

Research Article

Synthesis and Characterizations of Biobased Copolymer Poly(ethylene-co-butylene 2,5-Furandicarboxylate)

Nam Vu Trung , Mai Ngoc Nguyen , Anh Nguyen Thi Ngoc , Ni Pham Thi ,
Tung Tran Quang , and Thuy Tran Thi 

School of Chemical Engineering, Hanoi University of Science and Technology, Hanoi 100000, Vietnam

Correspondence should be addressed to Thuy Tran Thi; thuy.tranthi3@hust.edu.vn

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Homopolymers and copolymers derived from 2,5-furandicarboxylic acid have been extensively studied for their potential in the development of sustainable plastics. This research definitely spotlighted the synthesis of poly(ethylene-co-butylene 2,5-furandicarboxylate) copolymer via the two-step melting polycondensation with various ethylene glycol/1,4-butanediol molar ratios. The structural characterization of the obtained biobased copolymer was carried out by ATR-FTIR and ¹H NMR. The average molecular weight of the obtained copolymer was determined by the intrinsic viscosity measurements. It was found that ethylene glycol was preferentially incorporated into the copolymer structures when the molecular weight of the products was not high enough (>18000). The decomposition of two types of monomer units of the obtained copolymer was proven through the degradation two-step process by TGA measurements.

1. Introduction

Polyesters based on 2,5-furandicarboxylic acid (FDCA) have received the significant attention of many scientists in an effort to replace the dominant petroleum-based polymers in plastic engineering [1, 2]. Taking advantages of the synthesis from renewable biosources, FDCA as well as other biobased platforms plays an important role in overcoming the problems of environmental degradation, climate change, and finite fossil resources [3–5]. FDCA has drawn a special interest recently since its derived polymers have series of comparable properties with the corresponding polymers synthesized from terephthalic acid in terms of structures, crystalline, thermal and mechanical behaviors, sorption, and transportation of carbon dioxide, water, oxygen, etc. [6, 7].

Since the first discovery of poly(ethylene 2,5-furandicarboxylate) (PEF) was reported by Gandini et al. [8], intensive efforts have been made to investigate all aspects of these potential materials [9]. Besides, there are a considerable number of research publications relating to synthesis and characterization of copolymers based on FDCA block in

combination with conventional homopolymers [10]. Copolymers in general have been favored both in academic research and industrial manufacturing as an efficient method to modify the structure of polymers and exploit their special properties [11]. According to many recent reports in the literature, the ambitions of studying FDCA-based copolymers in particular have focused on two major objectives: controlling and enhancing polymers' desired characteristics and combining polymers' advantages of biosourced syntheses and biodegradation.

The modifications equipping FDCA-based homopolymers with biodegradation were achieved by copolymerizing with typical well-known biodegradable polymers such as poly(lactic acid) (PLA) [12, 13], poly(ethylene glycol) (PEG) [14–16], and polycaprolactone (PCL) [17, 18]. Their works have dedicated a great contribution to the development of advanced materials that are totally environmentally friendly. On the other hand, the other topics involving the improvement of polymers' mechanical and thermal behaviors via copolymerization are equally attractive. Among the series of potential FDCA-based polymers, PEF has received remarkable attention for modification since it is the first

