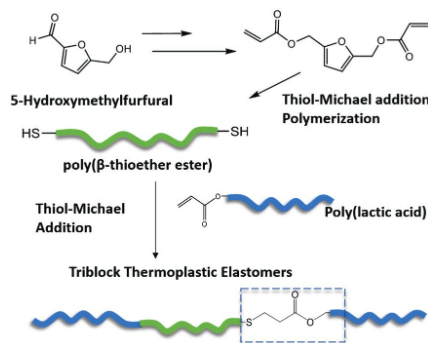


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5-Hydroxymethylfurfural Derivative Based Thermoplastic Elastomers Synthesized via Thiol-Michael Addition Reaction Utilizing Poly(lactic acid) as Hard End Blocks



5-Hydroxymethylfurfural derivative based thermoplastic elastomers (TPEs) are synthesized using the thiol-Michael addition reaction in combination with poly(lactic acid). The synthesis process occurs in a one-pot under mild reaction conditions. The properties of TPEs are tunable by varying the molecular weights of the soft segments or using the Diels–Alder reaction to dynamically crosslink the soft segments.

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5-Hydroxymethylfurfural Derivative Based Thermoplastic Elastomers Synthesized via Thiol-Michael Addition Reaction Utilizing Poly(lactic acid) as Hard End Blocks

Daihui Zhang and Marie-Josée Dumont*

5-Hydroxymethylfurfural derivative based thermoplastic elastomers (TPEs) are efficiently synthesized via a two-step thiol-Michael addition reaction using polylactide (PLA) as the hard segments in a one-pot reaction under mild conditions. The first step involves the synthesis of prepolymers having thiol groups as end groups. The macromolecular coupling reaction which occurred between the prepolymers and the PLA having acrylate-end groups is demonstrated via ^1H NMR and GPC. Additionally, by varying the ratio of 1,3-propanedithiol and 2,5-furan diacrylate, TPEs with soft segments having different molecular weights are synthesized, and then characterized. The cyclic tensile tests demonstrate the elasticity of the synthesized TPEs. Furthermore, the Diels–Alder reaction is used to dynamically crosslink the soft segments in the TPEs, leading to the increased mechanical properties in terms of Young's modulus and tensile strength.

1. Introduction

Renewable resources have been widely utilized for biofuels production, fine chemicals synthesis, and polymers synthesis.^[1–3] 5-Hydroxymethylfurfural (HMF) has shown its potential to be a versatile platform chemical.^[4] Despite various polymers synthesized from HMF and its derivatives, 2,5-furan dicarboxylic acid based (co)polyesters seems to be the most promising one.^[5,6] Due to the multiple functional groups of HMF available for derivatization, it is of interest to investigate the synthesis of new polymers from HMF and its derivative.^[4,7]

Thermoplastic elastomers (TPEs) are physically crosslinked polymers which can be prepared via several polymerization techniques.^[8–10] Research efforts have been made on the utilization of renewable resources to synthesize degradable TPEs.^[10] Due to the renewability, nontoxicity, biodegradability, and tunable crystallization behavior, polylactic acid (PLA), a bacterial biodegradable polyester, has been studied as hard blocks in the synthesis of TPEs.^[11] It has been suggested that the properties of soft middle

segments could influence the performance of PLA based TPEs.^[12] Therefore, various polymers with flexible polymeric chains have been evaluated as soft segments in PLA based TPEs.^[13–16] Recently, it has been shown that HMF derivative based poly(β -thioether ester) with tunable structures and properties could be efficiently synthesized via the thiol-Michael addition polymerization.^[7,17] The presence of thioether groups could be used as soft segments in TPEs.^[18,19] However, no information is available on the synthesis of PLA based TPEs using soft segments with thioether groups. Additionally, due to the presence of furan rings in the soft segments, HMF derivative based TPEs could be dynamically crosslinked by the Diels–Alder (DA) reaction to improve the mechanical properties

without losing other properties of TPEs.

Hence, this study reports the synthesis and characterization of HMF derivative based TPEs using PLA as the hard blocks. The first step was to synthesize 2,5-furan diacrylate (2,5-FDA) based prepolymers with thiol end groups. The TPEs were then synthesized by a coupling reaction between the prepolymers and the PLA having acrylate end groups. The structural, physical, and mechanical properties of the synthesized TPEs were investigated by NMR, Fourier transform infrared spectroscopy (FTIR), DSC, thermogravimetric analysis (TGA), and tensile tests. Furthermore, the effect of the DA reaction on the mechanical properties of TPEs was investigated. To the best of the authors' knowledge, this is the first example reporting the synthesis of PLA based TPEs using soft segments with thioether groups in a one-pot reaction under mild conditions. Moreover, the use of HMF derivative enabled the properties of TPEs to be adjusted.

