Full Length Research Article

Preparation and Characterization of Biobased Poly(Ethylene- 2,5-Furan Dicarboxylate)/Clay Nanocomposites

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ABSTRACT
Poly(ethylene 2,5-furan dicarboxylate)/Clay nanocomposites was prepared via esterification and polycondensation reaction. Biobased monomer was first intercalated into the interlayer regions of clay minerals by ion exchange reaction. Then, the clay was dispersed in the monomer at different loading degrees to conduct the polymerization process. Polymerization through the interlayer of the clay led to the exfoliated poly(ethylene-2,5-furan dicarboxylate)/montmorillonite nanocomposite formation. X-ray diffraction (XRD) analysis revealed that the resultant nanocomposites exhibited exfoliated polymer/clay nanocomposites
Keywords: Poly(ethylene-2,5- furan dicarboxylate); renewable polymers; nanocomposites, montmorinollite

INTRODUCTION
Research on nanocomposites derived from biodegradable polyesters and layered silicates have been a subject of great interest from the scientific community in recent years (Alexandre and Dubois, 2000, Kumar and Nanthini, 2009, Zhu et al., 2013). This is because layered clays such as Montmorillonite (MMT) are environmentally friendly, naturally abundant, and thus available at relatively low cost. Their dispersion within polyester matrices provides significant improvement in various properties, in contrast with the biodegradable polymers, which widens the application areas of these biopolyesters (Chen et al., 2008).

Polyester-layered silicate nanocomposites can be made by three different methods: polymer melt intercalation, solution adsorption/ intercalation and *in situ* intercalative polymerization (Chen and Evans, 2005, Chouli et al., 2012, Ray and

Okamoto, 2003). Chemicals from renewable feedstock have been proposed as monomers for polymer production and among the bio resources, carbohydrates which are obtained from the biorefinery can be transformed into varieties of products, including dehydrosugars, furans, and levulinic acid by dehydration. 2,5-furandicarboxylic acid (2,5-FDCA) is an important member of the furan family that can be formed by an oxidative dehydration of glucose (Werpy et al., 2004). For instance, 2,5-FDCA has a similar structure to teraphthalic acid (Figure 1) that is used in the production of polyethylene terephthalate (PET). Therefore, 2,5-FDCA has been found to be an alternative for the petroleum-based terephthalic acid (Bokanga, 1996, Nasirudeen et al., 2017). Furthermore, the US department of Energy has also identified 2,5-FDCA as one of the 12 top potential chemicals that can be derived from biomass (Holladay et al., 2004).
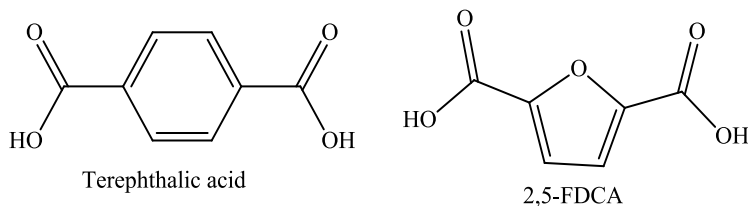

Figure 1. Structural similarity between terephthalic acid and 2,5-FDCA

Therefore, 2,5-FDCA has an enormous potential as a replacement for terephthalic acid, for the synthesis of various polyesters, such as poly(ethylene terephthalate) (PET), poly(propylene terephthalate) (PPT) and poly(butylene terephthalate) (PBT). PEF is the most studied and most important polyester from 2,5-FDCA and advantage of this biobased polymer as a PET analog provided an essential opportunity to address a high volume, high value chemical market. Roughly, 56 million tons of PET are manufactured every year leading to a market value of PET plastic in the range of $1.00 – 3.00/lb, depending on its usage (Yoshida et al., 2016).

