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SYNTHESIS AND PROPERTIES OF FURAN DERIVATIVES FOR EPOXY RESINS[§]

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Abstract

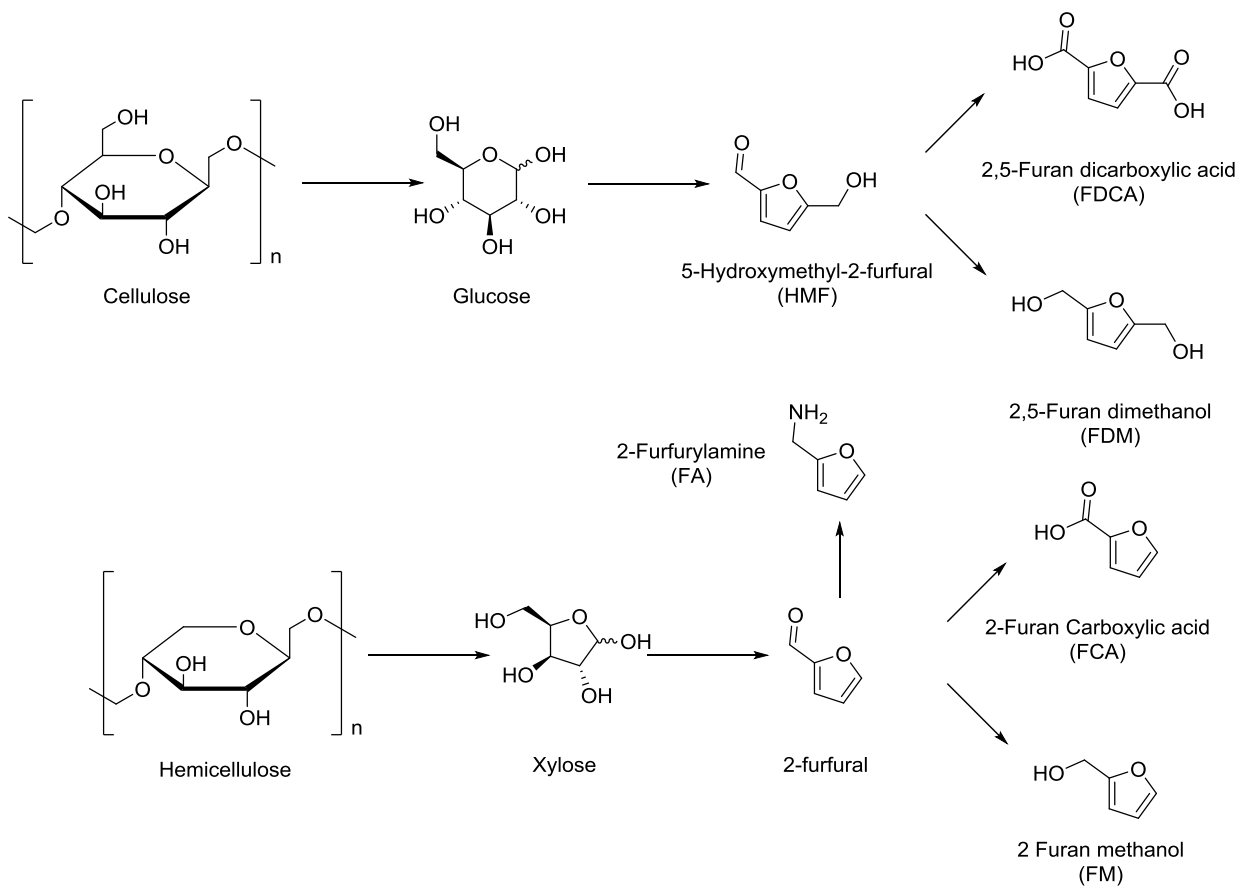
The discovery of huge petroleum reserves in the 19th century was a golden opportunity that promoted the industrial revolution, by offering a wide variety of cheap raw materials and a reliable source of energy. This caused an unprecedented increase of commodity and production of specialty chemicals in order to fulfill the needs of the global markets. However, as the global warming and the environmental issues has become a hazardous and worried situation, researchers are looking for bio renewable monomers with low toxicity in order to produce more sustainable polymers. This policy was also applied to epoxy resin materials because of their high volume production in industry for a wide range of applications. This review highlights the recent advances in the preparation of diamines and diepoxy monomers for the synthesis of epoxy resins, mainly from 2-furfural, 5-(hydroxymethyl)furfural (5-HMF), and 2,5-furandicarboxylic acid (FDCA), obtained from natural cellulose and hemicellulose feedstocks, respectively, and able to replace phthalic moieties in polyethylene terephthalate. In addition, the processes involved in the monomers preparation, such as reductive amination, etherification, esterification and carbonation are listed. This review, reporting quasi-exhaustive synthetic pathways of epoxy precursors containing furanic moieties and describing the resulting resins, is composed of seven main parts, based on the synthesis of glycidyl derivatives containing one or two or four furan nuclei bearing or not a spacer between the furan ring and the function. The influence of the substituents on furan moieties (O, CO, CH₂) and the spacer between these groups have also been evaluated. Finally, thermal and a few mechanical properties of the obtained bio-sourced epoxy resins were compared to their fossil fuel analogues (from bisphenol A), featuring the high potential of bio-based monomers as substituents for non-renewable ones.

Keywords: biomass; epoxy; furan; 2,5-furandicarboxylic acid; 5-hydroxymethyl furfural; telechelic; thermosets.