2. Results and Discussion

2.1. Synthesis and Characterization of Poly(β -thioether ester) and TPEs

2,5-FDA based TPEs were synthesized by a two-step thiol-Michael addition reaction, as shown in Figure 1A. The first step was to synthesize a prepolymer with thiol end groups. Then the prepolymer reacted with PLA having acrylate groups as end groups to generate triblock copolymers. Dimethylphenylphosphine (DMPP) has been observed to efficiently initiate the thiol-Michael

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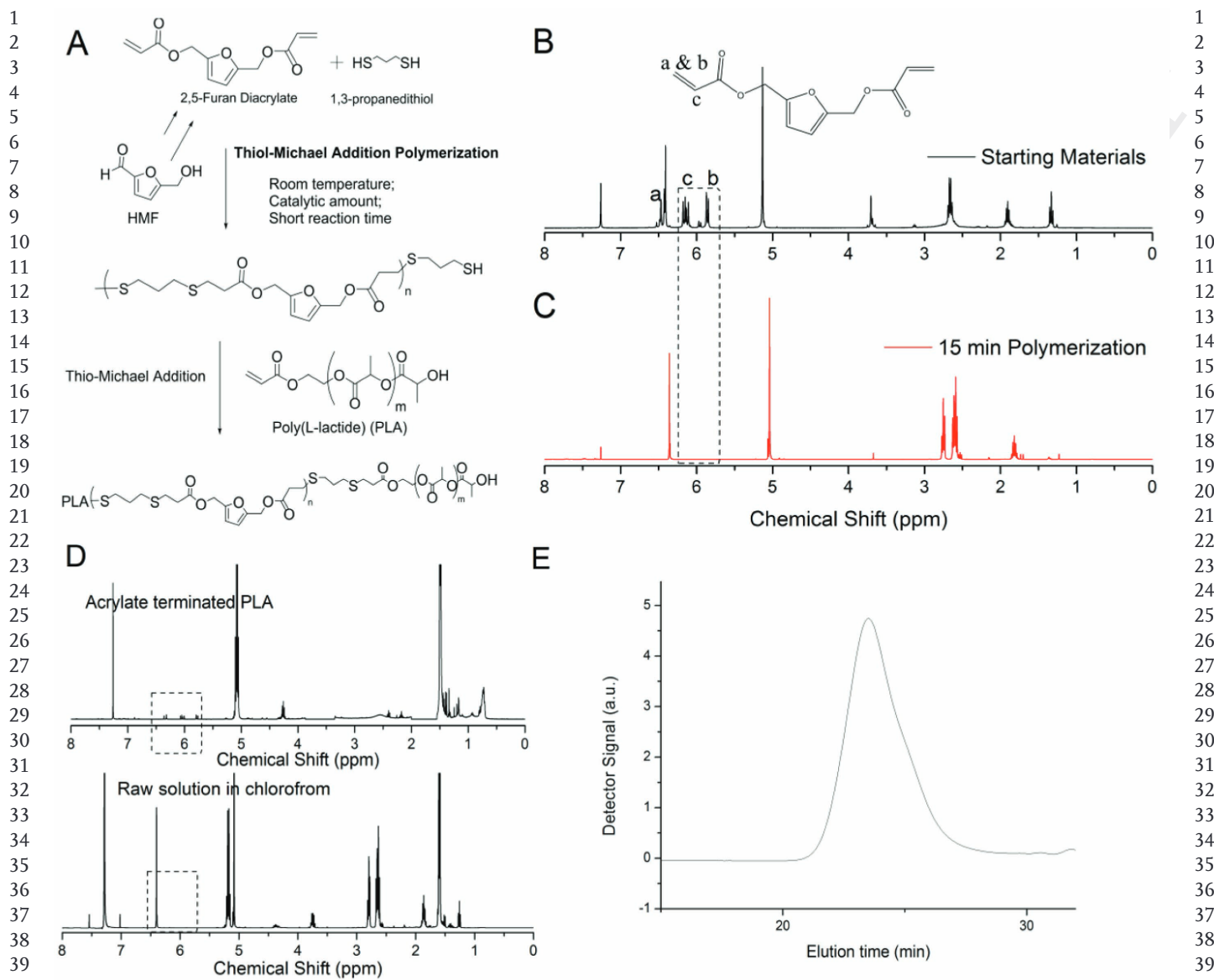