Biobased polymers derived directly from biomass are generally polysaccharides which are carbohydrates formed through the condensation of monosaccharide residues by hemi-acetal or hemi-ketal linkages. They can also be found as a short oligosaccharide sequence or polymeric repeat units linked to other biopolymers and serve as energy storage, structural and protective components, and for gel formation depending on their specific chemical structure, composition, molecular weight and ionic character (Alexandre and Dubois, 2000, Ramesh and Tharanathan, 2003). The major classes of polysaccharides are starches, celluloses and chitin which constitutes the bulk of polymers directly derived from biomass and are used in food and non-food industries due to their functional diversities (Ramesh and Tharanathan, 2003). Although they are naturally obtained directly from biomass, they generally need to have a bulk or surface modification chemically on the hydroxyl groups in their structure to pave the way for their application as biopolymers. In terms of bulk modification, some derivatives of these polymers are also desirable: an example of such a process is the formation of chitosan and the chemical modification involves the compatibility and minimization of the hydrophilicity of natural fibres between the fibres and the matrix (Gandini, 2008). Therefore, polysaccharides are generally modified for used as biopolymers by reducing

their hydrophilicity; achieved by lowering their surface energy or creating enough surface morphology in order to obtain a water contact angle higher than 90° (Cunha and Gandini, 2010, Gandini, 2008, Gandini, 2011). In this research work, preparation and characterization of biobased poly(ethylene 2,5-furan dicarboxylate)/clay nanocomposites is reported.

MATERIALS AND METHODS
Materials
Potassium per manganate, hydrochloric acid, titanium (iv) n-butoxide, triflouroacetic acid, 1,2-dichlorobenzene and 1,4-butandiol were purchased from Signa-Aldrich, Gilligham Dorset UK at 99% purity and montmorillorite clay (Nanofill 116) was obtained from Southern Clay products, UK. The 5-hydromethylfuran (5-HMF) used was our purified product synthesized previously (Nasirudeen et al., 2017) . All other reagents were used as received without further purification.

Methods
Synthesis of 2, 5-Furandicarboxylic acid (2,5 FDCA)
2,5-FDCA was synthesized according to the following procedure (Ma et al., 2012). Briefly, 5-hydroxymethyl furan (5-HMF) (1.26 g, 10 mmol) was added to a solution of sodium hydroxide (920 mg, 23 mmol) in a 100 ml round bottom flask equipped with magnetic stirrer. Potassium permanganate (363.5 mg, 2.3 mmol) was added to the contents in the 100 ml flask and stirred for 0.5 h at ambient temperature. The mixture was filtered and 1 mL of concentrated HCl was added to the filtrate, precipitate was formed and the pH was adjusted to 1 or less. The precipitate was washed with distilled water and a pale yellow solid was isolated by filtration and dried in a vacuum. The product was characterized by FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy.

Synthesis of polyester from 2,5-FDCA
Polymerization was performed based on the method described by Ma, et al., (2012). Briefly, 2,5-FCDA (4.682 g 30 mmol), 1, 4-butandiol

(13.523 g, 150 mmol) and titanium (IV) n-butoxide (0.102 g, (0.3mmol) were charged into a 50 mL round bottom flask fitted with a magnetic stirrer. The reaction flask was immersed into an oil bath heated at 160 °C for 6 h under N_2 atmosphere. After 6 h of reaction time, the excess diol was removed under vacuum and the reaction continued at 200 °C for further 2 h under vacuum. Upon cooling to room temperature, 6 mL of 1,2-dichlorobenzene was added to the reaction flask and heating continued at 200 °C under vacuum to remove traces of diol by azeotropic distillation with 1,2-dichlorobenzene.The resulting polyester was dissolved in 30 mL of triflouroacetic acid (TFA) and precipitated in 300 mL methanol. The precipitates were centrifuged at 3000 rpm for 10 minutes, washed with methanol (5 mL, 3 times) and dried at 50 °C under vacuum overnight and characterised by FTIR, ^{1}H NMR, [13]NMR, XRD and by elemental analysis.

