



Development of polylactic acid-based materials with highly and balanced mechanical performances via incorporating a furan ring-containing unsaturated copolyester

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ABSTRACT

Balanced strength and toughness of poly(lactic acid) (PLA)-based materials is highly desirable in academia and industry. In this work, 1,5-pentanediol and dodecanedioic acid with flexible alkyl chains, 2,5-furandicarboxylic acid with a rigid cyclic structure and itaconic acid with carbon-carbon double bond are integrated to synthesize a new bio-based unsaturated copolyester. Through dicumyl peroxide-induced simultaneous dynamic vulcanization and interfacial compatibilization of the copolyester with PLA, resulting blends display high and balanced mechanical properties, namely, the maximum elongation at break and notch impact strength are increased by ~35 times and ~17 times, as compared to neat PLA; while the tensile strength maintains at 57.4 MPa (only ~18% decrease). As evidenced from SEM images, stretching of copolyester domains that induces deformation of contacted PLA surfaces via strong interfacial bonding accounts for the toughening mechanism. This work offers a facile strategy for fabricating fully bio-based polymeric materials with highly comprehensive mechanical properties.

1. Introduction

Environment, economic, and safety challenges have triggered to replace petrochemical-based polymers with bio-based and biodegradable materials. PLA is regarded as one of the most promising alternatives due to high mechanical strength and stiffness, biodegradability, biocompatibility and nontoxicity [1,2]. Nevertheless, its intrinsic brittleness and slow crystallization are major drawbacks greatly restricting extensive commercialization and development. In past decades, extensive efforts have been devoted to toughen PLA [3–9]. Among current toughening strategies, physical blending with fully/semi bio-based flexible polymers or rubbers has been proved to be the most environmental, economic and efficient solution. However, 1) most toughening agents exhibit unfavorable compatibility with PLA matrix, and improvement of toughness, especially impact strength, cannot be realized without interfacial compatibilization [10–12]; 2) despite enhanced interfacial compatibility and tensile/impact toughness [13–18], serious decline of tensile strength, even up to 50%, is difficult to avoid as compared to pristine PLA.

Integrating rigid cyclic structures into molecular chains is an important approach for improving mechanical strength [19–22]. Among the 12 top value-added biomass chemicals approved by the U.S. Department of Energy [23,24], 2,5-furandicarboxylic acid (FDCA) is the sole aromatic monomer that has a more rigid structure compared to petroleum-based counterparts (especially, terephthalic acid) [25]. Jacquelin et al. reported a poly(butylene succinate-co-furanoate) copolyester with the increased tensile strength from 19.0 MPa of poly(butylene succinate) to 23.0 MPa [26]. Hu et al. demonstrated that the increased content of butylene furandicarboxylate unit was favorable to obviously enhanced tensile strength from 14.0 MPa to 59.2 MPa for Poly(butylene carbonate-co-furandicarboxylate) [27]. Therefore, maintaining the mechanical strength of PLA-based materials is expected to be achieved by using such rigid cyclic structure. Unfortunately, the concept has never been reported yet.

In this work, an FDCA-containing unsaturated copolyester is synthesized for toughening modification of PLA. A fully bio-based blend is produced through dicumyl peroxide (DCP)-induced simultaneous dynamic vulcanization and interfacial compatibilization. Due to the

