

Modifying Poly(propylene carbonate) with Furan-based Non-Isocyanate Polyurethanes

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 Electronic Supplementary Information

Abstract Poly(propylene carbonate) (PPC) is gaining significant momentum as a biodegradable polymer using CO₂ as an abundant, low-cost and renewable feedstock. Yet, PPC suffers from unsatisfactory thermal and mechanical properties, and its blends with other synthetic polymers as the second component typically exhibit poor compatibility. Herein, novel furan-based non-isocyanate polyurethanes (NIPUs) with high molecular weights and narrow distributions have been synthesized starting from 5-hydroxymethylfurfural (HMF) via a four-step procedure including reduction, glycidylation, carbonation of CO₂ and step-growth polymerization with diamines. Owing to the structural similarity and intermolecular hydrogen bonding interactions, furan-based NIPUs display good compatibility with PPC. A sea-island morphology can be observed in SEM images of PPC/NIPU blends, where the NIPU phases are randomly dispersed in the PPC matrix. Moreover, the blends exhibit only one *T_g* (higher than both that of PPC and the corresponding NIPU) on the DSC curves, which first increase and then decrease when increasing the content of NIPUs from 0 wt% to 15 wt%. Notably, the physical crosslinking formed by hydrogen bonding interactions, coupled with the rigidity of furan rings, confer simultaneous improvements of elongation at the break and tensile strength, affording high-performance CO₂-based biodegradable polymeric materials with low carbon footprint, good sustainability, and ideal biocompatibility.

Keywords PPC; CO₂; NIPU; HMF; Blends

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INTRODUCTION

Plastics have been widely used and become an essential part of human life, because of their lightweight, high performance, and good processability since their commercialization in the 1930s. Due to the growing concerns about plastic pollution and the exhaustion of fossil fuels, biodegradable and renewable polymers have been the subject of intensive research efforts during the past few decades.^[1–6] Among them, the biodegradable and biocompatible CO₂-based polycarbonates are of significant interest as they utilize greenhouse gas CO₂ as a low-cost and renewable building block.^[7–10] In particular, poly(propylene carbonate) (PPC), derived from the ring-opening copolymerization of CO₂ and propylene oxide (PO), is commercially available and shows great promise in a wide array of applications such as packing, agricultural mulch film, solid electrolyte, etc.^[11–17] However, PPC exhibits relatively low glass-transition temperature and unsatisfactory mechanical properties compared to its non-biodegradable counter-

parts.^[18,19] Chemical strategies such as block copolymerization offer a unique opportunity to tailor the properties and functionalities of PPC at the molecular scale.^[20–23] Yet, they are usually economically unsustainable and are not easy to be applied on large scale. Alternatively, physical methods, such as blending with other synthetic polymers, provide much easier processes to modify PPC. Due to the weak intermolecular interactions, PPC blends with polyesters, such as polylactide (PLA),^[24,25] polycaprolactone (PCL),^[26,27] poly(butylene adipate-co-terephthalate) (PBAT),^[28–30] as the second component suffer from poor compatibility and unsatisfactory mechanical properties. It is well accepted that the interfacial adhesion of polymer blends can be enhanced by the incorporation of hydrogen bonding interactions that provide a favorable enthalpic contribution facilitating mixing.^[31,32] Wang and coworkers found that the biocompatible and biodegradable small-molecular urethanes can effectively plasticize PPC while maintaining its mechanical strength.^[33] The hydrogen bonding interactions between the identical N-H moieties of urethanes and the carbonate unites within PPC not only confer good miscibility but also serve as physical crosslinking points that are beneficial for enhancing mechanical/thermal properties. Later, several works have reported that blending with thermoplastic polyurethanes can effectively improve the toughness and

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tensile strength of PPC.^[33–36]

