



# Article High-Performance Polyimide Films Derived from Biomass-Based Furfural: Fabrication and Properties

Lei Chen<sup>1</sup>, Weiyu Luo<sup>1</sup>, Yima He<sup>1</sup>, Lizhen Huang<sup>1</sup>, Jinjie Xu<sup>2</sup>, Kaixin Li<sup>1,\*</sup> and Yonggang Min<sup>1,\*</sup>

- <sup>1</sup> School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, China; cl223314@163.com (L.C.); weiyuluo64566@163.com (W.L.); yimahe0923@163.com (Y.H.); janly05011111@163.com (L.H.)
- <sup>2</sup> Guangzhou Emerging Material Institute Ltd., Guangzhou 510006, China; jinjie\_xu78@163.com
- \* Correspondence: li.kx@gdut.edu.cn (K.L.); ygmin@gdut.edu.cn (Y.M.)

Abstract: The development of renewable polymers as alternatives to the petroleum-based ones has received significant attention due to the increasing depletion of fossil oil and the associated environmental concerns. In this study, a semi-biomass-based polyimide (PI) film was successfully synthesized, using biomass-derived furfural (HMFA) as one of the raw materials. A two-step approach was first developed for this process: (1) conversion of HMFA to 3,3,4,4-biphenyltetracarboxylic acid dianhydride (BPDA) and (2) polymerization of BPDA with p-phenylenediamine (PPD) to form a PI film. The fabricated PI film demonstrated excellent properties, such as a high thermal decomposition temperature up to 600 °C, a satisfactory glass transition temperature (Tg) exceeding 365 °C, a coefficient of thermal expansion (CTE) of  $\approx$ 30 ppm/K, a tensile strength greater than 120 MPa, a dielectric constant value below 3.4, a dielectric loss value of less than 0.02, and a 24 h water absorption rate below 0.8%. These performances are comparable to the petrochemical-based PI. This work offers a promising strategy for utilizing biomass-derived materials in polyimide synthesis and would drive a new wave of advancements in polymer science.

Keywords: furfural; BPDA; polyimide; biomass; renewable polymer



Derived from Biomass-Based

Furfural: Fabrication and Properties.

Academic Editor: Conrado Aparicio

*Coatings* **2023**, *13*, 1726. https:// doi.org/10.3390/coatings13101726

Received: 22 August 2023

Accepted: 1 October 2023

Published: 3 October 2023

(†)

(cc)

Revised: 19 September 2023

Citation: Chen, L.; Luo, W.; He, Y.; Huang, L.; Xu, J.; Li, K.; Min, Y. High-Performance Polyimide Films

Polyimide is a high-performance polymer which is widely employed in aerospace and military fields due to its exceptional properties such as high heat resistance, low electrical conductivity, and intrinsic mechanical strength. It is generally synthesized via polycondensation between dianhydride and diamine [1–6]. However, the production of its monomers still relies on petroleum-based chemicals, which are associated with serious environmental issues and an energy crisis. Especially for the synthesis of diamines, it is reported that the carcinogenicity of petroleum-based diamines cannot be neglectable since it is significantly detrimental to the health of human beings [5]. Therefore, choosing green and renewable feedstock for the synthesis of dianhydride or diamine monomers is suggested as a feasible and efficient solution to alleviate the consumption of fossil oil and to achieve an environmental benefit. Moreover, the route for synthesizing PI film will be diversified by using different renewable resources, as they vary in chemical formula in nature [7–9]. Currently, the development of renewable PIs has been limited to the addition of biobased content, which is far from the early goals of revolutionary replacement. This limitation is mainly attributed to the design contradiction between the diversified characteristics of biobased resource and polymer properties.

Biomass is an abundant and potentially valuable resource that is easily accessible and widely available for a variety of chemical reactions, including ring-opening polymerization, copolymerization, and polytransesterification [10–15]. In the past two decades, a vast range of biomass-derived molecules have been employed as feedstock for polymerization process since their structure and functionality are similar to the petrochemical-based

**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). monomers after rational design [16,17]. Among these, furan-based chemicals were seldom reported [18]. In fact, most of them serve as top value-added chemicals and offer a rich source of derivatives that are potential renewable monomers. Especially furfural (HMFA), which is one of the key chemicals produced from lignocellulosic biorefineries, has recently been identified as a universal biomass-derived chemical. To the best of our knowledge, there are no works in the literature reporting the synthesis of biomass-derived polyimide from HMFA. In fact, polyimide is potentially prepared from HMFA owing to its unique properties and well-defined structure: (1) The aldehyde group of HMFA endows it with high chemical reactivity for the possible transformations into different targeted products. (2) The heteroaromatic furan ring of HMFA resembles the aromatic character of phenyl-based monomers, and it is readily converted to dianhydride via Diels–Alder for the fabrication of PI. Therefore, the synthesis of dianhydride or diamine monomers from furanbased chemical seems to be an efficient strategy to achieve the best balance between the biobased content in renewable PI and its polymer properties, such as its tensile strength or thermal stability.

Currently, many furan-based chemicals have been attempted as raw material for the synthesis of PI-based materials. For example, Hansol Jang et al. [19] used 2,5-furandicarboxylic acid (FDCA) as a raw material and copolymerized it with terephthalic acid,4,4'-(hexafluoroiso propylidene)diphthalic anhydride (6FDA), 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB), and terephthaloyl chloride to obtain a polyimide material with a biomass content of 11.32%. However, the resulting PI had significantly reduced thermal and mechanical properties, making it unsuitable for mass production. Similarly, Kai Ma et al. [20] also used FDCA as a raw material and combined it with a fluorinated para-nitroaniline to obtain a dinitro monomer, which was then reduced to an amino monomer. They then polymerized this amino monomer with bisphenol A dianhydride (BPADA) to obtain a polyimide monomer. Furthermore, they thermally crosslinked this polyimide with bismaleimide, resulting in a structurally responsible polyimide. Unfortunately, this polyimide did not exhibit outstanding thermodynamic properties.