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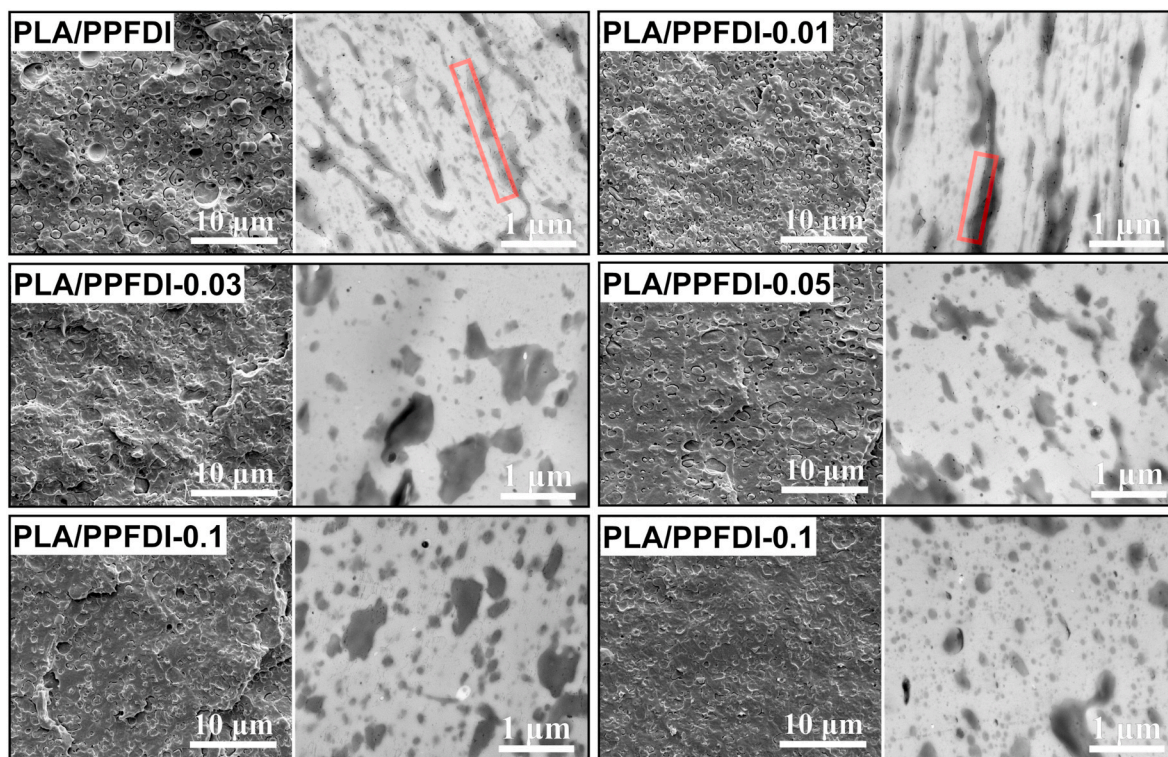


Fig. 1. SEM and TEM images of PLA/PPFDI blends prepared under different DCP contents.

