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Review

Production of bio-based 2,5-furan dicarboxylate polyesters: Recent progress and critical aspects in their synthesis and thermal properties

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Polymers based on 2,5-furandicarboxylic acid (2,5-FDCA), consist a new class of alipharomatic polyesters that can be prepared from monomers derived straight from renewable resources like furfural and hydroxymethylfurfural (HMF). For this reason, this class of materials has recently gained high interest. This review highlights the progress and fundamental aspects for the synthesis of bio-based 2,5-FDCA polyesters and their thermal properties. During time, several techniques, catalysts and conditions have been suggested in the literature for the synthesis of furan-based polyesters and are presented here. Some problems associated with the coloration and successful syntheses of polyesters with high molecular weights are thoroughly discussed in the current review. Moreover, the thermal properties of the resulting materials have been presented in detail, as they constitute some of the most important parameters for use and processing. Finally, the preparation and

Abbreviations: AA, adipic acid; ABA, 4-acetoxybenzoic acid; BG, 1,4 butanediol; BHEFDC, bis(hydroxyethyl)-2,5-furandicarboxylate; BHFD, bis-hydroxyalkylene furan dicarboxylate; c(BF)n, cyclic butylene 2,5-FDCA oligoesters; c(EF)n, cyclic ethylene 2,5-FDCA oligoesters; CALB, *Candida antarctica* Lipase B; COEs, cyclic oligoesters; DABP, 4,4′-diacetoxybiphenyl; DAI, 1,4:3,6-dianhydro-L-iditol; DAM, 1,4:3,6-dianhydro-D-mannitol; DAS, 1,4:3,6-dianhydro-D-sorbitol; DCM, dichloromethane; DI, polydispersity index; DMF, dimethyl furan; DMF, dimethylformamide; DMFD, dimethyl-2,5-furan dicarboxylate ester; DMSO, dimethylsulfoxide; DSC, differential scanning calorimetry; EG, ethylene glycol; FDCA, furandicarboxylic acid; GHG, greenhouse gas; GPC, gel permeation chromatography; HMF, hydroxymethylfurfural; LC, liquid crystalline; LC/TOF-MS, liquid chromatography/time-of-flight mass spectrometry; Mt, metric tonnes; Mw, molecular weight; NMR, nuclear magnetic resonance; NREU, non-renewable energy use; PAA, poly(adipic acid); PBAF, poly-(butylene adipate-*co*-butylene furandicarboxylate); PBF, poly(butylene 2,5-furanoate); PBF-PTMG, poly(butylene furandicarboxylate)-*b*-poly-(tetramethylene glycol) copolymers; PBHMF, poly(2,5-furandimethylene-2,5-furandicarboxylate); PBIS, poly(butylene-*co*-isosorbide succinate); PBS, poly(butylene succinate); PBSebF, poly(butylene sebacate-*co*-furanoate); PBSF, poly(butylene succinate-*co*-butylene furandicarboxylate); PBST, poly(butylene succinate-*co*-terephthalate); PBT, poly(butylene terephthalate); PBT, poly(butylene terephthalate); PCL, poly(ε-caprolactone); PDAIF, polyester from 2,5-furandicarboxyl chloride and isoiodide; PDASF, polyester from 2,5-furandicarboxyl chloride and D-isosorbide; PDeF, poly(decylene furanoate); PDMPF, poly (2,2-dimethyl-1,3-propylene furanoate); PDoF, poly(dodecylene furanoate); PE, polyethylene; PEF, poly(ethylene 2,5-furanoate); PEFS, poly(ethylene 2,5-furandicarboxylate-*co*-ethylene succinate); PEN, poly(ethylene napthalate); PET, poly(ethylene terephthalate); PHA, polyhydroxyalkanoate; PHepF, poly(hepthylene furanoate); PHF, poly(hexylene 2,5-furandicarboxylate); PHMBF, poly(1,4-phenylbismethylene-2,5-furandicarboxylate); PHQF, poly(1,4-phenylene-2,5-furandicarboxylate); PHQH, (poly(1,4-phenylene-2,5-furandicarboxylate); PLA, poly(lactic acid); PLGA, polylactide-glycolide; PNF, poly(nonylene furanoate); POF, poly(octylene 2,5-furandicarboxylate); POM, polarized optical microscopy; PPeF, poly(pentylene furanoate); PPF, poly(propylene 2,5-furandicarboxylate); PPN, poly(propylene napthalate); PPT, poly(propylene terephthalate); PTMG, poly(tetramethylene glycol); PTT, poly(trimethylene terephthalate); Py-GC/MS, pyrolysis-gas chromatography/mass spectroscopy; ROP, ring opening polymerization; SSP, solid state polymerization; TBT, tetrabutyl titanate; TCE, tetrachloroethane; TGA, thermogravimetric analysis; THF, tetrahydrofuran; TiBO, titanium (IV) *n*-butoxide; TMDSC, temperature-modulated differential scanning calorimetry; UPRs, unsaturated polyester resins; UPs, unsaturated polyesters; WAXS, wide-angle X-ray scattering; φBF, butylene furanicarboxylate unit content.