However, these studies indicate that research on converting biomass into polyimides is still limited to incorporating biomass as a segment unit into the structure of dianhydrides or diamines. Due to the direct incorporation of the furan ring, the intermolecular forces between main chains were reduced, ultimately leading to a significant decrease in the thermodynamic properties of the polyimides synthesized using these dianhydrides or diamines. This is insufficient to meet the demands of today's society for polyimide materials. To address this issue, a suitable method is to directly convert the furan ring into a benzene ring, which can solve the problem of reduced intermolecular forces caused by the furan ring and ensure that the performance of biomass-based polyimides is stable.

In this study, we divided the conversion route into three steps: HMFA oxidation to maleic anhydride (MAH) [21–24], MAH aromatization to phthalic anhydride (PA) [25,26], and PA coupling to 3,3,4,4'-biphenyltetracarboxylic dianhydride (BPDA) [27–29]. The BPDA obtained by this method has a synthesis material of furfural and furan, and furan has also been identified as a biomass chemical, making the dianhydride monomer a fully biomass-based monomer. Subsequently, we added the biomass-based BPDA (B-BPDA) and petroleum-based BPDA (P-BPDA) successively to N-methyl-2-pyrrolidone (NMP) and copolymerized them with p-phenylenediamine (PPD) to obtain a series of PI films with different segment structures. Through thermal and other property characterizations, we found that the addition of B-BPDA did not significantly reduce the performance of the resulting PI films. Moreover, when the B-BPDA to P-BPDA segment proportion was approximately 1:1, the material's tensile strength, dimensional stability, and hydrophobicity were even better than those of pure P-BPDA and PPD-derived PI. Through this phenomenon, we successfully demonstrated the feasibility of biomass in the PI synthesis field and proposed new ideas for subsequent research on pure biomass-based polyimides.

## 2. Experimental Section

# 2.1. Materials

Furfural (>99% purity) and 30% hydrogen peroxide ( $H_2O_2$ , analytical grade) were both purchased from Aladdin (Shanghai, China). Vanadium pentoxide ( $V_2O_5$ ,  $\geq$ 99%), was purchased from Macklin. Phosphoric acid (analytical grade) was purchased from Macklin (Shanghai, China). Furan (Fur, 99% purity) was purchased from Aladdin (Shanghai, China). Trimethylsilyl iodide (TMSI, analytical grade) was purchased from Aladdin (Shanghai, China). Liquid bromine (Br<sub>2</sub>, AR grade) was purchased from West Long Chemicals (Guangzhou, China). Hydroxylamine sulfate (analytical grade) was purchased from Acros Organics (City, Country). Palladium on carbon (55% water, 10% palladium content) was purchased from Puyang Binhe Chemical Co., Ltd. (Shanghai, China). Solvents such as ether, hydrochloric acid, and acetic anhydride were all of analytical grade and purchased from Aladdin or Macklin. The synthetic route for the conversion of HMFA to BPDA and its application to PI shown in Figure 1.



Figure 1. Synthetic route for the conversion of HMFA to BPDA and its application to PI.

#### 2.2. Preparation of MAH by Oxidation of HFMA

One equivalent of furfural was added to a solvent of formic acid, and the mixture was heated to 60 °C, resulting in the formation of a dark brown solution. Subsequently, 6 equivalents of hydrogen peroxide solution were added dropwise, followed by stirring the reaction mixture for a duration of 4 h. This addition of hydrogen peroxide induced a color change in the solution from dark brown to orange-red, which further transitioned into a light yellow shade after 30 min. Once the reaction was complete, the reaction mixture was transferred to a distillation flask and subjected to distillation at 60 °C under

reduced pressure, aiming to eliminate formic acid and any residual hydrogen peroxide. The resulting product was a pale yellow solid, constituting a mixture of maleic acid (MA) and fumaric acid, both of which were formed as a consequence of the oxidation of HMFA. By utilizing a combination of formic acid and hydrogen peroxide as the oxidation system, a highly potent oxidation capacity was achieved. Because of the low boiling point of formic acid and peroxide's ease of decomposition into water and oxygen, both of them could be easily removed after the completion of reaction.

<sup>1</sup>H NMR (600 MHz, CD3CN), δ 6.36 (2H, s, =CH-), δ 6.7 (2H, s, =CH-) ppm, at a 92% yield. As shown in Figure S1.

The mixture of maleic acid and fumaric acid obtained was added into acetic anhydride, along with the addition of 0.1 equivalent of phosphoric acid and 0.02 equivalent of vanadium pentoxide. Subsequently, the reaction mixture was transferred to a Parr reactor and heated at 120 °C under an oxygen atmosphere of 10 bar for 2 h. Following the completion of the reaction, the resulting solution underwent filtration, and the filtrate was collected. The acetic anhydride was effectively removed from the filtrate by distillation under reduced pressure, using an aubergine flask, resulting in the formation of solid maleic anhydride (MAH). To obtain the final MAH product, the solid was carefully washed with ice water and then dried using anhydrous sodium sulphate.

<sup>1</sup>H NMR (600 MHz, DMSO), δ 7.50 (2H, s, =CH-) ppm, yield 72%. As shown in Figure S1.

#### 2.3. Preparation of PA by Diels-Alder Reaction of MAH with Furan

A total of 1 equivalent of maleic anhydride (MAH) and 1.1 equivalents of furan were mixed and then added to an ether solvent. To maintain the reaction temperature below 20 °C, an ice bath was employed. The stirring of the reaction mixture continued for a duration of 12 h. The resulting solid was collected via filtration and subjected to freeze drying to eliminate any residual solvent, ultimately yielding o-oxynorbornene-dicarboxylic anhydride (ONDA). It should be noted that the Diels–Alder reaction involved in this process is reversible, and the utilization of a high-temperature environment can accelerate the inverse reaction, thereby leading to lower yields. <sup>1</sup>H NMR (600 MHz, DMSO)  $\delta$  6.54 (2H, dd, *J* = 2.7, 1.7 Hz),  $\delta$  5.35 (2H, ddd, *J* = 4.6, 2.9, 1.7 Hz), 3.28 (2H, dd, *J* = 3.1, 1.7 Hz) ppm, at a 98% yield. As shown in Figure S1.

