, and elongation at break of 493 MPa, 35.5 MPa, and 210%, respectively. The DSC results showed that the T_g and T_m were 28.1 and 148.2 °C, respectively. Papageorgiou *et al.* (2015b) studied the crystallization and thermal degradation behavior of PHF in 2015. They found that the T_m and T_g of the obtained PHF were 145 °C and 7 °C, respectively. Though the DSC analysis, it was revealed that PHF exhibited multiple melting behavior after the crystallization process, which was mainly due to partial melting, recrystallization, and final melting. It was found that the heat of fusion of pure crystalline PHF polyester was 34 kJ/mol, and further calculation gave an equilibrium melting temperature of 157 °C.

More recently, PHF was synthesized from FDCA and 1,6-hexanediol (HDO) *via* direct esterification (Fig. 8) (Zhang *et al.* 2019b). The obtained PHF had typical (110) plane, (010) plane, and (111) plane at 2θ = 13.78° (*d*=6.42 Å), 17.06° (*d*=5.19 Å), and 24.9° (*d*=3.58 Å) with intrinsic viscosity of 0.803 dL/g, average Young's modulus of 479 MPa, and maximum tensile strength pf 36.5 MPa. Its elongation at break was 216%, which was significantly higher than that of PET (90%) and PEF (3%). It was found that the high intrinsic viscosity caused the increase in the enthalpy of fusion with respect to as-synthesized PEF, in this case, the melting peak was particularly sharp, and the T_g and T_m was about 48 and 144 °C, which were relatively lower when compared to those of PEF.

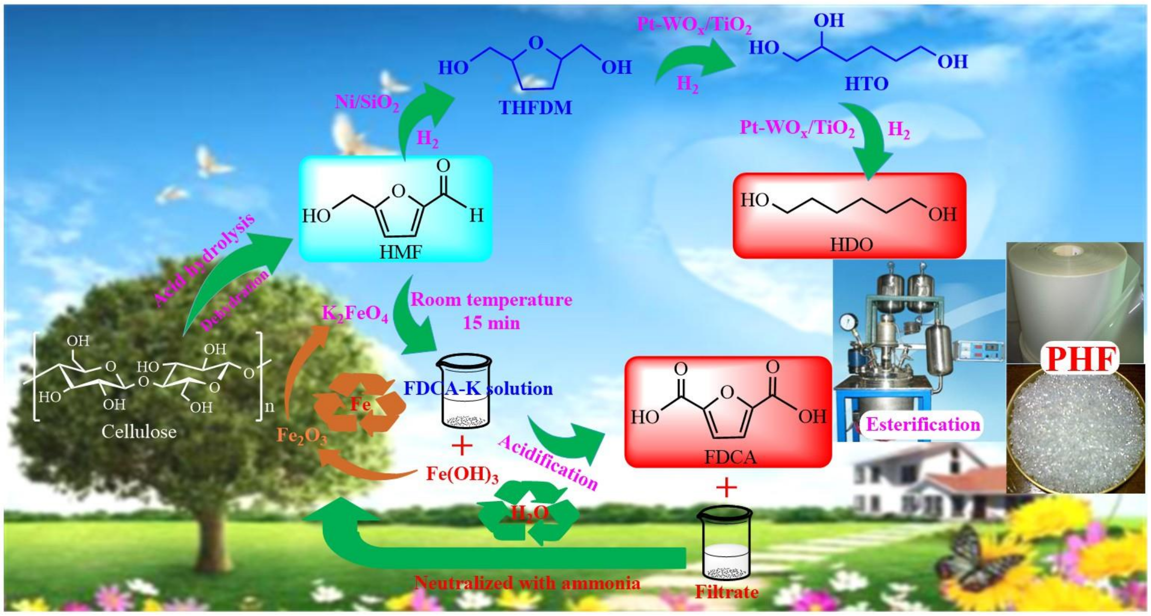

Fig. 8. Typical route for the synthesis of PHF from cellulose (Image from Zhang *et al*. 2019b)

Although the PHFs have been found to exhibit excellent mechanical properties, their applications have been limited due to the flammability. Recently, the synthesis of PHF-based copolyesters also attracted the attention of researchers (Wang *et al.* 2018a, b; Zhang *et al.* 2019b). Wang *et al.* (2018b) reported the use of renewable FDCA, HDO, and 2-carboxyetyly (phenyl)phosphinic acid (CEPPA) to synthesize phosphorus-containing poly(hexamethylene 2,5-furandicarboxylate)s (PHFCs) with different properties. They found that a series of synthetic PHFC showed good thermal performance, and the T_g decreased slightly as the molar content of CEPPA increased. In addition, they also synthesized the poly(hexamethylene 2,5-fruandicarboxylate)-b-poly(ethylene glycol) (PHFEGs) from FDCA, HDO and PEG *via* a two-step melt polycondensation method. Their results showed that the content of PEG in the prepared PHFEGs polyester was on different from that of the initial addition, and all of the PHFEGs were a dimorphic block copolymers and exhibited the excellent thermal stability with excellent shape-memory ability (Wang *et al.* 2018a). Poly(ethylene-co-hexamethylene 2,5-fruandicarboxylate) (PEHF) copolyesters with high intrinsic viscosity were synthesized by two-melt polycondensation using FDCA, EG and HDO as raw materials. They found that when a large amount of hexamethylene 2,5-furandicarboxylate (HF) ($\varphi_{HF} \geq 88$ mol%) was introduced, the prepared copolyesters were semi-crystalline, while for the remaining conditions they were amorphous polyesters. The synthesized copolyesters exhibited better thermal properties and had a single T_g which decreased as the amount of HF introduced increased. In addition, as the molar content of HF increased, the tensile modulus and tensile strength of the non-crystalline copolyester decreased, but the elongation at break and impact strength increased. The tensile properties of PEHF copolyesters were similar to those of bottle grade PET (Xie *et al.* 2018).

