



## PRODUCTION OF HYDROPHOBIC POLYMERS FROM BIO-BASED RESOURCES



M. B. Nasirudeen\*, H. C. Hailes and J. R. G. Evans

Department of Chemistry, University College London, 20 Gordon Street, WC1H 0AJ London, United Kingdom

\*Corresponding author: [n.m.baba.10@ucl.ac.uk](mailto:n.m.baba.10@ucl.ac.uk)

Received: March 26, 2018 Accepted: August 07, 2018

**Abstract:** 2,5-furandicarboxylic acid (FDCA) and 2,5-bis-(hydroxymethyl)furan (BHMF) were synthesised as monomers from bio-based derived 5-Hydroxymethylfuran (5-HMF). The aldehyde group of 5-HMF was oxidized using potassium permanganate to FDCA with 80% yield and BHMF was synthesised from 5-HMF using sodium borohydride at 88% yield. Polymerization of FDCA with the following diols: 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol and BHMF via esterification reactions at 160-200°C using titanium (IV) n-butoxide catalyst. All these diols produced hydrophobic polymers under the same conditions with PBH-2,5-F more hydrophobic with a contact angle of 91°. The differences within this family of polymers are the number of carbon atoms in the linking diols and that BHMF had a different diol structure with a furan ring attached.

**Keywords:** Carbohydrate, 5-hydroxymethylfuran, 2,5-FDCA, polymers

### Introduction

Petroleum and natural gas are currently the main raw materials for the production of about 95% of the world's chemicals. Predominantly, various chemicals such as ethylene, propylene, butadiene, butanes, benzenes etc. are derived from crude oil. These chemicals could be used as end-products, monomers for the polymer industries or as precursors for the production of chemicals for other applications. However, price fluctuations of these materials in the global markets and the effect of the emission of greenhouse gases to global climate coupled with increased public awareness of these effects, has renewed interest the search for an alternative to chemicals derived from fossil resources (Alonso *et al.*, 2010; Geboers *et al.*, 2011; Kobayashi *et al.*, 2012; Rosatella *et al.*, 2011). In this respect, biomass derived carbohydrate, which is abundant and relatively inexpensive can be converted into many useful renewable chemical feedstock (Gandini, 2008). Among those chemicals, 5-hydroxymethylfurfural (5-HMF), which can be easily produced by the dehydration of fructose is a potential intermediate. 5-HMF can be transformed into many other useful products, such as 2,5-furandicarboxylic acid (2,5-FDCA) which may replace terephthalic acid as a monomer in the production of plastics, and 2,5-dimethylfuran which is a potential liquid transportation fuel (Cao *et al.*, 2011).

Several known processes for the conversion of carbohydrates into energy and liquid fuels have been in existence for decades. For instance, liquefaction or pyrolysis of biomass leads to formation of bio-oils (Elliott *et al.*, 1991), Fischer-Tropsch synthesis has been employed for the production of alkanes or methanol from biomass-derived CO: H<sub>2</sub> gas and the production of aromatic hydrocarbons via the conversion of sugars or methanol was reported using zeolites as catalysts (Chen *et al.*, 1986, Weisz *et al.*, 1979). However, the most widely used process for producing liquid fuels from biomass is the conversion of glucose to ethanol (Katzen and Tsao, 2000). In this work, production of hydrophobic polymers from bio-based monomers is reported.

### Materials and Methods

#### Materials

Sodium borohydride, 1,4-butanediol, 1,6-hexanediol and 1,8-octanediol were obtained from Aldrich, Gilligham Dorset UK at 99% purity and 1-butyl-3-methylimidazolium chloride (BMIMCl) was obtained from Iolitec Deutschland Germany with 99% purity. All other reagents were used as received without further purification. <sup>1</sup>H and <sup>13</sup>C NMR were recorded

using a Bruker AMX 300 MHz spectrometer and data were processed by ACD/NMR Processor Academic Edition. Samples were made as dilutions of CDCl<sub>3</sub> unless otherwise stated. All chemical shifts (δ) are reported in parts per million (ppm). Multiplicities for <sup>1</sup>H coupled signals are denoted as s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). FTIR spectra were obtained in this work using ALPHA Bruker Optics FTIR spectrophotometer equipped with ZnSe ATR crystal.

#### Methods

##### Synthesis of 5-Hydroxymethylfuran (5-HMF)

This precursor was prepared according to our earlier paper (Nasirudeen *et al.*, 2017). Briefly, glucose (5.0 g, 0.028 mol) and BMIMCl (20.0 g, 0.11 mol) were heated in an oil bath at a temperature of 120 °C and stirred for 300 s to allow the dissolution of the glucose in the ionic liquid. The reaction was started by adding 10 mol. % of the following catalysts: CrCl<sub>3</sub>·6H<sub>2</sub>O, ZrO<sub>2</sub>, and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>. After completion of the reaction, 5-HMF was collected by vacuum distillation at 180 °C, 2.7 kPa. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>) δ 9.57 (1H, s, CHO), 7.22 - 7.21 (1H, d, *J* = 3.0 Hz, 3-H), 6.50 (1H, d, *J* = 6.0 Hz, 4-H), 4.70 (2H, s, OCH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz; CDCl<sub>3</sub>) δ 177.8 (C=O), 160.9 (C-5), 152.2 (C-2), 122.9 (C-3) 109.8 (C-4), 57.7 (OCH<sub>2</sub>); FT-IR (cm<sup>-1</sup>) 3377br, 1657s, 1250s, 1188s, 1160s.