[§]In memory of Dr Christian COLLETTE, Head of R&D Arkema

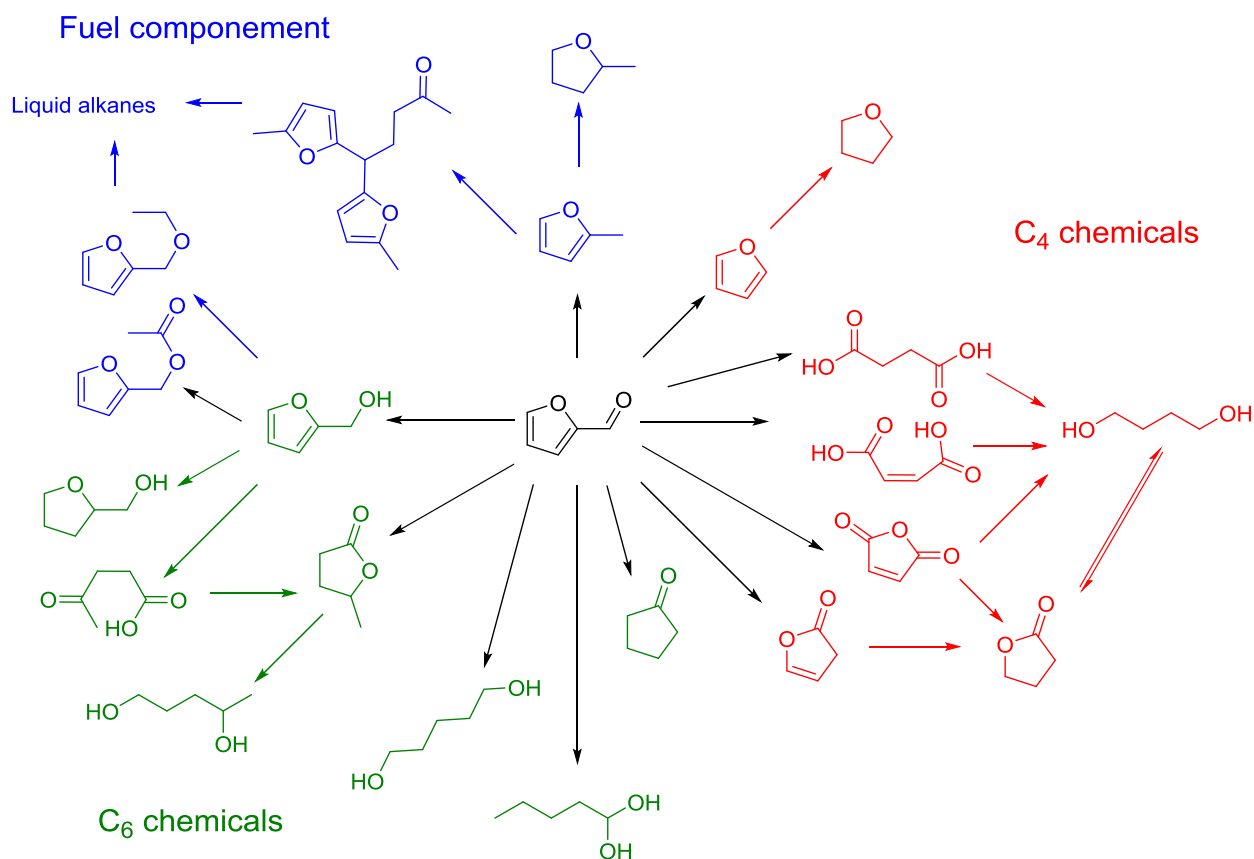
INTRODUCTION

Because of their attractive properties,¹ epoxy resins have widely been involved in many applications including coatings,² composites,³ electronic devices⁴ and as thermosets in aerospace industries.⁵ About 90% of epoxy resins are produced from fossil-based bisphenol A (BPA), named diglycidyl ether of bisphenol A (DGEBA).⁶ However, 10 % were synthesized from renewable resources,^{7,8} the overall production has reached almost 3 million tons per year.⁹ In addition, DGEBA, is obtained from BPA and epichlorhydrine which are considered as carcinogenic, mutagenic, reprotoxic and as endocrine disruptors.¹⁰⁻¹³ Consequently, many researchers have been launched in order to obtain original non-toxic substitutes for epoxy resins in petro-compounds as well as in biobased derivatives.^{8,14} A comprehensive review article that describes all kinds of reactants was reported by Chen *et al.*¹⁵ Actually, many issues have been highlighted on BPA,^{16,17} that can form a close attachment to estrogen receptors¹⁸ and affect body functions as cell regeneration,¹⁹ embryo development,²⁰ and also induces hormone-dependent tumors that may result in prostate or breast cancers.²¹ Thus, BPA containing substances have been prohibited in food packaging industries because of its leaching to the aliments, leading to human exposure to this harmful chemical.²² To remediate it, it is crucial to find out major resources from nature such as cellulose, polysaccharides, and fatty oils.²³⁻²⁷ The last ones afforded materials with low glass transition temperatures (Tg),^{28,29} and thus aromatic moieties, obtained from lignin, or pseudo-aromatic ones, afforded from hemicelluloses, are preferred due to the high physico-chemical properties induced by the presence of a rigid segment in the polymeric chain.³⁰⁻³² Actually, such above natural polymers, cellulose and hemicelluloses (Scheme 1), lead to glucose³³⁻³⁵ and xylose,³⁶ and can further generate 5-hydroxymethyl furfural (HMF)³⁷⁻⁴⁰ and 2-furfural⁴¹⁻⁴⁶



Scheme 1: Preparation of furanoic acids, aldehydes and alcohols from cellulose and hemicellulose⁴⁶

Furfural⁴¹⁻⁴⁷ is monofunctional and has been involved in various applications related to energy (new fuels) and original solvents in contrast to HMF that is telechelic, and thus, can be utilized in many strategies involving the synthesis of epoxy resins and reactions opening the way to a wide variety of polymers⁴⁷. Nevertheless, furfural is an interesting compound (Scheme 2) and several reviews report the main needs of chemistry (see below).^{44,45,47}



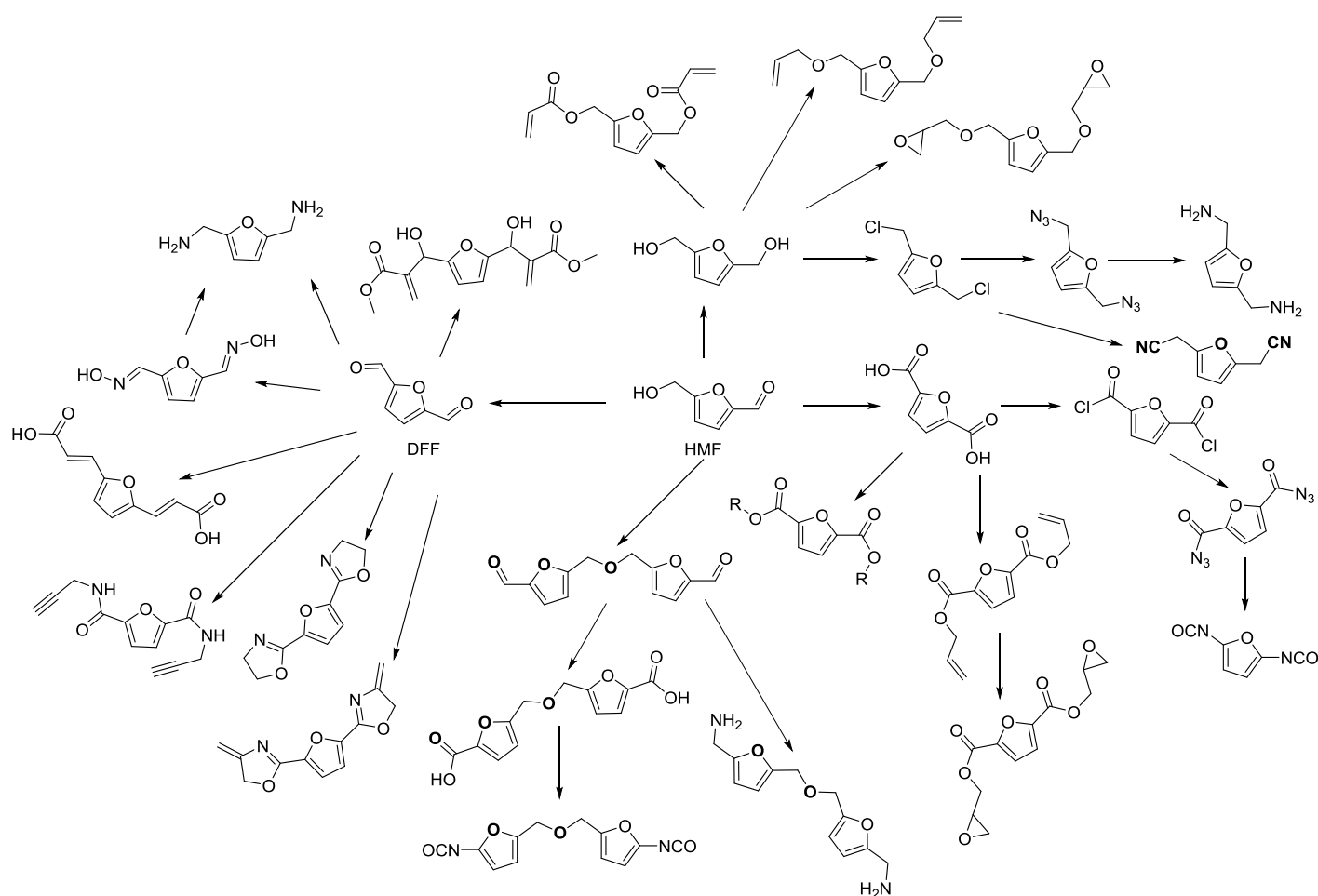
Scheme 2: Catalytic conversion of furfural to fuel components and synthons⁴⁷

Regarding HMF, as the specific goal of that present review, Zhang and Dumont⁴⁸ reported a comprehensive update highlighting the different sources of furanoic products (Scheme 3). This state-of-the-art deals with the synthesis of all types of polymers (polyesters, polyurethanes, polyacrylics, cyanate resins, etc).