Treatment of montmorillonite clay with 2,5-FDCA
A suspension of 1 g of montmorillonite clay (Nanofill 116) was made in 25 mL of ethyl acetate in a glass bottle with lid and 2 g of 2,5-FDCA was added. The contents were stirred with the aid of an ultrasonic probe (U200s control, IKA Labortechnik Germany) at 0.5 duty cycle, 60% amplitude and poured into a Petri dish and left to stand for 86 ks (24 h) for drying. Control samples were prepared with solvent but without 2,5-FDCA.

Dispersive intercalation of clay and 2,5-FDCA
1 g of montmorillonite clay was dissolved in 25 mL of DMSO in a 50 mL glass bottle and dispersed with an ultrasonic probe at 0.5 duty cycle, 60% amplitude for 20 minutes. To the contents in the 50 mL glass bottle, 2 g of 2,5-FDCA were added and the dispersion continued for further 20 minutes. The contents were poured into an evaporating basin and placed on a hot plate pre-set at 150 °C to evaporate the DMSO. After 30 minutes, the evaporating basin was cooled to room temperature and dried in a vacuum oven at 60 °C for 72 h.

Melt intercalation of clay and 2,5-FDCA
Montmorillonite clay and 2,5-FDCA were weighed in a ratio of 1:2 and placed into a 400 mL cylindrical glass vessel. Nitrogen gas was introduced into the glass vessel with the aid of a balloon as inlet and an empty balloon was placed at the outlet. The contents were heated in a furnace to 330 – 344 °C and allowed to cool to room temperature.

Preparation of Poly(ethylene-2,5-furan dicarboxylate)/Clay nanocomposites
Poly(ethylene-2,5-furan dicarboxylate/clay nanocomposites was prepared by intercalation from solution, *in situ* intercalative polymerization and melt intercalation as follows:

Intercalation method
Montmorillonite clay (10 mg) was weighed and dispersed in chloroform (25 mL) by ultrasonification. Polyester (200 mg) was added to the clay solution and dispersed for a further 30 minutes. The contents were transferred into a Petri dish and dried in a fume cupboard overnight to evaporate the chloroform. After drying, the mixture was ground with a pestle and mortar to a fine powder and the XRD pattern of the polyester/clay was obtained.

***In situ* intercalative polymerization**
2,5-FDCA (4.5 g), montmorillonite clay (0.225 g), 1,4-butandiol (13.53 g, 30 mmol) and titanium (IV) n-butoxide were charged into a 50 mL round bottom flask and heated in an oil bath set at 160°C under reflux and in a N_2 atmosphere for 6 hr. The excess diol was removed under vacuum and the reaction continued for further 2 hr at 200 °C under vacuum. The reaction mixture was cooled at room temperature and the resulting polyester was dissolved in triflouroacetic acid (30 mL). Methanol (100 mL was added to precipitate the polyester/clay and the precipitate was centrifuged at 300 rpm for 10 minutes, washed with methanol (10 mL 3 times) and dried under vacuum at 50 °C overnight.

Melt intercalation

Montmorillonite clay (10 mg) and polyester (200 mg) were charged into a 50 mL round bottom flask and heated at 40 °C with constant stirring at 300 rpm for 30 minutes. The melt sample was cooled to 4 °C and ground with a pestle and mortar to a fine powder and analyzed by XRD.

Characterization

^1H and ^{13}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 $CDCl_3$ unless otherwise stated. All chemical shifts (δ) are reported in parts per million (ppm). Multiplicities for ^1H 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.

For XRD analysis, the samples prepared from 5-HMF and 2,5-FDCA by the solution and melt intercalation methods were carefully ground into fine powders using a pestle and mortar and pressed with a microscope slide into a copper sample holder and analysed using an X-ray diffractometer (Siemens D500) in the Chemistry Department of UCL using Cu Kα1 radiation with wavelength of 0.154056 nm. The diffractometer running at 40 kV and 30 mA was set at a low initial angle of 2° and scanned to 25° 2θ in 0.05° steps. Counts were collected for 6 s at each step and the XRD pattern of the samples was obtained.