##### Synthesis of 2,5-Furandicarboxylic acid monomer

To 5-HMF (1.26 g, 0.01 mol) was added a solution of NaOH (0.92 g, 0.023 mol). Potassium permanganate (3.6 g, 0.023 mol) was added and the reaction stirred at ambient temperature for 0.5 h. The mixture was filtered and to the filtrate 1 mL of concentrated HCl was added to adjust the pH to 1 or less. The precipitate was collected by suction filtration, washed with distilled water (50 mL) and FDCA isolated as a yellow solid (1.25 g, 80%). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 13.56 (2H, s, COOH), 7.29 (2H, s, 2 x =CH); <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) δ 158.5 (COOH), 149.5 (C-2 and C-5), 118.3 (C-3 and C-4); FT-IR (cm<sup>-1</sup>) 3120s, 1670s, 1570s, 1418s, 960s, 851s.

##### Synthesis of 2, 5-bis-(hydroxymethyl) furan (BHMF) monomer

To 5-HMF (2.0 g, 0.016 mol) in methanol (40 mL, 0°C), sodium borohydride (2.4 g, 0.063 mol) was slowly added. The reaction was stirred for 3 h at r.t, quenched with saturated aqueous sodium chloride solution (40 mL) and stirred for a further 30 min. The methanol was removed *in vacuo* at 40°C. The product was extracted with ethyl acetate (3 x 40 mL), the

organic layers combined and washed with brine (60 mL) and dried (sodium sulfate). The solvents were removed *in vacuo* to give BHMf as a pale yellow powder (1.8 g, 88%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.22 (2H, s, 3-H and 4-H), 4.56 (4H, s,  $\text{OCH}_2$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  154.1 (C-2 and C-5), 108.7 (C-3 and C-4), 57.5 ( $\text{OCH}_2$ ); FT-IR ( $\text{cm}^{-1}$ ) 3330br, 1731s, 1240s, 971s, 810s, and 756s.

#### Synthesis of polyester from FDCA

FDCA (5.0 g, 0.03 mol), 1,4-butandiol (13.523 g, 0.15 mol) and titanium (IV) *n*-butoxide (0.102 g, 0.0003 mol) were heated at 160°C for 6 h under a  $\text{N}_2$  atmosphere. Excess diol was then removed under vacuum and the reaction heated at 200°C for further 2 h under vacuum. Upon cooling to room temperature, 6 mL of 1,2-dichlorobenzene was added and heating continued at 200°C under vacuum to remove traces of diol. The resulting polyester was dissolved in 30 mL of trifluoroacetic acid (TFA) and precipitated using methanol (300 mL). The precipitates were centrifuged at 3000 rpm for 10 min, washed with methanol (3 x 5 mL) and dried at 50°C under vacuum for 18 h.

#### Water absorption test

Water absorption tests were conducted by following ASTM D570-98: standard test method for water absorption of plastics (D570-98, 2010). Briefly, the samples were conditioned by drying in an oven for 24 h at  $50 \pm 3^\circ\text{C}$ , cooled in a desiccator and immediately weighed to the nearest 0.001 g. The conditioned samples were immersed entirely in a 50 mL glass beaker containing 25 mL of distilled water maintained at ambient temperature. The immersed samples were removed after specific time intervals and all surface water was gently wiped with dried lint-free filter paper and weighed to the nearest 0.001g. Percentage increase in weight during immersion was calculated using the following equation:

$$\text{Increase in weight, \%} = \frac{W_f - W_o}{W_o} \times 100 \quad (1)$$

$W_f$  is the weight of the water absorbed sample and  $W_o$  is the weight of the conditioned sample.

## Results and Discussions

### Structure characterization of 5-HMF

The synthesised 5-HMF was characterised by FT-IR analytical techniques in order to find out the functional groups that are present on the products. Both spectra were compared with a commercially available 5-HMF.

The results of the FT-IR spectra of 5-HMF synthesized is presented in Fig. 1(a). The absorption band at  $3377\text{ cm}^{-1}$  can be assigned to the OH functional group of the molecule. Similarly, the absorption at  $1657\text{ cm}^{-1}$  can be attributed  $\text{C}=\text{O}$ . Those at 1250, 1188 and 1160 can be assigned to  $\text{C}-\text{O}$  of the molecule. All these peaks were compared with a commercially sourced 5-HMF as can be seen in Fig. 1(b).