Figure 1. A) Scheme to synthesize 2,5-FDA based TPEs from HMF; ^1H NMR spectra of step growth polymerization of 2,5-FDA and 1,3-propanedithiol in chloroform-d. B) 0 min; C) 15 min; D) ^1H NMR of the macromolecular coupling between prepolymers and PLA with acrylate end groups in raw solution (chloroform); E) GPC of PLA-PPF1.1-PLA.

reaction in THF.^[7] However, PLA was poorly soluble in THF, which prevented the synthesis of TPEs occurring in a one-pot reaction system. Hence, chloroform was used to synthesize TPEs. A ^1H NMR spectra showed that the acrylate groups proton signals of 2,5-FDA disappeared within 15 min, indicating the full conversion of 2,5-FDA (Figure 1B,C). These results revealed that the thiol-Michael addition polymerization catalyzed by DMPP could be quickly performed in chloroform as well.

Then, a prepolymer with thiol end groups was synthesized using a ratio of 1,3-propanedithiol to 2,5-FDA equaling to 1.1–1, which was represented by PPF1.1. The presence of thiol groups in the raw solution after the thiol-Michael addition polymerization was analyzed by ^1H , ^{13}C NMR and HSQC (Figure S1, Supporting Information). The proton signals corresponding to the thiol groups and the protons next to the thiol groups were

observed at 1.34 ppm (h') and 1.87 ppm (f') (Figure S1A, Supporting Information). Moreover, carbon signals assigned to the carbon next to the thiol groups at the end of the prepolymer were observed at 23.47 ppm (g') (Figure S1B,C, Supporting Information). These results revealed the successful synthesis of prepolymers having thiols end groups.

Additionally, the macromolecular coupling between the prepolymers and PLA with acrylate end groups by the thiol-Michael addition reaction was investigated in chloroform (Figure 1A). The number average molecular weight of PLA with acrylate end groups was 5500 g mol^{-1} . First, a ^1H NMR spectrum of the raw solution showed that the protons signals of the acrylate groups disappeared after adding PLA to the prepolymer solution for 30 min (PLA-PPF1.1-PLA indicating triblock copolymers with PPF1.1 as the soft segments, Figure 1D). 59