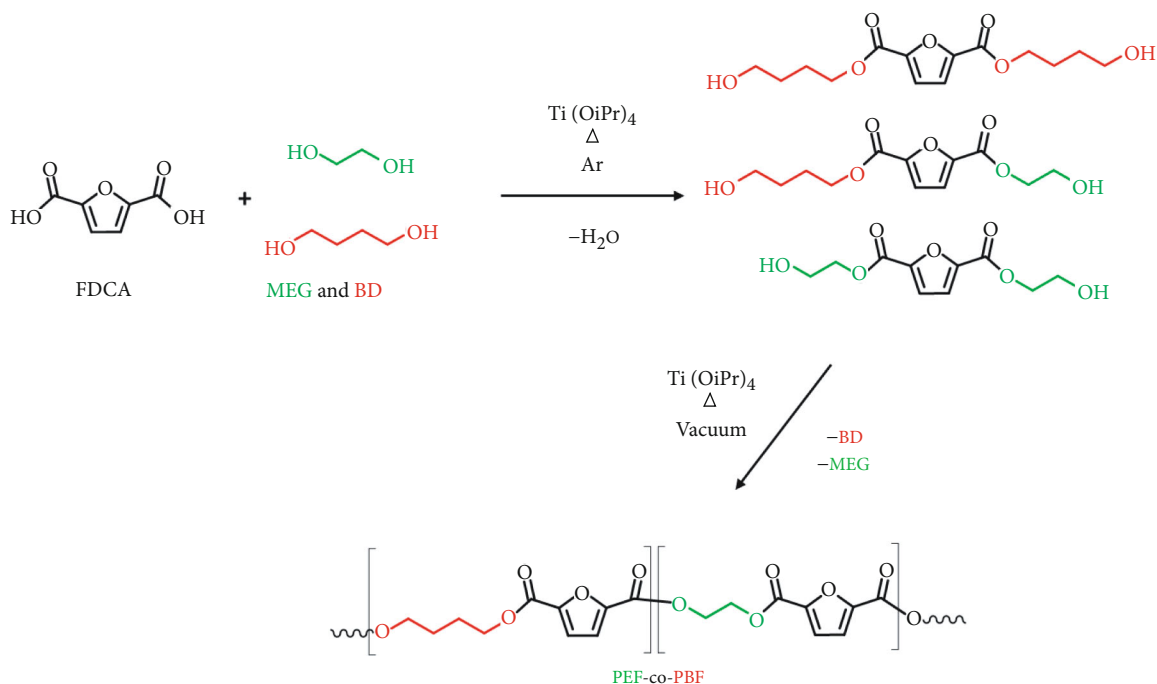


FIGURE 1: Schematic overview of the synthesis of PEF-co-PBFs by two-step melting polycondensation.

and the most basic polyester synthesized from FDCA. While PEF exhibits a lot of characteristics that are almost similar, even superior to the common poly(ethylene terephthalate) (PET) [6, 7, 19], it still has several inherent drawbacks in its thermomechanical properties such as the slow melt crystallization [20] and brittleness indicated by very limited elongation at break (1-5%) [21]. Copolymerization became a highly effective measure to toughen PEF, as well as to widen PEF-based materials' application range.

Recently, Xie et al. reported detailed investigations about poly(ethylene-co-hexamethylene-2,5-furandicarboxylate) (PEF-co-PHF) and poly(ethylene-co-1,5-pentylene 2,5-furandicarboxylate) (PEF-co-PPeF) [22, 23], indicating that the small contents of PPeF or PHF are capable of strengthening the ductility of copolymerized PEF. These results can be explained by the flexibility of the aliphatic long-chain diols; in fact, poly(alkylene furan-2,5-dicarboxylate)s with $C \geq 4$ are ductile materials with elongations at break exceeding 200% [22–24]. Previously, Ma et al. carried out a research about poly(ethylene-co-butylene 2,5-furandicarboxylate) [25]. In addition, 1,4-butanediol can be easily obtained via the HMF-based synthesis route by the recent successful transformations of 5-hydroxymethylfurfural (HMF), which is also the precursor of FDCA, to maleic anhydride [26]. Therefore, the present work is aimed at obtaining a deeper insight into the synthesis and characterization of polymers and copolymers based on FDCA.

In this contribution, the biobased copolymer poly(ethylene-co-butylene-2,5-furandicarboxylate) (PEF-co-PBF) was synthesized via the two-step melting polycondensation with varied ethylene glycol/1,4-butanediol molar ratios. The chemical structures of the obtained copolymers were analyzed with ^1H NMR and ATR-FTIR. The average molecular

TABLE 1: The preparations of copolymer synthesis.

Sample	Diol feed MEG : BD	m_{FDCA} (g)	$V_{\text{MEG}}, 25^\circ\text{C}$ (mL)	$V_{\text{BD}}, 25^\circ\text{C}$ (mL)
1	100 : 0	7.8	8.4	0
2	80 : 20	7.8	6.7	2.7
3	60 : 40	7.8	5.0	5.3
4	50 : 50	7.8	4.2	6.6
5	40 : 60	7.8	3.3	8.0
6	20 : 80	7.8	1.7	10.6
7	0 : 100	7.8	0	13.3

weights of obtained copolymers were estimated by the intrinsic viscosity measurements. Thermal properties of those samples were examined through TGA.