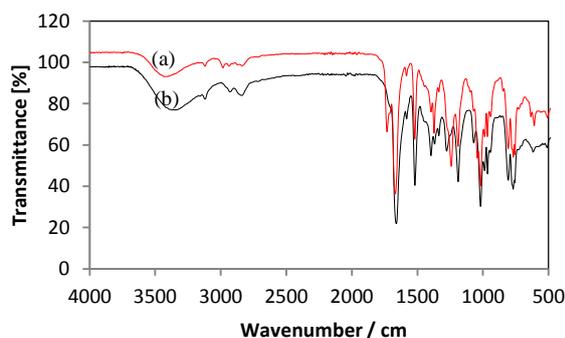


Fig. 1: FT-IR spectra of (a) synthesised 5-HMF (b) commercially sourced 5-HMF

### Synthesis of FDCA

Stated in the experimental section, FDCA was synthesised by oxidation of 5-HMF by potassium permanganate in a solution

of sodium hydroxide and a pale yellow solid was isolated by filtration as the product. The product was characterized by NMR and FT-IR spectroscopy.

### Characterization of FDCA

The structure of the synthesised FDCA was also characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR and the results are presented in Figs. 2 and 3. From Fig. 2, it can be seen that a singlet peak was observed at 7.29 ppm and this can be due to the proton resonances from H-3 and H-4 protons of the furan ring. Also observed on the spectra is the protons resonance associated with carboxylic acid at 13.56 ppm. These results are in agreement to those reported in literature (Gandini *et al.*, 2009a, Gandini *et al.*, 2009b, Silverstein *et al.*, 2005).

The result of the  $^{13}\text{C}$  NMR for the FDCA is presented in Fig. 3. It can be observed that a peak appeared at 118.31 ppm. This corresponds to the resonances of C3 and C4 of the furan ring while that at 146.92 ppm may be due to the resonances of C2 and C5. This is because these chemical shifts are characteristic of those associated with 2, 5-disubstituted furan rings (Gandini *et al.*, 2009b). Also, a  $^{13}\text{C}$  chemical shift associated with carboxylic acids usually occurs at 150 -185 ppm. This peaks associated the carboxylic acid were observed at 158.47 and 149.41, respectively.

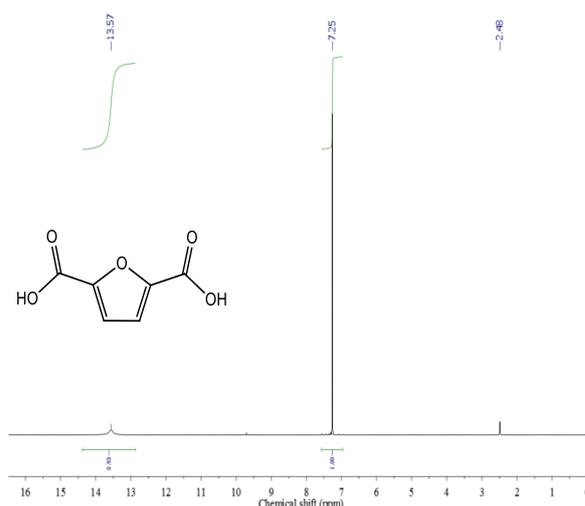


Fig. 2:  $^1\text{H}$  NMR of FDCA in  $\text{DMSO-d}_6$  (500 MHz)

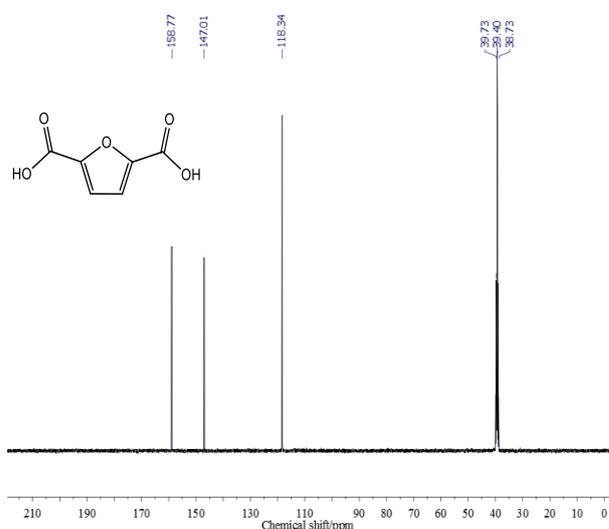


Fig. 3:  $^{13}\text{C}$  NMR of FDCA in  $\text{DMSO-d}_6$  (500 MHz)

In addition, the expected FT-IR absorption bands were observed. The  $\text{C}=\text{O}$  stretching vibration characteristic of the carbonyl group occurs at  $1670\text{ cm}^{-1}$  in agreement with others (Mohrig *et al.*, 2006). Using the  $\text{C}=\text{O}$  stretching absorption

resulting from of carboxylic acids occurs near  $1760\text{ cm}^{-1}$  (Silverstein *et al.*, 2005). This decrease may be attributed to the conjugation effects of the carbonyl group with the unsaturation of the furan ring which decreases the bond order of the C=O slightly and this leads to shifting of the absorption band to a lower frequency (Mohrig *et al.*, 2006).