RESULTS AND DISCUSSION

Structure characterization of FDCA

2,5-FDCA was synthesized from 5-HMF using 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 FT-IR and the result is presented in Figure 2.

From this result, the expected absorption bands of the characteristic functional groups associated with this compound such as stretching and bending absorption bands were observed. For instance, C = O stretching vibration characteristics of carbonyl group occurs at 1666 cm^{-1} and based on literature data, the absorption resulting from C = O stretching of carboxylic acids occurs near 1760 cm^{-1} (Silverstein et al., 2005a, Silverstein et al., 2005b). This decrease may be attributed to the conjugation effects of the carbonyl group with the unsaturation of the furan ring. Furthermore, some absorption bands were observed in the 2800 – 2200 cm^{-1} region associated with carboxylic acids and these may be as a result of the very intensive O-H stretching absorption. Also observed on the FT-IR spectrum are: C – O stretching and O – H bending which appears at 1270 and 1418 cm^{-1} respectively. The main peaks observed in the spectra are summarized in Table 1.

Table 1. Characteristic peaks of FDCA.

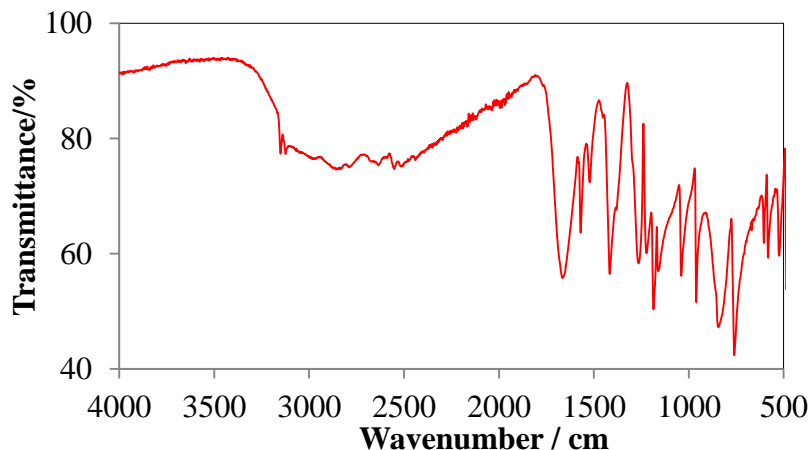| Assignment	Wavenumber / cm
C = O (Carboxylic acid)	1666
OH (Acid)	2700 - 3400
C = C (Furan ring)	1569
C – O – H bending (Acid)	1418
C – H bending and Furan ring	960, 849, 760

Figure 2. FT-IR Spectra of prepared FDCA.

Other vibrations that are associated with 2, 5-disubstituted furans were observed at 3149 cm^{-1} which may be as a result of O–H stretching of the carboxylic acid and also C–H stretching vibration at C-3, 4 positions. Another characteristic band occurs at 1569 cm^{-1} which results from C=C stretching absorptions and at 1039 cm^{-1} which corresponds to the characteristic band of heterocyclic breathing. Furthermore, bending motions that are typical of 2, 5-disubstituted furan were observed at 960, 843 and 759 cm^{-1} respectively. All these characteristic absorptions were similar to those peaks reported elsewhere (Gandini et al., 2009a, Gandini et al., 2009b, Mitiakoudis and Gandini, 1991, Silverstein et al., 2005a, Silverstein et al., 2005b).

The structure of the synthesized FDCA was further characterized by ^{1}H NMR and ^{13}C NMR and the results are presented in Figures 3 and 4. From Figure 3, 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 proton resonance associated with carboxylic acid group 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., 2005a).

The result of the ^{13}C NMR for the FDCA is presented in Figure 4. It can be observed that a

peak appeared at 118.31 ppm that 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-disubsituted furan rings (Gandini et al., 2009a). Also, a ^{13}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 ppm, respectively.