THE DECOMPOSITION OF FDCA-BASED POLYESTERS

It was known that the start of decomposing of FDCA-based polyesters will happen through the breaking of the polymer chain in the six-member transition stage due to the presence of a β-hydrogen atom, and most of the hetero-cleavage was continued instead of homogenization (Levchik and Weil 2004; Chebbi *et al.* 2019; Lu *et al.* 2019; Terzopoulou *et al.* 2019). Different cleavage methods will form different degradation products, such as -COOH and -CH_2=CH_2 products (Hetero-cleavage) or aldehydes, terminal alkyl, or methoxy terminal molecules (random chain scission).

The decomposition mechanism of FDCA-based polyesters was first studied by applying Py-GC/MS technology (Tsanaktsis *et al.* 2015b; Terzopoulou *et al.* 2016a,b; Terzopoulou *et al.* 2017a; Kasmi *et al.* 2018, 2019). In this research, the thermal degradation mechanism of FDCA-based polyester such as PEF, PPF, and PBF at 340, 390, and 500 °C was investigated, and mass spectrometry was carried out after gas separation in the GC capillary column. It was found that more complex pattern was present at high temperatures of 500 °C, whereas in the case of 340 and 390 °C, the chromatographic peak was less and chromatogram map was simpler. Some volatile substances (CO, CH_3CHO, *etc.*) obtained by decomposition of -COOH and -CH_2=CH_2 products were detected at low retention times. (Tsanaktsis *et al.* 2015b) The results of the Py-GC/MS analysis of PHF, PNF, and some other FDCA-based polyesters showed that the main thermal degradation products were similar to the PEF, PPF, and PBF (Terzopoulou *et al.* 2016a).

CONCLUSIONS AND OUTLOOK

On account of the excessive consumption of fossil resources and environmental issues, renewable biomass materials and sustainable economy have received wide attention in industry and academia. FDCA-based polyesters provide a viable solution to the environmental and economic issues arising from over-reliance on petroleum-based products. As described above, the synthesis of FDCA-based polyesters has made a major breakthrough, and a large number of preparation strategies are being implemented and improved. Of course, not all these FDCA-based copolyesters will reach industrial application, and their substitution for petroleum-based polymers remains challenging. This arduous task involves obtaining large quantities of biomass raw materials, producing high-performance FDCA-based polyesters, and their cost-effective performance. Academia and industry have devoted a lot of time and effort to the production of FDCA-based polymers and PEF, and there continues to be progress in the right direction. Base on the new trends of rational utilization of renewable biomass resources and the encouraging results, it is exciting to develop valuable products from biomass materials. On the other hand, the global organizations should provide additional funding and incentives to both industry and academia in the field of fully biobased polymers, though large-scale production of fully bio-based polymers is still difficult and has a long way to go.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from National Natural Science Foundation of China (Grant No. 21406208) and Natural Science Foundation of Zhejiang Province (Grant No. LY17C160008).

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

REFERENCES CITED

Amarasekara, A. S., Ha, U., and Okorie, N. C. (2018). “Renewable polymers: Synthesis and characterization of poly(levulinic acid-pentaerythritol),” *Journal of Polymer Science Part A-Polymer Chemistry* 56(9), 955-958. DOI: 10.1002/pola.28980

Amarasekara, A. S., Nguyen, L. H., Okorie, N. C., and Jamal, S. M. (2017). “A two-step efficient preparation of a renewable dicarboxylic acid monomer 5,5-[oxybis (methylene)] bis[2-furancarboxylic acid] from d-fructose and its application in polyester synthesis,” *Green Chemistry* 19(6), 1570-1575. DOI: 10.1039/C6GC03314H

Araujo, C. F., Nolasco, M. M., Ribeiro-Claro, P. J. A., Rudić, S., Silvestre, A. J. D., Vaz, P. D., and Sousa, A. F. (2018). “Inside PEF: chain conformation and dynamics in crystalline and amorphous domains,” *Macromolecules* 51(9), 3515-3526. DOI: 10.1021/acs.macromol.8b00192

Banella, M. B., Bonucci, J., Vannini, M., Marchese, P., Lorenzetti, C., and Celli, A. (2019). “Insights into the synthesis of poly(ethylene 2,5-furandicarboxylate) from 2,5-furandicarboxylic acid: Steps toward environmental and food safety excellence in packaging applications,” *Industrial & Engineering Chemistry Research* 58(21), 8955-8962. DOI: 10.1021/acs.iecr.9b00661

Bikiaris, D. N., Papageorgiou, G. Z., Giliopoulos, D. J., and Stergiou, C. A. (2008). “Correlation between chemical and solid-state structures and enzymatic hydrolysis in novel biodegradable polyesters. The case of poly(propylene alkanedicarboxylate)s,” *Macromolecular Bioscience* 8(8), 728-740. DOI: 10.1002/mabi.200800035

Burgess, S. K., Leisen, J. E., Kraftschik, B. E., Mubarak, C. R., Kriegel, R. M., and Koros, W. J. (2014). "Chain mobility, thermal, and mechanical properties of poly(ethylene furanoate) compared to poly(ethylene terephthalate)," *Macromolecules* 47(4), 1383-1391. DOI: 10.1021/ma5000199

Burgess, S. K., Kriegel, R. M., and Koros, W. J. (2015). "Carbon dioxide sorption and transport in amorphous poly(ethylene furanoate)," *Macromolecules* 48(7), 2184-2193. DOI: 10.1021/acs.macromol.5b00333

Burgess, S. K., Wenz, G. B., Kriegel, R. M., and Koros, W. J. (2016). "Penetrant transport in semicrystalline poly(ethylene furanoate)," *Polymer* 98, 305-310. DOI: 10.1016/j.polymer.2016.06.046

Chebbi, Y., Kasmi, N., Majdoub, M., Cerruti, P., Scarinzi, G., Malinconico, M., Dal Poggetto, G., Papageorgiou, G. Z., and Bikiaris, D. N. (2019). "Synthesis, characterization, and biodegradability of novel fully biobased poly(decamethylene-co-isosorbide 2,5-furandicarboxylate) copolyesters with enhanced mechanical properties," *ACS Sustainable Chemistry & Engineering* 7(5), 5501-5514.

