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To cite this article: Ming Wang, Ying Wu, Yi-Dong Li & Jian-Bing Zeng (2017): Progress in Toughening Poly(Lactic Acid) with Renewable Polymers, Polymer Reviews, DOI: [10.1080/15583724.2017.1287726](https://doi.org/10.1080/15583724.2017.1287726)

To link to this article: <http://dx.doi.org/10.1080/15583724.2017.1287726>



Accepted author version posted online: 08 Feb 2017.
Published online: 08 Feb 2017.



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Progress in Toughening Poly(Lactic Acid) with Renewable Polymers

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ABSTRACT

Poly(lactic acid) (PLA) is regarded as one of the most promising biobased and biodegradable polymers due its various advantages including high mechanical strength, easy processability, high melting temperature, renewability, biodegradability, and biocompatibility. However, the inherent brittleness significantly restricts its wide application. Therefore, toughening PLA has attracted more and more attention and various materials have been used to blend with PLA for toughening. Considering the fact that the use of petroleum-based species to toughen PLA would partially sacrifice the sustainability, various renewable polymers have recently been employed to toughen PLA. A series of important achievements have been obtained but not reviewed. This article aims to review progress in toughening PLA with renewable polymers. The toughening theories and compatibilization strategies are also briefly introduced.

KEYWORDS

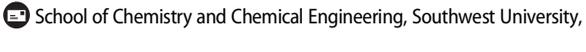
Poly(lactic acid); renewable polymers; toughening; sustainability

1. Introduction

Sustainable polymers that are derived from renewable resources have attracted more and more attention as they are not only petroleum independent but also environmentally benign.^{1,2} The wide use of sustainable polymers provides a good solution to reduce dependence of materials on fossil resources and to minimize plastic pollutions caused by indiscriminate use of petroleum-based polymers.³ Unfortunately, most of the sustainable polymers have some shortcomings that restrict their practical application. Therefore, property modification of sustainable polymers has become a very active and important realm of materials science.^{4–10}

Poly(lactic acid) (PLA), also known as polylactide, is one of the most investigated sustainable polymers,¹¹ because PLA has many excellent properties. PLA is renewable, biodegradable, and recyclable.^{12–14} After a lifetime, it can degrade completely into eco-friendly final products, such as CO₂ and H₂O.¹⁵ Both CO₂ and H₂O are essential feedstocks for growth of plants or crops via photosynthesis. **Figure 1** shows the typical synthesis and cyclic process of PLA.

PLA is biocompatible and its degradation products are safe for living organisms including the human body,¹⁶ making it the most attractive polymer for biomedical applications. The

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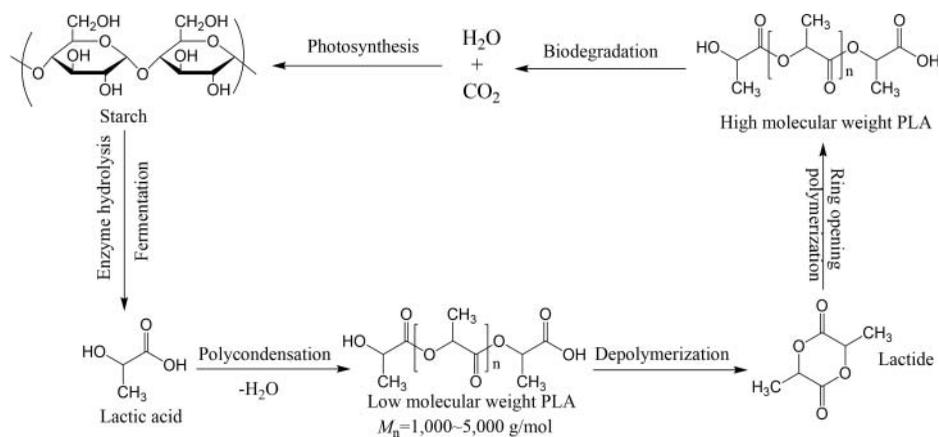


Figure 1. Typical synthesis and circulation of PLA.

safety of PLA has been approved by the Food and Drug Administration (FDA).¹⁷ PLA has good processability and can be converted into molded parts, foams, films, and fibers by conventional processing techniques with minimal modifications, which is very charming for practical applications in various fields.¹⁸

PLA exhibits high mechanical performance with tensile strength of 50~70 MPa and elastic modulus as high as 3.0~4.0 GPa, respectively, depending on the molecular weight and stereochemical composition.¹¹ In addition, PLA shows melting temperature of 170~180°C which is higher than many other sustainable polymers such as poly(butylene succinate) (PBS) and its copolymers. The high mechanical strength plus high melt point even helps PLA to find potential application in engineering plastics.¹⁹ All those combined advantages make PLA the most promising and attractive of sustainable polymers.

However, PLA also has some shortcomings which limit its use in some specific areas. The inherent brittleness, evidenced by the limited elongation at break and low impact strength, constitutes the greatest challenge for wide application of PLA.²⁰ Although it shows comparable tensile strength and modulus to poly(ethylene terephthalate) (PET), the elongation at break is less than 10% and the notched impact strength is smaller than 20 J/m.²¹ Another severe defect is the rather slow crystallization rate, which leads to low degree of crystallinity combined with low heat deflection temperature (HDT), thus resulting in narrowed application fields.^{22,23} The addition of nucleating agents or some nanoparticles provides an efficient way to accelerate crystallization rate thus improving the degree of crystallinity of PLA during thermal processing.^{22,24–26}

With respect to the lack of toughness, various techniques including chemical copolymerization, plasticization, and polymer blending have been applied to toughen PLA.^{21,27} Although chemical copolymerization is efficient in improving ductility of PLA, it usually causes serious loss in some merits of PLA; for example, it apparently reduces mechanical strength and melting temperature.^{28–30} In addition, the high cost, that results from the lengthy reaction period and rigorous copolymerization conditions, is another challenge for chemical copolymerization.¹⁹ In contrast, physical blending with plasticizers or flexible polymers represents an efficient and cost-effective way to improve toughness of PLA.^{16,21,27} Therefore, many plasticizers and flexible polymers have been widely used to blend with PLA for toughening.^{8,9,20,31–57}

Plasticization by addition of a suitable plasticizer is used not only to improve thermal processability but also to enhance flexibility of glassy polymers.²¹ Various plasticizers including poly(ethylene glycol), lactide monomer, citrate esters, glyceryl triacetate, dibutyl sebacate, epoxidized soybean oil, liquefied wood flour ester, and some oligomers have been widely used to plasticize PLA.^{31,33–35,58–70} Many of these plasticizers are very effective in improving ductility of PLA as evidenced by the drastic enhancement in elongation at break of the plasticized PLA. For example, the addition of 20 wt% citrate esters, PLA oligomer, or dibutyl sebacate could increase the elongation at break of PLA to 200~420% from less than 10% of neat PLA.^{31,62,69}

However, there are some significant problems associated with plasticization. Typically, substantial enhancement in tensile toughness requires relatively high content of plasticizers (15~20 wt%), which would cause a drastic reduction in tensile strength and elastic modulus.^{31,32,34,65} For example, addition of 15 wt% glyceryl triacetate as plasticizer significantly increased elongation at break of PLA from 11% to 233%, but the elastic modulus and tensile strength decreased drastically to 0.59 GPa and 29 MPa from 1.02 GPa and 65 MPa, respectively.⁶³ The durability of plasticized polymers are usually poor due to the migration of the plasticizers from bulk to surface, which would make the products brittle during storage or service.^{71,72} For example, migration of plasticizers such as lactide and epoxidized soybean oil in PLA matrix have been observed in some studies.^{71,72} In addition, the plasticization seems not so efficient in improving impact toughness, as most plasticizers, such as tributyl O-acetylcitrate and tributyl citrate, showed limited enhancement in notched impact strength compared to that of elongation at break.^{50,63} Due to these limitations, plasticization is not the best choice for toughening. It is therefore necessary to develop some other methods to simultaneously improve both tensile toughness and impact toughness of PLA and meanwhile to largely keep the mechanical strength, elastic modulus, and durability at a high level.

In contrast, blending with flexible or elastic polymers provides an alternative way of significantly improving tensile toughness and impact toughness simultaneously if fine morphology and suitable compatibility of blends are obtained.^{8,41,46,47,73,74} The loss in tensile strength and elastic modulus in polymer blends is usually much smaller than the plasticized polymers with similar compositions. For example, the elongation at break and impact strength of PLA were simultaneously increased to more than 200% and 400 J/m by incorporation of 20 wt% poly(ethylene glycol)-based crosslinked polyurethane (CPU) from less than 10% and 16 J/m, respectively. Meanwhile, the tensile strength and elastic modulus were only reduced by ~41% and ~29%, respectively.⁷⁴ While, by contrast, the tensile strength and elastic modulus of PLA plasticized by 20 wt% PEG were reduced by ~67% and ~82%, respectively.⁶⁰ Another advantage of polymer blending for toughening PLA is that the durability of the toughened blends is improved, since migration is avoided due to the high molecular weight and low mobility of the blending components.²³

Owing to these advantages, polymer blending has been widely used to toughen PLA.^{16,21,27} The flexible or elastic polymers used in earlier studies were usually produced from petroleum resources, including polyethylene (PE),^{36,37,75} poly(ethylene-co-octene) (POE) elastomer,^{76,77} acrylonitrile-butadiene-styrene (ABS) copolymer,⁴⁰ poly(ethylene-co-glycidyl methacrylate) (EGMA),⁴¹ EBA-GMA terpolymer combining EMAA-Zn ionomer,^{46,47,78} hydrogenated styrene-butadiene-styrene block copolymer (SEBS),⁷⁹ polycaprolactone (PCL),^{20,80–82} aliphatic-aromatic copolyesters,^{39,83–85} and polyurethanes.^{86–90} Some of these polymers showed very high toughening efficiency and even super-tough PLA

blends with impact strength of higher than 530 J/m achieved occasionally.^{41,46,47,75,79} However, it should be noted that the sustainability of the materials decreased by blending with petroleum-based polymers. In this regard, elastic fossil-based polymers are not the ideal toughening components for PLA.