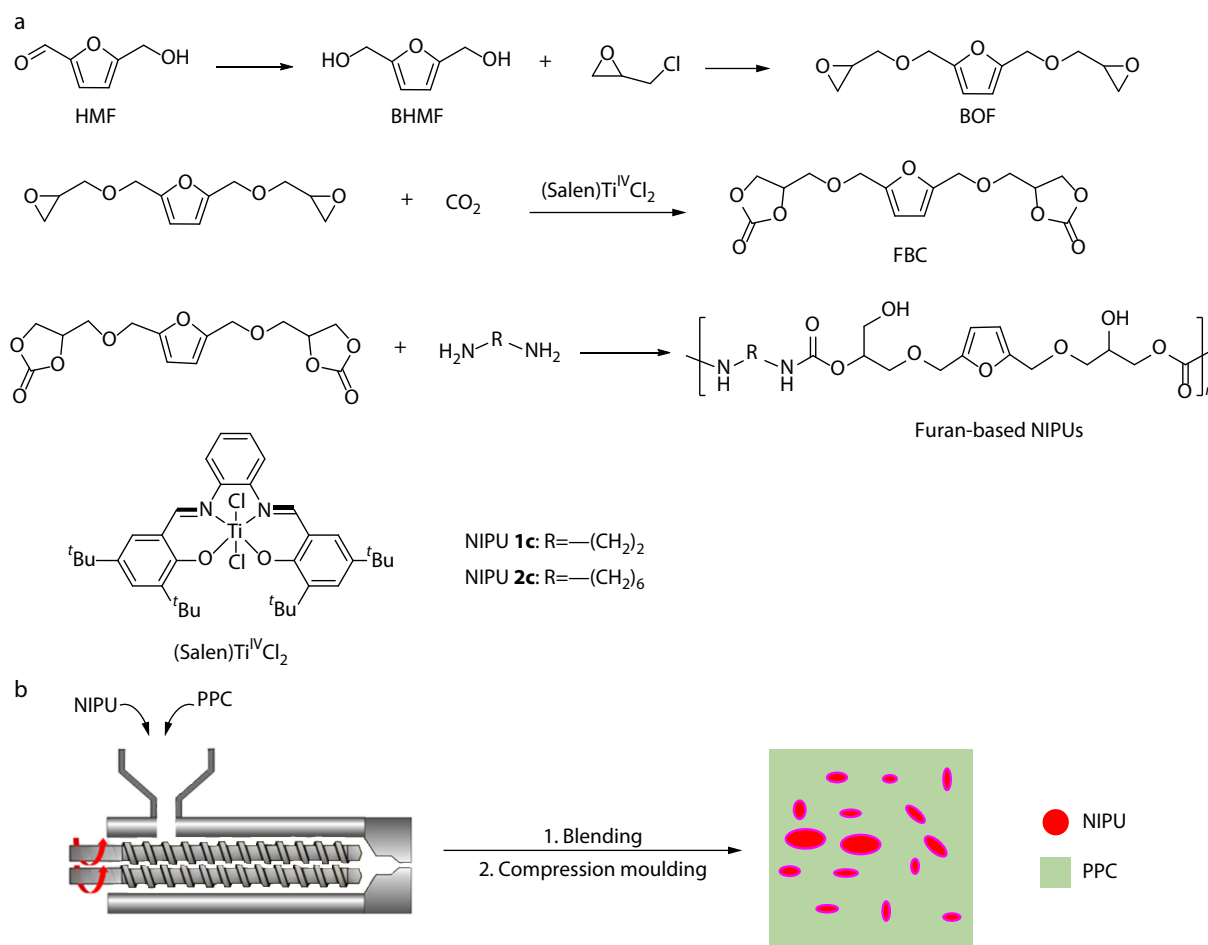
Polyurethanes are traditionally synthesized on basis of hazardous isocyanates, which may result in serious health effects.^[37–39] Alternatively, bis-5-membered cyclic carbonates that are accessible from the atom-economy coupling reaction between bis-epoxides and CO₂ can undergo step-growth polyaddition with diamines under mild reaction conditions, affording a myriad of non-isocyanate polyurethanes (NIPUs) bearing hydroxyl groups at the β -carbon atom of the urethane moieties.^[40–44] Notably, these NIPUs can be synthesized from renewable resources and possess structural similarities with CO₂-based polycarbonates.^[45–49] We rationalized that a well-designed NIPU shall exhibit good compatibility with PPC, thus affording high-performance CO₂-based biodegradable polymeric materials with good sustainability, low carbon footprint, and ideal biocompatibility. In this vision, two novel furan-based NIPUs with different chain lengths in diamine units have been synthesized starting from 5-hydroxymethylfurfural (HMF), which is readily accessible from the most abundant inedible biomass resource-lignocellulose and ranked in the “most value-added chemicals derived from biomass” list stated by the U.S. Department of Energy (Scheme 1a).^[50–52] In conjugation with tetra butyl ammonium bromide (TBAB), a salen titanium complex [(Salen)Ti^{IV}Cl₂] displayed high catalytic

activity in the coupling reaction between 2,5-bis[(2-oxiranylmethoxy)methyl]-furan (BOF) and CO₂, enabling the quantitative conversion of BOF to the targeted furan-based bis(cyclic carbonate) (FBC) within 3 h. The resulting NIPUs were further blended with PPC in an internal mixer (Scheme 1b). As both the -OH and -NH moieties of the NIPUs could form hydrogen bonding with carbonate units, PPC blends with furan-based NIPUs as the second components displayed good compatibility. Notably, the crosslinking effect of hydrogen bonding interactions, coupled with the rigidity of furan rings, endow the resulting PPC blends with simultaneous improvement in elongation at the break and tensile strength.

EXPERIMENTAL

Materials

N,N-dimethylformamide (DMF) was distilled from calcium hydride under an argon atmosphere before use. CO₂ (99.995%) was purchased from Wuhan Huaerwen gas Ltd. HMF was supplied by Aldrich. (Salen)Ti^{IV}Cl₂ was synthesized according to the procedure described in the literature.^[53,54] Other reagents and chemicals were used without further purification. PPC was supplied by the Changchun Institute of Applied Chemistry (CIAC). The number-average molecular weight (*M_n*) and



Scheme 1 (a) Synthesis of furan-based NIPUs starting from HMF via a four-step procedure including reduction, glycidylation, carbonation of CO₂, and step-growth polymerization with diamines; (b) Schematic representation of the fabrication process.

distribution ($\bar{M}_w/\bar{M}_n$) of PPC were determined by gel permeation chromatography (GPC) as 252 kDa and 1.4, respectively. According to ^1H -NMR spectroscopy, the content of carbonate unit in the main chain and cyclic carbonate by-product was determined as 91% and 6%, respectively (Figs. S1 and S2 in the electronic supplementary information, ESI).

