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Review

Recent Trends in the Synthesis of Monomers for Furanoate Polyesters and Their Nanocomposites' Fabrication as a Sustainable Packaging Material

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Abstract: Furanoate polyesters are an extremely promising new class of materials for packaging applications, particularly furanoate-based nanocomposites, which have gained a high interest level in research and development in both academia and industries. The monomers utilised for the synthesis of furanoate-based polyesters were derived from lignocellulosic biomass, which is essential for both eco-friendliness and sustainability. Also, these polyesters have a lower carbon footprint compared to fossil-based plastics, contributing to greenhouse gas reduction. The furanoate-based nanocomposites exhibit enhanced performance characteristics, such as high thermal stability, excellent mechanical strength, superior barrier resistance, and good bacteriostatic rate, making them suitable for a wide range of industrial applications, especially for food-packaging applications. This paper reviews the recent trends in the synthesis routes of monomers, such as the various catalytic activities involved in the oxidation of 5(hydroxymethyl)furfural (HMF) into 2,5-furandicarboxylic acid (FDCA) and its ester, dimethyl furan-2,5-dicarboxylate (DMFD). In addition, this review explores the fabrication of different furanoate-based nanocomposites prepared by in situ polymerization, by melt mixing or solvent evaporation methods, and by using different types of nanoparticles to enhance the overall material properties of the resulting nanocomposites. Emphasis was given to presenting the effect of these nanoparticles on the furanoate polyester's properties.

Keywords: 2,5-furandicarboxylic acid; dimethyl furan-2,5-dicarboxylate; furanoate polyesters; furanoate nanocomposites; thermal properties; mechanical properties; antibacterial properties; sustainable packaging

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1. Introduction

Chemical–synthetic polymers are bio-based polymers made from molecules obtained from natural resources, or by breaking down bio-based macromolecules using a combination of chemical and biological techniques [1]. These biobased polymers are produced mainly from the polysaccharide biomass, protein biomass, and lipid and wax biomass. To reduce greenhouse gas emissions and use fewer petrochemicals, sustainable or green packaging prioritises (1) materials derived from renewable resources or recycled materials; (2) lighter and thinner packaging made with energy- and cost-efficient processes; and (3) materials that are recyclable, compostable, biodegradable, or reusable, to minimise their negative environmental effects [2]. However, the mechanical properties of these biobased polymers are impacted by their inherent drawbacks, which include low water vapour barriers and high moisture sensitivity. The furanoate polyesters have a significant advantage

compared to other biobased polymers in terms of cost-effectiveness, lower environmental impact (such as lower carbon footprint and recyclability), efficient and better properties (mechanical, barrier, and thermal) than widely used petroleum derived polymers, and their practical processability [3].

The key monomer to produce furanoate polyesters is 2,5-furandicarboxylic acid (FDCA), which is generally produced by dehydration of polysaccharides and biomass feedstock (lignocellulosic biomass) to 5-hydroxymethylfurfural (5-HMF), followed by catalytic oxidation. There are numerous techniques that have been proposed for oxidising 5-HMF to FDCA, such as use of homogeneous (transition metal salts) and heterogeneous (precious metal) catalysts in water or organic solvents. However, using potent oxidizers like HNO_3, N_2O_4, and $KMnO_4$ is more effective in lab-scale and low-tonnage productions [4]. From a structural perspective of FDCA, a core furan ring is joined to two carboxylic acid groups at an angle of 129.4°. These structural features of FDCA can help to achieve carbon neutrality, and they provide several advantages over its predecessor TPA, including improved thermal stability and higher gas barrier qualities [5]. FDCA can be used to produce furanoate polyesters, mainly PEF, PBF and poly(propylene furanoate) (PPF), polyamides, and polyurethanes, as well as coating resins, plasticisers, and other chemicals, for use in textiles and packaging materials. Plans for a pilot-scale FDCA factory can be found in the Avantium and Stora Enso companies. Additionally, Petrobras and Novamont have made attempts to generate FDCA commercially. AVA Biochem made the announcement in 2016 that it will begin producing FDCA as well [6].

Besides FDCA, dimethyl-furan-2,5-dicarboxylate (DMFD), which has excellent solubility in most common solvents and a low boiling point, can also be used to produce polyesters. Above all, it can prevent FDCA from being decarboxylated at high temperatures. These benefits will help DMFD's prospective uses in the chemical, energy, and materials sectors [7]. Companies like DuPont and Archer Daniels Midland developed technology for converting fructose and methanol into DMFD, and this process is claimed to be less expensive than the processes for FDCA production [8]. However, the utilisation of precious metals, which have been found to have a good 5-(hydroxymethyl)furfural (HMF) oxidative esterification capacity, is the primary cause of the bottleneck issues in synthesising DMFD. However, their industrial applicability is hindered by their expensive cost. In the catalytic process, an extra base is needed; this goes against the idea of environmentally benign, green concepts [9].

Among the bio-based polymers that are classified as chemical–synthetic polymers, furanoate-based polyesters such as poly(ethylene furanoate) (PEF), poly(propylene,furanoate) (PPF), poly(butylene furanoate) (PBF), poly(pentylene furanoate), poly(hexamethylene furanoate) (PHF), poly(decylene furanoate) (PDeF), poly(dodecylene furanoate) (PDoF), and other poly(alkylene 2,5 furan-dicarboxylate)s (PAFs) have been researched extensively in the last decade, due to their excellent thermal properties, mechanical properties, and superior barrier properties for various industrial applications. PEF has excellent mechanical, thermal, and gas barrier properties in comparison to the widely used oil-derived plastics, such as poly(ethylene terephthalate) (PET). In comparison to PET, PEF's O_2 permeability drops by 5–11, its CO_2 permeability drops by 2–19 times, and its water sorption capacity has an increase of $\sim$1.8×. Brugess et al. made a detailed study on the O_2 permeability, CO_2 permeability, and water sorption properties of PEF compared to PET using different techniques. The author observed the reduced O_2 sorption values of PEF (0.094 ccSTP/ccPoly·atm) compared to the values of PET (0.102 ccSTP/ccPoly·atm), due to a decrease in the PEF chain segment mobility due to furan ring flipping obstruction [10]. In a similar study, the large reduction in CO_2 permeability of PEF 19× at 1 atm was observed in compared to PET. The increase in the solubility of PEF with CO_2 was observed, due to its higher affinity to polar ring [11]. In another work, the author observed higher equilibrium water uptake in PEF due to higher affinity between the water and polar ring in PEF. PEF exhibits a sorption value of 787 $\pm$ 110 (cm^3 STP/cm^3 Poly·atm) compared to PET's value of 290 $\pm$ 140 (cm^3 STP/cm^3 Poly·atm) [12]. Furthermore, it was estimated that the production of PEF

would require 45–55% less non-renewable energy use (NREU) and produce 45–55% less greenhouse gas emissions (GHGs) than PET [13]. These properties make PEF a suitable substituent for oil-derived plastics in food-packaging applications. It has gained substantial attraction from industries around the world, such as Avantium NV (Netherlands), AVA Biochem (Switzerland), Toyobo Co., Ltd. (Japan), Danone (France), Eastman (US), and others, for packaging, fibre and textiles, electronics and electrical, and pharmaceutical applications [14].

In comparison to their homologues based on ethylene–glycol or 1,4-butanediol, the polymers made from 1,3-propanediol have lower melting temperatures, less crystallinity and higher biodegradation rates, due to the odd number of methylene units in the diol segment. Recently, PPF has gained considerable attention, mainly from the packaging industries due to its high gas barrier properties, and from academia due to the production of 1,3 propanediol from renewable resources [15]. PBF is a promising bio-based polyester derived from renewable resources, specifically, synthesised from 2,5-furandicarboxylic acid (FDCA) and 1,4-butanediol. Its potential for packaging applications is underpinned by its favourable mechanical and thermal properties, although challenges remain regarding its crystallisation rate and biodegradability compared to other polyesters like poly(lactic acid) (PLA) and PET. Their lower ability to crystallise and lower hydrophilicity make them suitable to produce films and bottles for soft drinks via compression mouldings. Their overall properties help to increase the shelf life of foods and beverages, making them suitable for food-packaging applications [16,17].

In recent years, there has been a lot of interest in the advancement of study and creation of innovative technologies related to the manufacturing of "active," "smart," or "intelligent" food packaging. Active packaging systems, as opposed to conventional packaging, are designed to interact with the food. They can absorb unwanted substances like moisture, carbon dioxide, oxygen, ethylene, and odours, or they can act on the surface of the material at the interface with the food, releasing substances that aid in food preservation by preventing oxidation and the growth of microorganisms. Recent developments in natural antioxidants, nanoparticles, and biobased and biodegradable polymer nanocomposites used for food-packaging applications are displayed in Figure 1 [18]. Generally, polymer nanocomposites are fabricated by the intercalation method, in situ polymerisation, the sol–gel method, and direct mixing of a polymer and nanofillers [19].