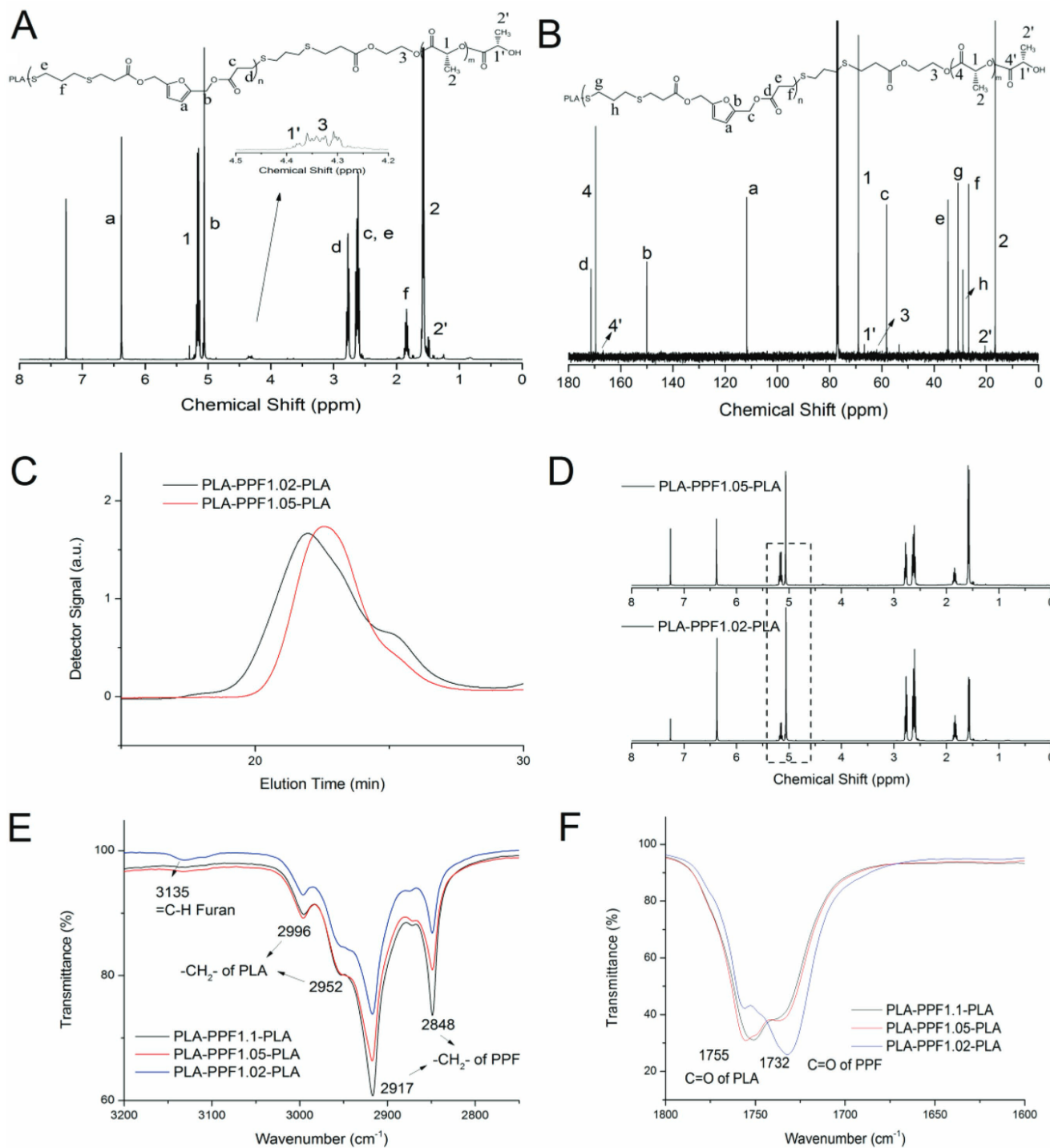


Figure 2. ^1H NMR A) and ^{13}C NMR B) of PLA-PPF1.1-PLA; C) GPC analysis of PLA-PPF-PLA with different soft segments; D) ^1H NMR of PLA-PPF1.05-PLA and PLA-PPF1.02-PLA; E) $-\text{CH}_2-$ regions; F) carbonyl regions.

Furthermore, a unimodal distribution of the synthesized polymers was observed by GPC analysis, and the number average molecular weight was $17\,001\text{ g mol}^{-1}$ ($M_w/M_n = 1.7$; Figure 1E and Table S1, Supporting Information). These results indicated the high efficiency of DMPP to catalyze the coupling reaction between the thiol and the acrylate groups of the polymers.

The TPEs were then precipitated in cold hexane, and the structure was confirmed by ^1H , ^{13}C (Figure 2A,B), COSY, and HSQC NMR analyses (Figure S2, Supporting Information). Furthermore, soft segments with higher molecular weights were synthesized to investigate their effects on the mechanical properties of TPEs. The ratios of 1,3-propanedithiol to 2,5-FDA were