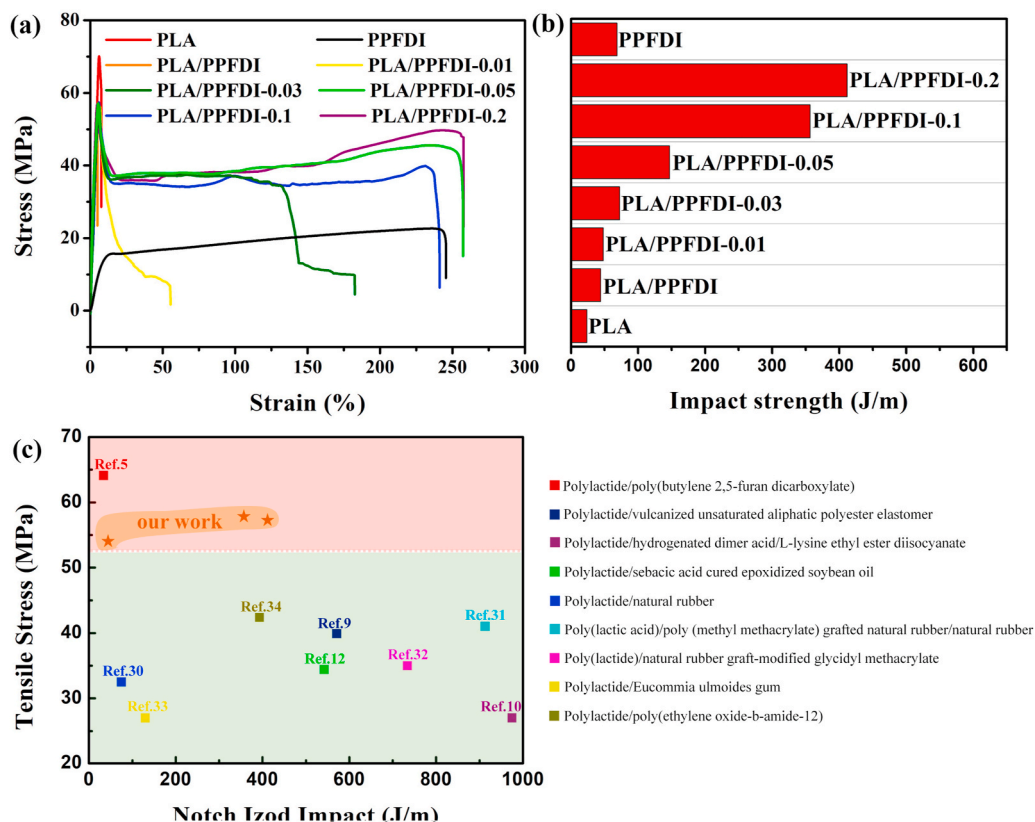


Fig. 2. (a) Tensile stress–strain curves and (b) notched impact strength of PLA, PPFDI, pristine PLA/PPFDI and PLA/PPFDI-x blends, (c) comparison of tensile strength and notch impact strength of the PLA-based blends in this work with previous works on semi/fully bio-based PLA blends.