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

A 100 mL three-neck flask was equipped with a magnetic stirring bar and placed in an ice bath, and then charged with 12.8 g of 5-hydroxymethylfurfural (HMF) (100 mmol) and 40 mL of de-ionized water. When HMF completely dissolved and formed a homogeneous brown solution, 11.3 g of NaBH_4 (300 mmol) was added in small portions. The mixture was allowed to react at 40 °C for 4 h before it turned to be a pale-yellow solution. After 20 mL of deionized water was added to quench the reaction, the reaction mixture was extracted with 50 mL of ethyl acetate three times. The combined organic phase was washed with 50 mL of saturated brine and dried with anhydrous Na_2SO_4 . After the solvent was removed under vacuum, 11.2 g of product was obtained as a pale-yellow solid with high purity. ^1H -NMR (400 MHz, CDCl_3 , δ , ppm): 6.16 (s, 2H), 4.50 (s, 4H). ^{13}C -NMR (100 MHz, CDCl_3 , δ , ppm): 154.0, 108.5, 57.4.

Synthetic Procedure for 2,5-Bis[(2-oxiranylmethoxy)-methyl]-furan (BOF)

To a 250 mL three-neck flask equipped with a constant-pressure dropping funnel and mechanical stirring device, was added a mixture of 96 g of 50% (W/W) aqueous sodium hydroxide (1.2 mol), 21.9 mL of epichlorohydrin (1.4 mol), and 3.22 g of tetrabutylammonium bromide (TBAB) (10 mmol). When stirred vigorously under an inert gas atmosphere, 12.8 g of BHMF (100 mmol) in 100 mL of THF was added dropwise. The reaction mixture was allowed to react at 50 °C for 2 h and then cooled to room temperature. After 100 mL of deionized water was added to quench the reaction, the reaction mixture was extracted with 50 mL of ethyl acetate three times. The combined organic phase was washed with saturated brine, dried with anhydrous MgSO_4 , and concentrated under vacuum, dark brown liquid residue was obtained and later purified by chromatography on silica gel (ethyl acetate:hexane=4:7). A clear yellow liquid was obtained as the product with an overall yield of 70%. ^1H -NMR (400 MHz, CDCl_3 , δ , ppm, Fig. S3 in ESI): 6.29 (s, 2H), 4.55–4.43 (m, 4H), 3.80–3.74 (m, 2H), 3.48–3.40 (m, 2H), 3.20–3.14 (m, 2H), 2.82–2.77 (m, 2H), 2.64–2.58 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3 , δ , ppm, Fig. S4 in ESI): 152.0, 110.5, 110.4, 70.9, 65.3, 50.9, 44.4.

Synthetic Procedure for Furan-based Bis(cyclic carbonate) (FBC)

In an argon-filled glove box, 0.03 mmol of $(\text{Salen})\text{Ti}^{\text{IV}}\text{Cl}_2$, and 17.3 mg of TBAB (0.03 mmol) were dissolved in BOF (15 mmol) and charged into a pre-dried 10 mL autoclave equipped with a magnetic stirrer. Then the autoclave was taken out of the glove box, put into an oil bath at 100 °C, and pressurized to 3 MPa with CO_2 . At the end of the reaction, the autoclave was cooled to room temperature. The crude mixture was used for ^1H -NMR spectroscopy analysis. The catalyst could be easily removed by chromatography on a short pad of silica gel with CH_2Cl_2 as eluent to afford purified furan bis(cyclic carbonate) for the preparation of NIPUs. ^1H -NMR (400 MHz, CDCl_3 , δ , ppm, Fig. S5 in ESI): 6.30 (s, 2H), 4.83–4.79 (m, 2H), 4.55–4.45 (m, 6H),

4.38–4.30 (m, 2H), 3.76–3.70 (m, 2H), 3.66–3.60 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3 , δ , ppm, Fig. S6 in ESI): 152.0, 110.5, 110.4, 70.9, 65.3, 50.9, 44.4.

Synthetic Procedure for Furan-based NIPUs

A 100 mL three-neck flask was equipped with a mechanical stirring device and linked with a Schlenk line. The flask was then charged with 10 mmol FBC and 10 mmol diamines. The mixture was allowed to react at 60 °C for 20 min, then 80 °C for 1 h, and 100 °C for another 1 h under an inert gas atmosphere.

NIPU 1c

^1H -NMR (400 MHz, $\text{DMSO}-d_6$, δ , ppm): 7.14–7.07 (m, 2H), 6.37 (s, 2H), 4.67 (m, 0.82H), 4.40 (s, 4H), 3.92–3.75 (m, 5.00H), 3.52–3.33 (m, 6.20H), 2.95 (m, 2H), 2.53 (m, 2H). ^{13}C -NMR (100 MHz, $\text{DMSO}-d_6$, δ , ppm): 156.8, 156.4, 152.2, 152.1, 110.5, 73.7, 71.9, 69.1, 68.3, 65.9, 64.8, 60.6, 45.1, 42.0.