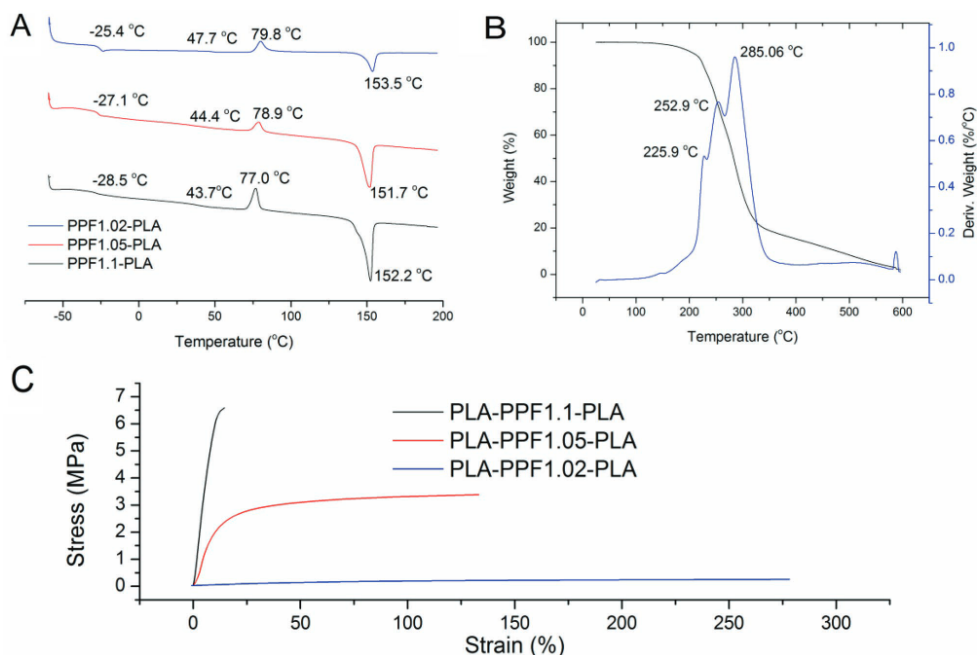


Figure 3. A) DSC curves of PLA-PPF-PLA; B) TGA curves of PLA-PPF1.05-PLA; C) stress-strain tensile tests of PLA-PPF-PLA.

set to 1.05-1 (PLA-PPF1.05-PLA) and 1.02-1 (PLA-PPF1.02-PLA), respectively. The molecular weights of the soft segments increased as the ratio of 1,3-propanedithiol to 2,5-FDA decreased from 1.05:1 to 1.02:1. As shown in Figure 2C, the molecular weights of TPEs increased from 28 125 g mol⁻¹ ($M_w/M_n = 1.6$) to 35 931 g mol⁻¹ ($M_w/M_n = 2.1$) (Table S1, Supporting Information). The structure of the synthesized TPEs analyzed by ¹H NMR and FTIR are shown in Figure 2D and Figure S3 (Supporting Information). The ratio of the signal intensity at 5.15 ppm (proton next to methyl groups of PLA) to the signal at 5.06 ppm (methylene groups next to the furan rings) decreased, indicating a decrease in the mass percentage of PLA in TPEs (Figure 2D). Additionally, as compared to the FTIR spectra of PPF (Figure S3A,B, Supporting Information), the characteristic bands of PLA were observed for PLA-PPF-PLA, including stretching vibration of -CH₂- at 2996 and 2952 cm⁻¹, and C=O stretching vibration at 1755 cm⁻¹ (Figure 2E,F and Figure S3C, Supporting Information).

2.2. Thermal and Mechanical Properties of TPEs

DSC was used to evaluate the thermal transitions of the TPEs (Figure S4, Supporting Information). A summary of the thermal transitions and the second heating curves are shown in Table S2 (Supporting Information) and Figure 3A, respectively. Two glass transition temperatures (T_g) for each synthesized TPEs were observed, corresponding to the soft segment and the PLA segment in the TPEs. For example, the T_g of the soft segment in PLA-PPF1.1-PLA was -28.5 °C, while the T_g of the PLA segment was 37.7 °C. As compared to PPF (-32.3 °C),^[17] the T_g of the soft segments in the copolymers increased due to the presence of PLA segments which restricted the flexibility of the chains. Furthermore, the crystallization

peaks were observed in the cooling step and the second heating curve. The cold crystallization temperature of PLA-PPF1.1-PLA was 89.2 °C, which was higher than the melt crystallization temperature (77.0 °C). As the molecular weight of the soft segments increased, the melt crystallization temperature observed in the second heating curve slightly increased from 77.0 to 79.8 °C. Moreover, the ΔH_m significantly increased from 10.0 J g⁻¹ (PLA-PPF1.02-PLA) to 34.1 J g⁻¹ (PLA-PPF1.1-PLA), indicating the presence of more crystals in the TPEs. This could be explained by the different mass percentage of PLA in the TPEs. When the molecular weight of the soft segments in the TPEs increased, the mass percentage of PLA decreased from 67.9% (PLA-PPF1.1-PLA) to 27.8% (PLA-PPF1.02-PLA), as determined by ¹H NMR. The thermal stability of the synthesized TPEs was evaluated by TGA (Figure 3B and Figure S5, Supporting Information). The temperature at 5% weight loss for the TPEs was around 209-240 °C (Table S2, Supporting Information). Moreover, the maximum decomposition temperatures of PLA-PPF1.05-PLA were observed to be 225.9, 252.9, and 285.1 °C, respectively. The first two decomposition steps were the results of the decomposition of the soft segments, corresponding to the first stage of the α -hydrogen bond scission and alkyl-oxygen homolysis, as well as the second stage of C-S bond scission.^[17] The decomposition step at 285.1 °C was due to the degradation of the PLA segment.^[20] However, for PLA-PPF1.02-PLA, only two decomposition stages were observed. This was probably due to the relatively low mass percentage of PLA present in TPEs (27.8%).