Codou, A., Guigo, N., van Berkel, J., de Jong, E., and Sbirrazzuoli, N. (2014). "Non-isothermal crystallization kinetics of biobased poly(ethylene 2,5-furandicarboxylate) synthesized *via* the direct esterification process," *Macromolecular Chemistry and Physics* 215(21), 2065-2074. DOI: 10.1002/macp.201400316

Collias, D. I., Harris, A. M., Nagpal, V., Cottrell, I. W., and Schultheis, M. W. (2014). "Biobased terephthalic acid technologies: A literature review," *Industrial Biotechnology* 10(2), 91-105. DOI: 10.1089/ind.2014.0002

Diao, L. C., Su, K. M., Li, Z. H., and Ding, C. K. (2016). "Furan-based co-polyesters with enhanced thermal properties: Poly(1,4-butylene-co-1,4-cyclohexane-dimethylene-2,5-furandicarboxylic acid)," *RSC Advances* 6(33), 27632-27639. DOI: 10.1039/c5ra27617a

Duo, J., Zhang, Z., Yao, G., Huo, Z., and Jin, F. (2016). "Hydrothermal conversion of glucose into lactic acid with sodium silicate as a base catalyst," *Catalysis Today* 263, 112-116. DOI: 10.1016/j.cattod.2015.11.007

Eerhart, A., Faaij, A. P. C., and Patel, M. K. (2012). "Replacing fossil based PET with biobased PEF; process analysis, energy and GHG balance," *Energy & Environmental Science* 5(4), 6407-6422. DOI: 10.1039/c2ee02480b

Firoozi, N., and Kang, Y. Q. (2019). "A highly elastic and autofluorescent poly(xylitol-dodecanedioic acid) for tissue engineering," *ACS Biomaterials Science & Engineering* 5(3), 1257-1267. DOI: 10.1021/acsbiomaterials.9b00059

Gandini, A., Coelho, D., Gomes, M., Reis, B., and Silvestre, A. (2009a). "Materials from renewable resources based on furan monomers and furan chemistry: Work in progress," *Journal of Materials Chemistry* 19(45), 8656-8664. DOI: 10.1039/b909377j

Gandini, A., Silvestre, A. J., Neto, C. P., Sousa, A. F., and Gomes, M. (2009b). "The furan counterpart of poly (ethylene terephthalate): An alternative material based on renewable resources," *Journal of Polymer Science Part A: Polymer Chemistry* 47(1), 295-298. DOI: 10.1002/pola.23130

Garcia-Campo, M. J., Quiles-Carrillo, L., Sanchez-Nacher, L., Balart, R., and Montanes, N. (2019). "High toughness poly(lactic acid) (PLA) formulations obtained by ternary blends with poly(3-hydroxybutyrate) (PHB) and flexible polyesters from succinic acid," *Polymer Bulletin* 76(4), 1839-1859. DOI: 10.1007/s00289-018-2475-y

Gomes, M., Gandini, A., Silvestre, A. J. D., and Reis, B. (2011). "Synthesis and characterization of poly(2,5-furan dicarboxylate)s based on a variety of diols," *Journal* *of Polymer Science Part A: Polymer Chemistry* 49(17), 3759-3768. DOI: 10.1002/pola.24812

Green, K. D., Turner, M. K., and Woodley, J. M. (2000). "*Candida cloacae* oxidation of long-chain fatty acids to dioic acids," *Enzyme and Microbial Technology* 27(3-5), 205-211. DOI: 10.1016/S0141-0229(00)00217-9

Guidotti, G., Soccio, M., Lotti, N., Gazzano, M., Siracusa, V., and Munari, A. (2018). "Poly(propylene 2,5-thiophenedicarboxylate) *vs.* poly(propylene 2,5-furandicarboxylate): Two examples of high gas barrier bio-based polyesters," *Polymers* 10(7). DOI: 10.3390/polym10070785

Haas, T., Jaeger, B., Weber, R., Mitchell, S. F., and King, C. F. (2005). "New diol processes: 1,3-propanediol and 1,4-butanediol," *Applied Catalysis A: General* 280(1), 83-88. DOI: 10.1016/j.apcata.2004.08.027

Haernvall, K., Zitzenbacher, S., Amer, H., Zumstein, M. T., Sander, M., McNeill, K., Yamamoto, M., Schick, M. B., Ribitsch, D., and Guebitz, G. M. (2017). "Polyol structure influences enzymatic hydrolysis of bio-based 2,5-furandicarboxylic acid (FDCA) polyesters," *Biotechnology Journal* 12(9). DOI: 10.1002/biot.201600741

Hartweg, M., and Becer, C.R. (2016). "Direct polymerization of levulinic acid *via* Ugi multicomponent reaction," *Green Chemistry* 18(11), 3272-3277. DOI: 10.1039/c6gc00372a

Herran, R., Amalvy, J. I., and Chiacchiarelli, L. M. (2019). "Highly functional lactic acid ring-opened soybean polyols applied to rigid polyurethane foams," *Journal of Applied Polymer Science* 136(37). DOI: 10.1002/app.47959

Hong, S., Min, K.-D., Nam, B.-U., and Park, O. O. (2016). "High molecular weight bio furan-based co-polyesters for food packaging applications: Synthesis, characterization and solid-state polymerization," *Green Chemistry* 18(19), 5142-5150. DOI: 10.1039/c6gc01060a

Hu, C., Bourbigot, S., Delaunay, T., Collinet, M., Marcille, S., and Fontaine, G. (2019a). "Synthesis of isosorbide based flame retardants: Application for polybutylene succinate," *Polymer Degradation and Stability* 164, 9-17. DOI: 10.1016/j.polymdegradstab.2019.03.016

Hu, H., Zhang, R. Y., Jiang, Y. H., Shi, L., Wang, J. G., Ying, W. B., and Zhu, J. (2019b). "Toward biobased, biodegradable, and smart barrier packaging material: Modification of poly(neopentyl glycol 2,5-furandicarboxylate) with succinic acid," *ACS Sustainable Chemistry & Engineering* 7(4), 4255-4265. DOI:

Hu, H., Zhang, R. Y., Sousa, A., Long, Y., Ying, W. B., Wang, J. G., and Zhu, J. (2018). "Bio-based poly(butylene 2,5-furandicarboxylate)-b-poly(ethylene glycol) copolymers with adjustable degradation rate and mechanical properties: Synthesis and characterization," *European Polymer Journal* 106, 42-52. DOI: 10.1016/j.eurpolymj.2018.07.007

Hu, H., Zhang, R. Y., Wang, J. G., Ying, W. B., Shi, L., Yao, C. K., Kong, Z. Y., Wang, K., and Zhu, J. (2019c). "A mild method to prepare high molecular weight poly(butylene furandicarboxylate-co-glycolate) copolyesters: Effects of the glycolate content on thermal, mechanical, and barrier properties and biodegradability," *Green Chemistry* 21(11), 3013-3022. DOI: 10.1039/c9gc00668k

Jerpdal, L., Schuette, P., Stahlberg, D., and Akermo, M. (2019). "Influence of temperature during overmolding on the tensile modulus of self-reinforced poly(ethylene terephthalate) insert," *Journal of Applied Polymer Science*. DOI: 10.1002/app.48334

Ji, N., Zhang, T., Zheng, M., Wang, A., Wang, H., Wang, X., and Chen, J. G. (2008). "Direct catalytic conversion of cellulose into ethylene glycol using nickel-promoted tungsten carbide catalysts," *Angewandte Chemie-International Edition* 47(44), 8510-8513. DOI: 10.1002/anie.200803233

Jia, Z., Wang, J. G., Sun, L. Y., Liu, F., Zhu, J., and Liu, X. Q. (2019). "Copolyesters developed from bio-based 2,5-furandicarboxylic acid: Synthesis, sequence distribution, mechanical, and barrier properties of poly(propylene-co-1,4-cyclohexanedimethylene 2,5-furandicarboxylate)s," *Journal of Applied Polymer Science* 136(13). DOI: 10.1002/app.47291

Jiang, M., Liu, Q., Zhang, Q., Ye, C., and Zhou, G. (2012). "A series of furan-aromatic polyesters synthesized *via* direct esterification method based on renewable resources," *Journal of Polymer Science Part A-Polymer Chemistry* 50(5), 1026-1036. DOI: 10.1002/pola.25859

Jiang, M., Lu, T. T., Zhang, Q., Chen, Y., and Zhou, G. Y. (2015). "From fossil resources to renewable resources: Synthesis, structure, properties and comparison of terephthalic acid-2,5-furandicarboxylic acid-diol copolyesters," *Journal of Renewable Materials* 3(2), 120-141. DOI: 10.7569/JRM.2014.634139

Kasmi, N., Terzopoulou, Z., Papageorgiou, G. Z., and Bikiaris, D. N. (2018). "Poly(1,4-cyclohexanedimethylene 2,6-naphthalate) polyester with high melting point: Effect of different synthesis methods on molecular weight and properties," *Express Polymer Letters* 12(3), 227-237. DOI: 10.3144/expresspolymlett.2018.21

Kasmi, N., Wahbi, M., Papadopoulos, L., Terzopoulou, Z., Guigo, N., Sbirrazzuoli, N., Papageorgiou, G. Z., and Bikiaris, D. N. (2019). "Synthesis and characterization of two new biobased poly(pentylene 2,5-furandicarboxylate-co-caprolactone) and poly(hexamethylene 2,5-furandicarboxylate-co-caprolactone) copolyesters with enhanced enzymatic hydrolysis properties," *Polymer Degradation and Stability* 160, 242-263. DOI: 10.1016/j.polymdegradstab.2019.01.004

Kieber, R. J., Ozkardes, C., Sanchez, N., and Kennemur, J. G. (2019). "Cationic copolymerization of isosorbide towards value-added poly(vinyl ethers)," *Polymer Chemistry* 10(25), 3514-3524. DOI: 10.1039/c9py00590k

Kwiatkowska, M., Kowalczyk, I., Kwiatkowski, K., Szymczyk, A., and Jedrzejewski, R. (2017). "Synthesis and structure-property relationship of biobased poly(butylene 2,5-furanoate)-block-(dimerized fatty acid) copolymers," *Polymer* 130, 26-38. DOI: 10.1016/j.polymer.2017.10.009

Landim, L. B., Pinto, J. C., Cabral-Albuquerque, E. C. M., Cunha, S., and Fialho, R. L. (2018). "Synthesis and characterization of copolymers of urea-succinic acid-ethylene glycol and copolymers of urea-succinic acid-glycerol," *Polymer Engineering and Science* 58(9), 1575-1582. DOI: 10.1002/pen.24746

Levchik, S. V., and Weil, E. D. (2004). "A review on thermal decomposition and combustion of thermoplastic polyesters," *Polymers for Advanced Technologies* 15(12), 691-700. DOI: 10.1002/pat.526

Li, N., Zheng, Y., Wei, L., Tenga, H., and Zhou, J. (2017). "Metal nanoparticles supported on WO_3 nanosheets for highly selective hydrogenolysis of cellulose to ethylene glycol," *Green Chemistry* 19(3), 682-691. DOI: 10.1039/c6gc01327a

Lomeli-Rodriguez, M., Martin-Molina, M., Jimenez-Pardo, M., Nasim-Afzal, Z., Cauet, S. I., Davies, T. E., Rivera-Toledo, M., and Lopez-Sanchez, J. A. (2016). "Synthesis and kinetic modeling of biomass-derived renewable polyesters," *Journal of Polymer Science Part A-Polymer Chemistry* 54(18), 2876-2887. DOI: 10.1002/pola.28173

Lu, J., Li, Z. S., Zhou, L. Z., Wu, L. B., and Li, B. G. (2019). "Biobased 1,5-pentanediol derived aliphatic-aromatic copolyesters: Synthesis and thermo-mechanical properties of poly(pentylene succinate-co-terephthalate)s and poly(pentylene adipate-co-terephthalate)s," *Polymer Degradation and Stability* 163, 68-75. DOI: 10.1016/j.polymdegradstab.2019.02.010