To a dichloroethane solvent, one equivalent of ONDA was added, followed by the slow addition of five equivalents of trimethyl iodosilane, while maintaining the temperature at 60 °C. Nitrogen gas was introduced as a protective agent, proceeding a 12-hour reaction period. The reaction solution was collected and filtered to remove any insoluble matter. The filtrate obtained was mixed with deionized water and then transferred to a separatory funnel. Within the separatory funnel, the liquid phase exhibited distinct stratification, characterized by a nearly colorless upper layer and a milky white lower layer. The lower milky liquid was collected and washed with deionized water 2–3 times. The resulting liquid was then transferred to an aubergine flask and subjected to distillation under reduced pressure at 60 °C to eliminate any residual solvent, resulting in the collection of a white crystalline substance, namely the desired phthalic anhydride. The addition of ONDA to a dichloroethane solvent, followed by the reaction with trimethyl iodosilane at 60 °C, led to the formation of phthalic anhydride. The e purity of the product was achieved through the utilization of nitrogen gas as a protective agent and the subsequent washing with deionized water. <sup>1</sup>H NMR (600 MHz, DMSO) δ 8.03 (2H, dd, J = 6.9, 3.5 Hz), δ 8.01–7.94 (2H, m) ppm at a 77% yield. As shown in Figure S1.

#### 2.4. Preparation of BPDA by PA Coupling

One equivalent of phthalic anhydride (PA) was added to deionized water, and the temperature was gradually increased to 75 °C until the solid was fully dissolved. Subsequently, 1.1 equivalents of sodium hydroxide were added slowly and stirred thoroughly, followed by the dropwise addition of 1.1 equivalents of liquid bromine. The reaction was allowed to proceed for 4 h, with liquid bromine added dropwise to prevent the accumulation of clusters. At the end of the reaction, the solvent and residual liquid bromine were removed via distillation under reduced pressure at 70 °C, and a significant amount of white solid was collected. The resulting solid was washed 2–3 times with ethanol and then dried to a constant weight in a blast oven; ultimately, the monosodium salt of 4-bromophthalic acid (4-BAMS) was yielded. Notably, the addition of sodium hydroxide in this step broke the anhydride group and enhanced the electron cloud density of the benzene ring, thereby increasing its reactivity at the position four and facilitating the binding of Br to the benzene ring.

<sup>1</sup>H NMR (600 MHz, DMSO) δ 8.12 (1H, d, J = 2.5 Hz), δ 7.57 (1H, d, J = 8.3 Hz), 7.48 (1H, dd, J = 8.2, 2.5 Hz) ppm at an 82% yield. As shown in Figure S1.

After the temperature was stabilized, 1 equivalent of aqueous hydroxylamine sulphate was slowly added to the reaction mixture. Following stirring, 0.05 equivalents of the palladium carbon catalyst were added slowly, and the reaction was stirred at the same temperature for 3 h. At the end of the reaction, the heated reaction solution was filtered to remove any insoluble catalyst, and the resulting filtrate was collected. Subsequently, the solution was cooled to room temperature, and hydrochloric acid was added dropwise, resulting in the formation of a white solid as the pH of the solution changed. Once the pH reached approximately 3, almost no additional solid precipitated. To create an acidic environment, an aqueous solution of hydrochloric acid at pH = 1 was prepared and was utilized to wash the solid product three times. Finally, the residual hydrochloric acid was removed by immersing the solid in deionized water and distilling it under reduced pressure at 70 °C. The resulting solid was dried until it reached a constant weight, and then 3,3,4,4-biphenyltetracarboxylic acid (BLCA) was obtained. Notably, the valuable palladium carbon catalyst can be recovered after filtering at the end of the reaction and reused for subsequent tests with minimal or no impact on catalytic efficiency.

<sup>1</sup>H NMR (400 MHz, DMSO) δ 8.37 (2H, d, *J* = 2.0 Hz), δ 8.06 (2H, d, *J* = 8.7 Hz), 7.78 (2H, dd, *J* = 8.6, 2.0 Hz) ppm at a 90% yield. As shown in Figure S1.

Ultimately, all the resulting BLCA was added to a three-necked flask, followed by the addition of an excess of acetic anhydride. Then, the reaction system was heated to 100 °C and reacted for 3 h. At the end of the reaction, the solution was collected and distilled under reduced pressure at 70 °C to obtain the final product, BPDA. To ensure the suitability of BPDA for subsequent PI synthesis experiments, the obtained BPDA was collected and transferred to a sublimation apparatus. The product was then purified by sublimation at 450 °C, under high vacuum, at 0.002 Pa, effectively enhancing the purity to exceed 98%.

<sup>1</sup>H NMR (400 MHz, DMSO) δ 8.59 (2H, d, *J* = 2.2 Hz), δ 8.36 (2H, d, *J* = 7.9 Hz), 8.04 (2H, dd, *J* = 7.9, 2.2 Hz) ppm at a 95% yield. As shown in Figure S1.

### 2.5. Preparation of PI by Polymerization of BPDA with PPD

While keeping the humidity below 40% relative humidity, 1 equivalent of p-phenylenediamine (PPD) was added to N-methyl-2-pyrrolidone (NMP), and then 1 equivalent of BPDA was added slowly with mechanical stirring to ensure uniform and sufficient polymerization. This was followed by stirring the reaction mixture for more than 2 h to obtain polyamido acids (PAAs).

NMR spectroscopy diagram of PAAs obtained by B-BPDA/P-BPDA and PPD polymerization with Bruker AVANCE III HD 600MHz. From the PAA spectrogram, it can be seen that  $\delta$  10.3 represents the peak position of H in CO-NH in PAA,  $\delta$  7.6~8.3 represents the peaks of benzene ring hydrogen in different chemical environments of PAA,  $\delta$  2.54 and 2.50 are the peaks of deuterated DMSO and its associated residual solvents, and  $\delta$  2.0 represents the peak position of H in -COOH.