DMA was used to evaluate the viscoelastic behavior of elastomers (Figure S6, Supporting Information). The storage modulus significantly decreased in the temperature regions of -35 to -10 and 40-60 °C, corresponding to the glass transition of the soft segments and PLA segments, respectively. In addition, when the temperature was lower than 40 °C, the storage

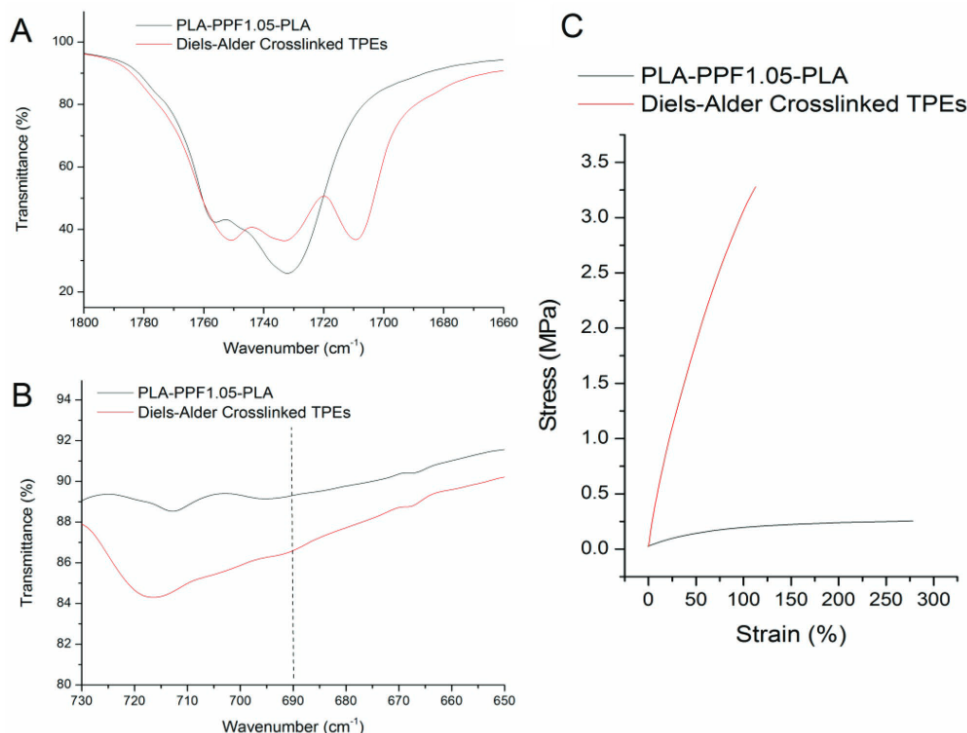


Figure 4. A) Carbonyl region of PLA–PPF1.02–PLA and DA crosslinked films; B) protons peak region of maleimide; C) stress–strain tensile tests of PLA–PPF1.05–PLA and crosslinked films.

modulus of PLA–PPF1.1–PLA was higher than the other two samples. This was consistent with other observations where increasing the mass percentage of PLA segments in the TPEs led to an enhancement of the storage modulus.^[12] The films used for the determination of the mechanical properties were prepared by solution casting. Several factors, such as the type of solvent used, the evaporation rate, and the concentration of polymer, can influence the crystallization of PLA during the solution casting process.^[21] Here, the effect of the solvent used (dichloromethane or chloroform) was investigated using PLA–PPF1.1–PLA. Similar to the behavior of pure PLA,^[22] the crystallinity percentage of TPEs in dichloromethane was higher (41.2%) than in chloroform (21.6%) (Figure S7, Supporting Information). Due to the brittleness of the films obtained in dichloromethane, chloroform was chosen for the film preparation. The mechanical properties of three TPEs were determined by stress–strain tensile tests (Figure 3C; Table S3, Supporting Information). A linear response was observed for the three samples at low strain. As the molecular weight of the soft segments increased, the Young's modulus and the tensile strength decreased from 45.6 MPa (PLA–PPF1.1–PLA) to 0.3 MPa (PLA–PPF1.05–PLA), and from 6.6 to 0.4 MPa, respectively. However, the elongation at break was increased from 14.5% to 277.8%. In addition, cyclic tests for PLA–PPF1.05–PLA were performed to evaluate the elasticity of TPEs (Figure S8, Supporting Information). It was observed that the residual strain for the first cycle was 2.4% as compared to 0.7% (second cycle), and 0.6% (third cycle). Moreover, the elastic recovery was increased from 70.2% (first cycle) to 93.4% (third cycle). It has been suggested that the mechanical properties of PLA