Lu, M., Zhu, X., Li, X. H., Yang, X. M., and Tu, Y. F. (2017). "Synthesis of cyclic oligo(ethylene adipate)s and their melt polymerization to poly(ethylene adipate)," *Chinese Journal of Polymer Science* 35(9), 1051-1060. DOI: 10.1007/s10118-017-1951-4

Ma, J. P., Yu, X. F., Xu, J., and Pang, Y. (2012). "Synthesis and crystallinity of poly(butylene 2,5-furandicarboxylate)," *Polymer* 53(19), 4145-4151. DOI: 10.1016/j.polymer.2012.07.022

Mao, Y. M., Kriegel, R. M., and Bucknall, D. G. (2016). "The crystal structure of poly(ethylene furanoate)," *Polymer* 102, 308-314. DOI: 10.1016/j.polymer.2016.08.052.

Matos, M., Sousa, A. F., Fonseca, A. C., Freire, C. S., Coelho, J. F., and Silvestre, A. J. (2014). "A new generation of furanic copolyesters with enhanced degradability: Poly (ethylene 2,5-furandicarboxylate)-co-poly (lactic acid) copolyesters," *Macromolecular Chemistry and Physics* 215(22), 2175-2184. DOI: 10.1002/macp.201400175

Matos, M., Sousa, A. F., Silva, N., Freire, C. S. R., Andrade, M., Mendes, A., and Silvestre, A. J. D. (2018). "Furanoate-based nanocomposites: A case study using poly(butylene 2,5-furanoate) and poly(butylene 2,5-furanoate)-co-(butylene diglycolate) and bacterial cellulose," *Polymers* 10(8). DOI: 10.3390/polym10080810

Menager, C., Guigo, N., Martino, L., Sbirrazzuoli, N., Visser, H., Boyer, S. A. E., Billon, N., Monge, G., and Combeaud, C. (2018). "Strain induced crystallization in biobased poly(ethylene 2,5-furandicarboxylate) (PEF); Conditions for appearance and microstructure analysis," *Polymer* 158, 364-371. DOI: 10.1016/j.polymer.2018.10.054

Montava-Jorda, S., Chacon, V., Lascano, D., Sanchez-Nacher, L., and Montanes, N. (2019). "Manufacturing and characterization of functionalized aliphatic polyester from poly(lactic acid) with halloysite nanotubes," *Polymers* 11(8). DOI: 10.3390/polym11081314

Moore, J. A., and Kelly, J. E. (1978). "Polyesters derived from furan and tetrahydrofuran nuclei," *Macromolecules* 11(3), 568-573. DOI: 10.1021/ma60063a028

Morales-Huerta, J. C., de Ilarduya, A. M., and Munoz-Guerra, S. (2018). "Blocky poly(-caprolactone-co-butylene 2,5-furandicarboxylate) copolyesters *via* enzymatic ring opening polymerization," *Journal of Polymer Science Part A-Polymer Chemistry* 56(3), 290-299. DOI: 10.1002/pola.28895

Morales-Huerta, J. C., de Ilarduya, A. M., and Munoz-Guerra, S. (2016a). "Poly(alkylene 2,5-furandicarboxylate)s (PEF and PBF) by ring opening polymerization," *Polymer* 87, 148-158. DOI: 10.1016/j.polymer.2016.02.003

Morales-Huerta, J. C., de Ilarduya, A. M., and Munoz-Guerra, S. (2016b). "Sustainable aromatic copolyesters *via* ring opening polymerization: Poly(butylene 2,5-furandicarboxylate-co-terephthalate)s," *ACS Sustainable Chemistry & Engineering* 4(9), 4965-4973.

Moreau, C., Belgacem, M. N., and Gandini, A. (2004). "Recent catalytic advances in the chemistry of substituted furans from carbohydrates and in the ensuing polymers," *Topics in Catalysis* 27(1), 11-30. DOI: 10.1023/B:TOCA.0000013537.13540.0e

Papadopoulos, L., Terzopoulou, Z., Bikiaris, D. N., Patsiaoura, D., Chrissafis, K., Papageorgiou, D. G., and Papageorgiou, G. Z. (2018). "Synthesis and characterization of in-situ-prepared nanocomposites based on poly(propylene 2,5-furan dicarboxylate) and aluminosilicate clays," *Polymers* 10(9). DOI: 10.3390/polym10090937

Papageorgiou, G. Z., and Bikiaris, D. N. (2005). "Crystallization and melting behavior of three biodegradable poly(alkylene succinates): A comparative study," *Polymer* 46(26), 12081-12092. DOI: 10.1016/j.polymer.2005.10.073

Papageorgiou, G. Z., Papageorgiou, D. G., Terzopoulou, Z., and Bikiaris, D. N. (2016). "Production of bio-based 2,5-furan dicarboxylate polyesters: Recent progress and critical aspects in their synthesis and thermal properties," *European Polymer Journal* 83, 202-229. DOI: 10.1016/j.eurpolymj.2016.08.004

Papageorgiou, G. Z., Papageorgiou, D. G., Tsanaktsis, V., and Bikiaris, D. N. (2015a). "Synthesis of the bio-based polyester poly(propylene 2,5-furan dicarboxylate). Comparison of thermal behavior and solid state structure with its terephthalate and naphthalate homologues," *Polymer* 62, 28-38. DOI: 10.1016/j.polymer.2015.01.080

Papageorgiou, G. Z., Tsanaktsis, V., and Bikiaris, D. N. (2014). "Synthesis of poly(ethylene furandicarboxylate) polyester using monomers derived from renewable resources: Thermal behavior comparison with PET and PEN," *Physical Chemistry Chemical Physics* 16(17), 7946-7958. DOI: 10.1039/c4cp00518j