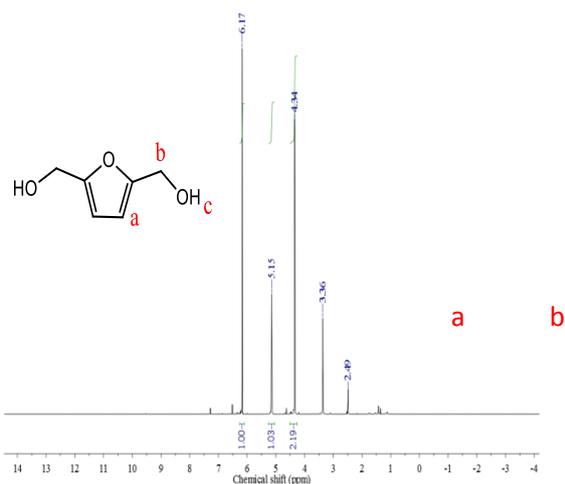
The FT-IR peaks observed are summarised in Table 2 which are in agreement with the values reported (Gandini *et al.*, 2009a, Gandini *et al.*, 2009b, Silverstein *et al.*, 2005, Mitiakoudis and Gandini, 1991).

**Table 1: Characteristic peaks of FDCA**

Assignment	Wavenumber / $\text{cm}^{-1}$
C = O stretching	1670
C – H	3150, 3120
OH (Acid)	2700 - 3400
C = C (Furan ring)	1569
C – O – H bending (Acid)	1418
C – H bending and Furan ring	960, 851, 762

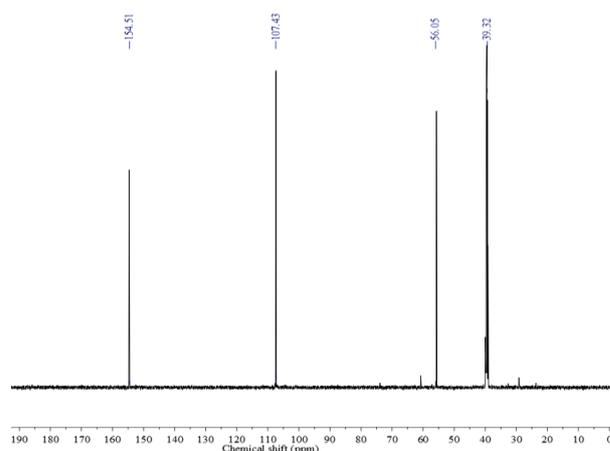
#### Synthesis of 2, 5-Bis (hydroxymethyl) furan (BHMF)

2, 5-Bis (hydroxymethyl) furan was synthesised by oxidation of 5HMF using  $\text{NaBH}_4$  and  $\text{KMnO}_4$ . The product was recrystallized in a refrigerator and a light yellow powder (4.4 g, 88.0% yield) was obtained. This product was characterized by NMR (500 MHz in  $\text{DMSO-d}_6$ ) as shown in Figs. 4 and 5. From Fig. 4, it can be observed that a singlet peak occurs at 6.17 ppm. This is attributed the 2H protons of the furan ring at H3 and H4. Also observed is a singlet peak at 5.15 ppm which is that of 2 protons attached on the OH and finally a doublet at 4.34 ppm of 4H on the  $-\text{CH}_2$  ends of the structure. Other peaks at 3.36 and 2.49 are those of water and  $\text{DMSO-d}_6$  solvents, respectively.



**Fig. 4:  $^1\text{H}$  NMR spectra of BHMF in  $\text{DMSO-d}_6$  (500 MHz)**

To further characterize the structure of the synthesized BHMF, a  $^{13}\text{C}$  NMR of the product was also obtained (Fig. 5). From this result, it can be observed that the peaks are attributed as follows: 154.62 ppm is assigned to the 2C of C2 and C5, 108.95 ppm is assigned to 2C of C4 and C5 and 55.71 is assigned to the 2C of  $-\text{CH}_2$ . These assignments confirmed to the peaks obtained by  $^1\text{H}$  NMR and were all in agreement to the ones reported elsewhere (Rass *et al.*, 2013).



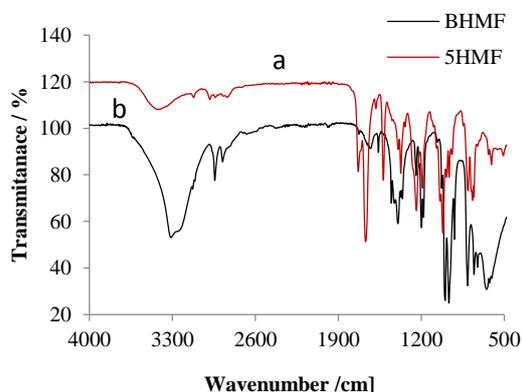
**Fig. 5:  $^{13}\text{C}$  NMR spectra of BHMF in  $\text{DMSO-d}_6$**

#### FT-IR spectra of BHMF

To further establish the structure of the BHMF synthesized, an FT-IR spectrum of the product was obtained to identify the functional groups that are present. This result is presented in Fig. 6(b) and compared with the starting material (5-HMF). From these results, it can be seen that the functional group of the C=O at  $1731\text{ cm}^{-1}$  on the starting material (5-HMF) in Fig. 6(a) was absent on the final product. On the other hand, functional groups around the OH region ( $3330\text{ cm}^{-1}$ ) and those at the C-O ( $1240\text{ cm}^{-1}$ ) were observed on both spectra. Similarly, functional groups of  $-\text{CH}$  on the furan structure were observed at about 971, 810 and  $756\text{ cm}^{-1}$ .