Polymerization Process
The polymerization reaction was conducted by the esterification method and followed by polycondensation reaction (Scheme 1), and at the end of the polymerization process, a fibrous lumps of polymer were obtained. The resulting polymer was characterized by NMR, FTIR and TGA.

NMR structure characterization
The ^{1}H NMR and ^{13}C NMR spectra for the polymer product are presented in Figures 5 and 6. From Figure 5, it can be observed that the resonance peaks of H3 and H5 of the furan protons appeared at 7.19 ppm and that at 4.38 is attributed to that of the ester -OCH$_2$ Also observed are two CH$_2$ next to the OCH$_2$ at 1.89 ppm.
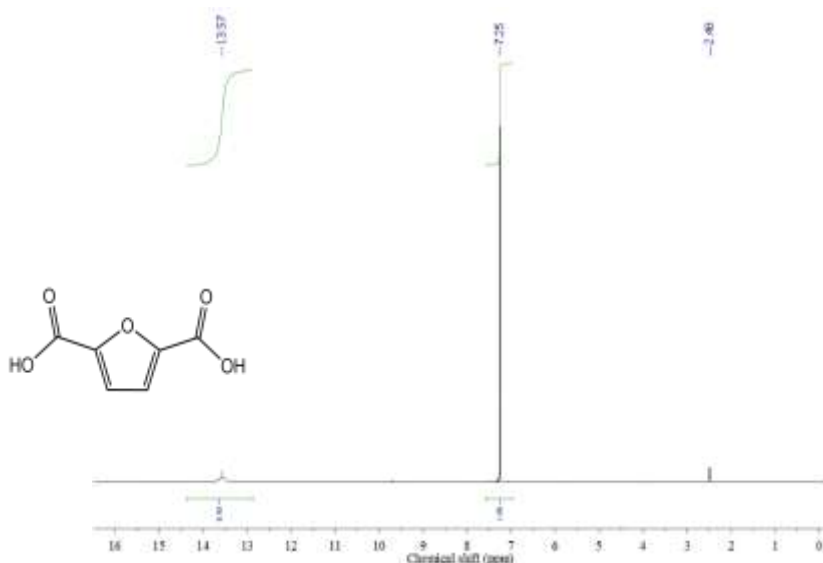
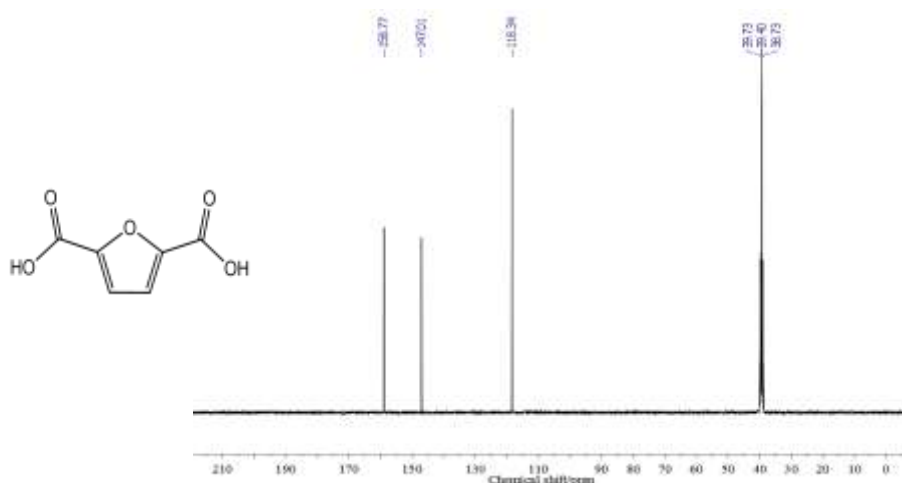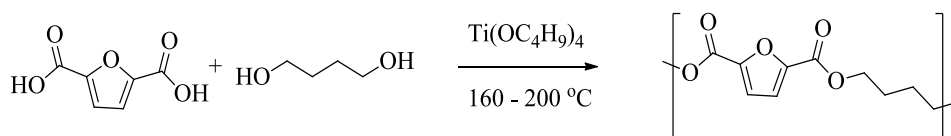**Figure 3**: ^{1}H NMR of FDCA in DMSO-d$_6$ (500 MHz)