In order to compare the performance of biomass-based BPDA and petroleum-based BPDA, both types of BPDA were added to N-methyl-2-pyrrolidone (NMP) and polymerized with p-phenylenediamine (PPD) to obtain different block types of polyamido acids (PAAs). The resulting PAA blocks were then thermally imidated to obtain polyimide (PI) films. To achieve PI films with varying compositions, the dianhydride content in the BPDA was

modified. The resulting PI films were denoted as PI-0 to PI-5, with PI-0 representing a film composed of 0% biomass-based BPDA, and PI-5 representing a film composed of 100% biomass-based BPDA. The remaining compositions represented films with 20%, 40%, 60%, and 80% biomass-based BPDA composition, respectively.

#### 3. Results and Discussion

# 3.1. FTIR Spectra Analysis

The synthesized monomers were optimized and characterized using Fourier-transform infrared spectroscopy (FTIR). Figure 2a illustrates the structural evolution from HMFA to MAH. HMFA was initially converted to MA, resulting in the disappearance of aldehyde characteristic peaks at 1758 cm<sup>-1</sup> and 1401 cm<sup>-1</sup> and the appearance of carboxyl vibration peaks at 1710 cm<sup>-1</sup> and 1265 cm<sup>-1</sup>. Subsequently, MA was further transformed into MAH, where the characteristic peaks at 1855 cm<sup>-1</sup> and 1783 cm<sup>-1</sup> represented the anhydride, and the C–O–C stretching vibration peak of the five-membered ring reappeared at 1401 cm<sup>-1</sup>, confirming the successful synthesis of MAH [30,31].



Figure 2. FTIR spectra of the synthetic monomer.

Figure 2b demonstrates the structural evolution from MAH to PA. Initially, the peaks at  $1226 \text{ cm}^{-1}$ ,  $1085 \text{ cm}^{-1}$ , and  $1022 \text{ cm}^{-1}$  represented the formation of ether bonds, confirming the synthesis of ONDA. Subsequently, upon conversion of ONDA to PA, characteristic peaks of the phenyl ring appeared at 1467 cm<sup>-1</sup> and 906 cm<sup>-1</sup>, and the benzyl anhydride's C-O-C characteristic peaks at 1263 cm<sup>-1</sup> and 1106 cm<sup>-1</sup> also emerged, confirming the successful synthesis of PA [24,32].

Figure 2c presents the structural evolution from PA to BPDA. PA was first transformed into 4-BAMS, with the carboxylic acid vibration peaks at 1700 cm<sup>-1</sup> and 1295 cm<sup>-1</sup> replacing the anhydride characteristic peaks. Subsequently, after the transformation into BLCA, the carboxylic acid peaks shifted to a double peak. Finally, upon dehydration to form BPDA, the anhydride characteristic peaks reappeared, confirming the successful synthesis of BPDA [33].

The as-prepared PI films from the polymerization with different block ratios of BPDAto-PPD were characterized by Fourier-transform infrared–attenuated total reflection spectroscopy (FTIR-ATR), and the results are shown in Figure 3. As can be seen, all the characteristic peaks for PI films remained essentially unchanged with varying BPDA-to-PPD ratios. The peaks at 1774 cm<sup>-1</sup>, 1710 cm<sup>-1</sup>, and 1358 cm<sup>-1</sup> are ascribed to the stretching vibrations of C=O in imide ring, the asymmetric stretching vibrations of C=O, and the stretching vibrations of C–N in the imide ring, respectively, confirming the completion of imidization. In addition, the peaks at 1514 cm<sup>-1</sup>, 831 cm<sup>-1</sup>, and 733 cm<sup>-1</sup> that correspond to the characteristic peaks of the phenyl ring are ascribed to the stretching vibration of C=C in the phenyl ring and the out-of-plane bending vibration of =C–H (two absorption peaks) [34]. Furthermore, no other peaks were observed in the FTIR-ATR spectra, indicating the high purity of the measured PI samples.



Figure 3. FTIR-ATR spectra of PIs.

## 3.2. Tensile Strength

To characterize the tensile strength ( $\sigma_t$ ) of the obtained PI films, we fabricated them into a long strip measuring 10 mm × 65 mm and tested the middle 25 mm length using a universal testing machine, at a pulling rate of 50 mm/min. In addition, we used a PSSMCX GPC gel chromatography column with a 0.05 mol/L lithium bromide NMP solution as the mobile phase at a flow rate of 1 mL/min and a column temperature of 35 °C to perform liquid-phase GPC characterization of PAA diluted to 2.0 mg/mL with NMP. The data summary table is shown in Table 1, where dispersity (D = Mw/Mn) represents the molecular weight distribution index, calculated as the ratio of Mw to Mn. Mw is the weight-average molecular weight, and Mn is the number-average molecular weight [35].

Sample	M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	$M_w/M_n$	σ <sub>t</sub> (MPa)
PI-0	525,795	459,602	1.144	116.67
PI-1	476,620	471,362	1.011	101.20
PI-2	607,368	494,040	1.229	117.34
PI-3	594,446	471,668	1.260	123.02
PI-4	460,682	390,995	1.178	109.34
PI-5	421,903	373,583	1.129	106.90

Table 1. Summary of GPC and tensile strength data for PI.

As shown in Table 1, with the gradual increase in B-BPDA content, the tensile strength of the PI film shows a trend of first increasing and then decreasing, reaching a maximum when the ratio of B-BPDA to P-BPDA is close to 1:1, with a maximum variation amplitude of about 13% for  $\sigma_t$ . The DI values of all PAA are around 1, indicating that the molecular weight distribution of the prepared PAA is uniform, which is the basis for the stable performance of the PI film. At the same time, we can see that the tensile strength of the PI film is proportional to both the weight-average molecular weight can improve the mechanical properties of the PI film to some extent. It is worth noting that when the input ratio of B-BPDA to P-BPDA is about 1:1, the molecular weight of PAA reaches the highest value, indicating that the block copolymerization of the two is beneficial to the growth of the chain. This is consistent with the XRD conclusion mentioned earlier that the "tightness of grain arrangement is the highest".