With the presence of these functional groups on the BHMF, it can be ascertained that reduction was successfully achieved on 5-HMF to yield a pale yellow powdered material at 97% (2.1g). Also, the melting point of this yellow powder was measured and found to be  $72^\circ\text{C}$  and compared with the literature value of  $74\text{--}77^\circ\text{C}$ .

Therefore, this product will either serve as a monomer or diol for esterification reactions and also will be treated with Na-MMT clay for an attempt to carry out an *in situ* polymerization for the synthesis of polymer-clay nanocomposite.

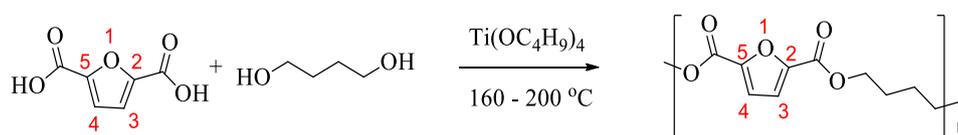


**Fig. 6: FT-IR spectra of (a) 5-HMF and (b) BHMF**

#### Synthesis of poly(butylene-2,5-Furandicarboxylate (PB-2,5-F)

Initial polymerisation reactions were conducted at  $200^\circ\text{C}$  using esterification and polycondensation method. At the end of the polymerization reaction, methanol was added to precipitate the polymer formed which was collected via centrifugation. A fibrous polymer was obtained and after drying was characterized by NMR, FTIR and TGA instruments. The reaction scheme is presented in Scheme 1.

## Hydrophobic Polymer Production



Scheme 1: Synthesis of poly (butylene-2, 5-furandicarboxylate) (PB-2,5-F)

### NMR structure characterization

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra for the polymer product are presented in Figs. 7 and 8. From Fig. 7, it was observed that the resonance peaks of 3-H and 4-H of the furan protons appeared at 7.19 ppm and that at 4.38 is attributed to ester  $\text{OCH}_2$  group. Also observed were two peaks due to  $\text{OCH}_2\text{CH}_2$  at 1.89 ppm as expected.

In the  $^{13}\text{C}$  NMR spectrum (Fig. 8), the  $\text{C}=\text{O}$ , C-2/C-5 and C-3/C-4 associated with the furan ring were observed at 160.0, 147.8 and 118.5 ppm, respectively. Also observed are the carbon atoms associated with the ester at 65.0 ppm and 25.2 ppm corresponding to  $\text{OCH}_2$  and  $\text{OCH}_2\text{CH}_2$ , respectively. These resonances were comparable to those for the same polymer reported elsewhere (Ma et al., 2012).

From these results, it was concluded that the furan ring remained thermally stable in the final product despite the extensive heating at 200°C during the polymerization reaction.

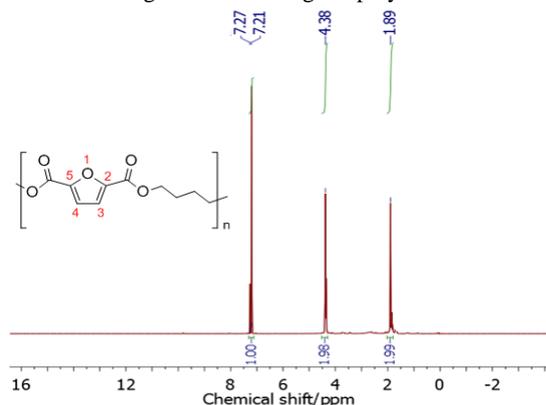


Fig. 7:  $^1\text{H}$  NMR spectra of polyester from FDCA and 1, 4-butanediol in  $\text{CDCl}_3$

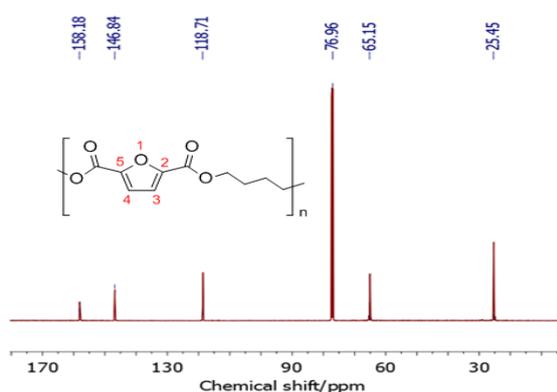


Fig. 8:  $^{13}\text{C}$  NMR spectra polyester from FDCA and 1, 4-butanediol

### FT-IR structure characterization

The resulting polymer synthesized from FDCA and 1,4-butanediol was characterized by FT-IR. The FT-IR spectra shown in Figure 9 provided evidence for characteristic absorptions of the furan ring at 3122, 1574, 1039, 975, 824 and 771  $\text{cm}^{-1}$ , and those of the ester carbonyl at 1728  $\text{cm}^{-1}$  which were all observed. This also confirmed the results obtained from the NMR spectrum. The detailed functional group assignments are presented in Table 3.