Bio-nanocomposites are novel, highly effective, lightweight, and environmentally benign materials that may be substituted in place of conventional, nonbiodegradable plastic packaging. While biodegradable and non-toxic, polysaccharides like starch, chitosan, and carboxymethyl cellulose do not harm the environment, but their low water resistance, poor mechanical qualities, and weak antibacterial activity lower their usage in food-packaging materials. Consequently, nanoparticles may be used to enhance their antibacterial activity, thermal, mechanical, and gas barrier capabilities [20].

Nanoparticles such as carbon nanotubes (CNTs), fullerenes, carbon black, nano clays, nanocrystals, and metallic nanoparticles (such as s Ag, Au, Pt, ZnO, and metal oxides such as copper oxide (CuO), SiO_2, TiO_2, aluminium oxide(alumina) (Al_2O_3), and iron oxides (Fe_3O_4, and Fe_2O_3)) are commonly used for the nanocomposite's fabrication. The incorporation of these nanoparticles into the polymer matrix improves the thermal, chemical, mechanical, optical, magnetic, and electrical properties to a much greater extent than conventional composites [19]. Similarly, different types of nanoparticles were incorporated into the furanoate polyesters, to fabricate their respective nanocomposites with aim of improving the thermal, crystallinity, mechanical, antimicrobial, and antioxidant properties, to expand their usage in a broad range of applications, especially in the field of food packaging [20]. Furanoate polyesters are amorphous in nature and have higher glass transition temperatures, higher transparency, strong barriers, and mechanical strength than the product's targeted qualities, especially for packaging applications [21]. PEF, PPF, and PBF were used commonly in food and beverage packaging, such as frozen food trays' manufacturing, beverages' packaging, and bottle manufacturing. The PBF-based copolymers were used for

processed fruits and vegetables under modified atmospheric packaging. Poly(neopentyl glycol furanoate) (PNF) is a member of the furanoate-based polyester family used in the packaging of low-moisture foods, fatty foods, alcoholic beverages, and acidic foods [22]. It must be considered that the migration of nanoparticles from food packaging into food products in specific concentrations might be the cause of toxicity. Thus, it is important to integrate them into materials in a way to avoid toxicity. However, regarding the safety of bionanomaterials, less information is currently known about the potential for migration and the effects of other bio-based nanomaterials, such as reinforcing agents or nanofillers. The European Union (EU) and the U.S. Food and Drug Administration (FDA) focus on regulating the use of nanomaterials in current food-packaging materials, and the development of new nanocomposite materials for food packaging must comply with these requirements [23].

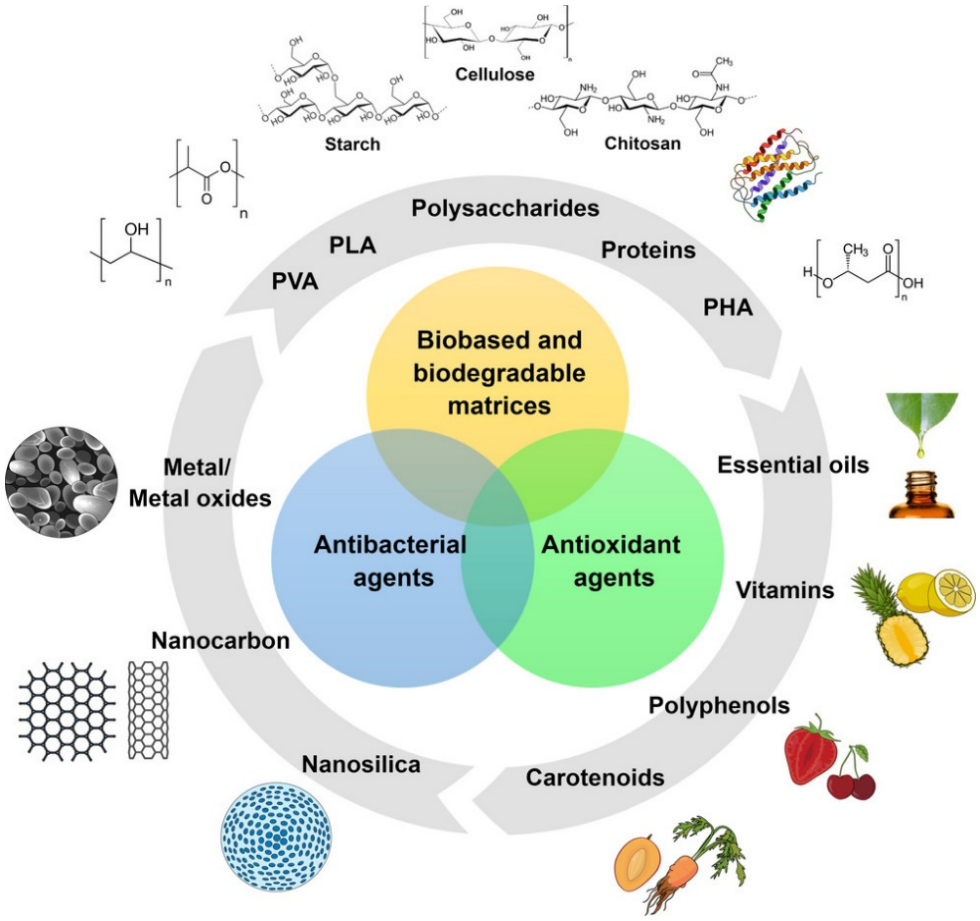


Figure 1. Scheme of natural antioxidants, nanoparticles, and biobased and biodegradable polymer nanocomposites for packaging applications. Adapted from ref. [18].

This paper reviews the recent trends in the synthesis routes of monomers (such as FDCA and its ester DMFD) used for the synthesis of furanoate polyesters and their nanocomposites. Various catalytic activities have been explored which are involved in the oxidation of HMF into FDCA and its ester DMFD. In addition, furanoate-based nanocomposites fabricated using different types of nanoparticles to improve the overall material properties (thermal, mechanical, antimicrobial, and antioxidant) of the nanocomposites has been studied toward packaging applications. These furanoate-based nanocomposites could potentially be used as a replacement for oil-derived polymers-based nanocomposites in packaging applications.

2. Recent Trends in the Synthesis of Monomers for Furanoate Polyesters

2.1. Synthesis Routes of FDCA

According to recent research, several catalyst types have been used to synthesise 2,5-FDCA employing a variety of methods. The hybrid catalysts, such as glucose–fructose oxidoreductase (GFOR) and gluconolactonase (GL), enzymes of the family of oxygen-dependent glucose oxidases or glucose dehydrogenases, enzymes of the family of uronate dehydrogenases, and metallic nanoreactors such as gold nanoparticles, were used in the conversion step. The 2,5-FDCA synthesis based on the dehydration of glucose derivatives (glucaric acid) by applying new-engineered nano catalysts (hybrid catalysts) helps to skip the highly expensive isomerisation step [24].

The synthesising route of FDCA from renewable furfural using conventional palladium catalysts (Pd (II)) proceeds to obtain >99% FDCA yield based on HPLC analysis. Increasing the catalytic effectiveness is observed by employing one equivalent of PPh_3 (in relation to the Pd (II) pre-catalyst) as sacrificial additives [25]. With four processes of successive bromination, esterification, carbonylation, and hydrolysis, furoic acid may be converted practically to 2,5-FDCA with a total yield of 65% and an isolated yield of more than 80% in each step. The carbonylation of ethyl 5-bromo-furan-2-carboxylate, which is a crucial step in the scale-up synthesis, is especially well preserved at 90% isolated yield when Pd is catalysed [26]. In another study, using a one-pot two-step procedure, under aqueous reaction conditions, the oxidation of HMF produced an 85% yield, while the dehydration of fructose and subsequent oxidation produced a 64% yield of pure FDCA utilising a Pd/CC catalyst and molecular O_2 as the oxidising agent. The Pd/CC catalyst is easily recoverable, reusable, and stable [27]. Manganese ferrite nanoparticles ($MnFe_2O_4$) were also found to be a most active and selective catalyst, which produces an 85% yield of FDCA in 5 h at 100 °C. The fluctuating oxidation state of manganese is the cause of the $MnFe_2O_4$ catalyst's greater activity. Comparing the $MnFe_2O_4$ catalyst and t-Butyl hydroperoxide (TBHP) oxidant combination to other documented FDCA synthesis techniques, the combination uses less time and energy [28].

Using the one-pot synthesis route, the FDCA was synthesised using fructose as the starting material and acetic acid (HOAc) as the solvent. Initially, the fructose was dehydrated catalytically to produce HMF and 5-acetoxymethylfurfural (AMF), which were then oxidised further to FDCA by air over homogeneous Co/Mn/Br catalysts in HOAc. Under ideal reaction conditions, a 50% total yield of HMF and AMF and a 35% yield of FDCA with a purity of 99.1% were obtained with a 100 wt. % conversion of fructose [29]. A two-step method is employed to synthesise FDCA directly from fructose without HMF separation, using Amberlyst-15 and Platinum Catalysts (Pt) supported with carbon (5 mol % Pt) catalysts. Initially, low-concentration fructose was dehydrated in Dimethyl sulfoxide (DMSO) with the aid of an Amberlyst-15 catalyst, to produce HMF with a 97.1% yield. Subsequently, the HMF that was produced in situ was subjected to atmospheric pressure oxygen oxidation in a 3/1 (w/w) alkaline Potassium carbonate (K_2CO_3) H_2O/DMSO medium. Pt/C catalysed the reaction, which resulted in a 91% yield of FDCA at 100 °C for 10 h [30]. The study on the synthesis of 2,5-FDCA by direct carboxylation of the biomass-derived 2-furoic acid (FA) and CO_2 promoted by low-cost (K_2CO_3) demonstrated the feasibility of the reaction, which was highly dependent on the temperature. The addition of potassium formate (HCOOK) in the K_2CO_3 system improved the yield of FDCA greatly, lowered the melting temperature of the reaction system from 386 °C to 200 °C, and reduced the activation energy barrier [31].