Therefore, more and more attention has been paid to toughen PLA with renewable polymers.^{54–57,73,91–102} Although some review articles in toughening PLA have been published,^{21,23,27} there is still a lack of comprehensive review papers to exclusively report the progress in toughening PLA with renewable polymers. As this topic develops very quickly and a series of significant achievements have been obtained recently, it is necessary to review the progress of this topic to show some detailed insights into renewable polymers toughened PLA blends and to guide future investigations on property modification of PLA.

2. Toughening theory

2.1 Toughness: Definition and influence factors

Before going to the main topic, we would like to briefly introduce the toughening theory. First, let us talk about the definition of toughness, which is defined as the ability to absorb energy before fracture. It is usually categorized into tensile toughness and impact toughness according to the different loading patterns. Tensile toughness is used to describe the ability to absorb tensile fracture energy during stretching, while impact toughness relates to the ability of absorbing sudden impact energy.²³ Two kinds of factors affect the toughness of materials—extrinsic and intrinsic. The extrinsic factors include temperature, notched or unnotched, sample geometry, loading pattern, and fracture mode. The intrinsic factors mainly involve phase behavior, chemical structure, and chain entanglement.¹⁰³ Even under given extrinsic conditions, different polymers or blends may behave differently due to the different intrinsic behaviors.

According to the fracture behaviors, Wellinghoff and Baer¹⁰⁴ classified neat polymers into two categories—brittle and ductile polymers. The brittle polymers are inclined to break while ductile polymers tend to yield when loaded. In consideration of the influence of microstructural and molecular parameters on the fracture behaviors, Wu¹⁰⁵ categorized neat polymers into brittle and pseudoductile polymers. The prefix “pseudo” was added to highlight the effect of intrinsic factors on the fracture behaviors of the polymers. Entanglement density ν_e and characteristic ratio C_∞ are the two parameters that control the fracture behavior of neat polymers. The crazing stress and yield stress are proportional to $\nu_e^{1/2}$ and C_∞ , respectively. In rubber/brittle polymer blends, the combination of rubber phase morphology and chain parameters of the brittle polymer determined the fracture behavior of the blends. Super-tough blends are obtainable if ν_e of the brittle polymer is 0.1 mmol/cm³, because considerable fracture energy can be absorbed due to occurrence of massive combined crazing and yielding of the matrix at this entanglement density level. The review paper by Wu can be referenced for further detailed understanding of these theories.¹⁰³

2.2 Toughening mechanisms

Since Merz et al.¹⁰⁶ proposed the microcrack toughening mechanism in 1956, many different mechanisms, such as shear yielding,^{107–109} multiple crazing,^{110–112} and their combination^{113,114}

have been proposed to describe rubber toughened brittle polymer blends. Shear yielding is reported as the main source for energy dissipation; therefore, to allow the brittle polymer matrix shear yielding is regarded as the key point to design highly toughened polymer blends.^{22,103,114,115} However, shear yielding and crazing usually occur competitively, and the intrinsic properties of the brittle polymers determine which mode dominates the deformation.^{22,103,114} The relationship between craze initiating stress and yield stress of matrix strongly affect the deformation mechanism. Shear yielding dominates the deformation when craze initiating stress is greater than yield stress. Otherwise, crazing is the main deformation mechanism if craze initiating stress is smaller than yield stress. Their combination occurs if both are comparable. In addition, the combination also takes place if interactions exist between the shear bands and crazes.²³ Generally speaking, the fracture process of glassy amorphous polymers such as polystyrene¹¹² is dominated by crazing, while that of brittle crystalline polymers such as polyamide¹⁰⁸ is controlled by shear yielding. PLA can be both amorphous and semi-crystalline by changing the stereochemical composition or processing conditions, and thus the three toughening mechanisms have been observed in rubbery polymer toughened PLA blends.^{22,23}

The first step for toughening is stress concentration, which is induced by the presence of dispersed rubber particles and usually leads to cavitation of the blends.^{23,115,116} Cavitation then initiates shear yielding or crazing, which further develops to cause large plastic deformation of matrix to dissipate a large amount of fracture energy. Either internal or debonding cavitation occurs for rubber toughened plastic blends, and which one dominates depends on the interfacial adhesion between the dispersed phase and the polymer matrix.¹⁰⁹ Internal cavitation relating to the cavitation in the dispersed rubber phase takes place when the interfacial adhesion is strong. Poor interfacial adhesion usually causes debonding cavitation, which involves the formation of cavities via interfacial debonding of dispersed rubber particles and matrix at the interface. It is noted that a combination of both cavitations is also possible for suitable interfacial adhesion.²³ Both cavitation mechanisms have been reported in rubbery polymers toughened PLA blends; however, the optimal impact toughness usually occurs at a suitable interfacial adhesion, which induces peaceable cavitation and then matrix shear yielding without catastrophic crack propagation.⁴⁷ Either too weak or too strong interfacial adhesion is unfavorable, as the former usually causes premature interfacial failure,^{117,118} while the latter generally delays the occurrence of matrix yielding.¹¹⁹

The tensile toughness (ductility) of PLA can be improved relatively easily, for example, by plasticization as introduced in the above section. But significant improvement in impact toughness is much more challenging. Similar to toughening other brittle polymers, physical blending with flexible or elastic polymers is also the most efficient strategy to improve impact toughness of PLA. However, it is worth noting that the most flexible or elastic polymers are immiscible with PLA.¹⁹ Thus, high toughened blends are usually unavailable by simple blending, due to the poor interfacial adhesion and coarse phase morphology which resulted from the inherent immiscibility of their blends.³⁷ Compatibilization is usually required for immiscible PLA blends to improve interfacial adhesion as well as to refine phase morphology and thus to enhance the mechanical properties. Therefore, improvement in compatibility between rubbery polymers and PLA during processing is a key issue for the production of high toughened PLA blends. Various compatibilization strategies have been reported in PLA-based blends, which have been reviewed in our previous paper.¹⁹ However, the principles in relationship between compatibility, phase morphology, and mechanical

properties have not been explained. It is therefore necessary to describe those fundamental principles in detail for better understanding the key factors in toughening PLA.

3. Compatibilization, phase morphology, and toughness

3.1 Compatibilization

Immiscible polymer blends generally show phase-separated morphology with low interfacial adhesion and coarse phase morphology, where the minor phase usually dispersed as large sized particles in the major polymer matrix.^{37,120} The effect of interfacial adhesion on the toughening efficiency and mechanisms have been discussed in the above section. As a matter of fact, the interfacial adhesion would not only affect the toughening mechanism and toughening efficiency but also influence various phase morphological parameters such as phase structure, particle shape, particle size and size distribution, as well as inter-particle distance. Those morphological parameters could in turn affect the toughening mechanism and final mechanical properties of the immiscible blends. Although the interfacial adhesion of immiscible blends is usually weak, it can be controlled by suitable compatibilization, which then enables the regulation of both phase morphology and final properties of the blends.¹²⁰

Although various strategies have been used to improve compatibility of immiscible PLA blends,¹⁹ there are many common characteristics among those strategies from the viewpoint of fundamental principles. Either pre-made or *in situ* generated blocky structured compatibilizers, with one block miscible with one blend component and a second block miscible with the other, are usually used to improve compatibility of immiscible blends.¹²⁰ The first role of the compatibilizer is to reduce the interfacial tension and thus the particle size of dispersed phase during melt processing. Usually, the average size of the dispersed phase can be reduced to sub-micrometer range under suitable compatibilization. The second role is to cause emulsification to prevent coalescence during processing or storage to stabilize phase morphology, and final properties of the resultant blends. The third role is to enhance interfacial adhesion through entanglement of each block with the corresponding miscible component. Suitable interfacial adhesion is necessary for stress transfer from one phase to the other, which is helpful in preventing catastrophic failure of the multiple crazing initiated at the interface.¹²⁰ Refined and stabilized phase morphology plus improved interfacial adhesion usually transform useless immiscible blends to useful high performance materials, which combines the advantages of individual components.