## 3.3. X-ray Diffraction Analysis

To observe the crystallization of different PI films, we prepared  $20 \times 20$  mm thin films and obtained their X-ray diffraction (XRD) patterns with a Rigaku Corporation Ultima IV, using a scanning rate of 5 °C/min, as shown in Figure 4. All the PI films exhibited a broad diffraction peak in the range of  $2\theta = 18^{\circ}-25^{\circ}$ , with similar peak positions. Upon close inspection, a weak diffraction peak was observed at  $2\theta = 18.3^{\circ}$ , indicating the presence of some microcrystalline regions in the PI films [36]. Based on the Bragg equation and Scherrer formula, we have the following:

 $\lambda = 2d_{002}\sin\theta$ 

$$D = 0.89\lambda/(B\cos\theta)$$

where  $\lambda$  is the X-ray wavelength of the Cu target (Ka = 0.154178 nm),  $\theta$  is the Bragg diffraction angle of the (002) plane of the graphite-like structure, d<sub>002</sub> is the interplanar spacing of the (002) plane, D is the average crystal size, and B is the FWHM of the diffraction peak at  $2\theta = 18.3^{\circ}$ . The data obtained are presented in the table below:



Figure 4. X-ray diffractograms of PIs.

According to Table 2, as the content of B-BPDA increases, the interplanar spacing of PI shows a trend of first increasing and then decreasing. When pure B-BPDA or pure P-BPDA is copolymerized with PPD, the interplanar spacing of PI is the smallest. It is known that the interplanar spacing can reflect the degree of atomic arrangement to some extent. The larger the interplanar spacing, the more compact the arrangement of grains in the same plane. A further analysis showed that when the input ratio of B-BPDA to P-BPDA is close to 1:1, the arrangement of PI grains is the most compact, indicating that the molecular interaction force between PI chains can be enhanced by the simultaneous presence of the two BPDA monomers in the block copolymerization with PPD, which promotes the compact arrangement of grains. Similarly, Table 2 also shows the variation trend of grain size, which shows an overall trend of first decreasing and then increasing and reaches a peak when the input ratio of the two BPDA monomers is approximately 1:1 [6,37]. This trend indicates that, in the process of block copolymerization, not only the molecular interaction force is improved but also the phenomenon of fine-grain strengthening is induced, providing a basis for subsequent performance testing.

Sample	20 (°)	FWHM (°)	d <sub>002</sub> (nm)	D (nm)
PI-0	18.60	0.163	0.4765	48.819
PI-1	18.46	0.153	0.4801	52.000
PI-2	18.32	0.167	0.4837	47.631
PI-3	18.36	0.168	0.4826	47.350
PI-4	18.44	0.158	0.4806	50.353
PI-5	18.48	0.155	0.4795	51.330

Table 2. Summary of XRD data for PI.

# 3.4. Thermal Properties

To characterize the thermal stability of the obtained PI films, 10 milligrams of the samples were cut into small pieces and subjected to a TGA analysis by using a METTLER TOLEDO TGA/DSC in a nitrogen environment, at a heating rate of 10 °C/min, over a temperature range of 35–800  $^{\circ}$ C, as shown in Figure 5. By observing the trend of the curves in Figure 5, it can be seen that all curves have only one obvious weight-loss gradient, which occurs at around 600 °C, indicating that all components of the PI are uniform and that the imidization process is complete. The Td5% and Td10% of PI-0 are 584 °C and 621 °C, respectively, and the residue at 800 °C (R800 °C) is 45.59%, which is comparable to the thermal performance of Upilex series PI films on the market [38,39]. Overall, as the content of B-BPDA gradually increases, the Td5% of the PI film shows a decreasing trend, with a maximum decrease of less than 7%, while the Td10% remains stable at around 600  $^{\circ}$ C, with a decrease of less than 5%. It can be seen that, regardless of the variation in the ratio of B-BPDA to P-BPDA, the obtained PI films can still ensure excellent thermal stability. The reason for this phenomenon should be that the benzene ring of B-BPDA is derived from the furan ring, and the bond energy within B-BPDA molecules is lower than that of petroleum-based benzene rings, leading to a decrease in the stability of the benzene ring structure of B-BPDA [40]. However, at the same time, the presence of two BPDA monomers with different bond energies in the block copolymerization process results in the entanglement of benzene ring chains with different bond energies, promoting the enhancement of molecular interactions and the stability of the PI crosslinking network. As the content of B-BPDA increases, the former effect gradually becomes dominant, eventually leading to a decrease in the thermal stability of PI.



Figure 5. Thermogravimetric analysis curves of PIs.

#### 3.5. Mechanical Properties

The thermal expansion coefficient (CTE) of PI was determined via a thermomechanical analysis (TMA) performed on a METTLE SDTA2+. PI films were prepared into  $4 \times 16$  mm strips in a nitrogen atmosphere, with a heating rate of 10 °C/min, in the temperature range of 100–500 °C. The thermal expansion coefficient (CTE) and the glass transition temperature (Tg) of the PI films were determined by using formulas and the method of auxiliary lines. The formula for the CTE is as follows:

$$\alpha = \Delta L / (L \times \Delta T)$$

where  $\alpha$  represents the coefficient of thermal expansion,  $\Delta L$  represents the dimension change under unit temperature variation,  $\Delta T$  represents the unit temperature variation, and L represents the original length of the tested PI film [41].

As shown in Figure 6, the dimension-change–temperature curve was fitted, and the inflection point of the curve was set as  $T_g$  [42].



Figure 6. TMA curves of PIs.