NIPU 2c

^1H -NMR (400 MHz, $\text{DMSO}-d_6$, δ , ppm): 7.14–7.08 (m, 2H), 6.37 (s, 2H), 4.67 (m, 0.82H), 4.40 (s, 4H), 3.92–3.73 (m, 5H), 3.55–3.34 (m, 6.18H), 2.96–2.92 (m, 4H), 1.38–1.22 (m, 8H). ^{13}C -NMR (100 MHz, $\text{DMSO}-d_6$, δ , ppm): 156.7, 156.3, 152.2, 152.1, 110.5, 73.5, 71.9, 69.1, 68.2, 66.0, 64.9, 60.5, 29.8, 26.4.

Preparation of PPC/NIPUs Blends

Before blending, PPC was dried in a vacuum drying oven at 30 °C for 24 h. Then, it was melting blended with furan-based NIPUs by an internal mixer under 110 °C for 10 min. The weight ratio of PPC/NIPU was set as 97.5/2.5, 95/5, 92.5/7.5, 90/10, and 85/15. To prepare the sample sheets for measurements, PPC and its blends were compression-molded at 110 °C under 10 MPa.

Characterization Methods

The ^1H -NMR and ^{13}C -NMR spectra of the samples were recorded on a Bruker AV400 MHz type spectrometer using CDCl_3 and $\text{DMSO}-d_6$ as solvent at 25 °C. Fourier transform infrared spectra (FTIR) were recorded in the wavenumber range of 500–4000 cm^{-1} with transmission mode on a Bruker Vertex 80 FTIR spectrometer. GPC analyses were performed on Waters 410 GPC instrument in DMF (flow rate 1.0 mL/min) at 30 °C calibrated with polystyrenes as standards. The thermal stability of PPC and its blends were measured under nitrogen with a TGA 4000 (PerkinElmer) thermogravimetric analyzer (TGA). About 5 mg of sample was heated at 10 °C/min from 40 °C to 700 °C. The fracture surface morphology of the PPC/NIPU blends was obtained using a Nova NanoSEM 450 field emission scanning electron microscope (FESEM). The cryo-fractured samples were immersed in methanol for 24 h to remove the NIPU phase before observation. Differential scanning calorimetry (DSC) measurements were performed on a Q2000 (TA Instruments). The samples (5–10 mg) were enclosed in an aluminum pan and placed in the heating cell with an empty pan as a reference. All the samples were heated under nitrogen.

RESULTS AND DISCUSSION

Synthesis of Furan-based Bis(cyclic carbonate)

BOF was synthesized starting from HMF on a ten-gram scale following a modified procedure described in the literature.^[55] Considering that the molar ratio of reagents acts as a vital factor in the molecular weight of the resulting NIPUs as well as the

corresponding thermal and mechanical properties, it is of great importance to use highly active and durable catalyst systems by which full conversion of epoxy groups should be achieved to spare the painstaking purification process in the carbonation process. Quaternary ammonium salts such as TBAB have been widely used for such a purpose, yet, a relatively high catalyst loading of up to 3 mol% was required. In our previous work, (Salen)Ti^{IV}Cl₂ was first introduced as an effective catalyst for the coupling reaction between CO₂ and epoxides.^[54] Notably, 100% conversion of cyclohexene oxide (CHO) could be achieved within 8 h at 120 °C under a catalyst loading of 0.1 mol%, although CHO is among the most inactive epoxy monomers and its full conversion has been rarely reported. To ensure the quantitative and rapid transformation from BOF to FBC, the coupling reaction was conducted with (Salen)Ti^{IV}Cl₂ and TBAB as the catalyst and cocatalyst ([BOF]/[catalyst]/[cocatalyst]=500/1/1), respectively (Table 1). The catalytic activity of (Salen)Ti^{IV}Cl₂ increased steadily with reaction temperature and the turnover frequency (TOF) increased from 382 h⁻¹ at 100 °C to 672 h⁻¹ at 120 °C (Table 1, entries 3 and 7). Notably, an ultra-high TOF of 1920 h⁻¹ was obtained at a catalyst loading of 0.01 mol%, indicating enhanced catalytic activity under a diluted reaction mixture (Table 1, entry 8). To our delight, BOF could be completely converted to FBC within 3 h, with a turnover frequency (TOF) of 333 h⁻¹ (Table 1, entry 6).

Synthesis of Furan-based NIPUs

With the successful synthesis of FBC, we first conducted the step-growth polymerizations with 1,2-ethanediamine (EDA) and 1,6-hexanediamine (HDA) in DMSO at room temperature (Table 2, entries 1 and 2). As determined by ¹H-NMR spectra, the conversion of carbonate moieties in 24 h for the synthesis of NIPU **1a** and **1b** was 91.6% and 93.2%, respectively. In comparative experiments with 5 mol% TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) as the organic catalyst, monomer conversion for both reactions reached 100%, accompanied by an increase in molecular weights and a slight decrease in distributions. Furthermore, we examined the solvent-free and catalyst-free reaction conditions at elevated temperatures. Owing to the volatility of EDA and HDA, a temperature program similar to the literature was chosen.^[56] In detail, the reactions were conducted at 60 °C until the advancement reaction caused viscosity to increase. Then it was raised gradually to 80 °C and finally 100 °C to ensure the effective mixing of the reactant (Table 2, entries 3 and 6). In both cases, full conversion of FBC