3.2 Influence of phase morphology on toughening efficiency

Except for interfacial adhesion, various phase morphological parameters of immiscible blends could be tuned by specific compatibilization strategy, which makes the final properties controllable. Among those phase morphological parameters, the effect of particle size of dispersed phase on the toughening efficiency of rubbery polymer toughened PLA blends were most widely investigated, since the particle size is the other important factor that determines the impact toughness of PLA blends besides interfacial adhesion.^{8,37,46,121} In fact, both interfacial adhesion and dispersed particle size relate to the compatibility of the blends. Generally, poor compatibility causes poor interfacial adhesion and large dispersed particle size, hence low impact toughness, while improved compatibility leads to increased interfacial

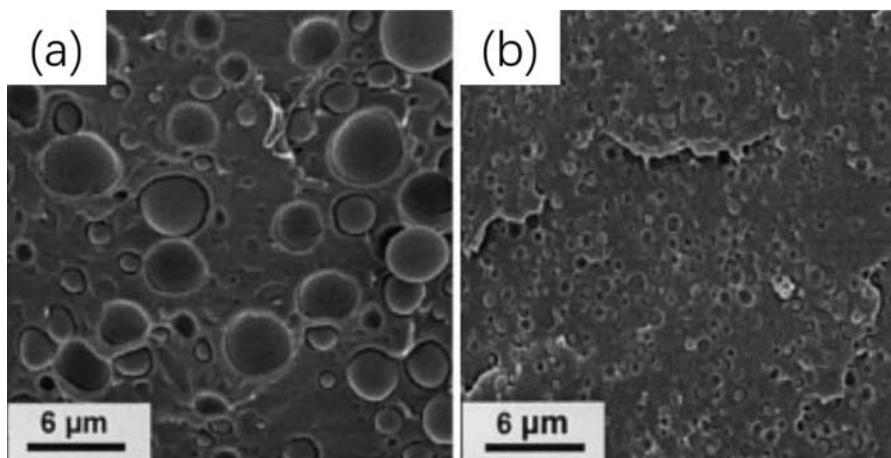


Figure 2. SEM images of cryofractured surfaces of PLA/LLDPE (80/20) (a) and PLA/LLDPE compatibilized with 5 wt% PLLA-PE (b).³⁷ © John Wiley and Sons. Reproduced by permission of John Wiley and Sons. Permission to reuse must be obtained from the rightsholder.

adhesion and reduced particle size and hence high impact toughness. For example, the average particle size of linear low-density polyethylene (LLDPE) in PLLA blends decreased from $6.4 \mu\text{m}$ of virgin PLA/LLDPE blends to $0.9 \mu\text{m}$ by addition of 5 wt% PLLA-PE block copolymer as compatibilizer, as shown in Fig. 2, and consequently the notched Izod impact strength increased from 34 J/m to 460 J/m , as reported by Anderson and coworkers.³⁷

However, it is not the case that the lower particle size always results in higher toughness. In fact, there is an optimum particle size in various rubber toughened brittle polymer systems, due to the fact that too small particles are inefficient in both initiating cavitation and terminating growth of crazes,^{47,82} while too large particles would induce premature crack propagation due to the coalescence of crazes.⁸² After correlating toughening efficiency with particle size and matrix chain parameters, Wu concluded that optimum particle size decreases obviously with increasing ν_e for rubber toughened brittle polymers ($\nu_e < 0.15 \text{ mmol/cm}^3$ and $C_\infty > 7.5$).¹⁰³ Therefore, the optimum particle size varies for different brittle polymers due to the different matrix chain parameters. In the case of amorphous brittle PLA matrix ($\nu_e = 0.1 \text{ mmol/cm}^3$), the optimum particle size as estimated by Bai et al.⁸² is ca. $0.75 \mu\text{m}$, which is in agreement with the experimental results in various studies, where the optimum particle size for high toughening efficiency is $0.7\text{--}1.1 \mu\text{m}$.^{47,74,82,121} It is worth noting that the optimum particle size for highly crystalline PLA matrix is much smaller, being $0.3\text{--}0.5 \mu\text{m}$.⁸² The difference in optimum particle size between amorphous and highly crystalline PLA matrix is attributed to the different dominating toughening mechanism. Generally, large particles are efficient in initiating multiple crazing which dominates in amorphous PLA matrix, while relatively small particles are effective in triggering the matrix shear yielding which dominates in highly crystalline PLA matrix.⁸²

Besides particle size, inter-particle distance is also an important factor in controlling the brittle/tough behavior of rubbery polymer toughened brittle polymer. It is widely accepted that there is a critical value (K_c) for the inter-particle distance of polymer blends. The blends are brittle if the inter-particle distance is above K_c , while they change to be tough if the inter-particle distance is below the K_c . The critical value is affected by many intrinsic

properties, such as modulus of the rubbery polymer, modulus ratio between matrix, and rubber dispersed phase. The critical inter-particle distance for toughening PLA is approximately $1.0\ \mu\text{m}$ as reported by Anderson et al.³⁷ A highly toughened PLA blend could be obtained if the inter-particle distance was less than $1.0\ \mu\text{m}$.⁸

Phase structure is believed to be another important factor in preparing highly toughened PLA blends. Although sea-island morphology with rubber particles dispersed in plastic matrix is the normally observed phase structure, the formation of a co-continuous phase structure is regarded as a very efficient way to reach remarkable improvement in impact toughness.^{51,96,122} The co-continuous phase structure in toughened PLA blends was occasionally observed for some specific blend systems.^{51,96,122} Dynamic vulcanization of PLA with natural rubber (NR) leads to a co-continuous phase structure when the content of NR was in the range 30~40 wt%. The obtained PLA/NR (65/35) showed the highest impact strength, almost eight times higher than that of PLA/NR (80/20) with sea-island phase structure.^{96,122} Besides the co-continuous phase structure, the formation of some other special phase structures such as quasi co-continuous structure and network-like structure is also believed to be helpful in enhancing impact toughness of rubbery polymer toughened PLA blends.^{10,73}

4. Toughening PLA with renewable materials

Various renewable substances including plant oils and their derivatives, natural rubber and its modified products, renewable aliphatic polyesters, microbial polyesters, bioelastomers, and aliphatic-aromatic copolyesters have been widely used for blending with PLA with the aim of toughening without reducing sustainability. Because most of the renewable substances are immiscible with PLA, direct blending usually leads to low performance PLA blends with poor interfacial adhesion and coarse phase morphology. Both are crucial factors for determining final mechanical properties of immiscible PLA blends. Therefore, the key issue in toughening PLA with renewable substances is to control interfacial adhesion and phase morphology. The strategies for improving compatibility and controlling phase morphology are various for different blending systems.

In the following section, while describing toughening PLA with renewable substances, we will briefly introduce some typical compatibilization strategies. It is worth noting that the use of some petroleum-based biodegradable polymer such as polycaprolactone to toughen PLA is out of the scope of this paper due to non-renewability. But, partially renewable polymers which may contain some non-renewable species are in the scope. In addition, some toughened PLA blends which contained renewable blending components and non-renewable compatibilizers are also included.

4.1 Biomass derived polyesters toughened PLA

Many dicarboxylic acids such as succinic acid, adipic acid and sebacic acid are obtainable from biomass related routes.¹²⁴ Those dicarboxylic acids can react with various diols to form renewable, biodegradable, flexible/elastic aliphatic polyesters. Various properties, such as mechanical modulus and elasticity, glass transition temperature, degree of crystallinity, melting temperature, and biodegradability of the biomass derived polyesters can be tailored through the selection of suitable monomers and regulation of their ratios.^{124–126} In addition, the abundance of ester groups makes them partially compatible with PLA, and direct melt

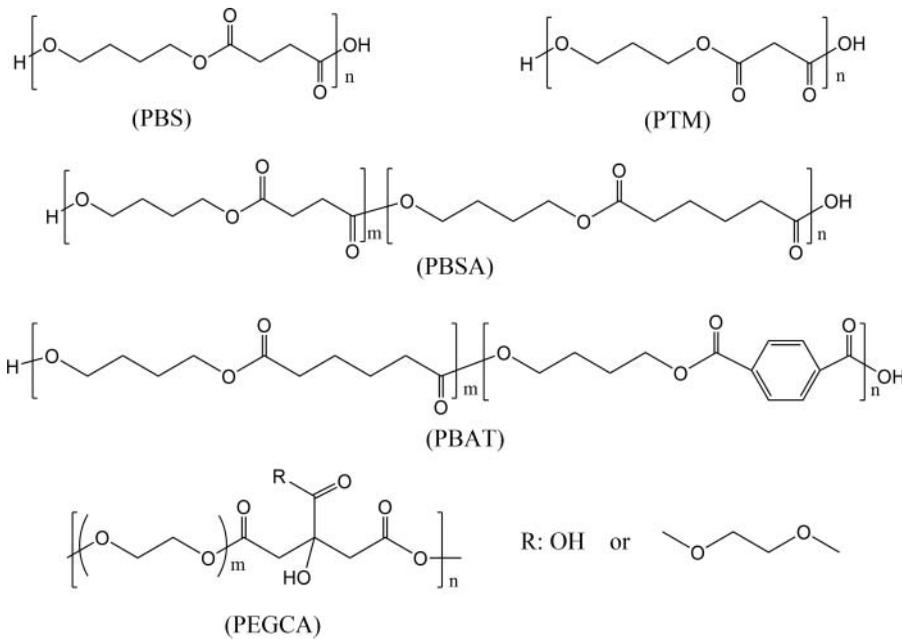


Figure 3. Chemical structures of biomass derived polyesters used in toughening PLA.

blending without compatibilization usually causes some degree of toughening, especially for improving tensile toughness.⁴² Those advantages make biomass derived polyesters the ideal toughening components for PLA, with neither reducing sustainability nor deteriorating biodegradability. Figure 3 shows the chemical structures of the biomass derived polyesters which were used to toughen PLA.