But, HMF is undergoing many issues which prevent it from commercialization: first, HMF is a hydrophilic and polar molecule that is hardly extracted from aqueous media. Polar aprotic solvents aqueous phase modifiers or ionic liquids have been potential alternatives but these candidates show cost, toxicity, stability, and recyclability limitations, as well as catalyst recovery.⁴⁹ Second, HMF is sensitive to acid conditions (the medium in which it is produced) yielding humic matter and by-products.^{50,51} Furthermore, high yield-production of HMF lies on fructose as a feedstock, although use of glucose or sucrose in presence of catalysts have already led to interesting solvents,^{52,53} none of these sugars will ever be competitive with raw cellulosic biomass for a commercial production of HMF.⁵⁴⁻⁵⁶

However, to the best of our knowledge, no review dealing with the synthesis of epoxy compounds starting from furan and HMF derivatives has been reported yet, that is the aim of this present review.

Several of the works outlined reflect studies in progress, or recently finalized ones, and thus are reported for the first time. Others were published in the last several years.



Scheme 3: wide range of monomers containing furan ring prepared from 5-HMF⁴⁸

Scheme 3 highlights the preparation of bio-based monomers, bearing a rigid moiety, as the obtained 2,5-furan dicarboxylic acid (FDCA) and 2,5-furan dimethanol (FDM) which are relevant building blocks for a wide range of polymers such as polyesters^{57–61} and polyamides.^{62–66} In addition, a more recent and comprehensive review on the microwave-assisted production of HMF from sugar, cellulose and polysaccharide feed has been discussed by Delbecq and Len.⁶⁷ This review is divided into three main categories: (i) the use of various homogeneous catalysts such as mineral or organic acids, metal salts, or ionic liquids; (ii) feedstock dehydration making use of various solid acid catalysts; and (iii) non-catalytic route.

Other strategies, starting from chloromethyl furfural (CMF), have been proposed and Mascall⁶⁸ developed many original routes of synthesis.

In addition, taking into account the large amounts of raw products (cellulose, sugars, etc) and the wide applications of furan synthons (from energy to polymers), it is not surprising to note how

the patents and publications are regularly increasing. In that area of polymer chemistry, it might be considered that one of the most important topics deals with polyesters and oxidation of HFM into 2,5-furan dicarboxylic acid, as well-mentioned in a recent review.⁶⁹

To complete on polyesters and substitution of PET by biosourced alternatives, recent studies from furanoic derivatives into aromatics⁷⁰ (e.g., dimethyl furane into paraxylene)⁷¹ can be mentioned, as well as those involving Diels Alder strategies.⁸

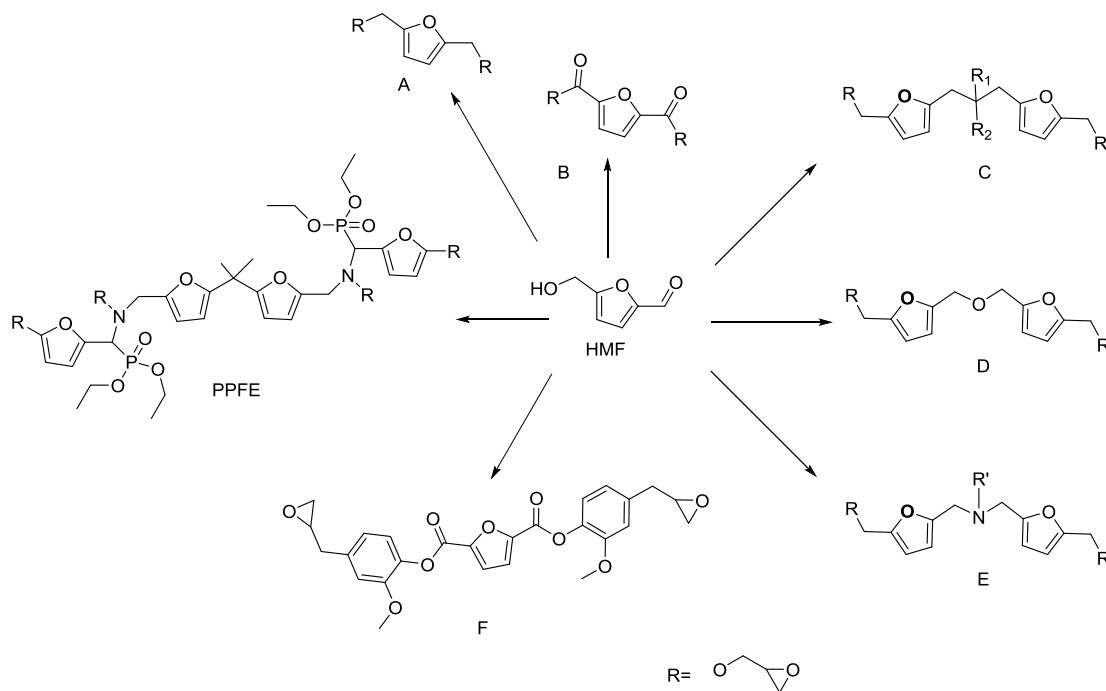
However, this review is devoted to the synthesis of epoxy compounds starting from furan derivatives.

Actually, two other criteria must be taken into account for the substitution of DGEBA: the quantity that can be produced and the price of the biobased substitute.⁷²⁻⁷⁶ Obviously, the mechanical performances of the resulting products resulting from such an alternative must be at least similar as those obtained from DGEBA. In addition, the products must be non-toxic.

All these requirements need to propose aromatic or *pseudo*-aromatic compounds, such as lignin or sugar derivatives as the most suitable substitutes.

First, vanillin,⁷⁷ eugenol⁷⁸ and cardanol⁷⁹ derivatives have been suggested while this present article reviews the furan products reported in the literature. Scheme 1 displays the process to get various furan derivatives from cellulose or hemicellulose. While furfural sounds straightforward from hemicellulose, hydroxymethyl furfural can be obtained from cellulose with levulinic acid as a side-product.⁸⁰

The goal of this present review aims at supplying *quasi*-exhaustive synthetic pathways of epoxy precursors containing furan moieties and describing the resulting resins. However, molecules suited to lead to epoxy derivatives have been supplied even if their applications are not reported. Nevertheless, many strategies have been devoted to obtain furan dicarboxylic acid that is able to replace phthalic derivatives in polyethylene terephthalate (PET),⁸¹⁻⁸³ which is a huge industrial challenge. Actually, other modifications of HMF moieties have been achieved to prepare acrylate, cyanate, urethane, etc...



Scheme 4: Various telechelic bis(glycidyl) furans obtained from 5-HMF

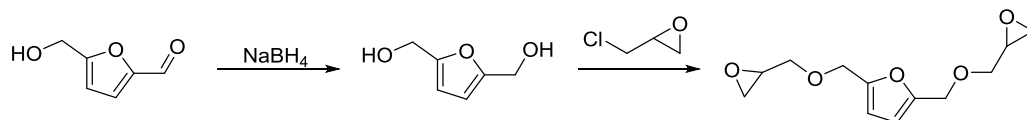
MAIN FAMILIES OF FURAN-CONTAINING DIEPOXY DERIVATIVES

This review is composed of seven main parts: the first one deals with the synthesis of derivatives containing one furan nucleus only; the second one on bisfuran bearing a spacer between the furan ring and the function; while the third one supplied strategies affording polycyclic monomer, then a conclusion and perspectives are supplied.

Scheme 4 displays overall pathways of the seven functional furan-containing epoxides, prepared from HMF.