Papageorgiou, G. Z., Tsanaktsis, V., Papageorgiou, D. G., Chrissafis, K., Exarhopoulos, S., and Bikiaris, D. N. (2015b). "Furan-based polyesters from renewable resources: Crystallization and thermal degradation behavior of poly(hexamethylene 2,5-furan-dicarboxylate)," *European Polymer Journal* 67, 383-396. DOI: 10.1016/j.eurpolymj.2014.08.031

Pasma, S. A., Daik, R., and Maskat, M. Y. (2019). "Enzymatic synthesis of biodegradable polyesters using succinic acid monomer derived from cellulose of oil palm empty fruit bunch," *Journal of Wood Chemistry and Technology* 38(6), 445-459. DOI: 10.1080/02773813.2018.1533976

Pileidis, F. D., and Titirici, M.-M. (2016). "Levulinic acid biorefineries: New challenges for efficient utilization of biomass," *ChemSusChem* 9(6), 562-582. DOI: 10.1002/cssc.201501405

Poulopoulou, N., Kantoutsis, G., Bikiaris, D. N., Achilias, D. S., Kapnisti, M., and Papageorgiou, G. Z. (2019a). "Biobased engineering thermoplastics: Ppoly(butylene 2,5-furandicarboxylate) blends," *Polymers* 11(6). DOI: 10.3390/polym11060937

Poulopoulou, N., Kasmi, N., Bikiaris, D. N., Papageorgiou, D. G., Floudas, G., and Papageorgiou, G. Z. (2018). "Sustainable polymers from renewable resources: Polymer blends of furan-based polyesters," *Macromolecular Materials and Engineering* 303(8). DOI: 10.1002/mame.201800153

Poulopoulou, N., Pipertzis, A., Kasmi, N., Bikiaris, D. N., Papageorgiou, D. G., Floudas, G., and Papageorgiou, G. Z. (2019b). "Green polymeric materials: On the dynamic homogeneity and miscibility of furan-based polyester blends," *Polymer* 174, 187-199. DOI: 10.1016/j.polymer.2019.04.058

Rosenboom, J. G., Hohl, D. K., Fleckenstein, P., Storti, G., and Morbidelli, M. (2018). "Bottle-grade polyethylene furanoate from ring-opening polymerisation of cyclic oligomers," *Nature Communications* 9(1), 2701. DOI: 10.1038/s41467-018-05147-y

Righetti, M. C., Marchese, P., Vannini, M., Celli, A., Tricoli, F., and Lorenzetti, C. (2019). "Temperature-induced polymorphism in bio-based poly(propylene 2,5-

furandicarboxylate),” *Thermochimica Acta* 677, 186-193. DOI: 10.1016/j.tca.2018.12.003

Rizescu, C., Podolean, I., Albero, J., Parvulescu, V. I., Coman, S. M., Bucur, C., Puche, M., and Garcia, H. (2017). “N-Doped graphene as a metal-free catalyst for glucose oxidation to succinic acid,” *Green Chemistry* 19(8), 1999-2005. DOI: 10.1039/c7gc00473g

Sharma, R., and Maiti, S. N. (2013). “Modification of tensile and impact properties of poly(butylene terephthlate) by incorporation of styrene-ethylene-butylene-styrene and maleic anhydride-grafted-SEBS (SEBS-g-MA) terpolymer,” *Polymer Engineering and Science* 53(10), 2242-2253. DOI: 10.1002/pen.23476

Sinisi, A., Esposti, M. D., Toselli, M., Morselli, D., and Fabbri, P. (2019). “Biobased ketal-diester additives derived from levulinic acid: Synthesis and effect on the thermal stability and thermo-mechanical properties of poly(vinyl chloride),” *ACS Sustainable Chemistry & Engineering* 7(16), 13920-13931.

Sousa, A. F., Coelho, J. F. J., and Silvestre, A. J. D. (2016a). “Renewable-based poly((ether)ester)s from 2,5-furandicarboxylic acid,” *Polymer* 98, 129-135. DOI: 10.1016/j.polymer.2016.06.015

Sousa, A. F., Fonseca, A. C., Serra, A. C., Freire, C. S. R., Silvestre, A. J. D., and Coelho, J. F. J. (2016b). “New unsaturated copolyesters based on 2,5-furandicarboxylic acid and their crosslinked derivatives,” *Polymer Chemistry* 7(5), 1049-1058. DOI: 10.1039/c5py01702e

Sousa, A. F., Guigo, N., Pozycka, M., Delgado, M., Soares, J., Mendonca, P. V., Coelho, J. F. J., Sbirrazzuoli, N., and Silvestre, A. J. D. (2018). “Tailored design of renewable copolymers based on poly(1,4-butylene 2,5-furandicarboxylate) and poly(ethylene glycol) with refined thermal properties,” *Polymer Chemistry* 9(6), 722-731. DOI: 10.1039/c7py01627a

Sousa, A. F., Matos, M., Freire, C. S. R., Silvestre, A. J. D., and Coelho, J. F. J. (2013). “New copolyesters derived from terephthalic and 2,5-furandicarboxylic acids: A step forward in the development of biobased polyesters,” *Polymer* 54(2), 513-519. DOI: 10.1016/j.polymer.2012.11.081

Sousa, A. F., Vilela, C., Fonseca, A. C., Matos, M., Freire, C. S. R., Gruter, G.-J. M., Coelho, J. F. J., and Silvestre, A. J. D. (2015). “Biobased polyesters and other polymers from 2,5-furandicarboxylic acid: A tribute to furan excellency,” *Polymer Chemistry* 6(33), 5961-5983. DOI: 10.1039/c5py00686d

Sukhawipat, N., Saetung, N., Pilard, J. F., Bistac, S., and Saetung, A. (2018). “Synthesis and characterization of novel natural rubber based cationic waterborne polyurethane effect of emulsifier and diol class chain extender,” *Journal of Applied Polymer Science* 135(3). DOI: 10.1002/app.45715

Tavener, S., Hardy, J., Hart, N., and Goddard, A. (2003). “Teaching green chemistry: From lemons to lemonade bottles,” *Green Chemistry* 5(3), G46-G48. DOI: 10.1039/b305233h