Poly(butylene succinate). The most well-known dicarboxylic acid derived polymer is poly(butylene succinate) (PBS) which shows excellent mechanical properties, processibility, and biodegradability.⁶ The commercially available PBS is produced by condensation polymerization of succinic acid and 1,4-butanediol. Succinic acid was previously produced through the petroleum route but now can be produced from a bioconversion route.¹²⁷ The biobased origin of succinic acid is believed to further stimulate the development of the PBS industry.^{5,128–130} PBS is a semicrystalline polyester with glass transition temperature of $\sim 37^\circ\text{C}$ and melting point of $\sim 114^\circ\text{C}$.⁶ Compared to brittle PLA, PBS exhibits much higher flexibility with elongation at break of more than 300%, thus it can be used to toughen PLA.

Wang et al.⁴² toughened PLA by melt blending with PBS. PLA/PBS blends showed phase-separated morphology with large PBS particle badly embedded in PLA matrix if not compatibilized. Although the elongation at break of PLA significantly increased from 4% to 250% via direct melt blending with 20 wt% PBS, the impact strength increased very slightly from 2.5 to 3.7 kJ/m² due to poor interfacial adhesion as evidenced by a large number of oval cavities left after the cryogenical fracture. After being compatibilized by 0.1 wt% dicumyl peroxide (DCP), the elongation at break almost remained unchanged, whereas the impact strength increased significantly to 30 kJ/m², due to enhanced interfacial adhesion and reduced PBS particle size (0.2–1.0 μm) as well as the narrowed particle size distribution, resulted from the free radical induced *in situ* interfacial compatibilization. Interfacial debonding induced matrix shear yielding was the toughening mechanism.

Except for *in situ* interfacial compatibilization, many other strategies have been used to improve compatibility of PLA/PBS blends. Our group compatibilized PLA/PBS blends by modifying PBS with 5 wt% PLA segments, which was incorporated through chain-extension reaction.^{28,44} Addition of 20 wt% modified PBS increased the elongation at break and impact strength of PLA from 7.2% and 1.86 kJ/m² to 320% and 2.81 kJ/m², respectively.

Persenaire et al.¹⁰¹ toughened PLA with PBS of different melt viscosities, and found that PBS with lower viscosity showed higher toughening efficiency. The PLA/PBS (80/20) blends with low PBS viscosity (melt flow rate of 18.5 g (10 min)⁻¹) showed a higher elongation at break with the value of 242%, compared to 190% of the blends with high PBS viscosity (melt flow rate of 4.5 g (10 min)⁻¹). The lower viscosity PBS showed higher mobility and lower entanglement during melt processing, thus dispersing with smaller size and narrower size distribution in PLA matrix, which accounts for the higher tensile strain. The elongation at break of the former blends could further increase to more than 350% when 2'-(1,3-phenylene)-bis-2-oxazoline (PBO), 1'-carbonylbiscaprolactam (CBC) or maleic anhydride-grafted PLA (PLLA-g-MA) was used as a compatibilizer.

Due to the reduction in tensile strength of PLA during toughening with PBS, Zhang et al.⁵⁶ have recently reinforced the DCP compatibilized PLA/PBS blends with poly(butylene succinate) (PBS)-grafted cellulose nanocrystal (PBS-g-CNC). They found that phase-separated morphologies formed for all blends or composites with PBS particles dispersed in PLA matrix, as shown in Fig. 4. The pristine PLA/PBS showed the largest PBS particle size. Both DCP and PBS-g-CNC were able to compatibilize PLA/PBS blends, thereby reducing particle size of PBS domains, and synergy effect between DCP and PBS-g-CNC occurred as evidenced by the further reduced PBS particle size with addition of both the components. In addition, the particle size distribution narrowed significantly in the DCP compatibilized

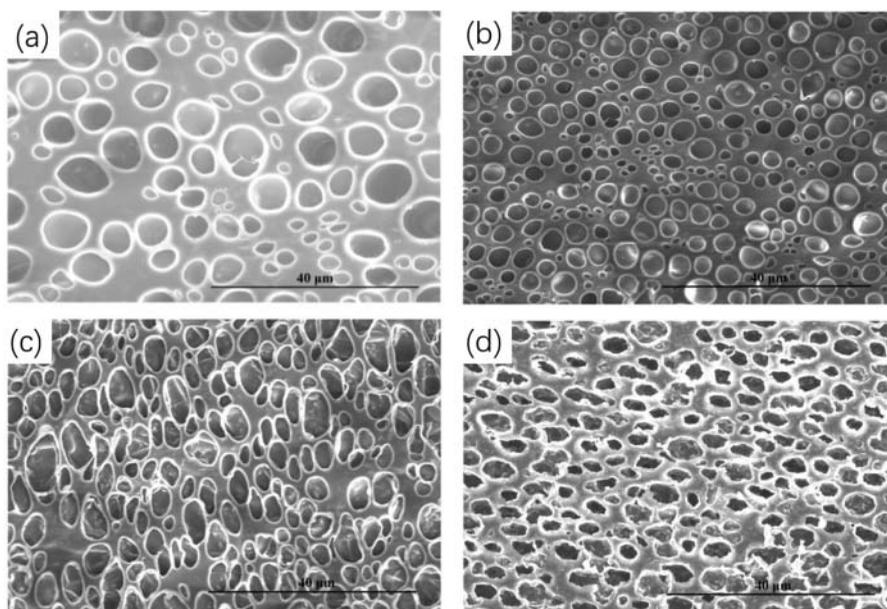


Figure 4. SEM images of etched cryogenically fractured surface of composites with PBS/PLA/DCP/(PBS-g-CNC) ratio of (a) (30/70/0/0), (b) (30/70/0.2/0), (c) (30/70/0/2) and (d) (30/70/0.2/2).⁵⁶ © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholder.

PLA/PBS/PBS-g-CNC ternary composites. Although all blends showed comparable elongation at break of 260~300%, the notched impact strength of DCP compatibilized PLA/PBS (70/30) increased from 105 J/m to 726 J/m by addition of 2% PBS-g-CNC; meanwhile, the stress at break increased from 30.9 MPa to 43.3 MPa, due to the improved crystallization by the presence of PBS-g-CNC. The impact strength and stress at break of pristine PLA/PBS binary blends were 52 J/m and 32.7 MPa, respectively.

Poly(butylene succinate-co-adipate) (PBSA) copolymer. PBSA is flexible biobased and biodegradable copolyester synthesized by condensation polymerization of 1,4-butanediol with succinic and adipic acids, and has an elongation at break of over 300%.¹³¹ The excellent flexibility also makes it a suitable potential toughening agent for PLA. However, simple blending could not lead to high toughened PLA/PBSA blends due to the immiscibility.¹³² Ojijo and Ray¹³³ compatibilized PLA/PBSA blends by addition of triphenyl phosphite (TPP), which induced chain extension and/or chain interchange reaction between both components and thus reduced the dispersed phase size and formed fibrillated links between the PLA and PBSA phases. As a result, the addition of 2 wt% TPP increased the elongation at break and impact strength of PLA/PBSA (70/30) blends from 6% and 6 kJ/m² to 20% and 11 kJ/m², respectively. Interfacial debonding induced matrix shear yielding was reported for the toughening mechanism of the compatibilized PLA/PBSA blends.

The same group recently compatibilized PLA/PBSA blends by addition of a multi-functional oligomeric chain extender (Joncryl[®] ADR 4368 CS), a copolymer containing pendent epoxy groups, which allows the formation of non-linear copolymer architecture at the interface through reaction between epoxy groups and terminal carboxyl groups of both components to improve the compatibility. The elongation at break and impact strength of PLA increased from 6% and 4.6 kJ/m² to 179% and 38.4 kJ/m² by blending with 40 wt% PBSA in the presence of 0.6 wt% Joncryl[®] ADR 4368 CS.¹⁰²

Poly(butylene adipate-co-terephthalate) (PBAT). PBAT is a flexible and fully biodegradable aliphatic-aromatic copolyester with strain at break of ~710%.⁸³ Although it includes a petroleum-based unit, it also contains a lot of biobased components. It is worth noting that a biomass derived route was also occasionally reported for terephthalic acid¹³⁴ which may be commercially available from renewable resources in the near future. Therefore, the aliphatic-aromatic copolyesters will be fully sustainable. The flexible nature makes it a possible toughening agent for PLA. Jiang et al.⁸³ melt blended PLA with PBAT through a twin screw extruder. The elongation at break of PLA increased to more than 200% from 3.7% of PLA by addition of only 5 wt% PBAT, indicating an excellent toughening efficiency on the tensile toughness. The impact strength increased from 2.6 kJ/m² of neat PLA up to 4.4 kJ/m² for the blends containing 20 wt% PBAT.

Several attempts have been made to improve the compatibility between PLA and PBAT so as to enhance mechanical properties. Zhang et al.⁸⁴ added glycidyl methacrylate (GMA) as a reactive processing agent for PLA/PBAT blends during melt blending. The epoxy group of GMA reacted with the terminal carboxyl group of both PLA and PBAT to form a block copolymer at the interface to improve their compatibility. Both the elongation at break and impact strength increased significantly for the blends with suitable content of GMA, depending on the blend compositions. Kumar et al.¹³⁵ also compatibilized PLA/PBAT blends with GMA. The results indicated that a PLA/PBAT (75/25) blend compatibilized by 5 wt% GMA showed impact strength of 76.56 J/m, compared to 50.44 and 21.09 J/m of pristine blends and original PLA, respectively; however, the improvement in elongation at break was very limited.