In another work, Pt catalysts were used in the liquid phase air oxidation of HMF to FDCA. The FDCA produced up to a 96% yield over Pt/c-Aluminium oxide (Al_2O_3) under ideal reaction conditions, which included a stepwise rise in the reaction temperature (75 and 140 °C for 12 h each) and 1 bar of oxygen pressure [32]. Gold (Au) catalysts were also used as a catalytic system for the aerobic oxidation of HMF into FDCA. It provides superior resistance to O_2, making them more stable and selective when compared to Pt and Pd catalysts. Nevertheless, in certain instances, it is also discovered that the intermediates or byproducts deactivate the Au catalysts. Due to the alloying effect, the addition of another metal (such as Pd, Cu, or Pt) to the Au results in bimetallic alloy catalysts that, typically, exhibit higher catalytic activity and stability than monometallic Au catalysts [33]. Au/Ceric oxide (CeO_2) was used as a catalyst, and O_2 was used as a green oxidant for fast and continuous conversion of HMF into 2,5-FDCA by using a micro packed-bed reactor. The improved gas–liquid mass transfer efficiency was achieved in just 41 s of a 100 wt. % HMF conversion and 90% FDCA selectivity. It provides a fresh opportunity to improve heterogeneous processes with limited mass transfer [34].

A unique method for the direct conversion of fructose into FDCA was studied via the one-pot synthesis route. Butyl methylimidazolium chloride ([Bmim]Cl) was used as a solvent with Amberlyst-15 and the non-noble metal (Fe-Zr-O) as a catalyst, with the goal of reducing the high prices of the starting material and catalysts. A 46.4% FDCA yield with a 100 wt. % of fructose conversion was achieved in base-free conditions [35]. $ZnFe_{1.65}Ru_{0.35}O_4$, a newly synthesised and effective magnetic catalyst, enables the aerobic oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfuran (DFF) or FDCA. It was established that the catalyst's active sites contain Ruthenium (Ru) (III) species. The reaction in water (H_2O)/DMSO (1:2, *v*/*v*) at 130 °C for 16 h produced the maximum FDCA yield (91.2%) with complete 100 wt. % of HMF conversion [36]. In most of the cases, DMSO/H_2O was selected as an effective medium. The ability of the DMSO/H_2O-mixed system to stabilise HMF in an alkaline environment permits effective HMF oxidation at high concentrations [37]. A different mixed system (2 equiv. sodium hydrogen carbonate ($NaHCO_3$), 3 h, 4 MPa O_2, and 140 °C) was also chosen over commercial Ru for the efficient synthesis of 2,5-FDCA via the two-step facial method. The HMF was converted about 10–25 wt. % in 1,4-dioxane/H_2O. The good stability of HMF in 1,4-dioxane/H_2O improves the superoxide radicals and leads to high FDCA yield (79%) at a high HMF concentration [38].

Greener synthesis of 2,5-FDCA from HMF was studied through microbial biotransformation and enzymatic biotransformation. The mechanism of biotransformation of HMF into FDCA in bacteria is displayed in Figure 2. The one-pot synthesis of FDCA from HMF was achieved using *Comamonas testosteroni* SC1588 cells and a laccase-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) system. At neutral pH, the cells converted HMF to 5-hydroxymethyl-2-furancarboxylic acid (HMFCA). The reaction mixture's pH was moved into an acidic range by the HMFCA production, which promoted the laccase–TEMPO catalytic oxidation. In just 36 h, 87% of the FDCA yield was produced, with a productivity of about 0.4 g/L h [39]. A novel whole-cell biocatalyst was produced for the sacrificial substrate-free cascade catalytic oxidation of 5-HMF to FDCA. The biocatalyst was built by co-expressing vanillin dehydrogenase (VDH_1) and HMF/furfural oxidoreductase (HmfH) in *Escherichia coli*. These biocatalysts made it possible to synthesise FDCA efficiently with a 96% yield under pH-controlled conditions. Additionally, FDCA was produced at a productivity of around 0.4 g/L h on a gram scale [40]. The commonly occurring process of hydrolysing glucose, dehydrating it, and then forming HMF followed by biological synthesis of FDCA using microorganisms and enzymes is illustrated in Figure 2.

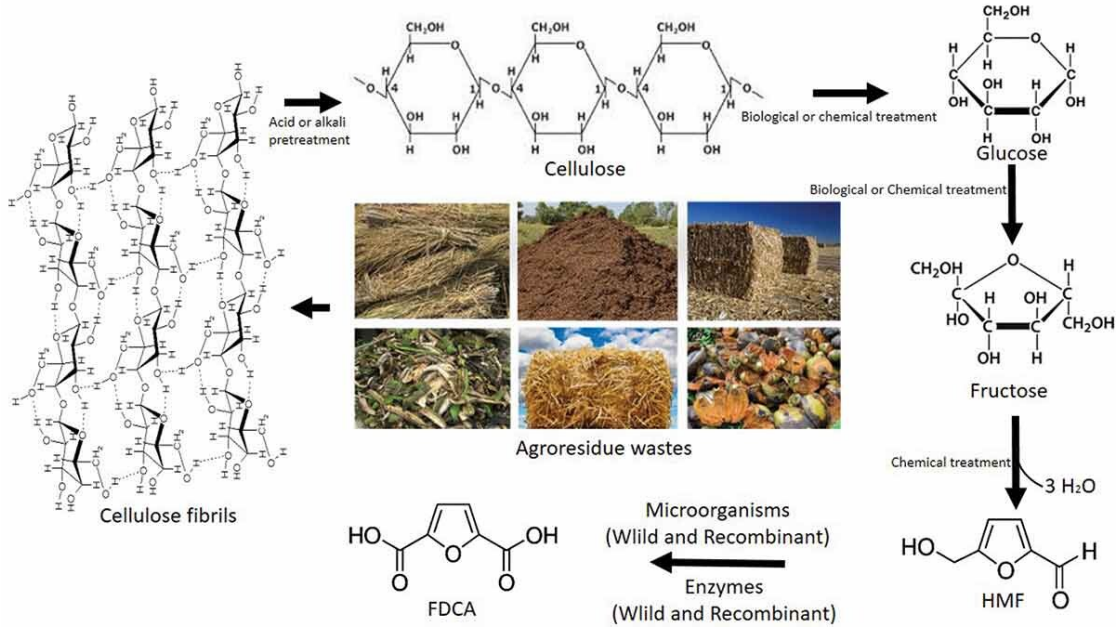


Figure 2. Conversion of biomass or agroresidue wastes into HMF by chemical catalysis, coupled by the biological synthesis of FDCA. Reproduced from ref. [41].

Using a TEMPO/laccase system in conjunction with *Pseudomonas putida* KT2440, an effective and highly selective biocatalytic method was used to produce FDCA from HMF. The selective oxidation of the hydroxymethyl group of HMF by TEMPO/laccase resulted in the main product 5-formyl-2-furancarboxylic acid, which *P. putida* KT2440 then oxidised to FDCA. By adjusting the reaction conditions, it was possible to achieve strong HMF conversion (100%) and excellent FDCA selectivity (100%) in less than 50 h [42]. An engineered *Raultella ornitholytica* BF 60 from 35 g/L HMF in a sodium phosphate buffer helped in the maximum FDCA production, 41.29 g/L, with a 95.14% yield in 72 h. Also, a system of natural and recombinant enzyme cascades, including HRP, catalase, galactose oxidase, and periplasmic aldehyde oxidase have been used to convert 6.3 g/L HMF to 7.81 g/L FDCA in phosphate buffer with a 100% yield in under 6 h [41]. When synthesising FDCA from HMF, employing a single enzyme can streamline the catalytic process in comparison to multi-enzyme reaction systems. However, only two enzymes, 5-Hydroxymethylfurfural Oxidase (HMFO) and HmfH, can complete this difficult task. For the effective production of FDCA, combining the catalytic activities of the enzymes in multi-enzyme systems with HMFO or HmfH may be a viable strategy [43]. Table 1 explores the other catalysts used for FDCA production from HMF using green pathways.

Table 1. List of FDCA synthesis from HMF using biocatalysts.