Figure 4: ^{13}C NMR of FDCA in DMSO-d$_6$ (500 MHz)

Scheme 1. Synthesis of poly (butylene-2, 5-furandicarboxylate)

In the ^{13}C NMR as shown in Figure 6, C = O, C2/C5 and C3/C4 associated with the furan ring were observed at 157.99, 146.75 and 118.51 ppm, respectively. Also observed on the spectra are the carbon atoms associated with the ester at 64.94 and 25.24 ppm. Since the diol used is 1, 4-butane diol, the ester group is represented here as –COOCH$_2$ – (CH$_2$)$_2$ – CH$_2$O-. Therefore, C is

the expected at 64.95 ppm and C at 25.24 ppm. These resonances were all comparable to those reported elsewhere (Ma et al., 2012b).

From these results, it could be concluded that the furan ring remained thermally stable in the final product despite the extensive heating at 200 °C during the polymerization reaction.
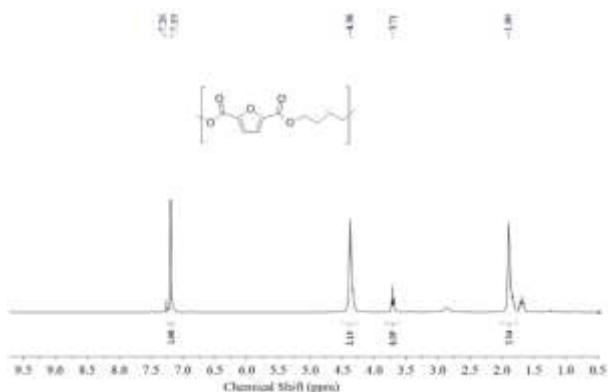
Figure 5: ^{1}H NMR spectra of polyester from FDCA and 1, 4-butanediol in CDCl$_3$

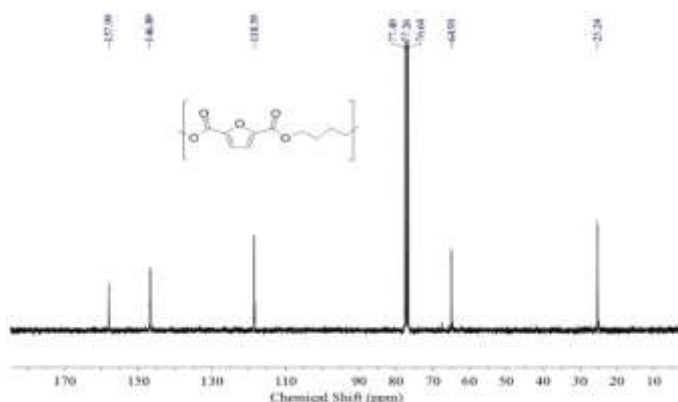**Figure 6**: ^{13}C NMR spectra polyester from FDCA and 1, 4-butanediol

FT-IR structure characterization

The resulting polyester synthesized from FDCA and 1, 4-butanediol was characterized by FTIR. The FTIR spectra shown in Figure 7 provided evidence for the chemical structure of the polyester. Characteristic absorptions of the furan ring at 3122, 1574, 1039, 975, 824 and 771 cm^{-1}, and those of the ester carbonyl at 1728 cm^{-1} were all observed. This also confirmed the results obtained from the NMR spectrum. The detailed functional group assignments are presented in Table 2.

To ascertain the total elimination of the 1,4-butanediol from the polyester, the FTIR spectrum of 1,4-butanediol was compared with that of the polyester product as shown in Figure 8 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.