Ma et al.⁸⁵ prepared *in situ* compatibilized PLA/PBAT blends by addition of DCP as a free-radical initiator, which induced branching and crosslink reactions between PLA and PBAT to improve their compatibility, which was confirmed by the reduced PBAT domain size and the enhanced interfacial adhesion. The content of DCP played an important role in phase morphology, deformation mechanism, and mechanical properties due to the different level of compatibilization. Phase-separated morphology formed with PBAT dispersed in PLA matrix. With increase in DCP content, the particle size decreased as shown in Figs. 5a–5c, while matrix shear yielding increased during fracture, leading to high energy dissipation and thus high toughness. Consequently, the elongation at break of PLA/PBAT (80/20) blend increased from ~200% to 300% with addition of 0.1~0.2 wt% DCP, while the maximum impact

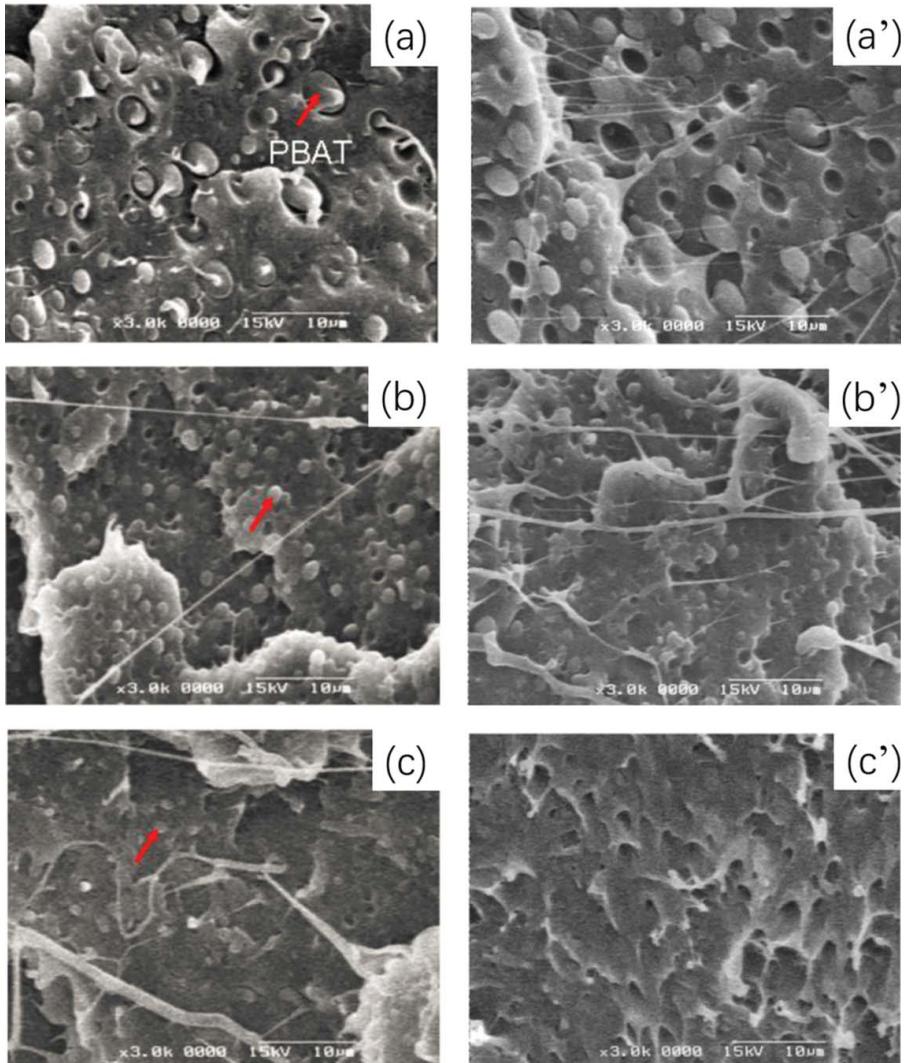


Figure 5. SEM images of cryo-fracture surfaces (a ~ c) and the notched Izod impact fracture surfaces (a' ~ c') of the PLA/PBAT (80/20) blends with DCP content: (a) (a') 0 wt%, (b) (b') 0.1 wt% and (c) (c') 0.5 wt%.⁸⁵ © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholder.

strength increased to 110 J/m with addition of 0.5 wt% DCP, compared to ~ 60 J/m of incompatible blend with the same composition. The chain branching and crosslinking of PLA/PBAT blends in the presence of DCP have also been observed by Signori et al. in a recent study.¹³⁶

Poly(trimethylene malonate). Eyiler et al.¹³⁷ toughened PLA films with a biobased polymer poly(trimethylene malonate) (PTM). PTM is miscible with PLA and can be synthesized from 1,3-propane diol and malonic acid via melt polycondensation. It is interesting to find that addition of PTM not only improves toughness but also enhances mechanical strength and modulus. For example, the respective tensile strength, Young's modulus, and toughness of PLA film were 21.2 MPa, 1.69 GPa, and 5.39 MPa, respectively, while addition of 10 wt% PTM increased those parameters to 105.6 MPa, 4.61 GPa, and 143.5 MPa, respectively.

Poly(polyethylene glycol-co-citric acid). Gui et al.¹³⁸ synthesized a biobased and biodegradable copolymer poly(polyethylene glycol-co-citric acid) (PEGCA) by condensation polymerization of polyethylene glycol and citric acid, and used the copolymer as a toughening modifier for PLA. PLA and the copolymer were partially miscible, as evidenced by the shift of T_g of both components. Maximum elongation at break and impact strength took place for the blends containing 15 wt% PEGCA, with the values of 242% and 103 J/m, respectively.

4.2 Bioelastomers toughened PLA

Polyester-based bioelastomers. Kang et al.⁹⁸ synthesized an unsaturated aliphatic polyester bioelastomer by condensation polymerization of itaconic acid, succinic acid, 1, 3-propanediol, and 1, 4-butanediol, and directly melt-blended the bioelastomer with PLA for toughening. The PLA blend containing 11.5 vol% elastomer showed the highest elongation at break of 179%, nearly 25-fold enhancement over neat PLA, and the highest notched

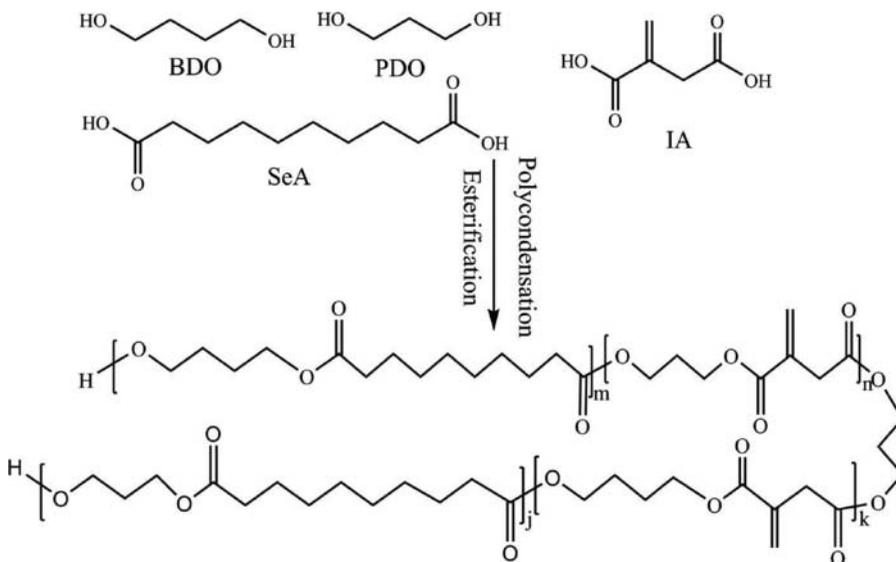


Figure 6. Synthesis of unsaturated aliphatic polyester elastomer from biobased monomers.⁷³ © The American Chemical Society. Reproduced by permission of The American Chemical Society. Permission to reuse must be obtained from the rightsholder.

impact strength occurred for the blend containing 22.6 vol% elastomer with the value of 13.4 kJ/m^2 compared to 2.4 kJ/m^2 of neat PLA.