A/A	Product	Catalyst	Medium	Monomer Yield	Ref.
1	FDCA	*Comamonas testosteroni* SC1588 cells	Laccase-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)	87%	[1]
2	FDCA	*Pseudomonas putida* S12 strain	5-hydroxymethylfurfural oxidase (HMFO)	70%	[44]
3	FDCA	*Acinetobacter calcoaceticus* NL14	Sodium carbonate (Na_2CO_3)	100%	[45]
4	FDCA	*Acinetobacter oleivorans* S27	-	100%	[46]
5	FDCA	CoO_x-MC (MC = mesoporous carbon)	Water using O_2 as the oxidant	95.3%	[47]
6	FDCA	Aryl-alcohol oxidase	Phosphate	100%	[48]

Table 1. *Cont.*

A/A	Product	Catalyst	Medium	Monomer Yield	Ref.
7	FDCA	Galactose oxidase (GO) and alcohol dehydrogenases (ADHs)	Water	95%	[49]
8	FDCA	*Aspergillus flavus* APLS-1	Phosphate	67%	[50]
9	FDCA	Aryl alcohol oxidase (AAO)/*Agrocybe aegerita* (AaeUPO)/galactose oxidase (GAO)	Phosphate	80%	[51]
10	FDCA	Laccase (CotA-TJ102@UIO-66-NH_2) and Novozym 435	Dimethylformamide (DMF)	95.5%	[52]

2.2. Synthesis Routes of DMFD

Similar to FDCA synthesis, several types of catalyst have been studied for the DMFD production via the oxidative esterification of HMF. A gold-supported catalyst, Au/Mg_3Al-HT, demonstrated superior catalytic activity, achieving 97.8% selectivity at 99.9% 2,5-furandiformaldehyde (DFF) using one-step oxidative esterification. Furfural and benzaldehyde oxidative esterification may also be accomplished using this catalyst. Notably, the basicity on the support surface decreased the Au nanoparticle's electronic state, which improved the catalytic selectivity of the oxidative esterification process [53]. In a similar kind of work, Au/CeO_2 showed strong catalytic performance in the oxidative esterification of methyl 5-formylfuran-2-carboxylate (MFFC) in methanol (10 wt. %), resulting in the production of DMFD in a high yield of 93%. Methanol serves as the formyl group of the HMF's solvent, reactant, and protective agent [54]. AuPd alloy nanoparticles (NPs) supported on Fe_3O_4 were used as the catalyst for one-pot oxidation of HMF into DMFD, with a 92% yield. The AuPd–Fe_3O_4 catalyst might also be repurposed effectively [55]

A tenable reaction mechanism was suggested for the oxidative esterification of HMF over Au–Cu/$_\gamma$–Al_2O_3. Reduction–oxidation pretreatment was used to create Au–Cu bimetallic catalysts using Au–CuO_x nanohybrids. The produced catalysts were employed in base-free conditions for the oxidative esterification of HMF into DMFD, with oxygen serving as the only oxidant. Through activity testing, the optimised Au–Cu/$_\gamma$-Al_2O_3 catalyst demonstrated an exceptionally high DMFD yield of up to 98% [56]. In similar work, mesoporous alumina nanospheres were embedded with CuO nanoparticles (CuO/m-Al_2O_3) as a catalyst for the oxidative methyl-esterification of HMF into DMFD, utilising tert-butyl hydroperoxide (TBHP) as an oxidising and methylating reagent. Oxidative methyl-esterification of HMF into DMFD results in a 92% yield, which demonstrates the outstanding catalytic activity of 6-CuO/m-Al_2O_3. The reaction mechanisms of oxidative methyl-esterification of HMF are displayed in Figure 3 [57]. The conversion of HMF into DMFD was also catalysed effectively by (Au NPs) supported on a nanostructured gamma alumina (γ-Al_2O_3) fibre. At about 45 °C, the catalyst exhibits outstanding recyclability and can achieve up to 99 wt. % of HMF conversion. A base is needed less often for HMF conversion, as the catalyst's Au concentration is raised [58].

In the presence of magnesium oxide (MgO)–Al_2O_3 and tetrabutylammonium bromide (TBAB), FDCA and dimethyl carbonate (DMC) were utilised to synthesise DMFD. The optimum yield and selectivity of the DMFD were reported to be 76.38% and 80.19%, respectively. The DMFD selectivity was increased by the combined action of the metal oxide and TBAB. A high-selectivity product was achieved when FDCA was deprotonated on the surface of MgO–Al_2O_3, and the TBAB enhanced its solubility in the organic reaction system [7]. Using both homogeneous and heterogeneous Pd–Co–Bi/C (5 mol% Pd (10 wt. % Pd/C), 5 mol% Co $(NO_3)_2$, 5 mol% Bi $(NO_3)_3$) catalysts under ambient oxygen, 5-HMF were esterified oxidatively to produce DMFD. The yields of oxidative esterification were produced at 93% and 96% via homogeneous and heterogeneous Pd–Co–Bi/C catalysts, respectively [59].

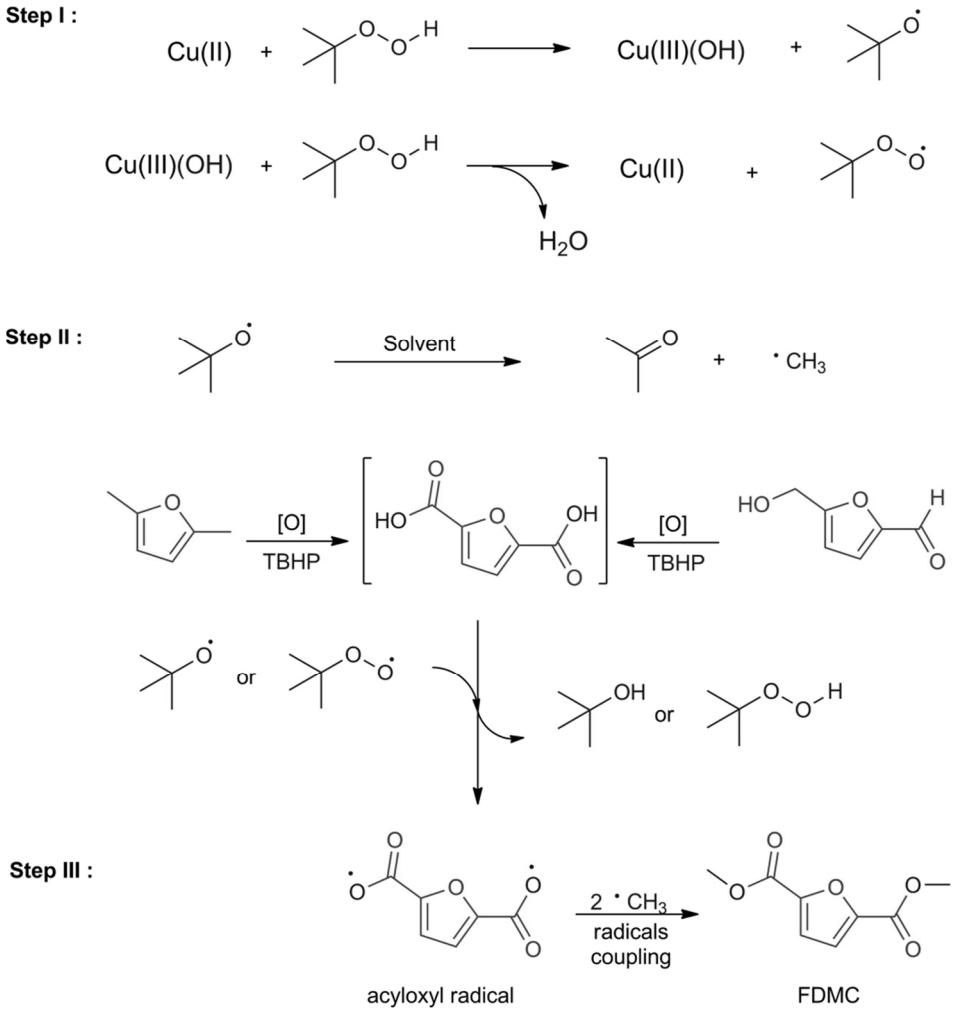


Figure 3. Scheme of the proposed reaction mechanisms for oxidative methyl-esterification of HMF. Adapted from ref. [57].

A different green method to synthesise DMFD was reported, which uses silica-supported solid acid catalysts for the dehydration of esterified galactaric acid into furan carboxylates in the presence of methanol. Further purification by the precipitation method produced DMFD with a 98% yield [60]. Further studies reported that furan carboxylates are produced when solid acid catalysts (silica-supported sulfonic acid catalysts) dehydrate aldaric acids in butanol. Over 90% furan carboxylate yields were obtained, with 80% selectivity to FDCA and its esters (DMFD) [61].

Using $Fe_2(SO_4)_3$ as the heterogeneous Lewis acid, dimethyl carbonate (DMC) as the green medium, and galactaric acid as the substrate, a 70% isolated yield of DMFD could be produced selectively by reaction condition optimisation; silica-based flash column chromatography was used to purify the final product [62]. Similarly, following the optimisation of the reaction conditions, DMFD was generated as a reaction between galactaric acid and dimethyl carbonate (DMC) in the presence of Amberlyst-36 at 200 °C for 2 h. With the purification procedure, the chemical was separated as a pure crystalline powder in a 70% yield [63]. Wisefeld et al. reported goal of the step-by-step conversion of acetal protected HMF (up to 20 wt. %) to DMFD was to maximise the production of DMFD and the recovery of the propane-1,3-diol (PDO)-protecting agent. PDO-assisted acetal protection prevented the reactive formyl group from degrading. Since a base was not used for carboxylate neutralisation during oxidative esterification in methanol, only 7.5 mol% Na_2CO_3 of base was required to stabilise the acetal in relation to PDO-acetalised HMF (PD-HMF) [64].