2. Materials and Methods

2.1. Chemicals. Titanium (IV) isopropoxide (99%) was provided by Energy Chemical. 2,5-Furandicarboxylic acid (FDCA) (97%), ethylene glycol (MEG) ($\geq 99\%$), and 1,4-butanediol (BD) (99%) were purchased from Sigma-Aldrich. Other chemical products were also purchased from Sigma-Aldrich.

2.2. Experimental Procedure. As displayed in Figure 1, the syntheses of PEF-co-PBFs with varied feed ratios of MEG and BD were carried out via the typical two-step melting polycondensation (an initial esterification, followed by a polycondensation with Ti(OiPr)_4 as a catalyst).

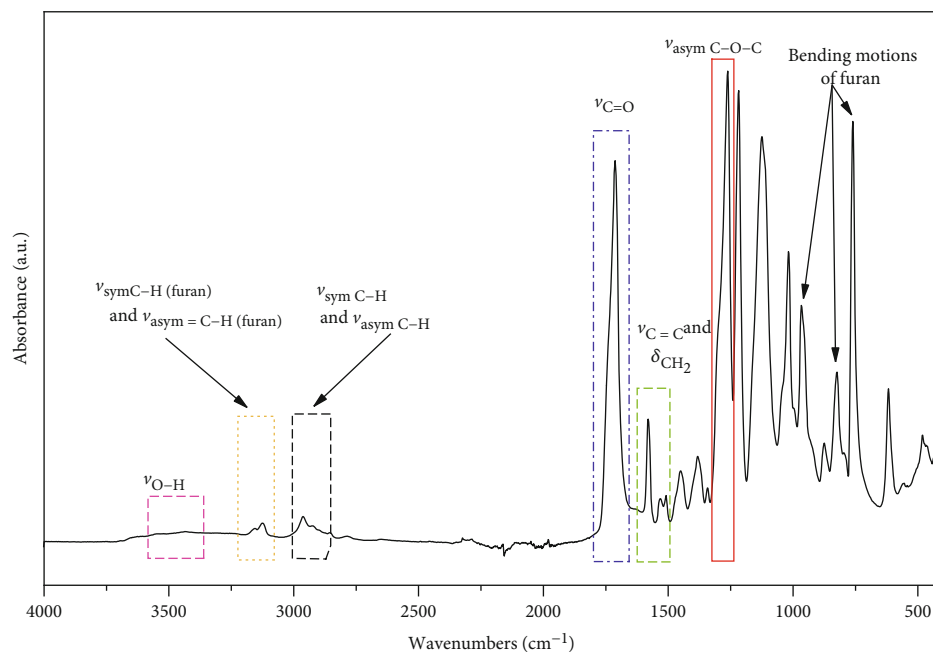


FIGURE 2: FT-IR spectrum of a copolymer synthesized with feed ratio of MEG : BD = 5 : 5.