Terzopoulou, Z., Karakatsianopoulou, E., Kasmi, N., Majdoub, M., Papageorgiou, G. Z., and Bikiaris, D. N. (2017a). “Effect of catalyst type on recyclability and decomposition mechanism of poly (ethylene furanoate) biobased polyester,” *Journal of Analytical and Applied Pyrolysis* 126, 357-370. DOI: 10.1016/j.jaap.2017.05.010

Terzopoulou, Z., Kasmi, N., Tsanaktsis, V., Doulakas, N., Bikiaris, D. N., Achilias, D. S., and Papageorgiou, G. Z. (2017b). “Synthesis and characterization of bio-based polyesters: Poly (2-methyl-1,3-propylene-2,5-furanoate), poly (isosorbide-2,5-

furanoate), poly (1,4-cyclohexanedimethylene-2,5-furanoate),” *Materials* 10(7), 801. DOI: 10.3390/ma10070801

Terzopoulou, Z., Tarani, E., Kasmi, N., Papadopoulos, L., Chrissafis, K., Papageorgiou, D. G., Papageorgiou, G. Z., and Bikiaris, D. N. (2019). “Thermal decomposition kinetics and mechanism of in-situ prepared bio-based poly(propylene 2,5-furan dicarboxylate)/graphene nanocomposites,” *Molecules* 24(9). DOI: 10.3390/molecules24091717

Terzopoulou, Z., Tsanaktsis, V., Nerantzaki, M., Achilias, D. S., Vaimakis, T., Papageorgiou, G. Z., and Bikiaris, D. N. (2016a). “Thermal degradation of biobased polyesters: kinetics and decomposition mechanism of polyesters from 2,5-furandicarboxylic acid and long-chain aliphatic diols,” *Journal of Analytical and Applied Pyrolysis* 117, 162-175. DOI: 10.1016/j.jaap.2015.11.016

Terzopoulou, Z., Tsanaktsis, V., Nerantzaki, M., Papageorgiou, G. Z., and Bikiaris, D. N. (2016b). “Decomposition mechanism of polyesters based on 2,5-furandicarboxylic acid and aliphatic diols with medium and long chain methylene groups,” *Polymer Degradation and Stability* 132, 127-136. DOI: 10.1016/j.polymdegradstab.2016.03.006

Tomar, N., and Maiti, S. N. (2008). “Mechanical properties and morphology of PBT/FE blends,” *Journal of Polymer Research* 15(1), 37-45.DOI:10.1007/s10965-007-9142-6

Tomar, N., and Maiti, S. N. (2010a). “Mechanical properties of mica-filled PBT/ABAS composites,” *Journal of Applied Polymer Science* 117(2), 672-681. DOI: 10.1002/app.30171

Tomar, N., and Maiti, S. N. (2007). “Mechanical properties of PBT/ABAS blends,” *Journal of Applied Polymer Science* 104(3), 1807-1817. DOI: 10.1002/app.25831

Tomar, N., and Maiti, S. N. (2010b). “Melt rheological properties of PBT/ABAS/Mica composites,” *Polymer-Plastics Technology and Engineering* 49(6), 617-623. DOI: 10.1080/03602551003664545

Tsanaktsis, V., Papageorgiou, D. G., Exarhopoulos, S., Bikiaris, D. N., and Papageorgiou, G. Z. (2015a). “On the crystallization and polymorphism of poly(ethylene furanoate),” *Crystal Growth & Design* 15(11), 5505-5512. DOI: 10.1021/acs.cgd.5b01136.

Tsanaktsis, V., Vouvoudi, E., Papageorgiou, G. Z., Papageorgiou, D. G., Chrissafis, K., and Bikiaris, D. N. (2015b). “Thermal degradation kinetics and decomposition mechanism of polyesters based on 2,5-furandicarboxylic acid and low molecular weight aliphatic diols,” *Journal of Analytical and Applied Pyrolysis* 112, 369-378. DOI: 10.1016/j.jaap.2014.12.016

van Berkel, J. G., Guigo, N., Visser, H. A., and Sbirrazzuoli, N. (2018). “Chain structure and molecular weight dependent mechanics of poly(ethylene 2,5-furandicarboxylate) compared to poly(ethylene terephthalate),” *Macromolecules* 51(21), 8539-8549. DOI: 10.1021/acs.macromol.8b01831

van Es, D. S. (2013). “Rigid biobased building blocks: current developments and outlook,” *Journal of Renewable Materials* 1(1), 61-72. DOI: 10.7569/JRM.2012.634108

Vannini, M., Marchese, P., Celli, A., and Lorenzetti, C. (2015). “Fully biobased poly(propylene 2,5-furandicarboxylate) for packaging applications: excellent barrier properties as a function of crystallinity,” *Green Chemistry* 17(8), 4162-4166. DOI: 10.1039/c5gc00991j

Wang, G. Q., Jiang, M., Zhang, Q., Wang, R., Qu, X. L., and Zhou, G. Y. (2018a). “Biobased multiblock copolymers: Synthesis, properties and shape memory behavior of poly(hexamethylene 2,5-furandicarboxylate)-b-poly(ethylene glycol),” *Polymer Degradation and Stability* 153, 292-297. DOI: 10.1016/j.polymdegradstab.2018.04.034

Wang, G. Q., Jiang, M., Zhang, Q., Wang, R., Qu, X. L., and Zhou, G. Y. (2018b). “Poly(hexamethylene 2,5-furandicarboxylate) copolyesters containing phosphorus: Synthesis, crystallization behavior, thermal, mechanical and flame retardant properties,” *Polymer Degradation and Stability* 153, 272-280. DOI: 10.1016/j.polymdegradstab.2018.05.010

Wang, G. Q., Jiang, M., Zhang, Q., Wang, R., and Zhou, G. Y. (2017a). “Biobased multiblock copolymers: Synthesis, properties and shape memory performance of poly(ethylene 2,5-furandicarboxylate)-b-ly(ethylene glycol),” *Polymer Degradation and Stability* 144, 121-127. DOI: 10.1016/j.polymdegradstab.2017.07.032