Our group has recently synthesized a similar unsaturated aliphatic copolyester bioelastomer via condensation polymerization of itaconic acid, sebacic acid, 1,3-propanediol, and 1,4-butanediol, as shown in Fig. 6, and blended the elastomer with PLA for toughening. The elongation at break of PLA containing 20 wt% bioelastomer increased from 7.8% of PLA to 302.3% and the impact strength increased from 16.8 J/m to 225.1 J/m . The impact strength further increased drastically when peroxide induced dynamic vulcanization and interfacial compatibilization were performed for the blends. The phase morphology was changed from discrete round-like elastomer droplets dispersed in PLA matrix for pristine blend to a quasi-co-continuous morphology for the compatibilized blends, as shown in Fig. 7. Super-toughened PLA blends with impact strength higher than 530 J/m were obtained by compatibilizing the blends with 0.05~0.2 wt% DCP, due to the formation of specific morphology and improved interfacial interaction. Internal cavitation induced matrix shear yielding, which is

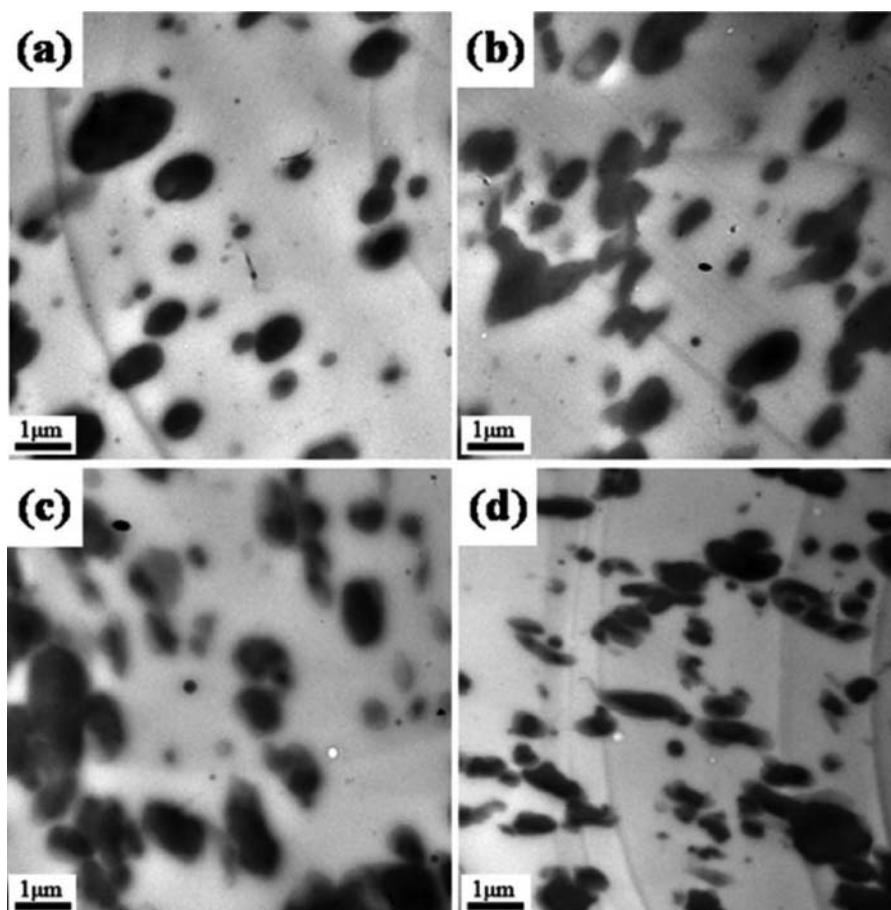


Figure 7. TEM micrographs of pristine PLA/UPE (80/20) blend (a), and PLA/UPE (80/20) blends compatibilized by different amount of DCP: (b) 0.03 wt%, (c) 0.05 wt% and (d) 0.1 wt%.⁷³ © The American Chemical Society. Reproduced by permission of The American Chemical Society. Permission to reuse must be obtained from the rightsholder.

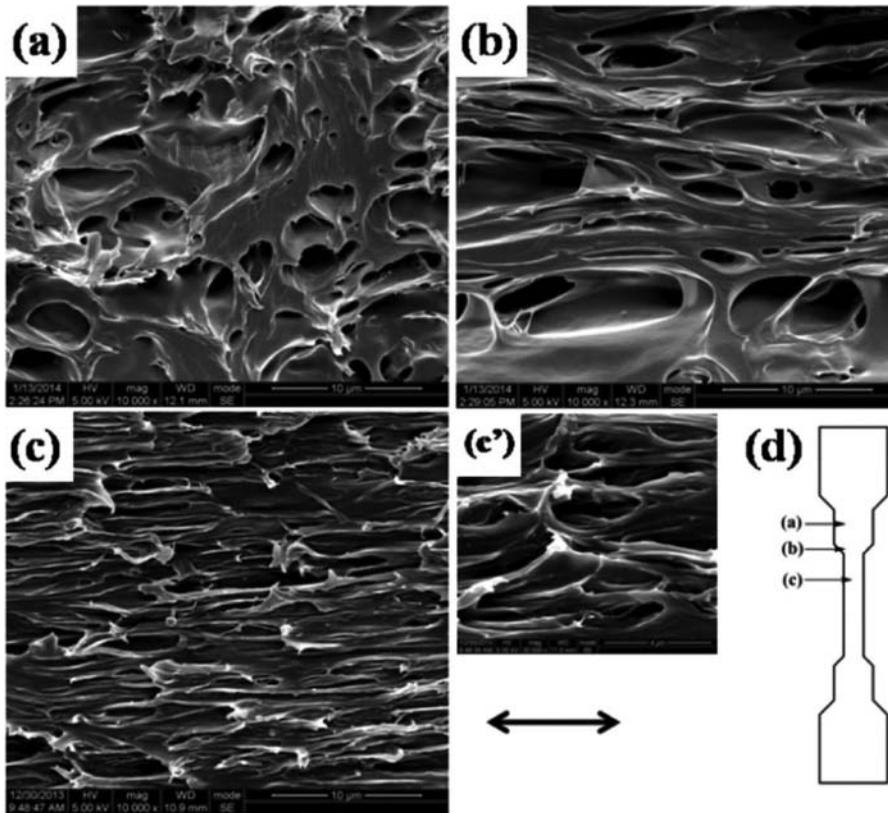


Figure 8. SEM images of stretched PLA blends compatibilized by 0.1 wt% DCP at different tensile stages as schematically indicated in (d) with the double-arrow line indicating the tensile direction.⁷³ © The American Chemical Society. Reproduced by permission of The American Chemical Society. Permission to reuse must be obtained from the rightsholder.

the most efficient way of energy dissipation, was observed for the toughening mechanism of the blends, as shown in Fig. 8.⁷³

Hu et al.¹³⁹ synthesized a renewable PLBSI bioelastomer by condensation polymerization of lactic acid, sebacic acid, itaconic acid and 1,4-butanediol (BDO) (Fig. 9), and melt blended the elastomer with PLA for toughening. The presence of LA units in PLBSI makes it compatible with PLA, and it disperses uniformly in PLA matrix with average particle diameter of $0.69 \mu\text{m}$. Consequently, both tensile toughness and impact toughness of PLA were highly improved by addition of 15 wt% PLBSI bioelastomer with respective elongation at break and impact strength of more than 300% and 35.3 kJ/m^2 , which was 30 times and 15 times higher, respectively than the corresponding value of neat PLA.

Polyamide-based bioelastomer. Poly[(ethylene oxide)-block-(amide-12)] (PEBA) is an elastic copolymer that derived from renewable resources, has high impact resistance, and hence can be used to toughen brittle polymers.¹⁴⁰ Zhang et al. toughened PLA by melt blending with PEBA, and found that addition of 30 wt% PEBA increased the elongation at break of PLA from 5.1% to 367.2%.¹⁴¹ Han et al.^{142,143} have recently toughened PLA with PEBA through melt mixing, and found that the elongation at break of PLA/PEBA blends increased to more than 300% and the impact strength increased up to 60.5 kJ/m^2 with the

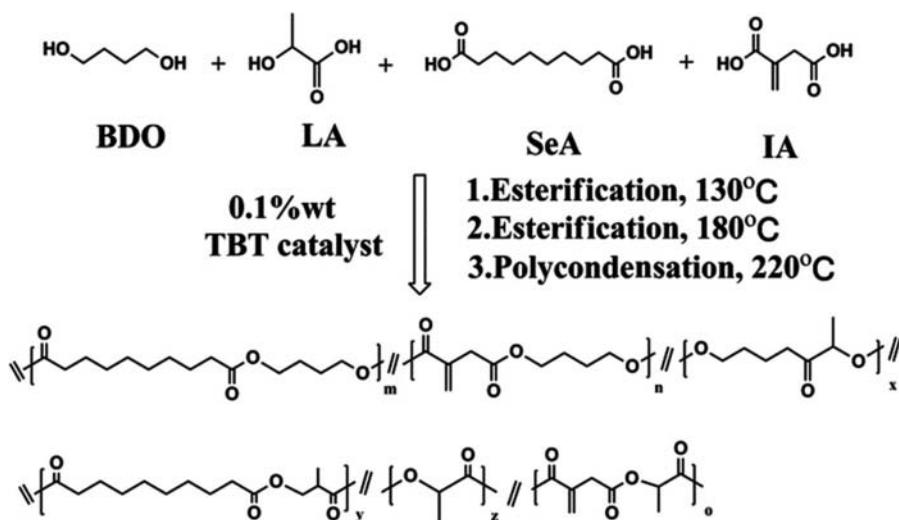


Figure 9. Polymerization reactions of PLBSI biobased copolyesters.¹³⁹ © The Royal Society of Chemistry. Reproduced by permission of The Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.

addition of 30 wt% PEBA. Those parameters of neat PLA were only 6.7% and 4.5 kJ/m², respectively.