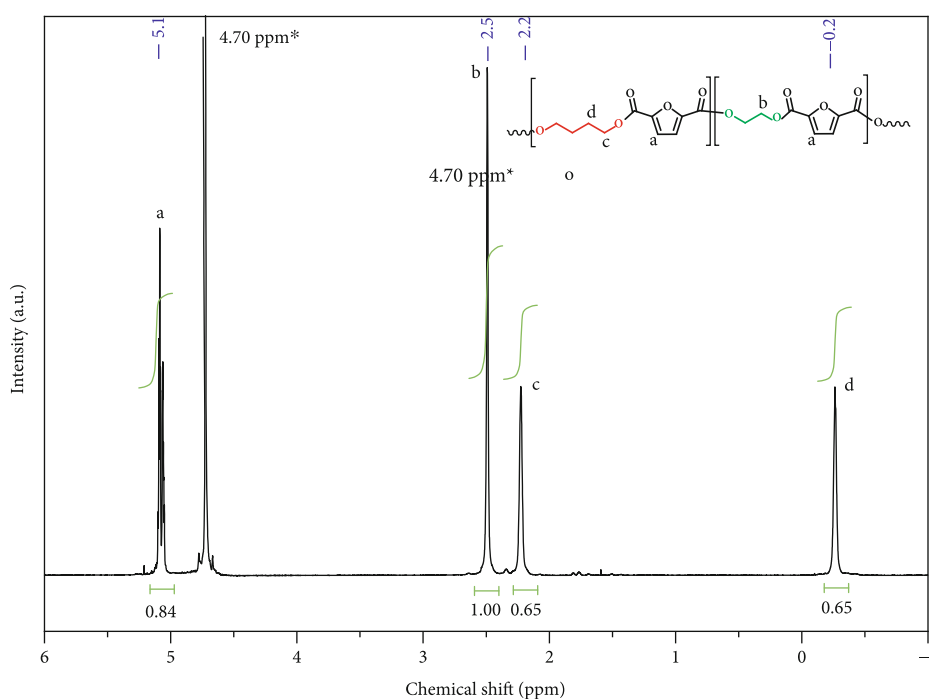


FIGURE 3: ^1H NMR spectrum of a copolymer synthesized with feed ratio of MEG : BD = 5 : 5 (internal standard D_2O and TFA- d_1 were tagged "*" at 4.7 ppm).

7.8 g of FDCA and an excessive amount of diols (FDCA : diol = 1 : 3) were charged into a two-neck round-bottom flask (Table 1), followed by adding a suitable volume of $\text{Ti}(\text{OiPr})_4$ (100 μL). The flask was connected to a reflux condenser and a mechanical stirrer. For the first stage, the reaction systems were kept stable at 175°C and were purged with argon periodically for 8 h. Then, in the second stage,

the reactions were performed at 200°C under high vacuum for the next 8 h to achieve high molecular weight polymers.

After that, the products were taken directly from reaction flasks by a spatula. The received samples were dried at 60°C overnight, and they did not undergo any further chemical process before being submitted for analytical measurements.

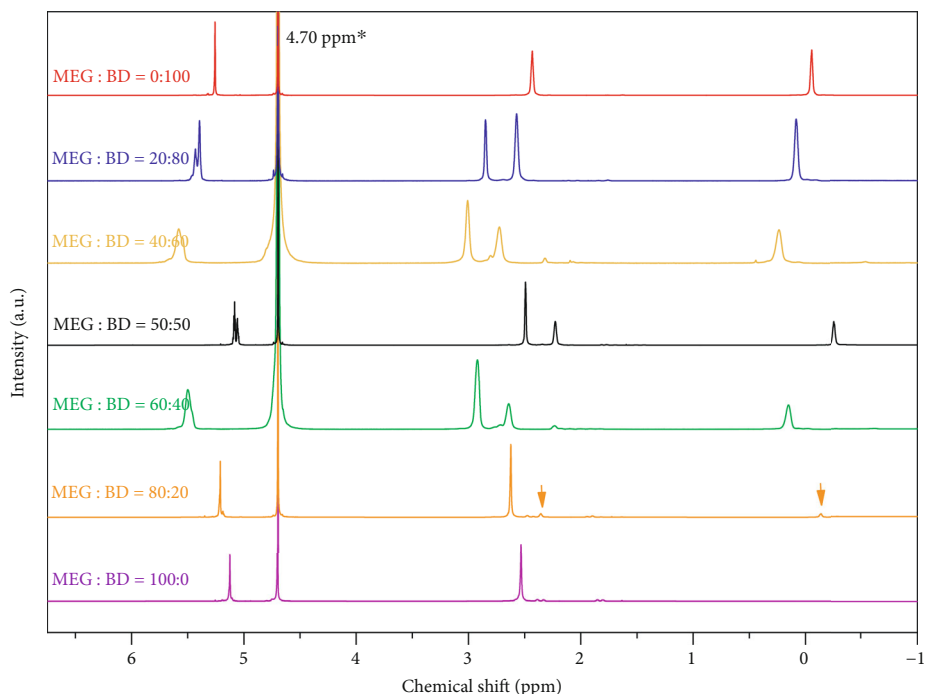


FIGURE 4: ^1H NMR spectra of prepared PEF, PBF, and PEF-co-PBFs (internal standard D_2O and TFA-d1 were tagged “*” at 4.7 ppm).