In our previous comparative study on the synthesis of high molecular weight furanoate polyester (PEF) using both FDCA and DMFD monomers, we evaluated factors such as molar ratios, catalysts, reaction times, and temperatures on synthesising high-molecular-weight polyesters for packaging applications. The results indicated that FDCA is more effective for synthesising high-molecular-weight polyesters. While both monomers exhibited similar degrees of crystallinity and thermal properties in their amorphous states, the increased content of DEG (diethylene glycol) in FDCA-based polyesters led to reduced hardness and elastic modulus values [65].

Conversely, DMFD is a commonly used monomer for synthesising furanoate polyesters and their nanocomposites at a laboratory scale due to its high purity, shorter polycondensation times, and reduced coloration in the final polyesters or nanocomposites.

3. Furanoate-Based Nanocomposites

3.1. Poly(ethylene furanoate) (PEF)-Based Nanocomposites

PEF nanocomposites were fabricated using neat multi-walled carbon nanotubes (MWCNTs) or functionalised MWCNTs, graphene oxide (GO), and graphene nanoplatelets (GNPs) via in situ polymerisation to improve the thermal stability of the nanocomposites. The thermal properties' evaluation demonstrated that all the fillers acted as nucleating agents for the PEF crystallisation, but to varying extents. It always favours the formation of the α-crystal phase [66]. The incorporation of CNT and GNPs induced changes in the lamellar thickness and increased the crystallinity of the PEF. The transmission electron microscopy (TEM) analysis further indicated that the formation of large CNT aggregates in the hybrid PEF nanocomposite was due to the ultrasonication process. Deep studies on the crystallisation kinetics and nanoindentation behaviour on the PEF/CNT nanocomposite revealed that CNTs have a more pronounced nucleating effect during melt crystallisation, with higher crystallisation rates observed in the PEF/2.5 CNTs nanocomposite. The nanoindentation results demonstrated that the addition of CNTs to the PEF matrix improved the nanomechanical properties of the PEF [67].

PEF/Montmorillonite (MMT) nanocomposites were synthesised using organically modified montmorillonite (OMMT) via in situ melt polycondensation, to improve the overall thermal and mechanical properties of the PEF. The results showed that the PEF chains grafted from the surface of the MMT and contributed to the partial exfoliation of the OMMT. The presence of OMMT improved the melt crystallisation, tensile modulus, and strength of the PEF nanocomposites containing 2.5 wt. % OMMT [68]. The results of wide-angle X-ray scattering (WAXS) and TEM indicated that the OMMT-based PEF nanocomposites exhibit primarily an intercalated morphology, with some individual exfoliated clay platelets. The DSC results showed that the presence of clays affected the sample crystallisation behaviour slightly, accelerating its rate due to the nucleating effect of the OMMT clays. Additionally, the thermogravimetric analysis (TGA) results indicated that PEF nanocomposites have higher thermal stabilities than pure PEF, both under inert and oxidative atmospheres. The TG and DTG results of the neat PEF and PEF/OMMT nanocomposites are displayed in Figure 4. The dispersed clay layers slow down the initial decomposition of the PEF, which could be advantageous for processing and material forming at high temperatures [69,70]. Biobased PEF/clay nanocomposites were synthesised using different methods, such as solution, in situ, and melt-intercalated methods. The results showed that exfoliated PEF/montmorillonite nanocomposite was formed because of polymerisation occurring through the clay's interlayer, which was confirmed by an XRD analysis [71].

The usage of nanoparticles was also studied in the fabrication of PEF nanocomposites. These nanocomposites were found to expand their applications in the packaging industry for food and cosmetics and were efficient photocatalysts for removing anti-inflammatory/analgesic drugs. Novel PEF/TiO_2 nanocomposites were fabricated using DMFD as the starting monomer, pyromellitic dianhydride (PMDA) (5‰ mol/mol of DMFD), and TiO_2 (60 nm, 0.5–10‰ wt./wt. of PEF and 30 nm) nanoparticles via one-

pot polycondensation. The nanocomposites with 60 nm TiO_2 nanoparticles had higher glass transition temperatures (T_g) and enhanced the crystallisation rate compared to neat PEF. Moreover, the impact strength increased. The PEF/TiO_2 nanocomposites exhibited an impact strength, which was 25 times higher than that of neat PEF. Importantly, all the PEF/TiO_2 nanocomposites demonstrated superior gas barrier properties compared to traditional packaging materials. The ultraviolet and blue light shielding of PEF/TiO_2 nanocomposites increased up to 97%. Also, the antibacterial activity of the nanocomposites against *E. coli* increased to 83% [72]. The solid-state polymerisation study on PEF-based nanocomposites synthesised using TiO_2 and SiO_2 nanoparticles showed that the addition of nanoparticles into the PEF matrix resulted in the higher transesterification kinetic rate constants and lower activation energies [73].

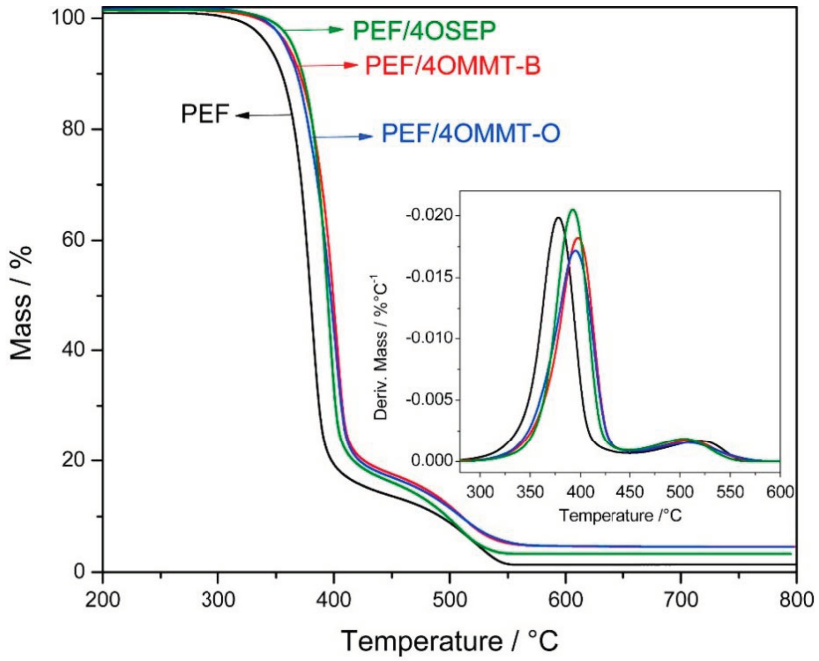


Figure 4. TG and DTG results of the neat PEF and PEF nanocomposites with 4 wt. % of clay content. Adapted from ref. [69].

The PEF bio-composite films prepared by incorporating ZnO NPs showed a water vapour permeability (WVP) value of 3.93×10^{-12} g·m m^{-2}·s·Pa and a visible-light transmittance of 80.5%. Moreover, these films exhibited a bacteriostatic rate of up to 97.0% after 3 h. As a result, PEF/m–ZnO films hold considerable potential for use in food- and beverage-packaging applications [74]. Our previous work was also focused on the synthesis of PEF-based nanocomposites containing Ce–bioglass, ZnO, and Zirconium dioxide (ZrO_2) nanoparticles (1 wt. %) via in situ polymerisation, targeting food-packaging applications. The crystallinity studies showed an increase in crystallinity above 20% for all the PEF-based nanocomposites. The antimicrobial studies exhibited an increased inhibition rate of bacterial strains by roughly 9–22% for Gram-positive bacteria (*E. coli*) and 5–16% for Gram-negative bacteria (*S. aureus*), as displayed in Figure 5 [75]. The PEF-based nanocomposites fabricated using Ag and TiO_2 displayed a significant rise in bacterial inhibition, over 15% against both bacteria, as shown in Figure 5 [76]. Our further studies on the thermal stability and decomposition mechanism of all the above nanocomposites were studied using TGA and pyrolysis-gas chromatography/mass spectrometry (Py–GC/MS). Except for the PEF–ZnO nanocomposite, all the other nanocomposites demonstrated good resistance to thermal degradation up to 330 °C without experiencing significant mass loss, and hydrogen bond scission products were noted in the PEF–TiO_2 and PEF–ZrO_2 nanocomposites.