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Crystallization
Melting
Thermal stability

properties such as biodegradability of several furanoate-based copolymers are also discussed.

Contents

1. Introduction

In recent years, the potential replacement of fossil fuels for the production of appropriate monomers by inexpensive and renewable starting materials such as cellulose, starch, lignin, proteins and vegetable oils is increasingly being explored [1–10], with the aim to develop a more sustainable bio-based economy. The production of polymers from renewable resources is an old practice and the first approach involved the modification of natural polymers. However, this practice is limited today and most efforts are focused on the preparation of bio-based monomers for polymer synthesis. Bioplastics and thermoplastic biopolymers that are either biodegradable or at least partly bio-based, constitute one of the fastest growing markets. The overall sum of 3.5 million tonnes that were produced during 2011 represent a share of 1.5% of the overall construction polymer production, which was almost 235 million tonnes [11]. Current producers of bio-based polymers estimate that production capacity will reach nearly 12 million tonnes by 2020. With an expected total polymer production of about 400 million tonnes in 2020, the bio-based share should be increased to 3%, meaning that bio-based production capacity will grow faster than overall production [12,13]. Regarding the European bioplastics market, it currently represents the 15% of the global production capabilities, which is higher than that of North and South America, but significantly smaller than the one of Asia, which represents the 58.1% [14]. However, the forecasts for 2019 reveal that more than 80% of the bioplastics will be produced in Asia, while Europe will be left with less than 5% of the world production capacity, as a result of austerity and lack of economic and policy measures, which will facilitate the scale up of production of bio-based polymers [14].

Isosorbide, 2,4:3,5-di-O-methylene-D-mannitol, bicyclic diacetalyzed galactaric acid, 2,5-furandicarboxylic acid, citric, 2,3-O-methylene L-threitol, dimethyl 2,3-O-methylene L-threarate, betulin, dihydrocarvone, decalactone, pimaric acid, ricinoleic acid and sebacic acid, are some important monomers derived from biomass, which are used for bio-based polyester manufacturing, consequently, replacing the petrochemical based polyesters used in various fields including packaging, coating, tissue engineering, drug delivery systems and many more [15]. Presently, various essential biomass-based biodegradable polyesters have been used in industrial-biological materials, such as polyhydroxyalkanoate (PHA) [16,17], poly(lactic acid) (PLA) [18,19], poly(glycolic acid) (PGA) and their lactide-glycolide (PLGA) copolymers [20,21], poly(ε-caprolactone) (PCL) [22,23], poly(alkylene succinates) [24–30], poly(alkylene adipates) [31,32] and other aliphatic polyesters [33–35]. In addition, several other thermoplastic polyesters are prepared by biomass-based diols and carboxylic acids, such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and poly(trimethylene terephthalate) (PTT) [36,37].

Extensive research efforts were triggered in 2004 towards the synthesis of bio-based chemicals, when the US Department of Energy published a list of "ten bio-based chemicals" of top priority [38]. 2,5-FDCA, which shows good potential as a replacement for terephthalic acid, a widely used component in various polyesters such as PET and poly(butylene terephthalate) (PBT), was among them. Recently, the production of furan derivatives from sugars has become exciting in chemistry and