TABLE 2: MEG and BD content of synthesized copolymers.

Sample	Diol feed		Copolymer		Name of copolymer
	ϕ_{MEG} (%)	ϕ_{BD} (%)	ϕ_{MEG} (%)	ϕ_{BD} (%)	
1	100	0	100	0	PEF
2	80	20	92	8	$\text{PE}_{92}\text{B}_8\text{F}$
3	60	40	70	30	$\text{PE}_{70}\text{B}_{30}\text{F}$
4	50	50	61	39	$\text{PE}_{61}\text{B}_{39}\text{F}$
5	40	60	55	45	$\text{PE}_{55}\text{B}_{45}\text{F}$
6	20	80	38	62	$\text{PE}_{38}\text{B}_{62}\text{F}$
7	0	100	0	100	PBF

3. Methods

Nuclear magnetic resonance (^1H NMR): the chemical structures and compositions of synthesized copolymers were characterized by ^1H NMR spectra using a Bruker Avance III HD 500 MHz spectrometer. D_2O with TFA-d1 was utilized as an internal standard instead of pure TFA-d1, which is a very hazardous organic solvent.

Fourier transform infrared spectroscopy (FT-IR): infrared spectra of samples were recorded on a Nicolet iS50 FTIR (Thermo Fisher Scientific) spectrometer in the ATR mode. The specimens were measured directly with a scan range from 400 cm^{-1} to 4000 cm^{-1} .

The intrinsic viscosity method: to determine the average molecular weight of synthesized products, the intrinsic viscosity method was employed. Viscosities of polymer solutions were measured with an Ostwald viscometer. The solutions were prepared with a phenol/1,1,2,2-tetrachloror-

TABLE 3: Intrinsic viscosities and estimated average of copolymer.

Copolymer	Intrinsic viscosity (dL/g)	Estimated M_v (g/mol)
PEF	0.364 ± 0.002	$17,546 \pm 133$
$\text{PE}_{92}\text{B}_8\text{F}$	0.338 ± 0.002	$16,132 \pm 114$
$\text{PE}_{70}\text{B}_{30}\text{F}$	0.275 ± 0.006	$12,125 \pm 358$
$\text{PE}_{61}\text{B}_{39}\text{F}$	0.326 ± 0.002	$15,439 \pm 125$
$\text{PE}_{55}\text{B}_{45}\text{F}$	0.274 ± 0.001	$11,494 \pm 80$
$\text{PE}_{38}\text{B}_{62}\text{F}$	0.323 ± 0.002	$14,756 \pm 153$
PBF	0.348 ± 0.002	$16,835 \pm 176$

othane (3:2, w/w) mix solvent. Intrinsic viscosities were obtained by extrapolating the linear plot η_{sp}/C -C.

Thermal gravimetric analysis (TGA) experiments: these experiments were performed by using a Shimadzu DTG-