XRD pattern of the polymer/clay nanocomposites

Assessments of intercalation and/or exfoliation of the polymer clay nanocomposites were investigated by XRD and the results are presented in Figure 9. From these results, it can be observed that the basal spacing (d$_{001}$) of the polymer-clay nanocomposite produced by an *in situ* polymerization is 1.413 nm. This revealed a decrease in the d-spacing when compared with that of the FDCA monomer (1.70 nm) and this suggests an exfoliation of the polymer into the clay galleries based on the basal spacing. Also, it was observed that the d$_{001}$ value of the polymer without the clay was absent in relation to its nanocomposite counterpart. Therefore, from this result it can be concluded that an exfoliated polymer/clay nanocomposite was prepared by an *in situ* polymerization technique.
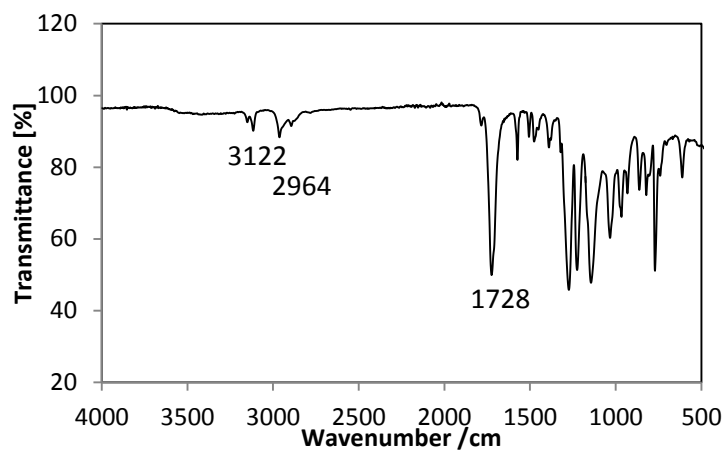
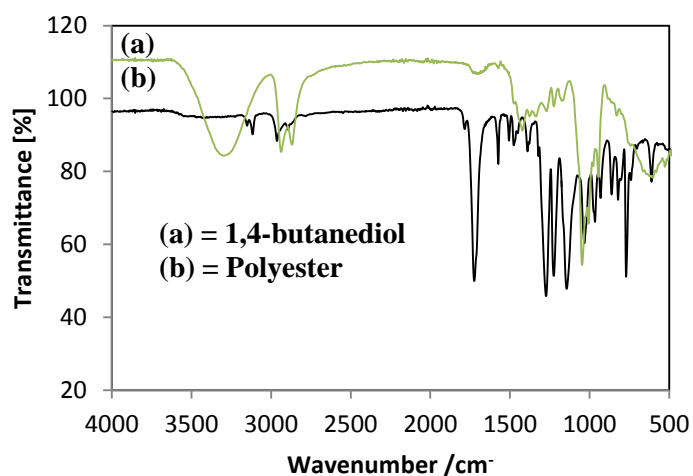**Figure 7**: FTIR spectrum of polyester from FDCA