Table 1 Coupling reaction of CO₂ and FBC by (Salen)Ti^{IV}Cl₂.^a

Entry	Temp (°C)	Time (h)	Yield ^b (%)	TON ^c	TOF ^d (h ⁻¹)
1	80	3	43.8	438	146
2	90	3	62.8	628	209
3	100	1	38.2	382	382
4	100	2	69.3	693	347
5	100	2.5	85.0	850	339
6	100	3	>99.9	1000	333
7	120	1	67.2	672	672
8	120	1	19.2	1920	1920

^a Reaction conditions: neat BOF, CO₂ pressure = 3.0 MPa, [epoxide]/[Cat.]/[Cocat.]=1000/1/1; ^b Obtained from the normalized integrals of the methylene resonances in ¹H-NMR spectra around 4.80 ppm; ^c TON = turnover number of epoxy groups per Ti, TOF = turnover frequency; ^d [epoxide]/[Cat.]/[Cocat.]=10000/1/10.

Table 2 Polyaddition reaction of FBC with EDA and HAD.^a

Entry	NIPU	TBD (mol%)	FBC ^b (conv.%)	M _n ^c (kDa)	Đ ^c
1	1a	0	92	26.2	1.32
2	1b	5	100	35.8	1.35
3 ^d	1c	0	100	26.7	1.26
4	2a	0	94	28.9	1.34
5	2b	5	100	39.2	1.36
6 ^d	2c	0	100	34.1	1.28

^a Reaction conditions: FBC 0.5 mmol, diamine 0.5 mmol, DMSO 0.5 mL, 25 °C, 24 h; ^b Calculated from ¹H-NMR; ^c Determined by GPC using DMF as the eluent and with polystyrene standards; ^d FBC 20 mmol, diamine 20 mmol, solvent free, 60 °C for 20 min, 80 °C for 1 h and then 100 °C for 1 h.

was achieved within 2 h, and the resulting NIPU **1c** and **2c** also exhibited relatively narrow distributions (1.26 and 1.28, respectively).

The characteristic signals of cyclic carbonate moieties at around 1791 cm⁻¹ on the FTIR spectra (Fig. S7 in ESI) of FBC disappeared after the polyaddition reactions. New bands at 3363 and 1703 cm⁻¹ could be observed, which are ascribed to hydroxyl groups and urethane moieties, respectively. Furthermore, ¹H-NMR and ¹³C-NMR spectra were exploited to analyze the structures of NIPU **1c** and **2c** (Figs. S8–S11 in ESI) as well as the regioselectivity of the polyaddition reaction. As mentioned above, the nucleophilic attack of primary amine could occur at both methylene and methine carbons adjacent to carbonyl groups, which results in the formation of primary and secondary hydroxyl groups, respectively. Taking the ¹H-NMR spectrum of NIPU **1c** as an example (Fig. S8 in ESI), chemical shifts around 4.68 ppm would be attributed to the protons of newly formed primary hydroxyl groups as described in the literature.^[47] According to relative integration areas, the ratio of primary OH and secondary OH within NIPU **1c** could be determined as 40:60, which is the same to that within NIPU **2c**.

Morphological Analysis of PPC/NIPU Blends

Next, NIPU **1c** and NIPU **2c** were physically blended with PPC by an internal mixer. To investigate the morphology of PPC/NIPU blends, the cryo-fractured surfaces of the blends were immersed in methanol to etch the NIPU phases. Fig. 1 and Fig. S12 (in ESI) show the cryo-fractured surfaces of the etched PPC/NIPU **1c** and PPC/NIPU **2c** blends. Cavities can be observed on the cryo-fractured surfaces of both PPC/NIPU **1c** and PPC/NIPU **2c** blends, displaying a sea-island phase structure, where the NIPU phases are randomly dispersed within the PPC matrix, suggesting strong interfacial adhesion resulted from the intermolecular hydrogen bonding interactions between PPC and furan-based NIPUs.^[36,57] At the same NIPU content, the NIPU particles in PPC/NIPU **2c** blends are smaller than those in the PPC/NIPU **1c** blends. This could be ascribed to the relatively lower density of urethane moieties within NIPU **2c**, which endows weaker intramolecular interactions and improves intermolecular interactions.^[58] Moreover, the size of NIPU particles increases with the increasing contents of NIPUs, which could be ascribed to the gradually enhanced intramolecular hydrogen-bonding interaction. To further investigate the interactions within the PPC/NIPU blends, glass-transition temperature (*T*_g) of PPC, furan-based NIPUs, and their blends were determined by DSC characterization (Fig. 2). Owing to the