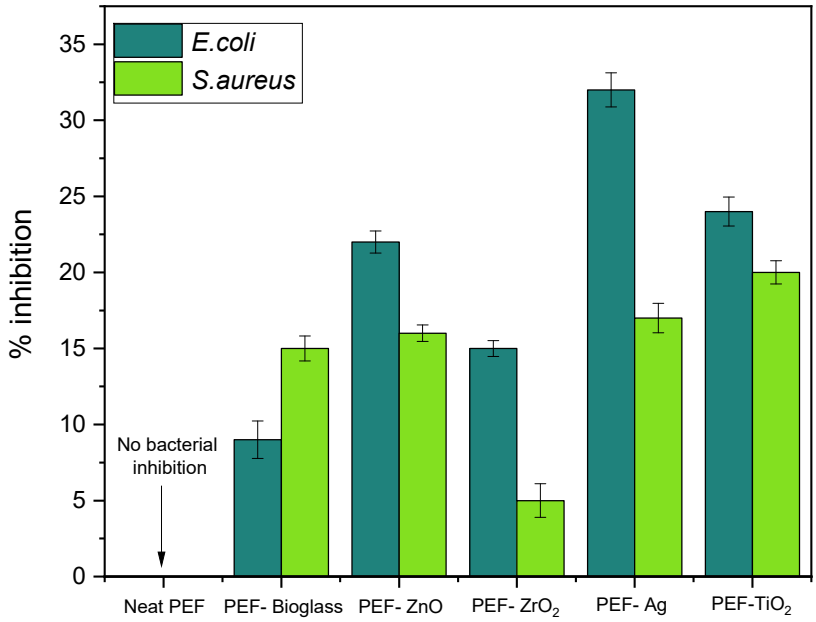


Figure 5. Antimicrobial efficacy of PEF-based nanocomposites against *E. coli* and *S. aureus*. Adapted from refs. [75,76].

3.2. Poly(propylene furanoate) (PPF)-Based Nanocomposites

Papadopoulos et al. from our group produced PPF-based nanocomposites using the nano clays Cloisite®-Na (MMT), Cloisite®-20A (MMT 20A), and halloysite nanotubes (HNT) by the in situ polymerisation technique. The nanocomposites showed good thermal stability and altered crystallisation rates. The MMT and HNT act as nucleating agents, and the MMT 20 A acts as a quaternary ammonium salt present in between its layers [77]. In a similar study, PPF-based nanocomposites were synthesised using 1 wt. % of CNT and GO platelets via the in situ polymerisation technique, resulted in a deceleration of crystallinity and suppression of the strength of T_g. The effects of the CNTs were greater than those of the GO, most likely because of the larger aspect ratio of the nanotubes. The bulk-like crystals and crystals growing onto the fillers (filler-induced crystals) in the case of nanocomposites containing unmodified fillers, with the majority of RAF matching to $RAF_{crystal}$, are illustrated in Figure 6 [78].

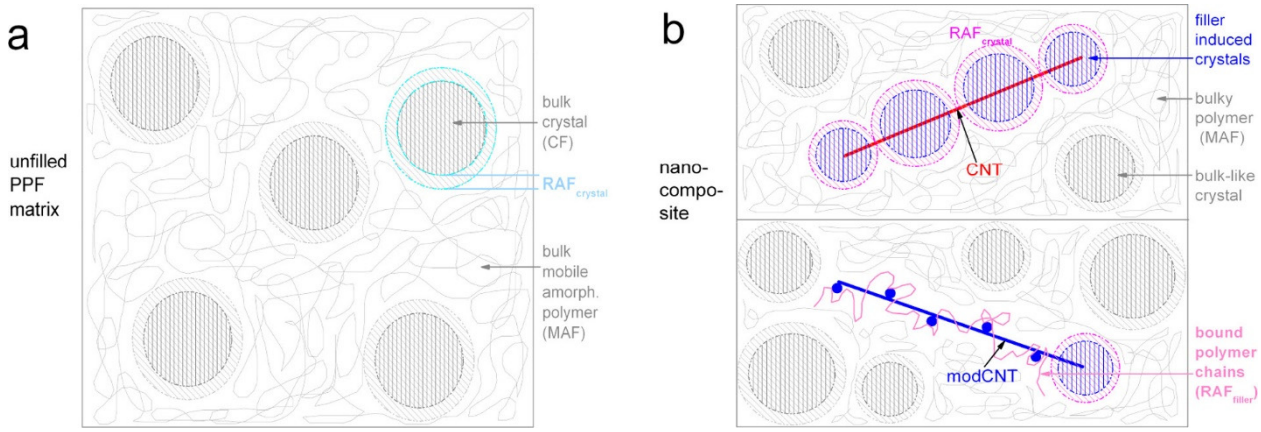


Figure 6. Schematic view of various polymer phases: (**a**) unfilled PPF, (**b**, **top**) PPF/CNT, and (**b**, **bottom**) PPF/modCNT in the semicrystalline state. Reproduced from ref. [78].

The thermal decomposition kinetics and mechanism of PPF/graphene nanocomposites synthesised via the in situ polymerisation technique demonstrated that the incorporation of

graphene nanoplatelets does not affect thermal stability, whereas it increases the activation energy values. Also, the decomposition mechanism of PPF was not affected, due to the addition of graphene nanoplatelets, but the secondary homolytic degradation reactions were improved [79]. Poly(trimethylene 2,5-furanoate) (PTF) reinforced with a few layers of graphene (FLG) (0.1 to 0.3 wt. %) were produced via in situ polymerisations to improve the thermal and mechanical properties. The addition of FLG does not affect the crystallisation/melting behaviour of PTF. The PTF/0.3 FLG nanocomposites resulted in a minor (about 5%) rise in the Young's modulus and a 200% increase in elongation at break. The decreased OTR values of the nanocomposites were observed due to the hydrophobic surface area of the FLG [80].

The PPF/CNT (0.5 to 2 wt. %) nanocomposites synthesised via the solution and coagulation method showed excellent thermal and storage modulus (e.g., 1240 MPa for PPF to 1768 MPa for the 2 wt. % nanocomposite). In addition, the thermal stability and dynamical mechanical properties were improved in all the PPF nanocomposites [81]. The PPF-based nanocomposites produced using a low content of cellulose nanocrystals (CNCs) by the solvent-casting method did not alter the crystal structure and crystallisation mechanisms of the PPF. However, the PPF/CNC nanocomposites exhibited excellent thermal stability [82]. The melt-compounded PPF with MCC via twin-screw extrusion showed a faster crystallisation rate and nucleating rate intensified by compounding the PPF with a low content of MCC. Also, the tensile modulus, strength, and elongation at break were increased with the addition of MCC [83].

3.3. Poly(butylene furanoate) (PBF)-Based Nanocomposites

Recent research has focused on enhancing PBF's properties through the development of nanocomposites. These efforts include blending PBF with other polymers and incorporating nanofillers to improve its performance in packaging applications. Blending with Other Polymers: Studies have explored various blends of PBF with other polyesters, such as PLA and PET, aiming to improve properties like biodegradability and mechanical strength. For instance, blending PBF with PLA has shown potential for increasing ductility while maintaining thermal stability. For instance, the synthesis of PBF nanocomposites with clay nano-inclusions has been achieved successfully, leading to enhanced mechanical properties and thermal stability compared to neat PBF. These nanocomposites have been characterised using techniques such as SEM and thermogravimetric analysis (TGA), which confirmed their improved structural integrity and thermal resistance.

PBF/TiO_2 (50 nm) nanocomposites synthesised via the in situ polymerisation technique with TiO_2 added into a mass ratio of 1 to 9%, demonstrated that the crystallisation rate of nanocomposites has been improved in comparison to neat PBF. Also, the elongation at break and impact strength of the PBF/TiO_2 nanocomposites enhanced by 118% and 200% compared to neat PBF. These nanocomposites were targeted for packaging-film applications [84]. The acetylated bacterial cellulose/PBF (Ac-BC) and acetylated bacterial cellulose/poly (butylene 2,5-furandicarboxylate)-co-(butylene diglycolate) (Ac-BC/PBF-co-PBDG-90/10) nanocomposites made from furanoate-based polyesters and bacterial cellulose were thermally stable up to 239–324 °C. Figure 7 displays the SEM images of the uniform dispersion of acetylated bacterial cellulose into PBF and a PBF-co-PBDG matrix. Additionally, these nanocomposites showed an increased Young's modulus of up to 1239 MPa compared to their neat copolyesters. The oxygen permeability results of the nanocomposites were reported as 3.49×10^2 for the Ac-BC/PBF-co-PBDG-90/10 sample, and 1.75×10^5 for the Ac-BC sample [85].

Our research group has studied a few PBF-based nanocomposites. Papadopoulos et al. fabricated PBF/clay nanocomposites using in situ transesterification and the polycondensation method. Nano clays such as Cloisite®-Na (MMT), Cloisite®-20A (MMT 20A), and Cloisite®-10A (MMT 10A) were synthesised and used. These nano clays acted as nucleating agents, and the crystallisation $t_{1/2}$ was almost half, compared to neat PBF. The nanoindentation results showed the elastic modulus and hardness values of both amor-

phous and annealed nanocomposites compared to pristine PBF. The amorphous MMT 20A-based sample showed an increase in elastic modulus of around 560% and an increase in the hardness value of 321.4%. These fillers act as an additional crystallisation nucleus, to improve both the crystallisation rate and crystallisation fraction (which almost doubled) compared to neat PBF [86].