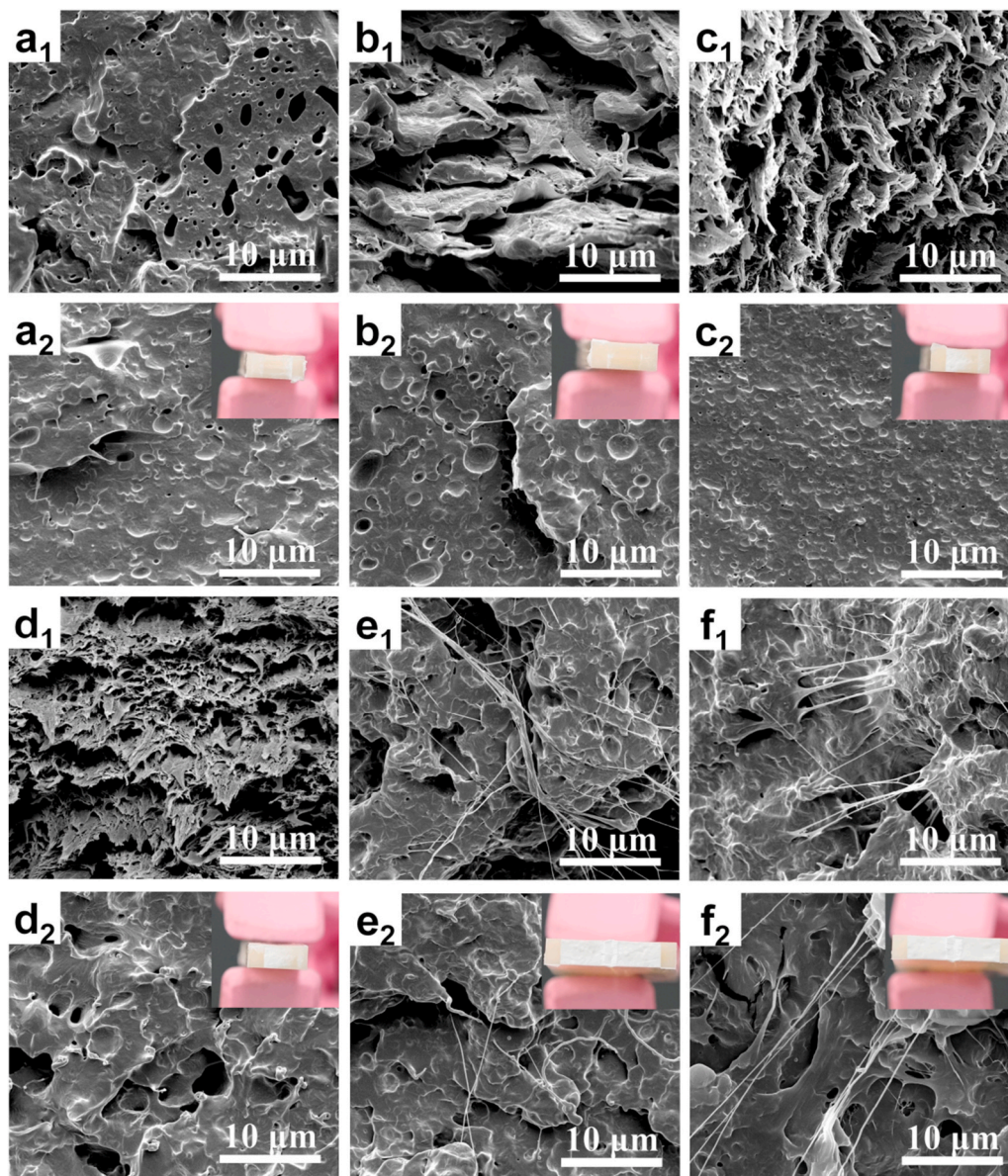


Fig. 3. SEM images of tensile and impact fracture surfaces of (a₁, a₂) pristine PLA/PPFDI blend, (b₁, b₂) PLA/PPFDI-0.01, (c₁, c₂) PLA/PPFDI-0.03, (d₁, d₂) PLA/PPFDI-0.05, (e₁, e₂) PLA/PPFDI-0.1, and (f₁, f₂) PLA/PPFDI-0.2.

presence of flexible 1,5-pentanediol (PeDO) and dodecanedioic acid (DDCA) as well as rigid FDCA in the copolyester chain, the toughness is improved significantly and the strength is well maintained, achieving good and balanced comprehensive mechanical properties. By controlling the content of DCP, notably, the maximum elongation at break and notch impact strength of the resulting materials are increased by ~35 times and ~17 times while the tensile strength only decreases by ~18%, as compared to those of neat PLA. This work provides an effective approach to develop PLA-based materials with highly comprehensive mechanical performances that are desirable for wide applications.

2. Results and discussion

The copolyester, PPFDI, for toughening PLA is synthesized by esterification and polycondensation, of which the ¹H NMR spectrum is shown in Figure S1. For the pristine PLA/PPFDI blend, the phase separation with easily distinguished interfaces as well as the inhomogeneous dispersion of PPFDI phase in the PLA matrix is observed (Fig. 1). When the content of DCP ≥ 0.03 wt%, very few voids are detected and the

interfaces are difficult to distinguish, indicating improved compatibility between PLA and PPFDI. TEM results further identify the morphological evolution, that is, decreased weight-average particle size of the PPFDI phase with the DCP content. According to previous reports [15,28], the change trend is conducive to the improvement of toughness of PLA materials. Additionally, DMA and DSC results further confirm the improved interfacial compatibility between PLA and PPFDI, due to that the *T_g*s of PLA and PPFDI approach to each other with the addition of DCP (Figure S2 and Figure S3). Moreover, from the corresponding data of DSC curves (Table S1), it can be deduced that adding DCP promotes the crystallization of PLA phase.

Fig. 2a presents typical tensile stress-strain curves of the blends, from which tensile strength, elongation at break and tensile toughness are summarized in Table S2. Neat PLA quickly fractures in a brittle mode after distinct yielding without necking, exhibiting the tensile strength and elongation at-break of 70.1 MPa and 7.4%, respectively. In contrast, PPFDI shows much higher elongation at break. After yielding at strain of 14.6%, the tensile stress gradually increases with strain before the breakage at ~245.5%. However, the pristine PLA/PPFDI binary blend