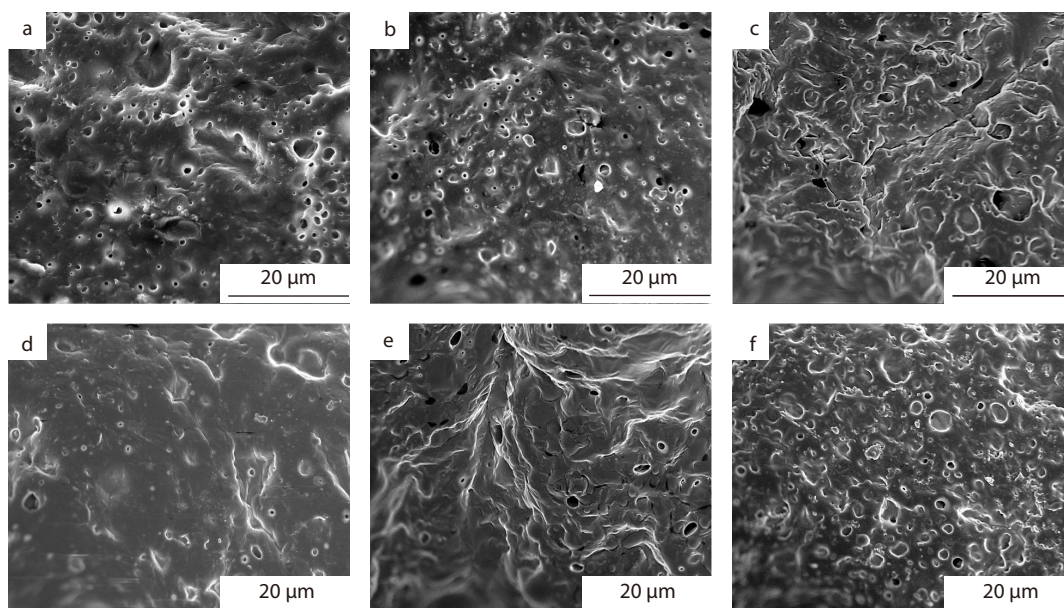


Fig. 1 SEM images of cryo-fractured surfaces of PPC/NIPU **1c** blends with a NIPU **1c** content of (a) 5.0 wt%, (b) 10.0 wt%, (c) 15.0 wt%, and PPC/NIPU **2c** blends with a NIPU **2c** content of (d) 5.0 wt%, (e) 10.0 wt%, (f) 15.0 wt%. The NIPU phases were etched by methanol before observation.

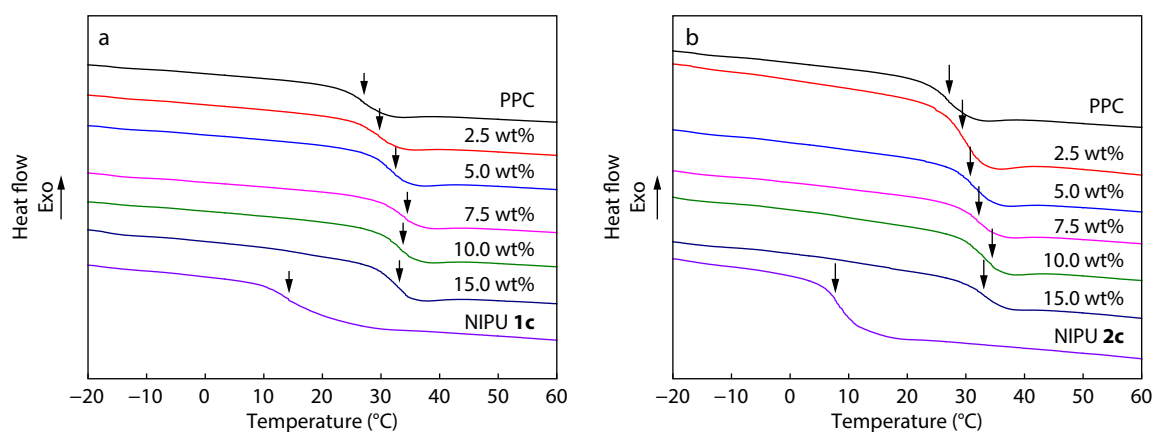


Fig. 2 DSC curves of (a) PPC/NIPU **1c** and (b) PPC/NIPU **2c**. The black arrows point out the T_g on the curves.

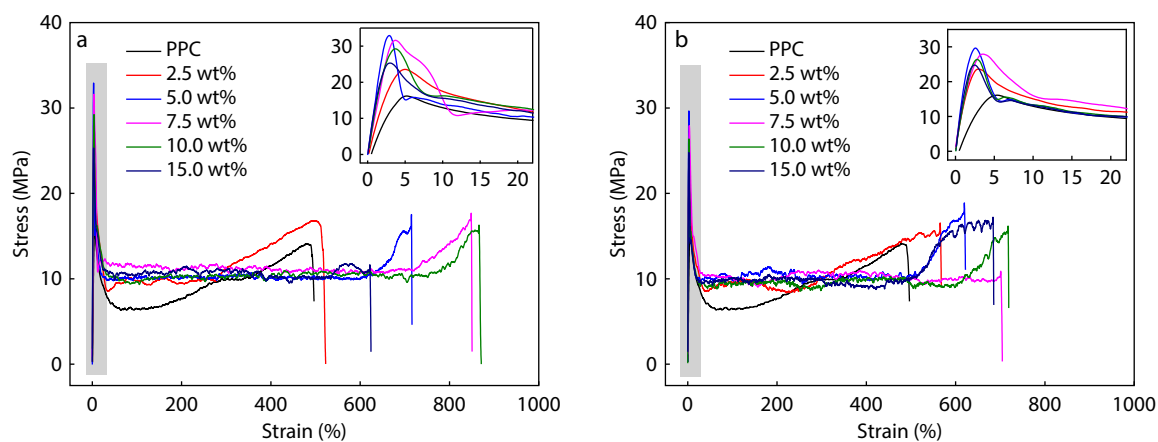


Fig. 3 Stress-strain curves of (a) PPC/NIPU **1c** and (b) PPC/NIPU **2c** blends with different furan-based NIPU contents. The grey areas of the curves are zoomed and displayed on the inserted graphs.