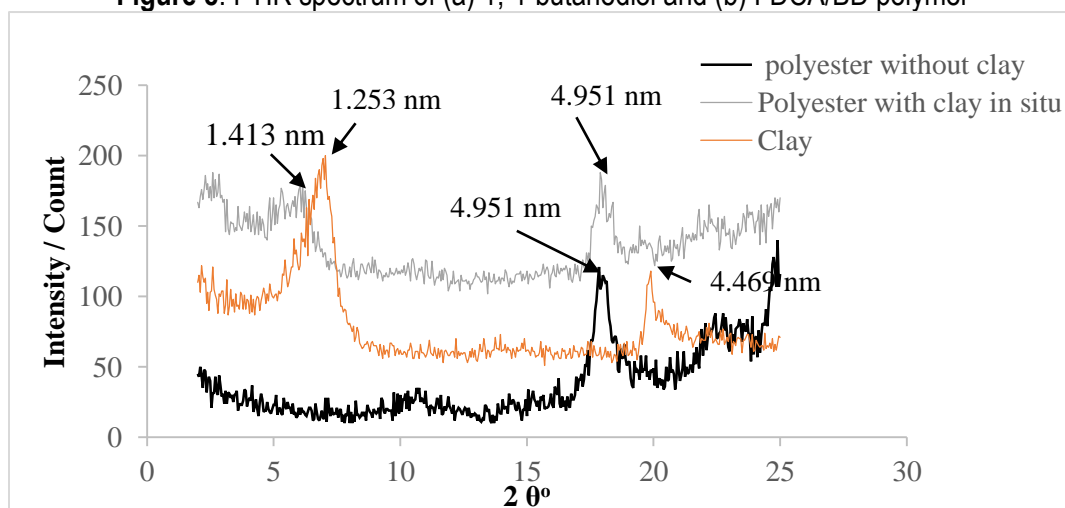**Figure 8**: FTIR spectrum of (a) 1, 4-butanediol and (b) FDCA/BD polymer

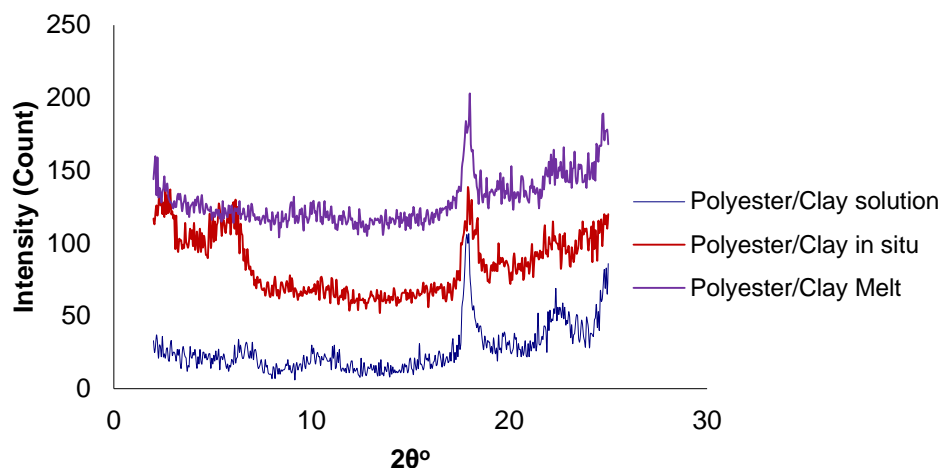**Figure 9**: XRD pattern polyester with and without clay

Figure 10: XRD pattern of polyesters/clay nanocomposites produced by various methods

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

XRD pattern of polymer/ Clay nanocomposites by different methods

The XRD patterns of polyester/clay nanocomposites as presented in Figure 10 revealed that there was no observed changes on polymer/clay nanocomposites produced by solution and melt intercalative methods. This might be due to the inability of these nanocomposite to form a thermodynamically homogeneous mixtures of the clay and polymer matrix. On the other hand, a slight increased on the d-spacing was observed in *in situ*

polymerization with a 2θ value of 6.25° and this suggests that the substrate used led to the formation of a polymer- clay nanocomposite.

CONCLUSION

In this study, biobased poly(ethylene- 2,5-furan dicarboxylate)/clay nanocomposites was prepared. The results obtained showed that an exfoliated polyester/clay nanocomposites were prepared by solution, *in situ* and melt intercalated methods as revealed by XRD chromatograms. Also, the interaction between the monomers and Na-montmorillonite clay showed that 5-HMF and 2,5-FDCA were able to intercalate between the clay layers which suggests that the production of polymer-clay nanocomposites are possible based on the *in-situ* polymerization of intercalated monomers and confirmed that the polymerization process produced the polyester accompanied by increased basal spacing of the montmorillonite, confirming that poly(ethylene- 2,5-furan dicarboxylate)/clay.

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