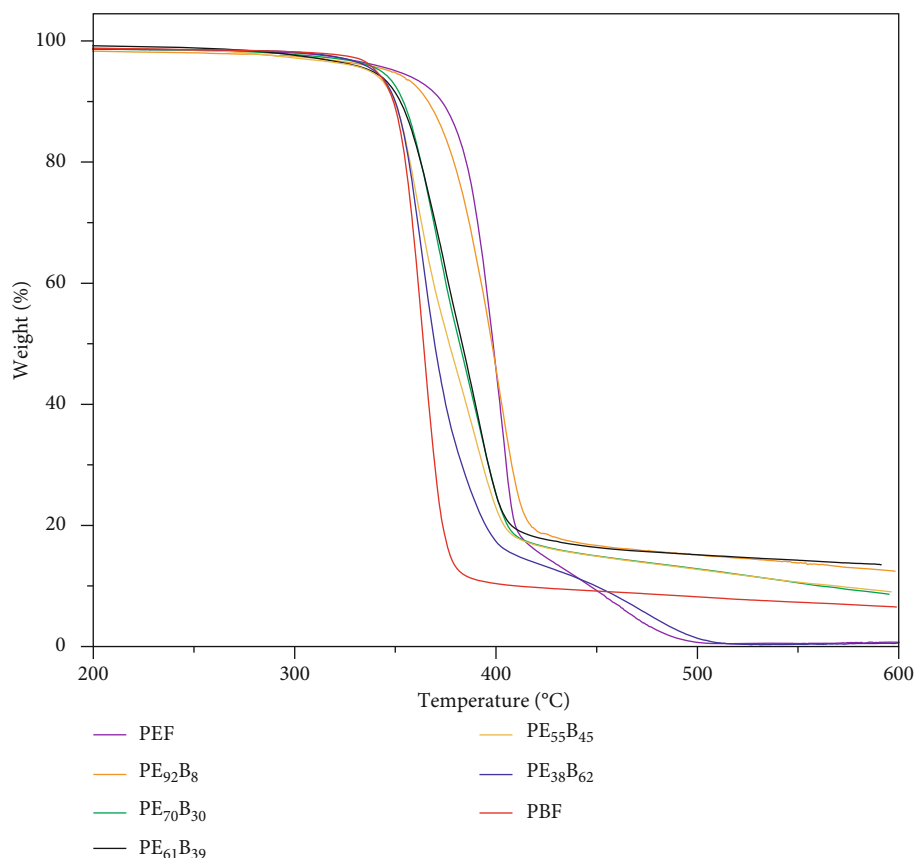


FIGURE 5: TGA plots of PEF, PBF, and PEF-co-PBFs.

60H analyzer with a heating rate of $10^{\circ}\text{C}/\text{min}$ under a nitrogen atmosphere and a temperature scan of $25\text{--}600^{\circ}\text{C}$.

4. Results and Discussion

4.1. Structures and Compositions of Copolymers. FT-IR analyses were employed to confirm the presence of various functional groups in polymer structures. There are no significant differences between the FT-IR spectra of the copolymer products and the PEF and PBF homopolymers. Figure 2 illustrates a typical FT-IR spectrum of a copolymer sample, which is the product synthesized with a feed ratio of MEG : BD = 5 : 5. The wavenumbers at 3157 and 3124 cm^{-1} were identified as symmetric and asymmetric C–H stretching of the furan ring ($\nu_{\text{sym}} = \text{C–H furan ring}$ and $\nu_{\text{asym}} = \text{C–H furan ring}$). The other two weak bands at 2962 and 2922 cm^{-1} belong to the symmetric and asymmetric C–H stretching properties of the methylene groups of the BD and MEG ($\nu_{\text{sym}} \text{C–H}$ and $\nu_{\text{asym}} \text{C–H}$). A very weak O–H hydroxyl group stretching vibration around 3434 cm^{-1} corresponding to end groups indicates that the copolymer has reached a rather high molecular weight. It is obvious that the stretching vibrations of the $\nu \text{C=O}$ bonds of the ester group can be observed at 1713 cm^{-1} . In addition, these spectra also showed a band near 1581 cm^{-1} assigned to both the C=C stretching and CH_2 in plane deformation ($\nu \text{C=C}$ and δCH_2 , respectively), a band near 1261 cm^{-1} originating from the $\nu_{\text{asym}} \text{C–O–C}$ stretching, and a series of signals assigned to the bending

motion of furan at 966 , 823 , and 760 cm^{-1} associated with the 2,5-disubstituted ring. Therefore, these spectroscopic results are consistent with the predicted molecular structures of the polyester products.

^1H NMR spectra were used to characterize structures and compositions of biobased polymers as can be seen in Figures 3 and 4. Because of the change in solvent, as well as the reference peak for aligning resonance signals, the measured signals were shifted in comparison with typical NMR spectra of FDCA-based polymers in TFA- d_1 [9].