4.3 Microbial polyesters toughened PLA

Microbial polyesters, also known as polyhydroxyalkanoates (PHAs), are a class of renewable and biodegradable polymers naturally produced by bacteria in general cultivated on agricultural raw materials.¹⁴⁴ Figure 10a shows the general chemical structure of PHA. The mechanical properties of PHAs vary from stiff thermoplastics to elastomers depending on the side alkyl chain length, and according to the side alkyl chain length, PHAs can be roughly divided into three categories, that is, short chain-length, medium chain-length, and long chain-length PHAs.¹⁴⁵

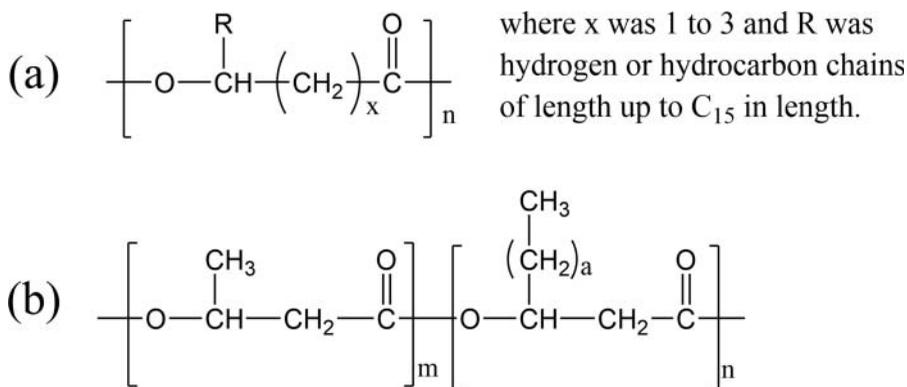


Figure 10. General chemical structures of PHAs (a) and PHA copolymers (b).

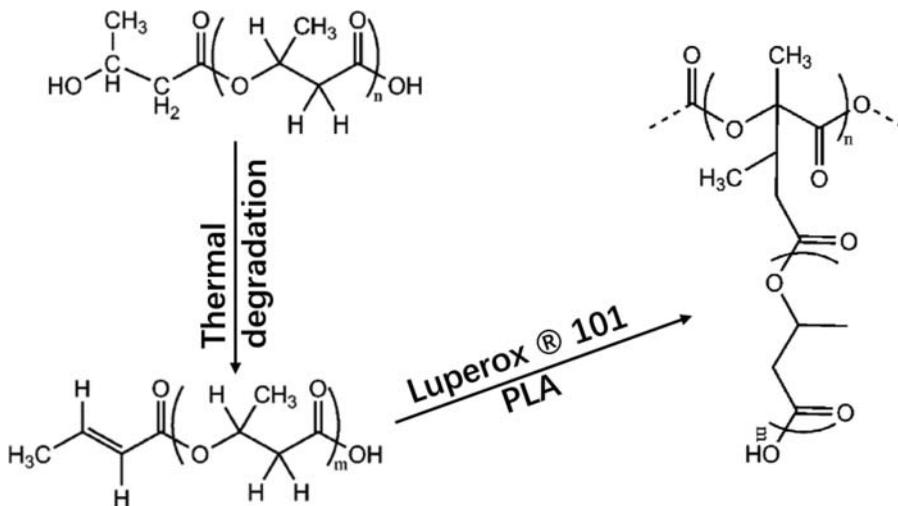


Figure 11. Thermal degradation of PHB to oligomers with crotonate end groups and subsequent grafting of the oligomers to the main chain of PLA.⁵² © The American Chemical Society. Reproduced by permission of The American Chemical Society. Permission to reuse must be obtained from the rights holder.

PHA homopolymers. The simplest PHA is poly([(R)-3-hydroxybutyrate] (PHB). Blending PHB with PLA is usually unable to obtain highly toughened blends regardless of being compatibilized or not, due to the inherent brittleness of both the polymers.¹⁴⁶ Yang et al.⁵² recently proposed a way of toughening PLA with PHB via a two-step extrusion process: thermally degrading PHB in an extruder to PHB oligomers (dPHB) with functional crotonate end groups and subsequent reactive extrusion to covalently anchor dPHB onto the main chain of PLA in the presence of a free radical initiator, as shown in Fig. 11. The results showed that PLA with 20% (w/w) grafted dPHB demonstrated an impressive elongation at a break of 538%, 66 times higher than that of pure PLA.

Poly(3-hydroxyoctanoate) (PHO) is a low- T_g medium chain-length PHA that can be used to toughen PLA, as reported by Takagi et al.¹⁴⁵ Addition of 30 wt% PHO increased Charpy impact energy from 0.052 J to 0.161 J. The Charpy impact energy can further increase to 0.26 J if the compatibility between PLA and PHO was improved by chemical modification of PHO via incorporation of epoxy groups.

Bartczak et al.¹⁴⁷ used atactic poly(R,S-3-hydroxybutyrate) (a-PHB), an amorphous synthetic analog of bacterial PHB with a low glass transition and elastomeric behavior as a bio-based toughening modifier for PLA, and found that the addition of 20 wt% a-PHB via solution mixing increased the elongation at break of PLA from 7% to 27%.

PHA copolymers. Copolymers of PHAs exhibit various physical properties depending on the structures and compositions, and the general chemical structure of PHA copolymers is shown in Fig. 10b. Nodax is a copolymer of 3-hydroxybutyrate (3-HB) with a small amount of medium chain-length 3-hydroxyalkanoate.¹⁴⁸ The presence of medium chain-length monomeric units decreases the melting point and crystallinity and hence improves the thermal processability and ductility as well as toughness of the microbial polyesters. The Nodax can be used as a biobased and biodegradable toughening agent for brittle PLA, as reported by Noda et al.³⁸ PLA blended with 10wt% NodaxH6, that is, poly(3-hydroxybutyrate-co-5mol% 3-hydroxyhexanoate) (P(3HB-co-5mol% 3HH)), showed an elongation at break of

more than 100%. The tensile energy was 10 times higher than that of neat PLA. Schreck and Hillmyer⁹⁵ melt blended PLA with a NodaxH6 containing 7 mol % 3HH, and found that addition of 15 wt% NodaxH6 resulted in a 2-fold enhancement in notched Izod impact strength with the value of 44 J/m compared to 22 J/m of neat PLA.

Poly(β -hydroxybutyrate-co- β -hydroxyvalerate) (PHBV) with 40% HV content is a soft copolymer with tensile strength and elongation at break of less than 10 MPa and \sim 15%, respectively. However, addition of 10~30 wt% PHBV interestingly changed the brittle PLA (elongation at break of \sim 4% and notched impact strength of 2.5 kJ/m²) to tough blends with elongation at break of 240~300% and impact strength increased up to 11 kJ/m², as reported by Ma et al.⁹⁴ The improved toughness for the blends was ascribed to the strain softening after yielding, which stabilized the neck growth to exhibit high flexibility. In spite of immiscibility between the two polymers, their blends showed a phase-separated morphology with rubbery PHBV dispersed finely in PLA matrix and the dispersed particle size increased with PHBV content in the blends. Fibrillation, interfacial debonding, internal cavitation, and matrix yielding are involved in the toughening mechanism of the PLA/PHBV blends.

Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P(3HB-co-4HB)) with a high molar fraction of 4HB behaves like an elastomer¹⁴⁹ and thus can be used to toughen PLA. Although PLA is immiscible with P(3HB-co-4HB), the elongation at break of PLA increased from 5% to 186% by direct blending with 30 wt% P(3HB-co-23.9 mol% 4HB) and further increased to 317% by incorporation of 0.1wt% DCP as an initiator, which induced branching/cross-linking of PLA with P(3HB-co-4HB) at the interface to improve interfacial adhesion, reduce dispersed particle size, and consequently enhance mechanical properties. As shown in Figs. 12a–12c, the blends showed phase-separated morphology. P(3HB-co-4HB) dispersed non-uniformly with large particles in the original blends, while dispersed uniformly with

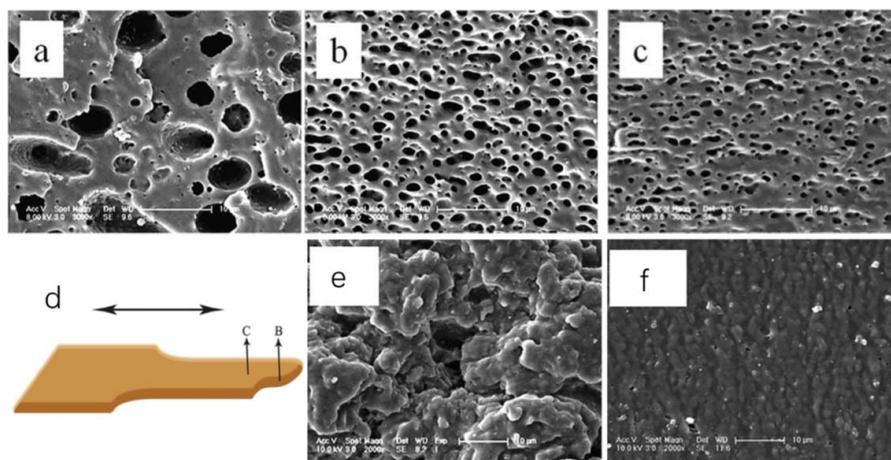


Figure 12. SEM micrographs of etched cryo-fractured surfaces of the PLA/P(3HB-co-4HB) (70/30) with different content of DCP: (a) 0, (b) 0.05 wt%, (c) 0.1 wt%, (d) A schematic diagram of the measurement locations (B) fractured surface and (C) surface parallel tensile direction near the broken points, and SEM images for the fractured surface (e) and surface parallel tensile direction near the broken points of the blends compatibilized by 0.1 wt% DCP.¹⁵⁰ © The Royal Society of Chemistry. Reproduced by permission of The Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.