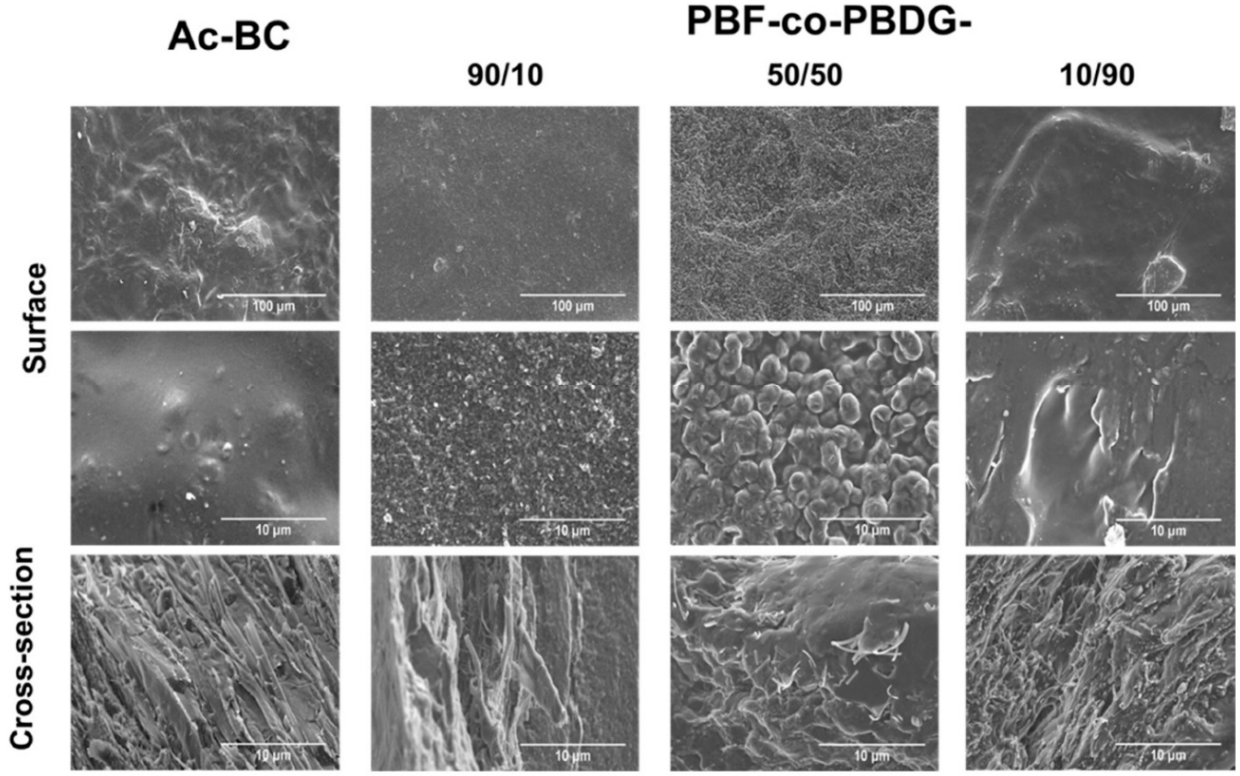


Figure 7. SEM images of (Ac-BC) and (Ac-BC/PBF-co-PBDG-90/10) nanocomposites. Reproduced from Ref. [85].

Montmorillonite and other layered silicates have been studied extensively for their ability to improve barrier properties and mechanical strength. These nanoparticles can create exfoliated structures that enhance the interaction between the polymer matrix and the filler, resulting in better performance characteristics [87].

A significant advancement involved the creation of nanocomposites using PBF and bacterial cellulose. These composites have demonstrated improved mechanical properties and gas barrier performance, making them suitable for packaging applications. The incorporation of acetylated bacterial cellulose into PBF-based matrices has been particularly promising, enhancing the overall structural integrity and functionality of the materials [88]. There is much less research on the incorporation of metal nanoparticles in PBF for packaging applications, thus, it is still very challenging. Silver and titanium dioxide nanoparticles have been incorporated into PBF to provide antimicrobial properties, which are crucial for active food-packaging applications [76].

PBF nanocomposites are being explored for various applications, including biodegradable packaging materials and textile fibres. The ability to tailor the properties of PBF through the use of nanofillers opens up new possibilities for creating sustainable materials that meet industry demands. Additionally, ongoing research is focused on optimising the compatibilisation of PBF with other biopolymers, to enhance its properties further. This includes the use of compatibilisers that improve interfacial adhesion in blends, which can lead to better mechanical performance and material longevity. In summary, the state of the art in PBF nanocomposites highlights their potential as versatile materials in the realm of sustainable polymers.

3.4. Other Furanoate-Based Nanocomposites

Apart from PEF, PPF, and PBF, other furanoate-based nanocomposites have also been explored, based on their material properties for industrial applications. Poly (hexamethylene 2,5-furandicarboxylate) (PHF)/MWCNT (with 0.25 and 0.5 wt. %) composites were produced using the in situ polymerisation method, as shown in Figure 8. These nanocomposites exhibited enhanced isothermal and non-isothermal crystallisation behaviour, with thermal decomposition temperatures of about 370 °C. In addition, the Young's modulus, storage modulus and tensile strength of the composites were higher, due to uniform dispersion of the MWCNT's into the PHF matrix [89].

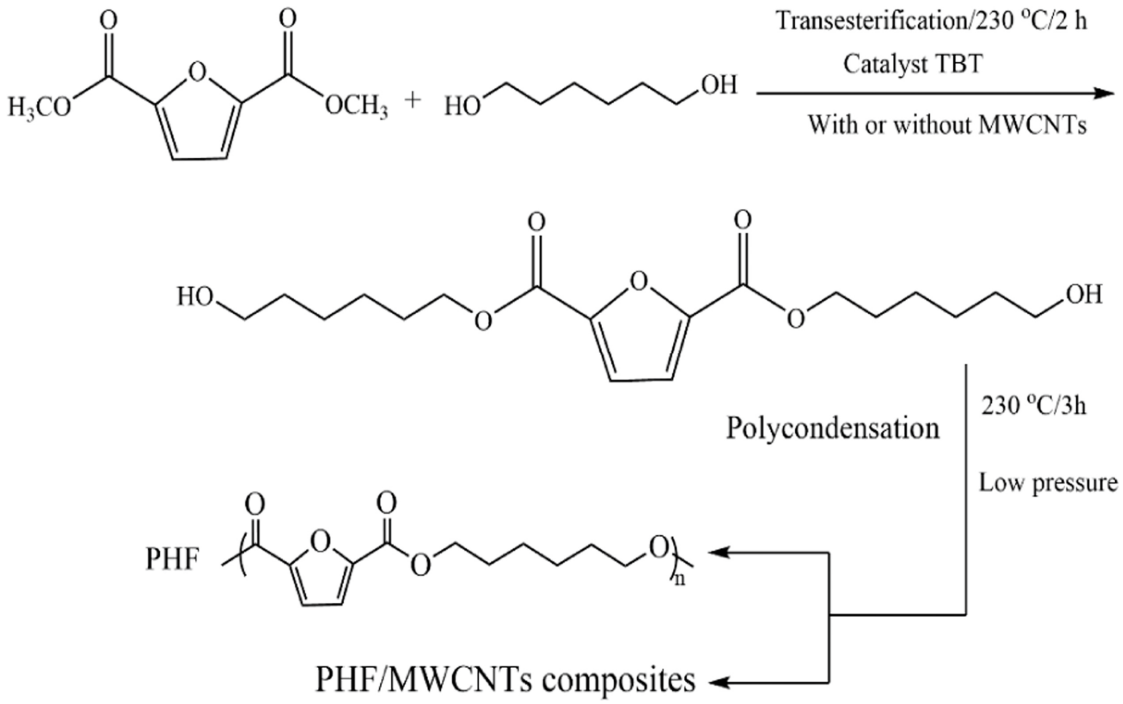


Figure 8. Synthesis route of PHF and (PHF)/ (MWCNT) composites. Reproduced from ref. [89].

Biobased poly(decylene-2,5-furanoate) (PDeF)/CNT nanocomposite films were prepared using solution mixing and the film-casting method, where the CNTs were incorporated from a 0.25 to 2 phr concentration. According to the dynamic–mechanical analysis (DMA) results, the nanocomposites' Cole–Cole graphs exhibited a qualitative similarity to neat PDeF, indicating the systems' homogeneity and strong filler–matrix adhesion. The CNTs acted as a nucleating agent and enhanced the crystallinity degree from 43.2% of neat PDeF to 55.0% PDeF/CNT-2 nanocomposites. In addition, the nanocomposites exhibited increased mechanical performance, as the elastic modulus increased up to 123% and the stress at break up to 131%, as displayed in Figure 9. Among the nanocomposites, the PDeF/CNT-1 nanocomposite was electrically dissipative, and the PDeF/CNT-2 nanocomposite was conductive [90].

Klonos et al. from our group produced poly(alkylene 2,5 furan-dicarboxylate) (PAFs)-based nanocomposites using inorganic nanofillers, graphene nanoplatelets, carbon and halloysite nanotubes, nano clays, and silica nanoparticles in the range 0.5–2.5 wt. %. The nanocomposites were synthesised using the in situ polymerisation technique aimed at food-packaging applications. The nanosized nucleating agents used were MMT nano clays, natural (MMT-Na) and two modifications (MMT-DD, MMT-DBe), HNT, CNT and modified CNT (modCNT), graphene (Gr), GO and modified GO (modGO), SiO_2, and mixed Gr and SiO_2 particles (mixGrSi). All the nanoparticles tended to enhance the crystallisation rate in correlation to the NP's surface area. It was reported that the NPs had an indirect impact on the mechanical performance by raising the elastic modulus because of the latter effect [91].