The CTE and  $T_g$  of the PI films were determined using formulas and plotted curves, as shown in Table 3. The CTE value reflects the dimensional stability of the product, with a higher CTE value indicating lower dimensional stability. The Tg value generally represents the highest long-term use temperature of plastic products, and both are closely related to the degree of crosslinking between molecular chains. As can be seen from the table, with the increase in B-BPDA content, the CTE value shows a trend of first decreasing and then increasing, with a variation amplitude of about 15%, while the Tg shows a trend of first increasing and then decreasing, with a variation amplitude of about 15%, while the Tg shows a trend of the undergo a mutation when the B-BPDA content is 100%. From this trend, it can be seen that when B-BPDA and P-BPDA are copolymerized with PPD, the entanglement between the chains is significantly increased, and the degree of crosslinking is higher. Therefore, when both BPDA monomers are present, the CTE value becomes significantly smaller and the Tg value slightly increases, which also verifies the conclusion inferred from the previous TG analysis.

## 3.6. Dielectric Properties

The obtained PI films were subjected to gold spraying on both sides for 1 min and then tested for their dielectric properties at frequencies ranging from 0.1 to 2 MHz [43].

To analyze the dielectric properties of the PI film more specifically, the dielectric data obtained at a frequency of 1 MHz were taken as the standard. As shown in Table 4, with

the increase in B-BPDA content, the Dk and D<sub>f</sub> values of the PI film generally increase, indicating that the addition of B-BPDA is unfavorable to the insulation performance of the PI film. Analyzing the specific numerical values, the range of variation of Dk is between 3.26 and 3.38, with a variation amplitude of less than 5%, and the range of variation of Df is between 0.0119 and 0.0150, with an order of magnitude in the range of  $10^{-2}$ . These data indicate that the addition of B-BPDA affects the electron cloud density of PI to some extent, but the impact is within the fluctuation range of conventional PI and has little effect on its practical application. The reason for this phenomenon could be that the benzene ring of B-BPDA is derived from the furan ring, and its electron cloud density is higher, and its stability is lower, compared to P-BPDA. During the copolymerization with PPD, the dispersion of free electrons is higher, ultimately leading to a decrease in the insulation performance of PI. This is also consistent with the trend of the TG test data of PI.

Table 3.	Summary	of	TMA	data	for	PI.
----------	---------	----	-----	------	-----	-----

Sample	CTE (ppm/K)	Τ <sub>g</sub> (°C)
PI-0	30.77	365.71
PI-1	27.16	371.77
PI-2	28.46	368.56
PI-3	26.41	373.92
PI-4	25.49	375.86
PI-5	31.50	365.63

Table 4. Summary of dielectric properties data for PI.

Sample	Dielectric Constant	<b>Dielectric Loss</b>
PI-0	3.26	0.0119
PI-1	3.30	0.0133
PI-2	3.31	0.0127
PI-3	3.36	0.0155
PI-4	3.28	0.0144
PI-5	3.38	0.0150

#### 3.7. Hydrophobic

To characterize the hydrophobic properties of the obtained PI films, we conducted contact angle measurements and water absorption tests. The test samples were PI films measuring  $20 \times 20$  mm with a thickness of 20–40 µm and a mass of about 10 mg. For the contact angle measurements, we dropped 10 µL of distilled water onto the PI films and measured the contact angle. For the water absorption tests, we immersed the PI films in 30 mL of distilled water for 24 h, removed them, and weighed them to determine the percentage change in mass before and after immersion [44].

As shown in Table 5 and Figure 7, with the continuous increase in B-BPDA content, the contact angle of the PI film shows a trend of first increasing and then decreasing, with a variation amplitude of less than 5%. The water absorption shows a trend of first increasing and then decreasing, and the water absorption rate is less than 1%. This indicates that the hydrophobic property of the PI film reaches its optimum when the ratio of B-BPDA to P-BPDA is approximately 1:1, and the addition of B-BPDA has a weak impact on the hydrophobic property of the PI film. Since the hydrophobic property is closely related to the degree of crosslinking and the tight arrangement of the grains in PI, this suggests that when the ratio of B-BPDA to P-BPDA is approximately 1:1, the crosslinking degree of PI chains is high, and the arrangement of the grains is tight. This further confirms the previous analysis using XRD and TMA.

Sample	Contact Angle (°)	Absorbent (%)
PI-0	67.8	0.73%
PI-1	69.1	0.66%
PI-2	69.6	0.67%
PI-3	70.8	0.58%
PI-4	66.3	0.70%
PI-5	65.8	0.80%

Table 5. Summary of hydrophobic performance data for PI.



Figure 7. Contact angle spectra of PIs.

## 3.8. Comprehensive Performance

In summary, the performance summary in Figure 8 indicates that the addition of B-BPDA has a weak impact on the properties of the PI film. Moreover, when B-BPDA/P-BPDA is copolymerized with PPD, it effectively increases the molecular weight of PI chains, the degree of entanglement between molecular chains, and intermolecular forces. This is manifested in the improvement of the tensile strength, dimensional stability, and hydrophobic properties of the PI film. At the same time, due to the influence of biomass bond energy, it has a certain impact on the thermal stability and dielectric properties of the PI film. In order to better apply biomass to the synthesis of polyimides, the next step is to optimize the synthesis route from HMFA to B-BPDA and explore the modification route from biomass to diamine in order to break through the pure biomass-based PI synthesis technology as soon as possible.



Figure 8. Summary graph of PI performance.

# 4. Conclusions

Using HMFA as a biomass feedstock, a suitable dianhydride monomer BPDA for PI synthesis can be obtained through chemical modification, which injects vitality into the production of PI monomers.

The semi-biomass-based PI film obtained through this method has a thermal decomposition temperature of  $\approx 600$  °C, a coefficient of thermal expansion of  $\approx 30$  ppm/K, a glass transition temperature > 365 °C, a tensile strength >120 MPa, a dielectric constant value < 3.4, a dielectric loss value < 0.02, and a 24 h water absorption rate <0.8%.

Moreover, when the input ratio of B-BPDA to P-BPDA is close to 1:1, the tensile strength, dimensional stability, and hydrophobicity of the material can be further improved.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings13101726/s1, Figure S1: The <sup>1</sup>H NMR spectrum for the transformation of HMFA to BPDA.