I. 2,5-Bis [(2-oxiranylmethoxy)methyl] furan (A).

In 2013, Cho *et al.*⁴⁶ pioneered the preparation of telechelic diepoxy, 2,5-bis[(2-oxiranylmethoxy)methyl] furan (BOF) starting from 2,5-bis(hydroxymethyl) furan, as depicted in Scheme 5.



Scheme 5: Preparation of 2,5-bis [(2-oxiranylmethoxy)methyl] furan (BOF) from 5-HMF⁴⁶

The resulting product was purified by column chromatography leading to a yellow liquid obtained in 60% yield. Surprisingly, the authors did not perform any classic epoxy networks but they studied its photoinitiated cationic homopolymerization. The targeted application of the resulting resins was adhesives.

In 2014, Palmese's team⁸⁴ synthesized and studied the properties of the same epoxy monomer (A) crosslinked by the diamines (4,4'-methylenebis(cyclohexylamine) (PACM) and diethyl toluene diamine (EPI)), as depicted in Figure 1.

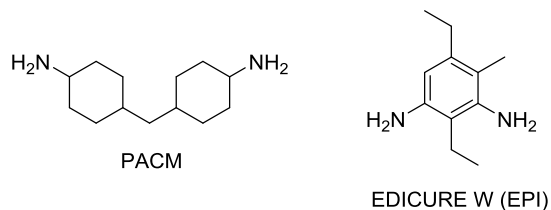


Figure 1: diamines used for crosslinking epoxy resins by Palmese team⁸⁴

These authors reported an interesting comparison of the obtained products with that achieved from the aromatic homologue diepoxy (1,4-bis[(2-oxiranylmethoxy)methyl]-benzene, BOB) and the furan counterpart (BOF), Figure 2.

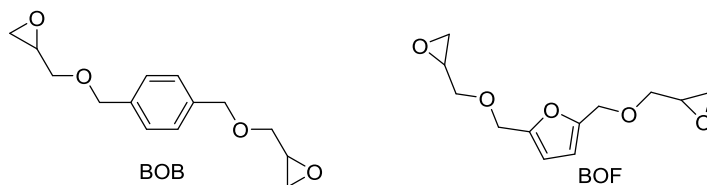


Figure 2: Aromatic (1,4-bis[(2-oxiranylmethoxy)methyl]-benzene, BOB) and furanoic homologue (2,5-bis[(2-oxiranylmethoxy)furan, BOF) diepoxy monomers

Another diepoxy compound, named hydroquinone diepoxy (HQ), was also added for such a comparison in order to evaluate the effect of the methylene group between the aromatic (or *pseudo* aromatic) group and the ether function, starting from hydroquinone derivative (Figure 3).

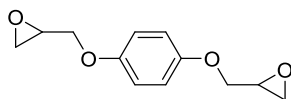


Figure 3: Hydroquinone derivative of BOB (HQ)

Table 1 lists the Tg values (obtained from DMA) of the different resins, compared to those achieved from DGEBA.

Table 1: Glass transition temperature (Tg) of epoxy resins produced from BOF, BOB, HQ and DGEBA with various telechelic diamines (Figure 1)⁸⁴

	PACM BOF	PACM BOB	EPI BOF	EPI BOB	EPI HQ	PACM DGEBA	EP DGEBA
Tg (°C)	71	55 100*	88	80 132*	193	167	185

*corrected

Several comments can be raised from these results:

- i) the furan derivatives favor slightly higher Tg values, attributed to the hydrogen bonding brought by the furan moieties;
- ii) All these Tg values are much lower (of ca. 100 °C) than those of materials prepared from DGEBA due to the presence of the methylene spacer between the (*pseudo*)aromatic group and the epoxide moiety.

Actually, this methylene group induces some mobility that contributes to the decrease of the Tg values. These results are confirmed by the high Tg of the network produced from HQ that does not contain any CH₂ group.

A similar behavior was also observed in the case of diepoxy-base vanillin (Figure 4).⁷⁷

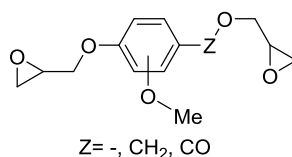


Figure 4: Telechelic diepoxy aromatic compound-based vanillin⁷⁷

Palmese *et al.*⁸⁴ also reacted these furan diepoxides by mixing BOF with DGEBA and studied the properties of the resulting networks. They noted that the Tg values followed the Fox-Flory's law. These authors hence supplied a basic contribution for the understanding of the effect of the substitution of aromatic to furan series in reactants. Indeed, the furan derivatives always bear a linker (CH₂ or C(=O)).

Similarly, the same team⁸⁵ reported the synthesis of epoxy resins starting from both furan reactants containing diepoxy and diamine functions (Figure 5). The diamine was prepared *via* the condensation of 2-furfurylamine with the corresponding aldehyde or ketone, in acidic medium. The experimental protocols were simple, and the monomers were obtained in high yields without the need to especially protect the amine function since the acid plays the role of both the catalyst and the protecting agent.⁸⁶⁻⁸⁸

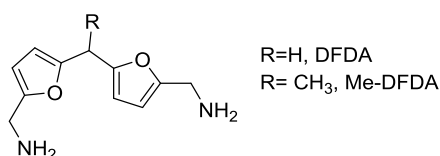


Figure 5: Diamine monomers prepared from furanoic starting materials⁸⁵

The T_g values, listed in Table 2, were compared to those observed from DGEBA resins.

Table 2: T_g values of epoxy resins from BOF and DGEBA with furfurylamines as hardners⁸⁵

	BOF DFDA	BOF Me-DFDA	BOF PCAM	DGEBA DFDA	DGEBA Me-DFDA	DGEBA PCAM
T _g (°C)	62	69	80	128	142	177

As above, the T_g values are lower than those noted from DGEBA. However, from a totally furan resin, the char yield was ca. 40% while it was 6% from a network produced from other amines and DGEBA.

Various authors^{89–91} reported theoretical calculations on the influence of the moieties inserted in the structures of such compounds: the role of the spacer between both furan nuclei and those of oxygen and the methylene adjacent to the epoxy groups.

More recent investigations have been devoted to the development of BOF diepoxide. First, Guo *et al.*⁹¹ cured the furan epoxy using two diamines, 3,3'-diaminodiphenyl sulfone (33 DDS) and 4,4'-diaminodiphenyl sulfone (44 DDS), at high temperatures (Figure 6).

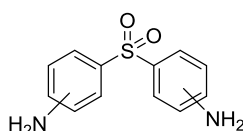


Figure 6: Telechelic diaminodiphenyl sulfone (33DDS and 44 DDS)⁹¹

A comparison on the thermal properties of the resulting epoxy resins with DGEBA in the same conditions is listed in Table 3.

Table 3: Glass transition temperature (T_g), decomposition temperature (5 wt% loss, T_{dec} 5%) and char of epoxy resins produced from BOF (or DGEBA) and DDS derivatives⁸⁵

	T _g (°C)	T _{dec} 5% (°C)	char (%)
BOF - 33 DDS	102	380	44
BOF - 44 DDS	114	460	42
DGEBA - 33 DDS	184	418	20
DGEBA - 44 DDS	238	416	14

(BOF, 33DDS and 44DDS stand for 2,5-bis[(2-oxiranylmethoxy)methyl]furan, 3,3-diaminodiphenyl sulfone and 4,4-diaminodiphenyl sulfone, respectively). Except the thermal stabilities of the resulting resins, the tendency is similar as that noted above.

Recently, Marotta *et al.*⁹² studied the copolymerization of BOF with methyl-5-norbornene-2,3-dicarboxylic anhydride (MNA) (Figure 7) at 130 °C and 180 °C in the presence of imidazole or dimethylbenzylamine, respectively (Table 4).