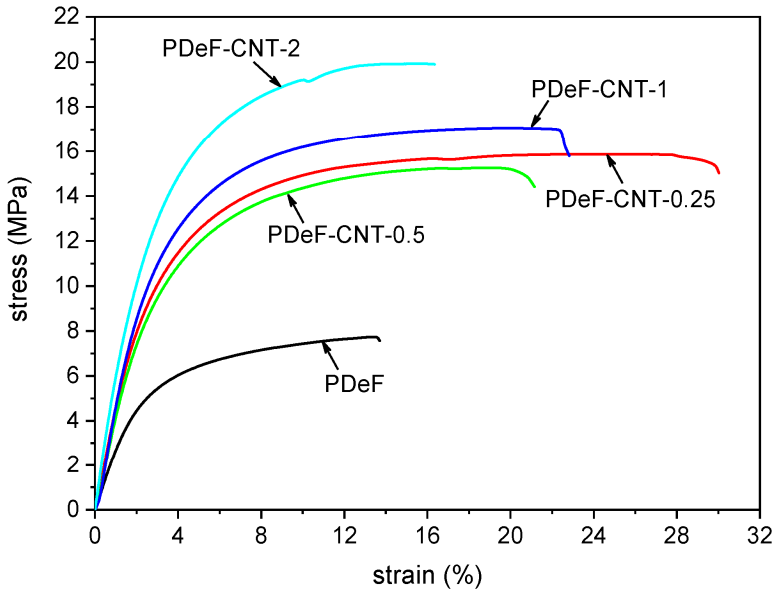


Figure 9. The stress–strain curves obtained in quasi-static tensile tests on (PDeF)/CNT nanocomposite films. Reproduced from ref. [90].

Poly(hexylene 2,5 furan-dicarboxylate) (PHF)-based nanocomposites were fabricated using graphene nanoplatelets and fumed silica nanoparticles (low wt. %), targeting food-packaging applications. Both the nanocomposites facilitated the crystallisation of the PHF; however, the graphene nanoplatelets tended to be more effective at improving the crystallisation rate. The differential scanning calorimetry (DSC) and X-ray diffraction (XRD) results demonstrated potential differences in the semicrystalline morphology between the nanocomposites and the neat PHF [92].

The addition of metallic nanoparticles and nano clays into furanoate polyesters improves the overall thermal stability of these nanocomposites to produce food-packaging films. The ability of polymer nanocomposite films to dissipate heat is essential for processing thermo-forming films on a wide scale without shrinking once food-packaging materials are processed at a higher temperature. The incorporation of carbon tropes like graphene, carbon nanotubes, carbon black, and other nanoparticles, including clay and montmorillonite, have demonstrated improved crystallinity and mechanical performance to extend the shelf life of food products, such as bottles for carbonated drinks, paper coatings, beer-packing material, multi-layer films, and containers. The fabrication of nanocomposites with active agents (metallic nanoparticles) helps to synthesise antimicrobial packaging films for the improved safety and quality of food products [93].

4. Challenges and Future Scope

In recent years, several studies have been carried out on the synthesis of FDCA or DMFD using different catalysts and substrates for the oxidation of HMF into FDCA or DMFD. From the present study, the following observations can be made:

Synthesis of FDCA: Catalysts such as Pd, Pt, and Au are commonly employed for the oxidation of HMF to FDCA, achieving high yield percentages. In addition, microbial and enzymatic catalysts, including *Pseudomonas putida* KT2440, *Acinetobacter calcoaceticus* NL14, *Acinetobacter oleivorans* S27, and aryl-alcohol oxidase, have been utilised to produce FDCA with nearly 100% yield. A novel whole-cell biocatalyst has been developed for a sacrificial substrate-free cascade for the effective oxidation of HMF to FDCA with an impressive yield.

Synthesis of DMFD: Metallic catalysts, particularly Au- and Al_2O_3-supported catalysts, are generally used for the oxidative esterification of HMF into DMFD, also resulting in high yield percentages. Furthermore, green substrates, such as galactaric acid and aldaric

acid, have been effectively utilised for the synthesis of DMFD, highlighting a sustainable approach in the process.

Even though the metallic catalyst exhibits good catalytic performance, the usage of such a catalyst is endangering the ecosystems. Further research should focus on more usage of bio-based catalysts, for catalytic oxidation and to attain maximum yield percentage of monomers, including the costs of the catalyst for large-scale synthesis. Furthermore, the current PET production plants may readily switch from using terephthalic acid as the initial monomer to FDCA. However, the prices of these monomers are now too high to produce low-cost polyesters that could be competition for the extensively used terephthalate polyesters. Mass production of these monomers should take place to make it more affordable and accessible to the market. In order to match the properties and satisfy the demand for a packaging material, further research must be carried out, investigating the most optimal combinations of reactants, catalysts, and reaction conditions to produce high-purity FDCA and DMFD monomers and to resolve the colouration of furan polyesters.

Thus, there is a great deal of room for research in the following area such as cost-effectiveness, recyclability and biodegradability to synthesise furanoate polyesters and their nanocomposites with improved material properties as a sustainable alternative to conventional plastics in food-packaging applications, especially in a field like bottle manufacturing. The eco-friendly nature of furanoate-based polyesters during their production and contribution to the circular economy in recycling and reuse, attracts the industries to shift towards furanoate-based polyesters. From the present study on fabrication of furanoate polyesters and its nanocomposites, the following observations were made:

- PEF, PPF, PBF, and other furan-based nanocomposites fabricated using different nanoparticles, like MWCNT's, CNT's, GO, and nano clays, improve the crystallinity of the overall material, resulting in improved thermal and mechanical properties.
- Metallic nanoparticles such as TiO_2, ZnO, ZrO_2, and Ag were incorporated into furan-based polyesters to improve the gas barrier and antimicrobial properties of nanocomposites to make them suitable for food-packaging applications.

Most of these nanocomposites were synthesised using metallic nanoparticles due to their high performance and low cost. Furan-based nanocomposites represent a significant advancement in the field of sustainable packaging materials. Ongoing research aims to overcome existing challenges, focusing on enhancing properties and reducing costs to enable wider commercial use. However, it is important to weigh their challenges associated with developing strategies for specialised biosafety risk assessment and regulatory framework formulation carefully, especially in fields like food packaging. To mitigate various environmental and safety challenges, it is imperative that the non-ecofriendly and volatile chemicals used in the production of biobased nanocomposites be replaced with more environmentally friendly alternatives. Expanding the breadth of applications for furanoate-based nanocomposites in packaging industries also depends on improving our fundamental understanding of the surface chemistry and interactions of these matrix systems containing fillers and additives. Most of these furanoate-based nanocomposites studies concentrated on mechanical characteristics, thermal stability, molecular weight, crystallisation rate, and other factors. Research on the novel properties that nanoparticles can impart to the matrix, like antibacterial, UV, blue-light shielding, and light-shielding, should also be explored from the perspective of packaging-material development.

The ongoing advancements in synthesis techniques and property enhancement strategies will likely lead to broader applications and increased market acceptance of these innovative materials, but the following must be considered:

Production Costs: the economic feasibility of producing furanoate-based polyesters at scale remains a concern, as the costs associated with its synthesis from biomass are currently higher than those of traditional petroleum-based polymers.

Biodegradability: While furanoate-based polyesters show improved properties over conventional polyesters, their non-biodegradable nature limits their appeal in certain applications. Further research on degradation and end-of-life aspects is crucial, since the

degradation behaviour of furanoate-based polyesters may also lead to a distinct sustainability challenge involving the creation of microplastic fragments.

Recyclability: In general, recyclability of the plastics was difficult due to its contamination, multilayered structures, etc. Whereas furanoate-based polyesters, such as PEF, can be recycled by both mechanical (re-extrusion) and chemical (hydrolysis and methanolysis) processes. Hence, these polyesters provide a great pathway for the development of a circular economy in which recycling has a crucial role.

Market Penetration: The overall market for bio-based polymers is still small, and furanoate-based polyesters need to compete with established materials like PET and PLA. Continued research and development are necessary to improve their properties and reduce production costs, to facilitate broader adoption in the packaging industry.

Social applications: Using furanoate-based polyesters as sustainable packaging material reduces environmental pollution and reliance on fossil fuels. Furanoate-based polyesters can be used in the textile industry for making sustainable fibres to avoid microplastic pollution caused by synthetic fibres. Consumer products such as bottles, containers, and other everyday items can be produced by furanoate-based polyesters, promoting a circular economy by allowing for recycling and composting. These polyesters can be used in agricultural films and biodegradable mulch to improve soil health and reduce plastic waste in farming. Since furanoate-based polyesters are derived from renewable resources, their production can lead to lower greenhouse gas emissions, aligning with global sustainability goals.

Role of society and politics: the development and promotion of furanoate-based polyesters can serve as a platform for raising awareness about the importance of sustainable materials and practices in society.

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