**Author Contributions:** Conceptualization, L.C.; Methodology, K.L.; Software, Y.H.; Validation, L.C.; Formal analysis, W.L.; Investigation, L.H.; Data curation, J.X.; Writing—original draft, L.C.; Writing—review & editing, W.L. and Y.H.; Supervision, K.L. and Y.M. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Key Research and Development Program of China (2020YFB0408100), the Natural Science Foundation of Guangdong Province of China (2023A1515011751), the Science and Technology Planning Project of Guangzhou city (2023B03J1285), the National Natural Science Foundation of China (22008037), the National Natural Science Foundation of China (220208037), the National Natural Science Foundation of China (U20A20340), the Guangzhou Hongmian Project (HMJH-2020-0012), and the Guangdong Innovative and Entrepreneurial Research Team Program (2016ZT06C412).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy.

**Acknowledgments:** We would also like to thank the Guangzhou Institute of Emerging Materials for providing financial assistance to support part of our testing equipment.

Conflicts of Interest: The authors declare no conflict of interest.

#### References

- 1. Sezer Hicyilmaz, A.; Celik Bedeloglu, A. Applications of polyimide coatings: A review. SN Appl. Sci. 2021, 3, 363. [CrossRef]
- 2. Yamashita, T. Photosensitive Polyimides: Fundamentals and Applications; CRC Press: Boca Raton, FL, USA, 2017.
- 3. Ji, D.; Li, T.; Hu, W.; Fuchs, H. Recent progress in aromatic polyimide dielectrics for organic electronic devices and circuits. *Adv. Mater.* **2019**, *31*, 1806070. [CrossRef] [PubMed]
- 4. Jiang, L.Y.; Wang, Y.; Chung, T.-S.; Qiao, X.Y.; Lai, J.-Y. Polyimide membranes for pervaporation and biofuels separation. *Prog. Polym. Sci.* **2009**, *34*, 1135–1160. [CrossRef]
- Li, Y.; Sun, G.; Zhou, Y.; Liu, G.; Wang, J.; Han, S. Progress in low dielectric polyimide film—A review. *Prog. Org. Coat.* 2022, 172, 107103. [CrossRef]
- Weng, M.; Luo, X.; Jian, L.; Liang, J.; Hu, J.; Liu, Y.; Zhang, J.; Feng, X.; Min, Y. Lutidine catalyzed highly thermal conductive graphite polyimide films via controlling grain size. *Appl. Surf. Sci.* 2022, 578, 152029. [CrossRef]
- Kabir, G.; Hameed, B.H. Recent progress on catalytic pyrolysis of lignocellulosic biomass to high-grade bio-oil and bio-chemicals. *Renew. Sustain. Energy Rev.* 2016, 70, 1131–1154. [CrossRef]
- 8. Isikgor, F.H.; Becer, C.R. Lignocellulosic biomass: A sustainable platform for the production of bio-based chemicals and polymers. *Polym. Chem.* **2015**, *6*, 4485–4500. [CrossRef]
- 9. Kirtika, K.; Ravindra, P.; Sharma, B.K. Bio-Based Chemicals from Renewable Biomass for Integrated Biorefineries. *Energies* **2019**, 12, 244.
- Long, H.; Li, X.; Wang, H.; Jia, J. Biomass resources and their bioenergy potential estimation: A review. *Renew. Sustain. Energy Rev.* 2013, 26, 344–352. [CrossRef]
- 11. Ferreira, S.; Monteiro, E.; Brito, P.; Vilarinho, C. Biomass resources in Portugal: Current status and prospects. *Renew. Sustain. Energy Rev.* **2017**, *78*, 1221–1235. [CrossRef]
- 12. Tursi, A. A review on biomass: Importance, chemistry, classification, and conversion. Biofuel Res. J. 2019, 6, 961–980. [CrossRef]