To ascertain the total elimination of the 1,4-butanediol from the polymer, the FT-IR spectrum of 1,4-butanediol and FDCA was compared with that of the polyester product as shown in Figure 10 and it can be seen that the absorption band of the OH group present on the 1,4-butanediol spectra was absent on the polyester. This indicates that the polymerization reaction proceeds and the expected product was obtained.

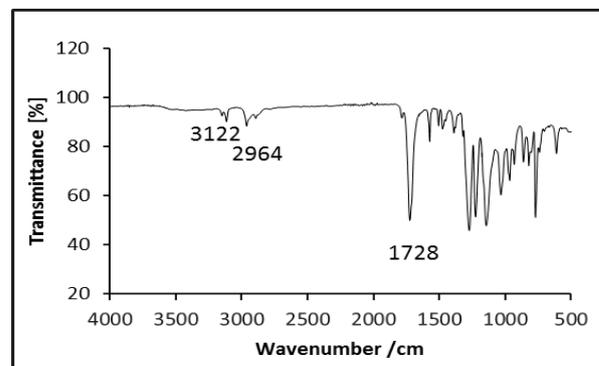


Fig. 9: FTIR spectrum of polyester from FDCA

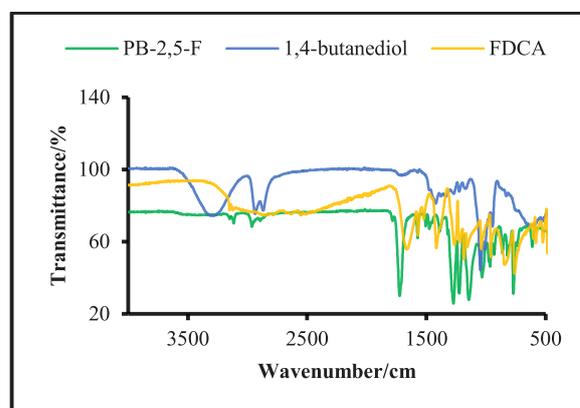


Fig. 10: FTIR spectrum of PB-2,5-F polymer, 1, 4-butanediol and FDCA

Table 2: FT-IR absorption bands of polyester from FDCA

Assignment	Wavenumber/cm
=CH	3122
C-H	2964, 2894
C=O	1724, 1785
C=C	1574
C-O	1272
Furan breathing	1039
Furan bending motion	975, 824, 771

### Water contact angle

The water contact angle gives an indication of hydrophobicity which in turn is related to the number of permanent dipoles in the structure and hence to dielectric constant. This reveals how a water drop on a solid or liquid surface spreads. Water contact angle is defined as the included angle that water makes with a solid surface or capillary walls of a porous material when both materials come into contact (Zhang et al., 2014).

As one of the aims of this research is the synthesis of hydrophobic polymers, contact angle of the polymer surface

was determined to study wettability and the results are presented in Fig. 11. The contact angle as measured with a protractor on printed images of droplets such as those displayed in Fig. 12 was 91° for PBH-2, 5-F polymer (Fig. 11). During the measurements of the contact angle, the advancing angles were measured and not the receding angle. This is because the measurements were conducted within 10-120 seconds and the formation of receding angles was prevented by buffering the atmosphere to stop evaporation from the water droplets. Therefore, the results suggest that the PBH-2,5-F polymer is slightly more hydrophobic than the others based on their water contact angle measurements (Zhang *et al.*, 2014; Yuan and Lee, 2013). In general, a material or surface is designated hydrophobic if the water contact angle is greater than 90° but this is an arbitrary criterion. An angle less than 90° corresponds to high wettability or hydrophilicity of the surface as illustrated in Fig. 12. However, others have argued that 65° should be the criterion for hydrophobic surfaces (Vogler, 1998; Guo *et al.*, 2008). As shown in Table 4, the other polymers: PB-2, 5-F, PH-2, 5-F and PO-2, 5-F also have contact angles close to 90° and therefore also fall into the category of hydrophobic.