based TPEs were highly dependent on several factors, such as the composition of TPEs and the crystalline structure of PLA blocks.^[12] Although only the effect of the molecular weight of soft segments on the mechanical properties was investigated, the observed mechanical behavior of PLA–PPF–PLA could be the result of microphase separation, due to the presence of two T_g values as observed by DSC analysis. PLA segments acted as physical crosslinks to provide the strength, while the PPF soft segments were responsible for the ductility. In addition, the presence of residual strain for PLA based TPEs has been suggested to be the results of either crystals orientation or “slippage” effect.^[14]

2.3. Diels–Alder Reaction of Furan Rings in the TPEs

The DA reaction has been widely used to tune the properties of polymers, modify the films to increase the functionality and synthesize self-healing materials.^[23–26] Due to the presence of furan rings in the soft segments of TPEs, it was hypothesized that the DA reaction between the furan rings and the maleimides groups could be utilized to modify the synthesized TPEs. PLA–PPF1.02–PLA was used as model, and the DA reaction was investigated to tune the mechanical properties of TPEs. The DA crosslinked films were prepared by mixing the polymer solution and bismaleimide. The weight ratio of TPEs to crosslinkers was 10:1, corresponding to a furan ring to maleimide group molar ratio of 4:1. After curing at 40 °C for 48 h, the FTIR and mechanical properties of the crosslinked films were determined (Figure 4 and Figure S9, Supporting



Information). A new peak at 1715 cm⁻¹, assigned to the carbonyl groups of maleimide, appeared (Figure 4A), while the signal at 690 cm⁻¹ attributed to the protons of the maleimide ring disappeared (Figure 4B). These results indicated that most of the maleimide groups had efficiently reacted with the furan rings in the TPEs. The stress–strain curves of DA crosslinked TPEs showed that the Young's modulus and ultimate tensile strength were significantly improved to 5.5 and 3.3 MPa, respectively, despite the decrease in elongation at break (112.7%) (Figure 4C). These results indicated that the mechanical properties of PLA–PPF–PLA could be efficiently improved in terms of Young's modulus and tensile strength, due to the ability of the DA reaction to form new crosslinking points.^[27]

3. Conclusions

HMF derivative based TPEs were synthesized using the thiol–Michael addition reaction in a one-pot system under mild conditions. Chloroform was used as solvent to initiate the thiol–Michael addition reaction using DMPP as catalyst. The macro-molecular coupling between the thiols and the acrylate groups of the polymers could be achieved under the same conditions. The molecular weights of the middle soft segments were adjustable depending on the ratio of the two monomers. Therefore, TPEs with different molecular weights were prepared, leading to TPEs films with varied thermal and mechanical properties. DSC analysis revealed two *T_g*, indicating the presence of microphase separation. Similar to pure PLA, PLA in the TPEs crystallized during the solvent casting process in chloroform, which was important for the mechanical properties of TPEs films. TGA analysis showed that all the TPEs were thermally stable to at least 210 °C. The presence of furan rings in the soft segments could function as reactive sites to be dynamically crosslinked via the DA reaction. As a result, the tensile strength of PLA–PPF1.02–PLA could be significantly improved from 0.4 to 3.3 MPa (crosslinked PLA–PPF1.02–PLA). Although the mechanical properties of the synthesized HMF derivative based TPEs were not comparable to some of other renewable TPEs, the presence of furan rings, available for properties adjustment, might broaden their applications. Moreover, the compositions and properties of the soft segments could be adjusted by the copolymerization of different monomers to yield a variety of TPEs.^[17]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

5-hydroxymethylfurfural, poly(lactic acid), thermoplastic elastomers, thiol–Michael addition

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