long flexible chains of aliphatic diamine, NIPU **2c** displays a T_g of 7.7 °C, much lower than that of NIPU **1c** (14.1 °C). It should be noted that, although phase separation was observed in the SEM images, the glass transition of furan-based NIPUs phase in the blends has not been detected in the DSC curves. It should be noted that the T_g of a PPC/NIPU blend is higher than the corresponding NIPU and neat PPC (T_g =26.8 °C), suggesting that the inter-molecular hydrogen-bonding interactions between PPC and NIPUs endow the blends with good compatibility. Also, the physical crosslinking between PPC and NIPUs significantly constrains the molecular movement of the PPC-rich phase. It can also be observed that the T_g first increases and then decreases with the increasing content of NIPUs. The maximum T_g of PPC/NIPU **1c** and PPC/NIPU **2c** blends are 34.3 °C at a NIPU **1c** content of 7.5 wt% and 34.5 °C at a NIPU **2c** loading of 10 wt%, respectively. This suggests that the intramolecular hydrogen-bonding interactions gradually dominate over their intermolecular counterparts in PPC/NIPU blends when the contents of NIPUs increase. To confirm this, an FTIR analysis of the blends was conducted (Figs. S13 and S14 in ESI). Taking the FTIR spectra of PPC/NIPU **1c** for example, the identical signals of carbonate moieties at 1739 cm^{-1} are gradually shifted to 1737 cm^{-1} when increasing the loading of NIPU **1c** from 0 wt% to 15 wt%, while signals corresponding to carbonyl groups of NIPU **1c** could not be observed (Fig. S13 in ESI). The simultaneous changes of these two characteristic signals well elucidate the formation of hydrogen bonding interactions between urethane

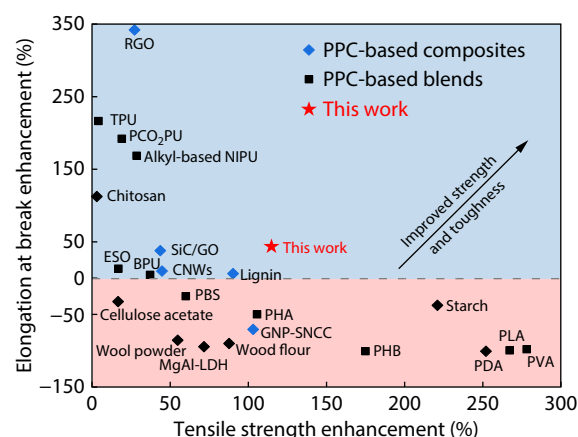


Fig. 4 Comparisons of enhancements of elongation at the break and tensile strength among different PPC-based blends and PPC-based composites with red stars representing results of PPC/NIPU **1c** blends in this work. (Data were from Table S2 in ESI).

moieties and carbonate units.

Tensile Properties of PPC/NIPU Blends

The tensile stress-strain curves and the tensile properties of neat PPC and its blends are shown in Fig. 3 and Table S1 (in ESI). Neat PPC displays a poor tensile strength of 15.5 MPa. Most of the current modification achievements on PPC can hardly enhance both the tensile strengths and their elongation at break of PPC,