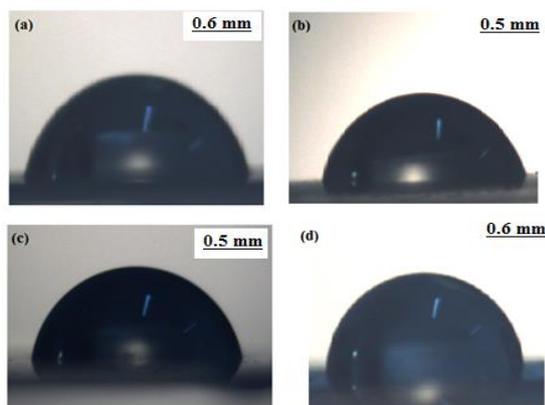


Fig. 11: Water contact angle of: (a) PB-2,5-F (b) PH-2,5-F (c) PO-2,5-F and (d) PBH-2,5-F

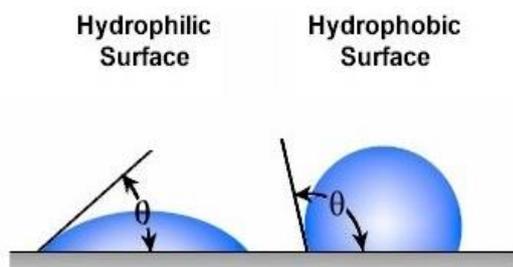


Fig. 12: Hydrophilic and hydrophobic surfaces based on contact angle

Table 3: Water contact angles of polymers derived from FDCA and various diols

Polymers	Water contact angle/ °		
	Mean	95%*	n**
PB-2,5-F	83	1	6
PH-2,5-F	85	1	6
PO-2,5-F	87	2	6
PBH-2,5-F	91	1	6

\*Confidence limit; \*\*Number of population

**Variation of contact angle with time**

The relationship between contact angle and time was investigated and the results are presented in Fig. 13. The contact angles of the sessile drops were also measured

between 10-120 seconds and it was found out that PB-2, 5-F, PH-2, 5-F and PO-2, 5-F polymers have the same contact angles of 83° at 10s while PBH-2, 5-F has an angle of 89°. This study revealed that the contact angles on these polymers increase slightly with time as observed on different polymers (Taylor *et al.*, 2007). The reason is that the approach to equilibrium is slow: some authors have advised vibrating the sessile drop to obtain an equilibrium angle (Ruiz-Cabello *et al.*, 2011).

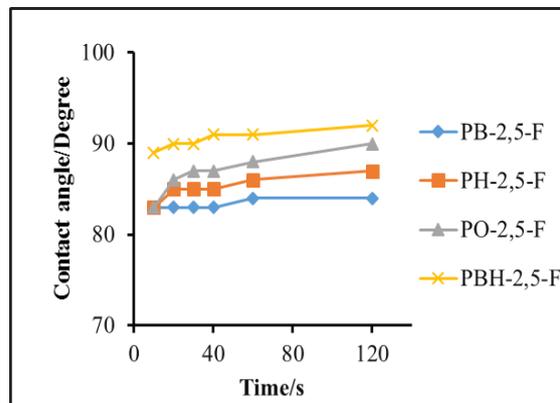


Fig. 13: Water contact angle as a function of time of the various polymers

In conclusion, water droplets on these polymers rest on their surfaces with a high contact angle which is stable in a 100% RH buffered atmosphere.

**Water absorption**

Water absorption tests were conducted on the polymers produced at different times and the results are presented in Fig. 14. It can be seen that all the polymers have absorbed a significant but low amount of water rising to about 1 % at saturation. Among the four polymers produced, PHB-2, 5-F shows the least water absorbed compared to others. After 14 days of immersion in water, this polymer was able to absorb only about 0.8 % water. This correlates with the contact angle value of this polymer: it gave the highest contact angle of about 91° compared to others. Similarly, PB-2, 5-F polymer was observed to have the highest water absorption value of 1% after 14 days of immersion which correlates with lowest water contact angle as earlier shown in Table 4. In general therefore, these polymers are able to absorb about 1% of water when in contact with water for extended times during their potential applications.

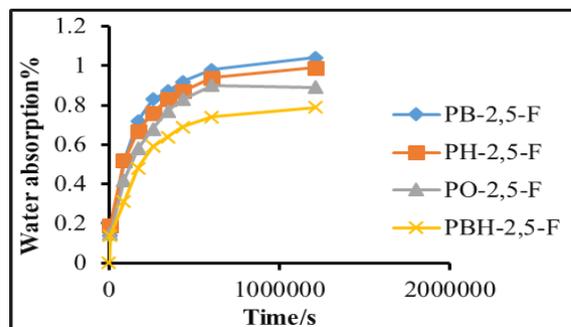


Fig. 14: Water absorption of the polymers derived from FDCA and various diols

**Conclusion**

Polymerization of FDCA monomer with various diols including BHMf as the reduction production of 5-HMF was conducted. The diols used were 1, 4-butandiol, 1, 6-hexanediol, and 1, 8-octanediol and the FDCA monomer was used to produce polymers using the various diols. There

polymers are: poly (butylene-2, 5-furandicarboxylate) (PB-2, 5-F), poly (hexylene-2, 5-furandicarboxylate) (PH-2, 5-F) and poly (octylene-2, 5-furandicarboxylate) (PO-2, 5-F). Another polymer, poly (2, 5-furandimethylene 2, 5-furandicarboxylate) (PBH-2, 5-F) was produced from FDCA and BHMF. Their structures were confirmed by <sup>1</sup>H NMR and FT-IR spectroscopies after precipitated in methanol. These bio-based polymers can serve as alternatives to those produced from fossil fuels.