still shows a typical brittle fracture, as manifested by the comparably low fracture strain to that of neat PLA. On contrary, introducing DCP induces significantly improved elongation at break. The maximum elongation at break of PLA/PPFDI-x blends increases to 257.4%, which is 35-time higher than that of neat PLA. In addition, the tensile toughness changes similarly to the variation of elongation at break of the samples. The maximum tensile toughness of PLA/PPFDI-x blends shows a value of 106.8 MJ/m³, which is 31 times improvement compared to 3.4 MJ/m³ of neat PLA. It's worth noting that the tensile strength of the PLA/PPFDI-x blends is still maintained at a relatively high level. PLA/PPFDI-0.1 shows the highest tensile strength with a value of 57.4 MPa, which is only decreased by ~18% compared with that of neat PLA, achieving a good balance of tensile strength and toughness. On the other hand, compared with neat PLA, both PLA/PPFDI and PLA/PPFDI-0.01 exhibit no obviously increased notched impact strength. When the DCP content exceeds 0.03 wt%, the notched impact strength is improved significantly. Notably, PLA/PPFDI-0.1 shows the maximum impact strength of 412.0 J/m, which is 17-time higher than that of neat PLA. Considering the comprehensive mechanical properties, the optimum DCP content in this work is 0.1 wt%. The comprehensive mechanical performance is superior over previously reported semi/fully bio-based PLA blends (Fig. 2b) [6,13,14,16,29–33]. Here, two aspects are considered accounting for the highly comprehensive mechanical properties: 1) the rigid furan rings restrict the internal rotatory degrees of freedom [34], minimizing the sacrifice of tensile strength (Scheme S2); 2) from gel content and XRD results, DCP-induced simultaneous dynamic vulcanization and interfacial compatibilization are favorable to stress transfer and energy dissipation (detailed discussion provided in the supplementary information, Figure S4).

To explore the toughening mechanism, SEM images of the tensile and impact fracture surfaces of the blends are observed (Fig. 3). The neat PLA shows a typically smooth fracture surface, attributing to the brittleness. For the pristine PLA/PPFDI blend, a relatively smooth brittle tensile fracture surface is also noted; however, some micrometer-sized voids are detected, which, according to some relevant works [28], is ascribed to the low interfacial adhesion and obvious phase separation between PLA and PPFDI. With the addition of DCP, rougher tensile-fracture surfaces as well as larger deformations are observed, and the fracture surface displays the morphological transition from short and coarse filament to slender fiber. This phenomenon is due to the easy stretching of the PPFDI domains that simultaneously induces the deformation of the contacted PLA surfaces via interfacial chain entanglements [12]. The above results imply the significantly improved elongation at break. Moreover, the neat PLA shows a smooth impact fracture surface without slight stress-whitening zones. For pristine PLA/PPFDI blend, inhomogeneous PPFDI domains are seen to disperse in PLA matrix. Some micrometer-sized voids or pits are also detected, ascribing to the delamination of PPFDI from PLA matrix under the external impact force. No obvious morphology change is seen until increasing the DCP content to 0.03 wt%. In this case, the size of PPFDI phase decreases sharply, and the interfaces cannot be identified easily. Further increasing the DCP content induces the formation of homogeneous impact fracture surface and “fold faults”, reflecting the higher shear yield and plastic deformation. When DCP content is ≥ 0.1 wt%, the impacted specimens are not broken completely. Especially, the PLA/PPFDI-0.2 blend shows an entirely stretched and deformed fracture surface. These results are consistent with those in Fig. 1.

3. Conclusions

A fully bio-based unsaturated copolyester containing a rigid cyclic structure, PPFDI, is synthesized and used to toughen PLA. Reactive compatibilization between the two phases is accomplished via one-step DCP-induced dynamic vulcanization. A sharp brittle-ductile transition of the resulting blends occurs at the DCP concentration of 0.03 wt%, accounting for the significantly improved compatibility. Notably, the

maximum elongation at break and notch impact strength are increased by ~35 times and ~17 times (as compared to neat PLA) to 257.4% and 412.0 J/m, respectively, while the maximum tensile strength maintains at 57.4 MPa that only decreases by ~18%, achieving a good balance between strength and toughness. Featured with the superior mechanical properties, such PLA-based material has high potential for wide applications.

CRedit authorship contribution statement

Lu He: Methodology, Investigation, Writing - original draft. Fei Song: Supervision, Conceptualization, Writing - review & editing. Lijin Qi: Investigation. Xi Zhao: Writing. Xiuli Wang: Supervision, Funding acquisition, Project administration. Yuzhong Wang: Supervision, Resources, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.coco.2020.100543>.

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