The designation of peaks is indicated in detail in Figure 3, which is the ^1H NMR spectrum of a copolymer synthesized with a feed ratio of MEG : BD = 5 : 5. Despite the shifting, it was clear to assign major signals to respective protons in the structure of PEF-co-PBF. The characteristic signal appearing at 5.1 ppm was assigned to the furan ring protons. The resonance of protons in $-\text{CH}_2\text{O}-$ of MEG and BD units exhibited signals at 2.5 and 2.2 ppm correspondingly, while protons of middle $-\text{CH}_2-$ in BD units were attributed to the peak at -0.2 ppm.

The designation of NMR signals of other samples in Figure 4 followed a similar pattern as the typical spectrum shown above. In summary, the characteristic signals of MEG and BD units detected in these spectra confirmed the successful synthesis of the expected copolymers.

Besides, the compositions of the copolymer samples were determined from integrated intensities of the signals assigned to two different diol units. Specifically, the content of BD

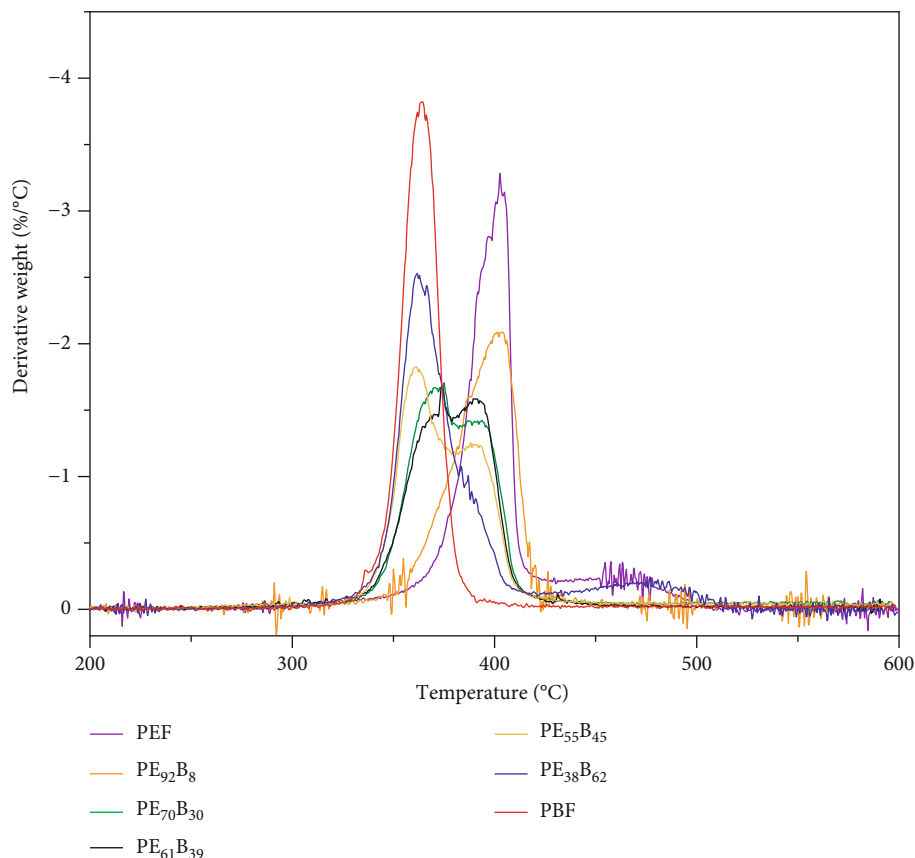


FIGURE 6: DTGA plots of PEF, PBF, and PEF-co-PBFs.

units ϕ_{BD} and MEG units ϕ_{MEG} in synthesized copolymers were calculated by

$$\phi_{MEG} = \frac{I_b}{I_b + I_d}, \quad (1)$$

$$\phi_{BD} = \frac{I_d}{I_b + I_d}. \quad (2)$$

I_b and I_d were the integrated intensities of protons of MEG and BD units, respectively, which were dubbed b and d in the ^1H NMR spectra as shown in Figure 3.

The calculation results are shown in Table 2. The copolymers are named as $\text{PE}\phi_{MEG}\text{B}\phi_{BD}\text{F}$, where ϕ_{MEG} and ϕ_{BD} are the percentage of diol in the copolymer.