- 13. Zhu, J.; Cai, J.; Xie, W.; Chen, P.-H.; Gazzano, M.; Scandola, M.; Gross, R.A. Poly(butylene 2,5-furan dicarboxylate), a biobased alternative to PBT: Synthesis, physical properties, and crystal structure. *Macromolecules* **2013**, *46*, 907–915. [CrossRef]
- Okuda, T.; Ishimoto, K.; Ohara, H.; Kobayashi, S. Renewable biobased polymeric materials: Facile synthesis of itaconic anhydridebased copolymers with poly(l-lactic acid) grafts. *Macromolecules* 2012, 45, 4313–4321. [CrossRef]
- 15. Gallezot, P. Conversion of biomass to selected chemical products. Chem. Soc. Rev. 2012, 41, 1538–1558. [PubMed]
- 16. Feng, L.; Iroh, J. Polyimide-b-polysiloxane Copolymers: Synthesis and Properties. *Inorg. Organomet. Polym. Mater.* **2013**, *23*, 477–488. [CrossRef]
- 17. Zhang, Y.; Huang, Z.; Ruan, B.; Zhang, X.; Jiang, T.; Ma, N.; Tsai, F.-C. Design and Synthesis of Polyimide Covalent Organic Frameworks. *Macromol. Rapid Commun.* **2020**, *41*, 2000356. [CrossRef]
- Li, N.; Zong, M. (Chemo)biocatalytic Upgrading of Biobased Furanic Platforms to Chemicals, Fuels, and Materials: A Comprehensive Review. ACS Catal. 2022, 12, 10080–10114. [CrossRef]
- Ma, K.; Chen, G.; Wang, W.; Zhang, A.; Zhong, Y.; Zhang, Y.; Fang, X. Partially bio-based aromatic polyimides derived from 2,5-furandicarboxylic acid with high thermal and mechanical properties. *J. Polym. Sci. Part A Polym. Chem.* 2018, 60, 646–656. [CrossRef]
- Jang, H.; Jang, H.W.; Kim, A.Y.; Youk, J.H. Partially Bio-based Colorless and Transparent Poly(amide-imide)s Derived from 2,5-Furandicarboxylic Acid. *Fibers Polym.* 2020, 21, 2159–2166. [CrossRef]
- 21. Milas, N.A. Catalytic oxidations in aqueous solutions I. The oxidation of furfural. J. Am. Chem. Soc. 1927, 49, 2149–2152. [CrossRef]
- Mariscal, R.; Maireles-Torres, P.; Ojeda, M.; Sádaba, I.; Granados, M.L. Furfural: A renewable and versatile platform molecule for the synthesis of chemicals and fuels. *Energy Environ. Sci.* 2016, 9, 1144–1189.
- Li, X.; Ko, J.; Zhang, Y. Highly Efficient Gas-Phase Oxidation of Renewable Furfural to Maleic Anhydride over Plate Vanadium Phosphorus Oxide Catalyst. *ChemSusChem* 2018, 11, 612–618.
- 24. Tachibana, Y.; Kimura, S.; Kasuya, K. Synthesis and verification of biobased terephthalic acid from furfural. Sci. Rep. 2015, 5, 8249.
- 25. Windmon, N.; Dragojlovic, V. Diels-Alder reactions in the presence of a minimal amount of water. Green Chem. *Lett. Rev.* 2008, 1, 155–163.
- Mahmoud, E.; Watson, D.A.; Lobo, R.F. Renewable production of phthalic anhydride from biomass-derived furan and maleic anhydride. *Green Chem.* 2014, 16, 167–175. [CrossRef]
- 27. Xiong, Y.; Ouyang, W. Synthesis and application of 4-bromo-phthalic anhydride. Fine Chem. Intermed. 2001, 2, 10–12. (In Chinese).
- 28. Li, X.J.; Li, C.Y.; Chen, W.; Wang, Y.F. Synthesis of 3,3',4,4'-biphenyltetracarboxylic dianhydride. J. Hebei Univ. Technol. 2007, 1, 64–67. (In Chinese)
- 29. Ballard, C.E. Green reductive homocoupling of bromobenzene. J. Chem. Educ. 2011, 88, 1148–1151.
- Soták, T.; Hronec, M.; Gál, M.; Dobročka, E.; Skriniarová, J. Aqueous-phase oxidation of furfural to maleic acid catalyzed by copper phosphate catalysts. *Catal. Lett.* 2017, 147, 2714–2723.
- 31. Li, X.; Ho, B.; Zhang, Y. Selective aerobic oxidation furfural to maleic anhydride with heterogeneous Mo-V-O catalysts. *Green Chem.* **2016**, *18*, 2942–2950. [CrossRef]
- 32. Tachibana, Y.; Yamahata, M.; Ichihara, H.; Kasuya, K.-I. Biodegradability of polyesters comprising a bio-based monomer derived from furfural. *Polym. Degrad. Stab.* **2017**, *146*, 121–125. [CrossRef]
- Xie, K.; Wang, X.; Dai, L.; Chen, Y. Synthesis process of 3,3',4,4'-biphenyltetracarboxylic dianhydride. *Chem. Ind. Eng. Prog.* 2005, 9, 1805–1808. (In Chinese)
- 34. Diaham, S.; Locatelli, M.; Lebey, T.; Malec, D. Thermal imidization optimization of polyimide thin films using Fourier transform infrared spectroscopy and electrical measurements. *Thin Solid Film.* **2011**, *519*, 1851–1856. [CrossRef]
- Xu, Z.; Croft, Z.L.; Guo, D.; Cao, K.; Liu, G. Recent development of polyimides: Synthesis, processing, and application in gas separation. J. Polym. Sci. 2021, 59, 943–962. [CrossRef]
- Gupta, A.K.; Bajpai, R.; Keller, J.M. PVDF: PI nano composite films: Mechanical, FT-IR, XRD, AFM and hydraulic study. J. Polym. Res. 2008, 15, 275–283. [CrossRef]
- 37. Weng, M.; Jian, L.; Feng, X.; Luo, X.; Hu, J.; Zhang, J.; Liu, Y.; Min, Y. High oriented graphite film with high thermal conductivity prepared by pure polyimide film formed with catalyst pyridine. *Ceram. Int.* **2021**, *47*, 25436–25444. [CrossRef]
- 38. Hergenrother, P.M. The use, design, synthesis, and properties of high performance/high temperature polymers: An overview. *High Perform. Polym.* **2003**, *15*, 3–45. [CrossRef]
- 39. Liu, X.-J.; Zheng, M.-S.; Chen, G.; Dang, Z.-M.; Zha, J.-W. High-temperature polyimide dielectric materials for energy storage: Theory, design, preparation and properties. *Energy Environ. Sci.* **2022**, *15*, 56–81. [CrossRef]
- 40. Lee, K.; Jing, Y.; Wang, Y.; Yan, N. A unified view on catalytic conversion of biomass and waste plastics. *Nat. Rev. Chem.* **2022**, *6*, 668–686. [CrossRef]
- Ando, S.; Sekiguchi, K.; Mizoroki, M.; Okada, T.; Ishige, R. Anisotropic Linear and Volumetric Thermal-Expansion Behaviors of Self-Standing Polyimide Films Analyzed by Thermomechanical Analysis (TMA) and Optical Interferometry. *Macromol. Chem. Phys.* 2018, 219, 1700354. [CrossRef]
- 42. Shi, S.; Yao, L.; Ma, P.; Jiao, Y.; Zheng, X.; Ning, D.; Chen, M.; Sui, F.; Liu, H.; Yang, C.; et al. Recent progress in the high-temperature-resistant PI substrate with low CTE for CIGS thin-film solar cells. *Mater. Today Energy* **2021**, *20*, 100640. [CrossRef]

- 43. Luo, J.; Liu, Y.; Liu, H.; Chen, W.; Cui, T.; Xiao, L.; Min, Y. Synthesis and Characterization of Polyimides with Naphthalene Ring Structure Introduced in the Main Chain. *Materials* **2022**, *15*, 6908. [CrossRef] [PubMed]
- 44. Constantin, C.P.; Aflori, M.; Damian, R.F.; Rusu, R.D. Biocompatibility of polyimides: A mini-review. *Materials* **2019**, *12*, 3166. [CrossRef] [PubMed]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.