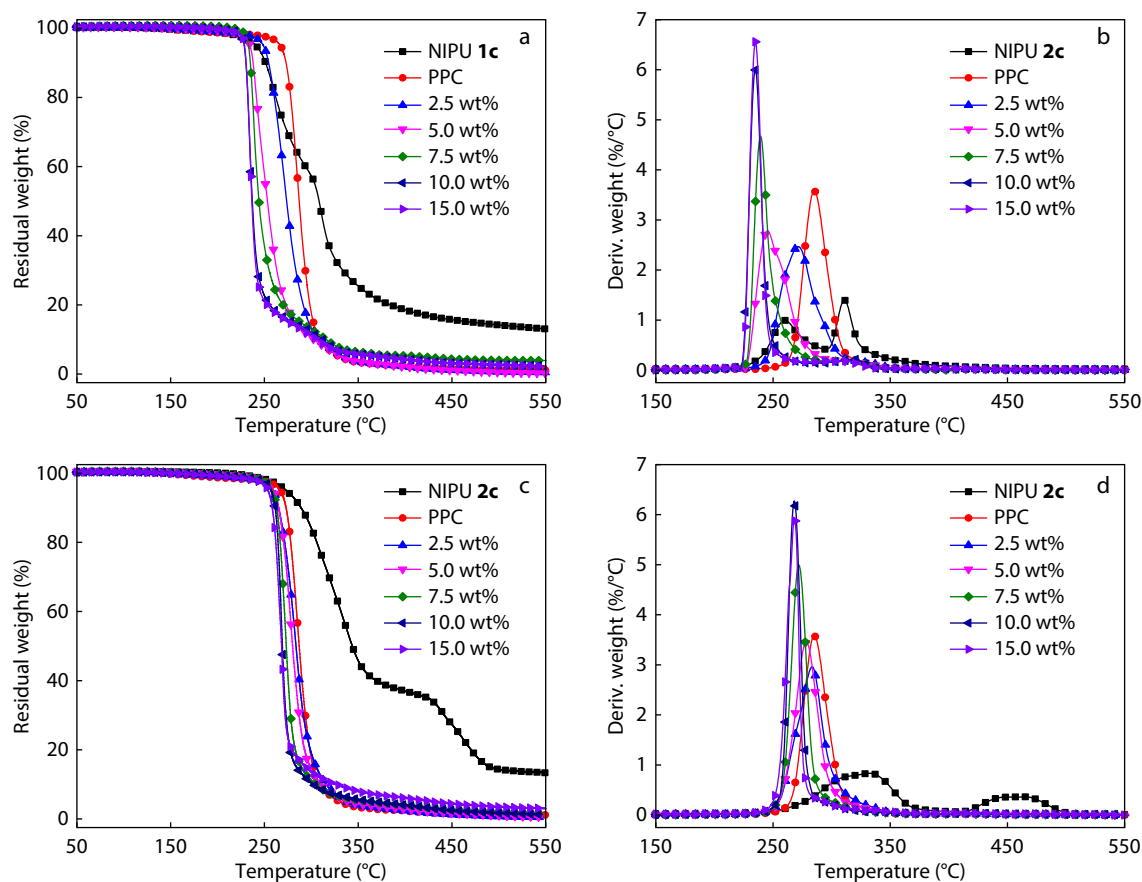


Fig. 5 TGA and DTG curves of PPC and their blends with (a, b) NIPU **1c** and (c, d) NIPU **2c** at different furan-based NIPU contents.

simultaneously (Fig. 4). In this work, incorporating furan-based NIPUs into PPC has enhanced the tensile strengths and elongations at break at the same time, displaying a simultaneous reinforcing and toughening effect on PPC. At a NIPU content of 5.0 wt%, the tensile strengths of PPC/NIPU blends are above 30 MPa, which are about twice that of neat PPC.^[59] When NIPU contents are higher than 5.0 wt%, the tensile strength of PPC/NIPU **1c** and PPC/NIPU **2c** blends start to decrease. Similarly, the elongations at break increase with increasing furan-based NIPU contents at the NIPU range of 0 wt%–10 wt% for PPC/NIPU **1c** as well as PPC/NIPU **2c**, further verifying the good interfacial interactions between PPC and furan-based NIPUs. While the areas of the NIPU phase become larger when further increasing the NIPU content, which brings more stress concentration and leads to the decrement in elongations at the break. The tensile strengths of PPC/NIPU **1c** blends are higher than those of PPC/NIPU **2c** blends, which might be ascribed to the higher density of hydrogen bonding interactions.

Thermal Stability of PPC/NIPU Blends

Thermal stabilities of PPC, furan-based NIPUs, and PPC/NIPU blends were measured by TGA and the results are shown in Fig. 5. The onset degradation temperature (T_{onset}) of PPC, NIPU **1c**, and NIPU **2c** are 267.0 °C, 241.1 °C, and 273.1 °C, respectively. Both NIPU **1c** and NIPU **2c** have two maximum degradation temperatures (T_{max}), which might be ascribed to the degradation of urethane moieties feathering primary and secondary OH, respectively. As urethane moieties are less thermally stable than aliphatic carbon chains and furan rings, NIPU **2c** possesses better thermal stability than NIPU **1c**. As is well known, the degradation of PPC occurs via the “back-biting” pathway (Scheme S1a in ESI) According to TGA analysis, PPC/NIPU blends exhibit inferior thermal stability compared to neat PPC when the temperature is above 200 °C. We envisioned that the hydrogen bonding interactions between PPC and NIPUs are gradually damaged when temperature increases and a large amount of free hydroxy groups within NIPUs undergo nucleophilic attack on the carbonate units, thus promoting the unzipping reaction of PPC (Scheme S1b in ESI).^[18,19,60]

CONCLUSIONS

In this work, furan-based NIPUs were synthesized starting from readily available HMF via a four-step procedure including reduction, glycidylation, carbonation of CO₂, and step-growth polymerization with diamines. In combination with onium salt TBAB, (Salen)Ti^{IV}Cl₂ displayed high catalytic activity in the carbonation process even under extremely diluted reaction conditions, and a remarkable TOF of 1920 h⁻¹ was obtained with a catalyst loading of 0.01 mol%. Under programmed reaction temperature, the step-growth polymerization proceeded under solvent-free and catalyst-free conditions, affording furan-based NIPUs with high molecular weights and narrow distributions. Due to the abundant N—H and O—H groups in furan-based NIPUs and C=O groups in the PPC matrix, strong intermolecular interactions have been formed through hydrogen bonding. Thus, the glass transition temperatures, tensile strengths, and elongations at break have been

significantly improved. Especially, upon the addition of 5.0 wt% furan-based NIPUs, the tensile strengths of the blends reached above 30 MPa, which are about twice that of neat PPC and can be equivalent to that of commercial polyethylene. This work demonstrates the preparation of high-performance CO₂-based biodegradable polymeric materials with low carbon footprint, good sustainability, and ideal biocompatibility.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-023-2904-8>.

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