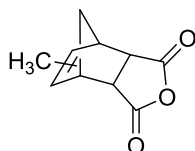


Figure 7: structure of methyl-5-norbornene-2,3-dicarboxylic anhydride (MNA)

Table 4: Glass transition temperature (T_g) and decomposition temperature 5 wt% loss (T_{dec} 5%), under nitrogen, of epoxy resins produced from BOF (or DGEBA) and MNA derivatives.⁹²

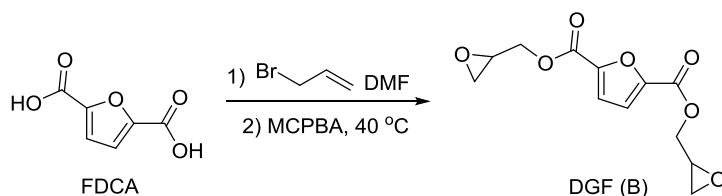
	T _g (°C)	T _{dec} 5% (°C)
BOF:MNA (1:1)	50	256
DGEBA:MNA (1:1)	152	271

The authors also used these formulations (BOF/MNA) incorporating TiO₂ nanoparticles as fillers to elaborate original nanocomposite coatings.⁹³

Furthermore, in an interesting article, Shen *et al.*⁹⁴ studied the modification of BOF with maleimide via a Diels Alder reaction in order to introduce a flexible pendant chain by the maleimide functions with the objective to supply a method for toughening the biobased epoxy resin. These authors inserted various modified BOF (such as MBOF) amounts and showed that the T_g values decreased when increasing MBOF contents were used: 60 °C for 0% MBOF to 40 °C when MBOF = 100%. However, 25% of maleimide remained present after curing although the retro Diels Alder reaction occurred. An optimum of 50% of MBOF led to better mechanical properties (e.g., impact resistance). Furthermore, the presence of free maleimide and MBOF enabled both a toughening effect of DA-BOF and a plasticizing effect.

II – Diglycidyl ester of 2,5-furandicarboxylic acid (B)

The first synthesis of diglycidyl ester of 2,5-furandicarboxylic acid (B) was reported by Liu *et al.*⁸⁹ from 2,5-furandicarboxylic acid (FDCA) in 2015, according to Scheme 6.



Scheme 6: Two step-synthesis of telechelic diglycidylester of 2,5-furandicarboxylic acid DGF from FDCA⁸⁹

Actually, FDCA is one of the twelve building blocks that is regarded as a platform for the synthesis of high-value biobased chemicals or materials.⁹⁵ Indeed, a recent review⁶⁹ reports some advances in catalytic oxidation of HMF towards FDCA as well as other HMF oxidation intermediates: 2,5-diformylfuran, 5-hydroxymethyl-2-furancarboxylic acid, 5-formyl-2-furancarboxylic acid. More recently, the same group⁹⁶ also obtained FDCA from HMF under microwave-assisted heating using hydrogen peroxide and various ruthenium catalysts.

Liu's group⁸⁹ compared the reactivity of telechelic diepoxy DGF to the corresponding diglycidyl terephthalate (DGT) and the resulting epoxy resins were produced after curing *via* two kinds of crosslinkers: an anhydride (methyl hexahydrophthalic anhydride MHHPA) and a telechelic diamine polyether, poly(propylene glycol)-bis(2-aminopropylether), Jeffamine®D230 (Figure 8).

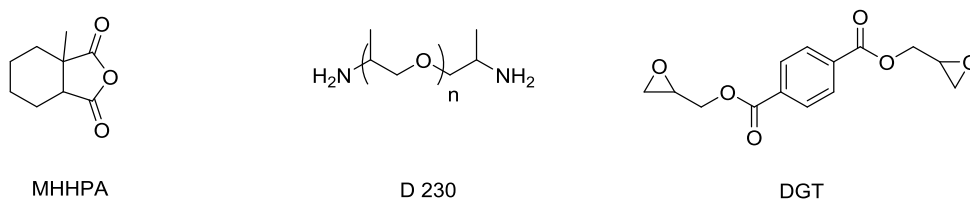


Figure 8: Hardeners used with FDGA diepoxyes: methyl hexahydrophthalic anhydride (MHHPA), poly(propylene glycol)-bis(2-aminopropylether) (D230) and diglycidyl terephthalate (DGT)

The curing behavior was highlighted by DSC, occurring at 120 °C-140 °C in presence of the anhydride and at 90-110°C with the bisamine.⁸⁹ The T_g values of the epoxy resins are listed in Table 5.

Table 5: T_g values of resins prepared from glycidyl reactants (where D230 stands for poly(propylene glycol)-bis(2-aminopropylether) (Jeffamine®D230)⁸⁹)

	DGF	DGF	DGT	DGT	DGEBA	DGEBA
	MHHPA	D230	MHHPA	D230	MHHPA	D230
T _g (°C)	152	129	101	92	125	97

Table 5 highlights several features: i) the T_g value of the resulting resins obtained from DGF is higher than those prepared from DGT and DGEBA, and ii) the T_g value of the material produced from DGT was slightly lower than that achieved from DGEBA and iii) . The

introduction of carbonyl group in the structure enabled to increase the rigidity of the resin and, consequently, the Tg, as this was already observed in the vanillin series.⁷⁷

In addition, the thermal stabilities are almost similar in the presence of the same crosslinkers.

Liu's group⁹⁷ revisited that work by comparing the products obtained from telechelic furan dicarboxylic and aromatic bis(carboxylic epoxy derivatization, starting from isophthalic isomer and 4,4'-diaminodiphenylmethane (DDM) aromatic diamine (figure 9). As above, the Tg value of the resulting network from the furan product was higher than that involving the aromatic one (156 °C versus 124 °C), as well as other physical characteristics (surface energies, and mechanical properties as tensile strength higher than corresponding aromatic network). These authors explained such features by the formation of hydrogen bonding arising from the oxygen atom in the furan core.

Guo's team⁹⁸ reported the *quasi* same synthesis but these authors substituted DDM by 33 and 44 DDS (Figure 9) to yield epoxy resins, the thermal and mechanical properties of which are listed in Table 6.



Figure 9: Telechelic diamine hardeners, 4,4'-diaminodiphenylmethane (DDM) and 4,4'-diaminodiphenylsulfone (44 DDS) used in the curing reaction⁹⁸

Table 6: Thermomechanical and mechanical properties of resins produced from DGF, DGEBA, 33 DDS and 44 DDS⁹⁸

Entry	Sample	Tg ^a (°C)	E ^b (MPa)	E ^c (MPa)	V _e (mol/dm ³)	Tensile Strength (MPa)	Elongation at break (%)	Shore hardness (HD)
1	DGF/ 33 DDS	180	3921	26	2.48	56	8.5	88.3
2	DGF/ 44 DDS	216	2510	25	1.39	50.2	13.8	86.9
3	DGEBA/ 33 DDS	178	1858	18	1.46	49.9	8.2	76.6
4	DGEBA/ 44 DDS	237	1932	16	1.18	44.6	10.3	80.5

^a From DMA ^b Values at 20 °C ^c Values at Tg +30 °C; E and V_e stand for storage modulus and crosslinking density, respectively

Although the Tg value of the material obtained from **B** is quite high, that from DGEBA achieved with the same hardener is even higher (237 °C). These results are different from those

reported by Liu *et al.*⁹⁷ who used an anhydride as the hardener and, surprisingly, with polyether diamine but no explanation has been given so far

In addition, Marotta *et al.*⁹⁹ investigated two methods to synthesize **B**:

i) the first one involves FDCA with epichlorhydrine as the conventional pathway used for vanillic acid⁷⁷ or gallic acid.¹⁰⁰ The product was purified by column chromatography. ¹H NMR spectroscopy confirmed the structure but the ratio of integrals of the signals assigned to furan and epoxide functions led to an average degree of polymerization of 0.17 highlighting the formation of oligomers (Figure 10).