### References

- Alonso DM, Bond JQ & Dumesic JA 2010. Catalytic conversion of biomass to biofuels. *Green Chemistry*, 12: 1493-1513.
- Geboers JA, Van De Vyver S, Ooms R, Op De Beeck B, Jacobs PA & Sels BF 2011. Chemocatalytic conversion of cellulose: Opportunities, advances and pitfalls. *Catalysis Science & Technology*, 1: 714-726.
- Kobayashi H, Ohta H & Fukuoka A 2012. Conversion of lignocellulose into renewable chemicals by heterogeneous catalysis. *Catalysis Sci. & Technology*, 2: 869-883.
- Rosatella AA, Simeonov SP, Frade RFM & Afonso CAM 2011. 5-Hydroxymethylfurfural (Hmf) as a building block platform: Biological properties, synthesis and synthetic applications. *Green Chemistry*, 13: 754-793.
- Gandini A 2008. Polymers from renewable resources: A challenge for the future of macromolecular materials. *Macromolecules*, 41: 9491-9504.
- Cao Q, Guo XC, Yao SX, Guan J, Wang XY, Mu XD & Zhang DK 2011. Conversion of hexose into 5-hydroxymethylfurfural in imidazolium ionic liquids with and without a catalyst. *Carbohydrate Research*, 346: 956-959.
- Elliott DC, Beckman D, Bridgwater AV, Diebold JP, Gevert SB & Solantausta Y 1991. Developments in direct thermochemical liquefaction of biomass - 1983-1990. *Energy & Fuels*, 5: 399-410.
- Chen NY, Degnan TF & Koenig LR 1986. Liquid fuel from carbohydrates. *Chemtech*, 16: 506-511.
- Weisz PB, Haag WO & Rodewald PG 1979. Catalytic production of high-grade fuel (gasoline) from biomass compounds by shape-selective catalysis. *Science*, 206: 57-58.
- Katzen R & Tsao GT 2000. A view of the history of biochemical engineering. *Advances in Biochemical Engineering/Biotechnology*, 70: 77-91.
- Nasirudeen MB, Hailes HC & Evans JRG 2017. Preparation of 5-hydroxymethylfurfural from glucose and fructose in ionic liquids by reactive vacuum distillation over a solid catalyst. *Current Organic Synthesis*, 14: 596-603.
- D570-98, A 2010. Standard Test Method for Water Absorption of Plastics, pp. 1-4.
- Gandini A, Silvestre AJD, Neto CP, Sousa AF & Gomes M 2009a. The furan counterpart of poly(ethylene terephthalate): An alternative material based on renewable resources. *J. Polymer Sci. Part a-Polymer Chem.*, 47: 295-298.
- Gandini A, Coelho D, Gomes M, Reis B & Silvestre A 2009b. Materials from renewable resources based on furan monomers and furan chemistry: Work in progress. *J. Materials Chem.*, 19: 8656-8664.
- Silverstein R, Webster F & Kiemle D 2005. Spectrometric Identification of Organic Compounds. Hoboken: John Wiley & Sons Inc.
- Mohrig JR, Hammond CN & Schatz PF 2006. Techniques in Organic Chemistry. 2nd ed. New York: WH Freeman and Company.
- Mitiakoudis A & Gandini A 1991. Synthesis and characterization of furanic polyamides. *Macromolecules*, 24: 830-835.
- Rass HA, Essayem N & Besson M 2013. Selective aqueous phase oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over Pt/C catalysts: Influence of the base and effect of bismuth promotion. *Green Chemistry*, 15: 2240-2251.
- Ma J, Pang Y, Wang M, Xu J, Ma H & Nie X 2012. The copolymerization reactivity of diols with 2,5-furandicarboxylic acid for furan-based copolyester materials. *J. Materials Chem.*, 22: 3457-3461.
- Zhang L, Zhao N & Xu J 2014. Fabrication and application of superhydrophilic surfaces: A review. *J. Adhesion Sci. & Techn.*, 28: 769-790.
- Yuan Y & Lee TR 2013. Contact angle and wetting properties. In: Bracco G & Holts B (eds.) *Surface Science Techniques*. 51 ed. Berlin Heidelberg: Springer-Verlag.
- Vogler EA 1998. Structure and reactivity of water at biomaterial surfaces. *Advances in Colloid and Interface Science*, 74: 69-117.
- Guo CW, Wang ST, Liu H, Feng L, Song YL & Jiang L 2008. Wettability alteration of polymer surfaces produced by scraping. *J. Adhesion Sci. & Techn.*, 22: 395-402.
- Taylor M, Urquhart AJ, Zelzer M, Davies MC & Alexander MR 2007. Picoliter water contact angle measurement on polymers. *Langmuir*, 23: 6875-6878.
- Ruiz-Cabello FJM, Rodriguez-Valverde MA & Cabrerizo-Vilchez MA 2011. Comparison of the Relaxation of Sessile Drops Driven by Harmonic and Stochastic Mechanical Excitations. *Langmuir*, 27: 8748-8752.