Wang, J. G., Liu, X. Q., Zhang, Y. J., Liu, F., and Zhu, J. (2016). “Modification of poly(ethylene 2,5-furandicarboxylate) with 1,4-cyclohexanedimethylene: Influence of composition on mechanical and barrier properties,” *Polymer* 103, 1-8. DOI: 10.1016/j.polymer.2016.09.030

Wang, J. G., Liu, X. Q., Zhu, J., and Jiang, Y. H. (2017b). “Copolyesters based on 2,5-furandicarboxylic acid (FDCA): Effect of 2,2,4,4-tetramethyl-1,3-cyclobutanediol units on their properties,” *Polymers* 9(9). DOI: 10.3390/polym9090305

Wang, J. G., Sun, L. Y., Shen, Z. S., Zhu, J., Song, X. L., and Liu, X. Q. (2019). “Effects of various 1,3-propanediols on the properties of poly(propylene furandicarboxylate),” *ACS Sustainable Chemistry & Engineering* 7(3), 3282-3291. DOI: 10.1021/acssuFig.ng.8b05288

Wang, X. S., Wang, Q. Y., Liu, S. Y., and Wang, G. Y. (2018c). “Biobased copolyesters: synthesis, structure, thermal and mechanical properties of poly(ethylene 2,5-furandicarboxylate-co-ethylene 1,4-cyclohexanedicarboxylate*,” Polymer Degradation and Stability* 154, 96-102. DOI: 10.1016/j.polymdegradstab.2018.05.026

Wu, B., Xu, Y., Bu, Z., Wu, L., Li, B.-G., and Dubois, P. (2014). “Biobased poly(butylene 2,5-furandicarboxylate) and poly(butylene adipate-co-butylene 2,5-furandicarboxylate)s: From synthesis using highly purified 2,5-furandicarboxylic acid to thermo-mechanical properties,” *Polymer* 55(16), 3648-3655. DOI: 10.1016/j.polymer.2014.06.052

Wu, N. J., Yu, J. H., Lang, W. C., Ma, X. B., and Yang, Y. (2019). “Flame retardancy and toughness of poly(lactic acid)/GNR/SiAHP composites,” *Polymers* 11(7). DOI: 10.3390/polym11071129

Xie, H. Z., Wu, L. B., Li, B. G., and Dubois, P. (2018). “Biobased poly(ethylene-co-hexamethylene 2,5-furandicarboxylate) (PEHF) copolyesters with superior tensile properties,” *Industrial & Engineering Chemistry Research* 57(39), 13094-13102. DOI: 10.1021/acs.iecr.8b03204

Xie, H. Z., Wu, L. B., Li, B. G., and Dubois, P. (2019). “Modification of poly(ethylene 2,5-furandicarboxylate) with biobased 1,5-pentanediol: significantly toughened copolyesters retaining high tensile strength and O_2 barrier property,” *Biomacromolecules* 20(1), 353-364. DOI: 10.1021/acs.biomac.8b01495

Yu, Z., Zhou, J., Cao, F., Wen, B., Zhu, X., and Wei, P. (2013). “Chemosynthesis and characterization of fully biomass-based copolymers of ethylene glycol, 2,5-furandicarboxylic acid, and succinic acid,” *Journal of Applied Polymer Science* 130(2), 1415-1420. DOI: 10.1002/app.39344

Zhang, C., Deng, H., Kenderes, S. M., Su, J. W., Whittington, A. G., and Lin, J. (2019a). "Chemically interconnected thermotropic polymers for transparency-tunable and impact-resistant window," *ACS Applied Materials & Interfaces* 11(5), 5393-5400. DOI: 10.1021/acsami.8b19740

Zhang, J. H., Li, J. K., Tang, Y. J., Lin, L., and Long, M. L. (2015). "Advances in catalytic production of bio-based polyester monomer 2,5-furandicarboxylic acid derived from lignocellulosic biomass," *Carbohydrate Polymers* 130(10), 420-428. DOI: 10.1016/j.carbpol.2015.05.028

Zhang, J. H., Liang, Q. D., Xie, W. X., Peng, L. C., He, L., He, Z. B., Chowdhury, S. P., Christensen, R., and Ni, Y. H. (2019b). "An eco-friendly method to get a bio-based dicarboxylic acid monomer 2,5-furandicarboxylic acid and its application in the synthesis of poly(hexylene 2,5-furandicarboxylate) (PHF)," *Polymers* 11(2). DOI: 10.3390/polym11020197

Zhou, H., Xu, H. H., and Liu, Y. (2019). "Aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over Co/Mn-lignin coordination complexes-derived catalysts," *Applied Catalysis B-Environmental* 244, 965-973. DOI: 10.1016/j.apcatb.2018.12.046

Zhou, W., Wang, X., Yang, B., Xu, Y., Zhang, W., Zhang, Y., and Ji, J. (2013). "Synthesis, physical properties and enzymatic degradation of bio-based poly(butylene adipate-co-butylene furandicarboxylate) copolyesters," *Polymer Degradation and Stability* 98(11), 2177-2183. DOI: 10.1016/j.polymdegradstab.2013.08.025

Zhu, J., Cai, J., Xie, W., Chen, P.-H., Gazzano, M., Scandola, M., and Gross, R. A. (2013). "Poly(butylene 2,5-furan dicarboxylate), a biobased alternative to PBT: Synthesis, physical properties, and crystal structure," *Macromolecules* 46(3), 796-804. DOI: 10.1021/ma3023298

Zou, G. J., Wang, P. L., Feng, W. T., Ren, Z. L., and Ji, J. H. (2018). "Poly(decamethylene terephthalamide) copolymerized with long-chain alkyl dodecanedioic acid: Toward bio-based polymer and improved performances," *Journal of Applied Polymer Science* 135(31). DOI: 10.1002/app.46531

Article submitted: November 1, 2019; Peer review completed: January 23, 2020;
Revisions accepted: February 10, 2020; Published: February 14, 2020.
DOI: 10.15376/biores.15.2.Zhang