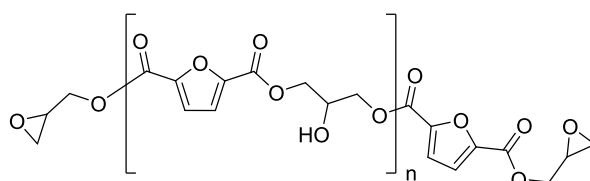


Figure 10: Telechelic Diepoxy terminated oligo(2,5-furanoic glycerol)⁹⁹

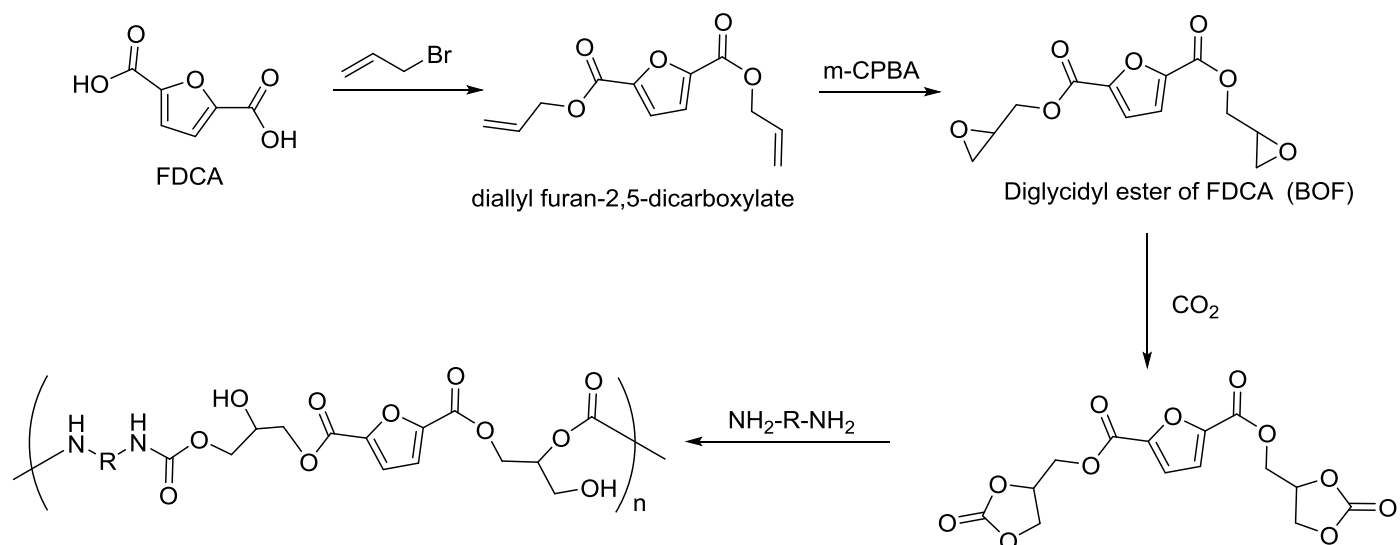
ii) The second method dealt with the transesterification of methyl ester of FDA with an excess of glycidol at low temperature in the presence of KOCN as the catalyst. As above, the purification of the product was achieved by column chromatography. In that case, the epoxy equivalent weight (EEW) value was low (135 compared to 152) with an average degree of polymerization of 0.011 while its melting point was 88 °C (DSC). Unfortunately, the authors did not report any yield of the product obtained from both pathways.

In 2018, Johansson *et al.*¹⁰¹ studied the copolymerization of **B** with epoxidized fatty methyl esters, either thermally or under UV-induced cationic initiation (onium salt). **B** was obtained from diallyl furan-2,5-dicarboxylate (DAFDC) and meta-chloroperbenzoic acid (mCPBA), epoxidation (Scheme 7). The decreasing order of the reactivity, monitored by DSC, was as follows, for various oil : furan epoxy mixtures ranging from 5:1 to 1:5:
oil monoepoxy > oil diepoxy > oil triepoxy >> furan epoxy (**B**).

The T_g values varied between -23 °C to 65 °C, considering the increasing furan content. When DGEBA replaced FDCA (**B**) with epoxidized oil, the T_g values of the obtained epoxy resin were almost the same. Finally, the storage modulus varied from 1.0 to 2.7 GPa, rather similar as that of PET.

As a matter of fact, one fashionable application from BOF deals with the synthesis of non-isocyanate polyurethanes (NIPUs).¹⁰² The carbonatation of BOF led to telechelic

bis(cyclocarbonate) which, added onto telechelic poly(methylene) diamines, yielded original NIPUs (Scheme 7).



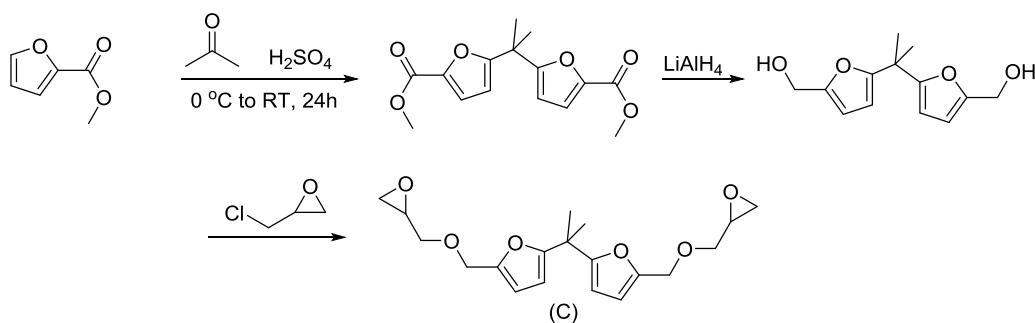
Scheme 7: Synthesis of non-isocyanate polyurethanes (NIPUs) from the dimethylol furan (BOF).¹⁰²

According to the nature of the telechelic diamine, the obtained NIPUs were amorphous with a broad range of Tgs varying from 63 °C to 113 °C. As expected, the rigid chemical structure of cycloaliphatic diamine led to higher Tg of the resulting NIPUs than that observed when softer linear aliphatic diamines were used.

To conclude in this section, it can be noted that such a B derivative is the logically most used but the presence of ester moieties enables to increase the Tg of the resulting epoxy resins but they also induced weak points toward hydrolysis.

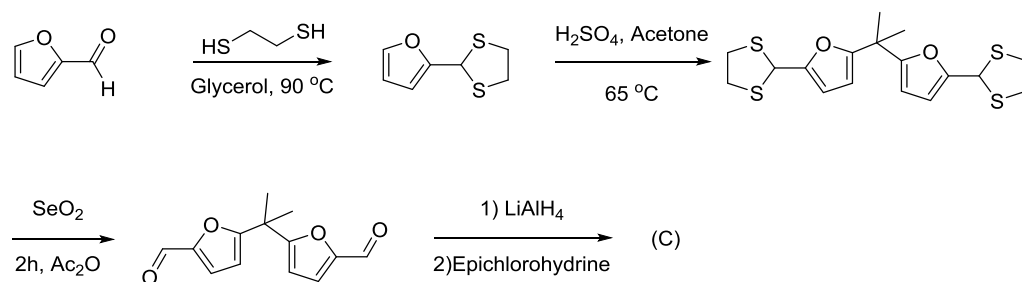
III) Bis(furan) Bearing Alkyl Spacers (C)

In 2013, *Cho et al.*⁴⁶ described a three-step synthesis of diepoxy bis(furan) in which both furan groups are separated by an isopropyl group (Scheme 8).