It can be seen that the content of each diol in the copolymers was proportional to its fraction in feed composition. Moreover, the results also indicated that the fractions of MEG in copolymers were higher than that in the diol feed, or MEG units were preferred to be formed in conditions set up for the polycondensation. This observation was unusual, as in previous investigations, MEG was found to be less reactive compared to the other diols [22, 23, 25]. It is possible that the reason related directly to specific conditions of the polycondensation.

4.2. Intrinsic Viscosities. The intrinsic viscosity figures obtained from the extrapolations are presented in Table 3.

Intrinsic viscosities of the synthesized polymer samples were in the range 0.27-0.35 g/dL.

There was no noticeable variation of intrinsic viscosities with the change of copolymer compositions. By applying Mark-Houwink's equation with available parameters for PET (Equation (3)) [27], the viscosity-average molecular weights of polymer samples were estimated in Table 3. In general, the molecular weights of synthesized polymers were lower than that reported by Ma et al. [25]. This was because the experimental conditions including temperature and vacuum control are not yet optimized for further increases of molecular weights of polymers. Furthermore, the low molecular weights may explain the higher reactive ethylene glycol in the polycondensation. When the polycondensation had not reached a certain extent of equilibrium, kinetic control may be preferred, which allowed a more kinetically active molecular, or a smaller molecular otherwise—ethylene glycol, to participate in the esterification with FDCA.

$$[\eta] = 4.68 \times 10^{-4} M_v^{0.68}, \quad (3)$$

in which M_v is the viscosity-average molecular weight of the synthesized polymer.

4.3. Thermal Stability. TGA (thermo gravimetric analysis) and DTGA (derivative thermo gravimetry) curves of copolymer samples are shown in Figures 5 and 6.

TABLE 4: Decomposition temperatures of PEF, PBF, and PEF-co-PBFs.

Polymer sample	$T_{d,5\%}$ (°C)	$T_{d,50\%}$ (°C)	$T_{d,max}$ (°C)	
PEF	351	399	403	
PE ₉₂ B ₈ F	348	398	—	407
PE ₇₀ B ₃₀ F	343	382	367	397
PE ₆₁ B ₃₉ F	338	383	386	403
PE ₅₅ B ₄₅ F	337	377	383	403
PE ₃₈ B ₆₂ F	340	370	368	—
PBF	340	364	369	

In general, the thermal stability of copolymer varied slightly between the properties of PEF and PBF. It was evident that the MEG content increased the decomposition temperature of the copolymer, as the thermal stability of PEF ($t_{d,5} = 351^\circ\text{C}$, $t_{d,50} = 399^\circ\text{C}$) with shorter saturated carbon chains was better than PBF ($t_{d,5} = 340^\circ\text{C}$, $t_{d,50} = 364^\circ\text{C}$). It was also concluded that copolymers were more thermally stable with higher content of ethylene units. Besides, DTGA curves described the two-step degradation corresponding to the appearances of two differential peaks at around 403°C and 368°C . These referred to the decompositions of BD and MEG units, respectively, as they did not occur simultaneously. In addition, the decomposition peaks of copolymers became broader compared to homopolymers. Although DTGA curves of PE₉₂B₈F and PE₃₈B₆₂F did not exhibit clearly separated peaks, this broadening was observed.

The data can be summarized in Table 4 with temperatures of decompositions at 5% and 50% weight loss ($T_{d,5\%}$, $T_{d,50\%}$) and temperatures at which the degradation rates are maximum ($T_{d,max}$).

5. Conclusions

Poly(ethylene-co-butylene 2,5-furandicarboxylate) copolymers were synthesized successfully from biobased FDCA and the two diols, i.e., ethylene glycol and 1,4-butanediol, by the two-step melting polycondensation. The structures of the obtained products were confirmed and were consistent with the prediction. The average molecular weights of the obtained copolymer nearly reached 18,000, followed by an unusual trend in compositions of copolymers compared to available results in the literature. The degradations of copolymers were typical two-step processes, in which higher stability was correlated with higher MEG content in copolymers.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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