Scheme 8: synthesis of telechelic diepoxy bis(Furan) starting from methyl furanoic methyl ester⁴⁶

The overall yield was low (40%) and these steps require toxic or hazardous reactants. Thus, Sucheck's group¹⁰³ suggested another pathway (Scheme 9) and could reach 47% overall yield. To the best of our knowledge, such a telechelic bisepoxy bis(furan) has never been involved in the synthesis of epoxy resins, though *Cho et al.*⁴⁶ used them under cationic photopolymerizations. Surprisingly and based on the structure of the precursor diol, the authors deduced that this compound cannot display any estrogenic activity in contrast to that of bisphenol A (BPA).¹⁰³ While with aromatic synthons, this is the most used method, and in the case of furans, only one has been reported.⁴⁶

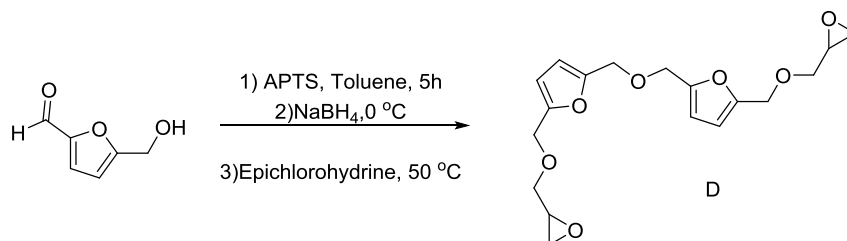


Scheme 9: synthesis of telechelic diepoxy bis(furan) (C) from furfural in a 5 step-reaction¹⁰³

To conclude on this short section, because furfural is a quite abundant, cheap, and stable compound in contrast to 5-HMF, this strategy to prepare furan C is remarkable and will probably lead to many innovations.

IV) Bis(furan) with an Ether Spacer between furan rings (D)

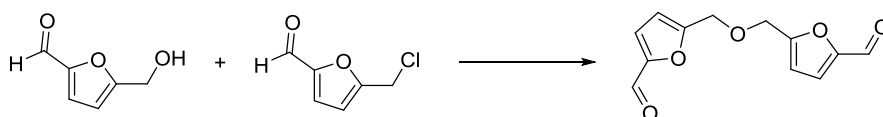
Meng *et al.*¹⁰⁴ have recently proposed the preparation of a new telechelic bis(epoxy) derivatives directly obtained from HMF *via* a simple self-etherification in acidic conditions (Scheme 10). This etherification reaction was inspired from Casanova *et al.*¹⁰⁵ and Bell's team¹⁰⁶ for searching new bio-diesel alternatives.



Scheme 10: new telechelic bis(epoxy) from hydroxymethyl furfural (HMF) via self-etherification¹⁰⁴

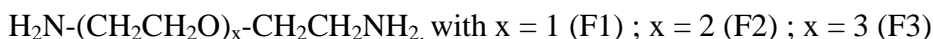
Another method to produce a (bis)aldehyde intermediate to avoid the levulinic acid side product was reported by Chundury and Szmant,¹⁰⁷ starting from HMF and 5-chloromethyl

furfural (Scheme 11), although these authors have not further developed the synthesis of the resin.



Scheme 11: Preparation of bis(aldehyde) from 5-HMF and 5-chloro HMF¹⁰⁷

Actually, such a novel diepoxy (**D**) has been reacting onto Jeffamine® hardener:



The thermal properties (T_g) of the resulting materials were compared to those obtained from BOF (**A**) and the results are summarized in Table 7.¹⁰⁴

Table 7: T_g values of epoxy resins prepared from (D)F and (A)Fi (where Fi stands for a telechelic diamine)¹⁰⁷

Resin	(D) F ₁	(D) F ₂	(D) F ₃	(A) F ₁	(A) F ₂	(A) F ₃
T _g (°C)	25	21	7	14	13	8

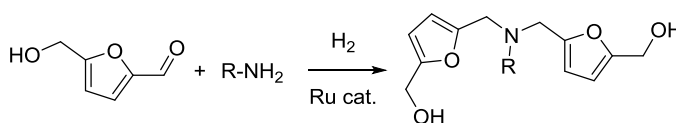
Obviously, such determined T_g values were low but not as low as those observed in epoxy resins achieved from BOF. This is not expected taking into account the presence of a soft spacer (as -CH₂-O-CH₂-) between both furan groups.

The thermal stabilities are slightly lower (of 20 to 30 °C) compared to that of network from BOF. Interestingly, all the resulting materials displayed satisfactory fire resistance properties.¹⁰⁴

In conclusion of this sub-section, this etherification strategy in the presence of a strong acid is simple, cheap and direct, and would deserve to be further continued in the future.

V) Bis(furan)s containing an amine spacer (E)

Zhang *et al.*¹⁰⁸ successfully prepared an HMF-based diol monomer with an amine spacer using reductive amination in the presence of a ruthenium catalyst (Scheme 12).



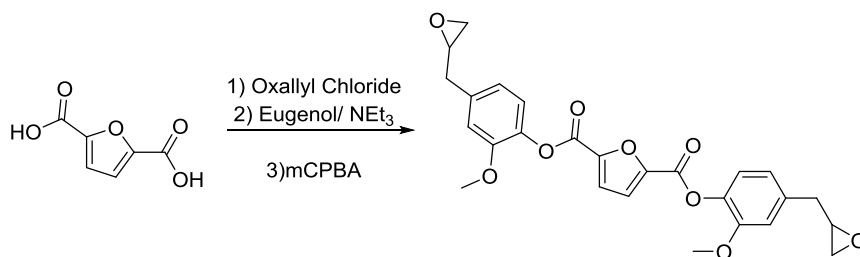
Scheme 12: Condensation of HMF with a primary amine to lead to a telechelic diol bis(furan) (where R stands for a benzyl or aliphatic substituent)¹⁰⁸

First, the nature of the ligand in the catalyst is essential and homogeneous ruthenium (II) having sterically hindered ligand was preferred. Actually, the best yields were achieved when aliphatic in alpha-C position and benzyl amine were used, reaching 90% when the reaction was carried out under 20 bar-hydrogen at 110 °C for 12 hours. Indeed, no reaction occurred when an aromatic or an aliphatic primary amine were used. The authors proposed a mechanism that led to an imine formation that can further be hydrogenated to its corresponding secondary amine. Then, this latter reacted onto the other HMF, thus yielding the bis(furan) diol. However, the authors did not further use these derivatives in specific reactions.

To conclude, the presence of that secondary amine may help in the catalysis of the reaction between the epoxy reactant and the hardener.

VI) Furan Dicarboxylic acid Modified Eugenol (F)

In 2017, Gu's team¹⁰⁹ synthesized an original and totally biobased telechelic epoxy in three steps from 1,4-bis(dicarboxylic acid) furan, involving eugenol in the second step (Scheme 13):



Scheme 13: the three step-synthesis of an aromatic telechelic glycidyl Furan from FDCA.¹⁰⁹

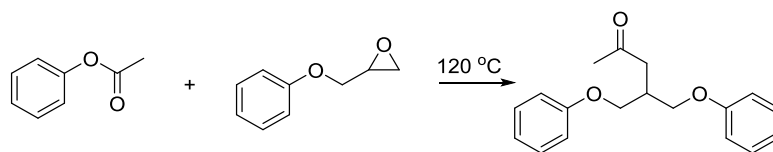
This diepoxy can be cured by MHPA and the DSC thermograms revealed a reaction starting from 142 °C (140 °C in the case of DGEBA). They led to materials, the T_g values of which were 153 °C (144 °C from DGEBA).

When F was involved in that curing, the thermal stabilities of the produced resins were 50 °C lower than those obtained from DGEBA. On the contrary, the char yield was much higher as well as the fire resistance, compared to those of the product obtained from DGEBA.

In 2020, Gu *et al.*¹¹⁰ claimed (in a patent) the process for the preparation of the molecule. Surprisingly, this patent does not refer the previous article¹⁰⁹ published three years before by the same authors.

In a similar manner, Chen *et al.*¹⁵ studied the curing process of compound F in the presence of 4-dimethylaminopyridine (DMAP). In addition, the authors also used another diacid chloride, ClC(O)(CH₂)_n-C(O)Cl with n = 1, 2, 3, without any furan group. The originality of this

survey arises from the curing mechanism. Actually, using model compounds, the authors showed that the activated ester reacted onto the epoxide ring in the presence of DMAP,¹¹¹ as in the reaction model displayed in Scheme 14.



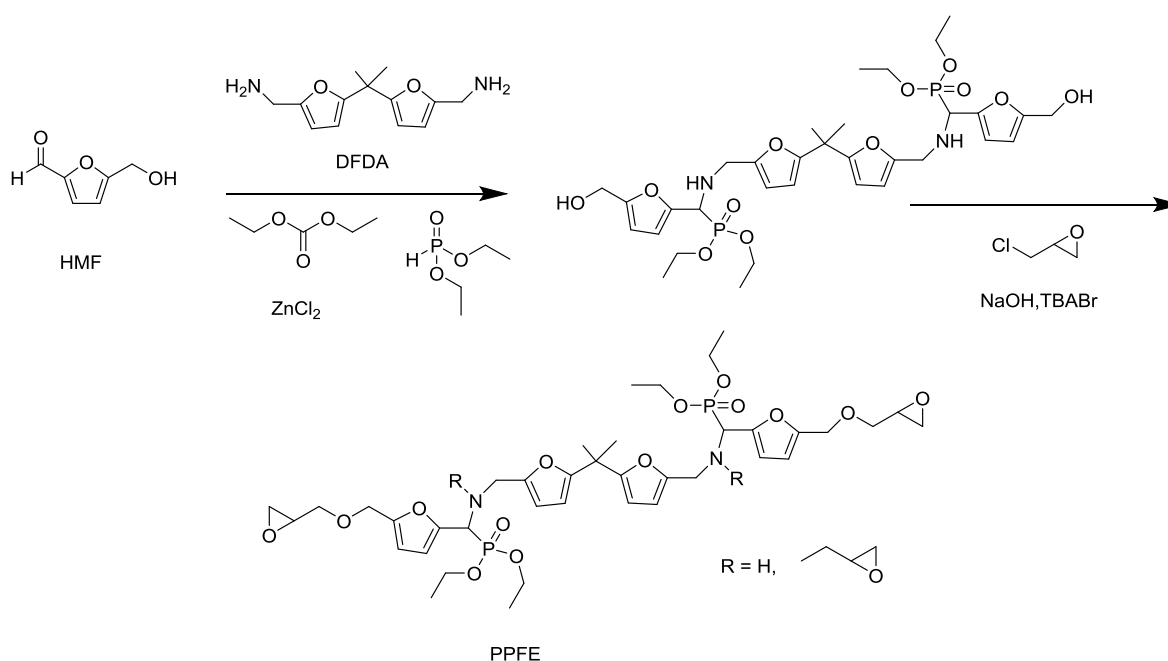
Scheme 14: Condensation between an aromatic acetate derivative and an epoxide compound¹¹¹

By DSC, the authors assigned an exothermal peak (at ca. 170 °C) in the reaction from compound **F**.

However, that strategy requires a diacyl chloride and thus, it potentially induces some issues for an industrial scale up.

VII) Telechelic bisepoxy(furan) containing a bisfurfurylamine and phosphonate functional group (G)

Park et al.¹¹² prepared a furan-based epoxy resin containing phosphorus group (PPFE) by Kabachnic-Field reaction,^{113,114} using HMF, difurfuryl diamine (DFDA) and diethylphosphite (Scheme 15).



Scheme 15: synthesis of a tetra(furan)containing diethyl phosphonate function (PPFE)¹¹²

The thermosets were formulated from BOF, BOF/PPFE and in presence of DFDA as the curing agent. The thermal, mechanical, and flame retardancy properties of the resulting materials were compared to those achieved from DGEBA as the reference. Owing to the furan and phosphonate

groups, those materials display enhanced properties compared to those of BOF-DFDA, as well as the flame-retardant behavior compared to the reference product.

CONCLUSION AND PERSPECTIVES

This review shows that all developed research favor opportunities to replace BPA-based epoxy resins by epoxy containing furan. It can be concluded that these latter led to materials having T_g values lower than those obtained from BPA because of the presence of the methylene group adjacent to furan ring induces softness, except if the reactant is FCDA, this latter possessing a C=O function in α -position. Similarly, thermal stabilities are generally lower, but flame retardancy and char yield are much higher compared to those of materials produced from BPA. Interestingly, the synthesis of amine hardener starting from furfural enabled the synthesis of totally biobased epoxy derivatives.

To complete all these surveys, it could be of interest to plan new approaches. First, oxidation reactions of HMF are much more studied (as well as more simple) and preparing a telechelic dicarboxylic furan acid had been the first motivation. On the contrary, the reduction of HMF by NaBH₄, and in a further extend, the reduction of acid (or ester) by LiAlH₄ represents innovative challenges. Second, using furfural, that is a more abundant raw material, and much easier to obtain, remains one of the hottest topics of research since it is involved in various topics as green solvents and energy (clean fuels). However, this is a monofunctional compound and it will be of interest to have bis or multifunctional derivatives. In addition, HMF leading to various polymers, undergoes some hydrolysis side reactions into levulinic acid that induces low yield and hence its purification must be optimized. Except the investigations from Cho *et al.*⁴⁶ and Sucheck *et al.*¹⁰³ and the diepoxydation of furfuryl amine,¹¹⁴ quite a few articles and patents have been published compared to the homologue series of products from aromatic reactants (e.g. addition of aldehydes and ketones onto aromatic rings of phenolic compounds).

The direct production of 5-(chloromethyl) furfural, proceeds in high yields directly from cellulose and cellulosic biomass, as reported by Mascal.⁶⁸ Hence, further studies are expected in the coming decades and should attract the interest of many academic as well as industrial researchers.

Finally, regarding the future of biosourced resins, as mentioned above, furan and fatty oils are promising building blocks for epoxy resin preparation because of huge available feedstocks.

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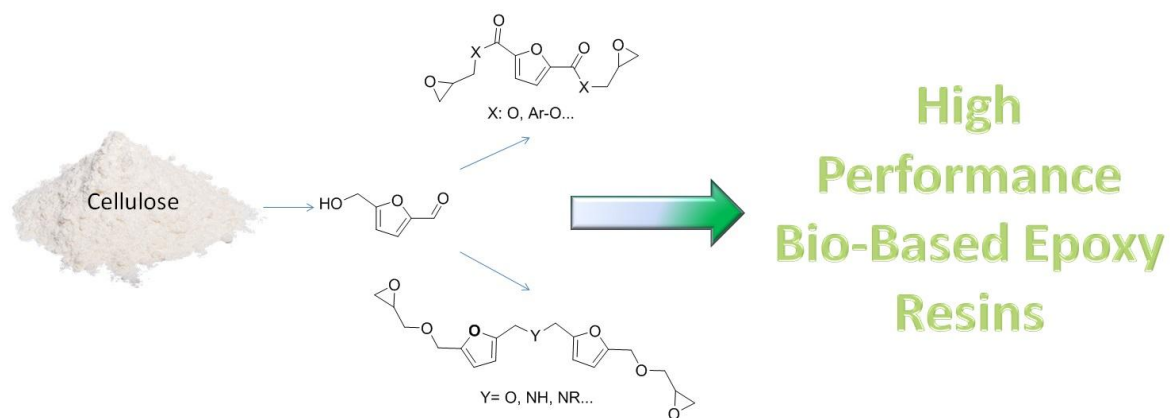
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This review reports synthetic strategies of epoxy monomers from biosourced 2-furfural, 5-(hydroxymethyl)furfural, and describes the resulting resins as well as their thermal and mechanical properties, compared to their fossil fuel analogues.