smaller particle size in the compatibilized blends. Toughening mechanism of cavitation and matrix shear yielding were observed for the blends as shown in Figs. 12d–12e.¹⁵⁰

4.4 PLA-based copolymers toughened PLA

Copolymers consisting of PLA segment and other flexible components show enhanced compatibility compared to the flexible homopolymers, due to the identical structure of PLA segment and PLA matrix. The presence of flexible components provides the copolymers with toughness. Therefore, the improvement in toughness of PLA can be realized by direct melt blending with PLA-based copolymers without external compatibilization. Therefore, various PLA-based copolymers have been designed and synthesized to toughen PLA.^{151–156}

Odent et al.¹⁵¹ synthesized poly(ϵ -caprolactone-co-D,L-lactide) (P[CL-co-LA]) random copolymer to toughen PLA, and found that the blend showed a phase-separated morphology with nanosized rubbery-like microdomains regularly dispersed within the PLA matrix. The effect of LA molar content played an important role in compatibility and toughening efficiency. PLA blend with 10 wt% P[CL-co-LA] copolymer containing 28 mol% LA exhibited a 4-fold increase in impact strength compared to neat PLA (11.4 kJ/m² versus 2.7 kJ/m²).

Rathi et al.¹⁵² synthesized PDLA-PEG-PDLA triblock copolymer by ring-opening polymerization of D-lactide using PEG 1000 as an initiator and stannous octoate as a catalyst, and melt blended the copolymer with PLLA using a twin screw mini-extruder. The elongation at break of PLA increased from 20% to 72% with addition of 15 wt% PDLA-PEG-PDLA; meanwhile the modulus that was kept at a high level only decreased from 1.88 GPa to 1.75 GPa. The formation of stereocomplex between PDLA chains and PLLA matrix as well as specific phase structure with flexible PEG dispersed in crystalline regions may contribute to the improved mechanical properties. When the content of PDLA-PEG-PDLA increased to 35 wt%, the elongation at break was further increased to 424%.¹⁵³

Sun and He¹⁵⁴ prepared “Core-Shell” rubber nanoparticles (POSS-rubber-D) with polyhedral oligomeric silsesquioxane (POSS) grafted poly(ϵ -caprolactone-co-lactide) (PCLLA) as rubbery core and poly(D-lactide) (PDLA) as outer shell as shown in Fig. 13 and blended POSS-rubber-D with commercial PLA via solution blending. The elongation at break of PLA increased first and then decreased with increasing content of POSS-rubber-D. The blends containing 10 wt% POSS-rubber-D showed the largest elongation at break with the value of 131.6%, compared to 11.5% of neat PLA. Strong rubber/matrix interaction formed for the blends due to the formation of stereocomplex between PDLA block of POSS-rubber-D and PLA matrix. Multiple crazing was observed for the toughening mechanism during tension. What is more interesting is that not only toughness but also the mechanical strength and Young's modulus were improved due to the formation of stereocomplex.

Qi et al.¹⁵⁵ synthesized a multiblock copolymer consisting of Pluronic F68 and poly(D-lactide) (PDLA-Pluronic F68-PDLA) by ring-opening polymerization of D-lactide using Pluronic F68 as an initiator and stannous octoate as a catalyst. Pluronic F68 is a flexible copolymer composed of 80% PEO segment and 20% PPO segment. Both elongation at break and impact strength of the melt blended PLA blends increased with increasing content of PDLA-Pluronic F68-PDLA. Addition of 10 wt% copolymer increased the elongation at break of PLA from 5% to 95% and impact strength from 2.4 kJ/m² to 12.8 kJ/m², respectively.

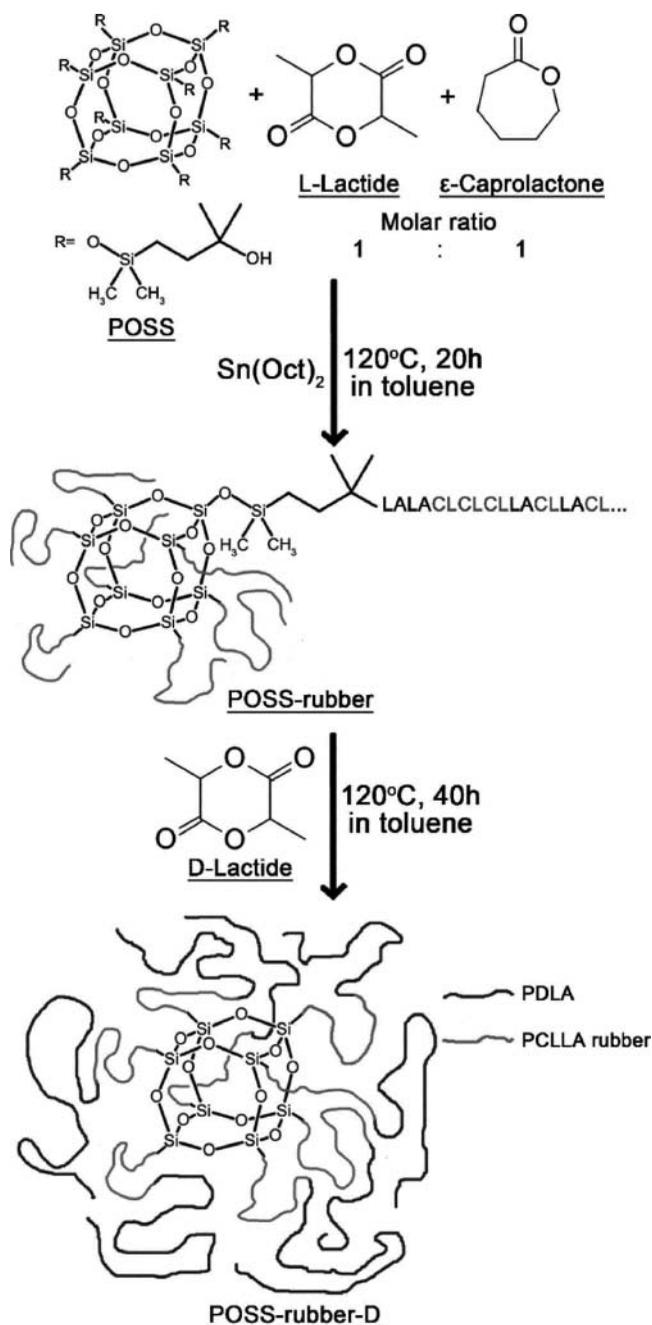


Figure 13. Synthesis of POSS-Rubber-D core-shell particles by ring-opening polymerization.¹⁵⁴ © The American Chemical Society. Reproduced by permission of The American Chemical Society. Permission to reuse must be obtained from the rights holder.

Feng et al.¹⁵⁶ have recently toughened PLA with a polyurethane (PELU) which contained PLA segments and was synthesized by chain extension reaction between PLA-PEG-PLA triblock copolymer with isophorone diisocyanate. It was found that PELU was partially miscible with PLA and the extent of miscibility increased with PLA segment content in PELU.

The blend was further compatibilized by an epoxy group containing polymeric modifier (ADR). As a result, all the elongation at break, tensile strength, and Young's modulus increased with increasing PLA segment content of PELU for the given blend composition. The elongation at break could increase to more than 300% with the addition of 15 wt% or higher PELU containing more than 30 wt% PLA segments.

The addition of PLA-based copolymers is very efficient in improving tensile toughness while it seems less efficient in enhancing impact toughness of PLA. The PLA-based copolymer usually showed very high compatibility with PLA, where the interfacial adhesion is too strong. The ductile copolymers act more like polymeric plasticizers for PLA to significantly improve the tensile toughness. Although the interfacial adhesion between highly compatible blends is too strong, it is not preferred for impact strength enhancement as it usually causes catastrophic crack propagation before occurrence of matrix yielding.

4.5 Natural rubber and its derivatives toughened PLA

Natural rubber (NR), a renewable polymer, is derived from the sap of some plants. The main constituent of NR is poly(cis-1,4-isoprene) (Fig. 14a), which exhibits a unique combination of low glass transition temperature, elasticity, toughness, renewability, biocompatibility, biodegradability, as well as low cost.^{157,158} Those advantages make it an ideal candidate to improve toughness of brittle PLA. Although PLA is immiscible with NR,¹⁵⁸ the presence of abundant reactive double bonds within NR enables compatibilization of PLA/NR blends via free radical induced interfacial reaction or some other treatments to improve polarity of NR.^{159,160} In addition, NR can be changed to epoxidized natural rubber (ENR, Fig. 14b) via oxidation of the double bonds under suitable oxidizing condition.⁵¹ PLA shows better compatibility with ENR than NR due to the improved polarity after incorporation of epoxy groups. Therefore, both NR and ENR have been used to toughen PLA in recent literatures.

Natural rubber. Bitinis et al.¹⁵⁸ found that PLA and NR were immiscible and their blends exhibited phase-separated morphology. The formed NR particles with a diameter of 1.1~2.0 μm dispersed in PLA matrix and the interfacial adhesion is low. PLA blends with 10 wt% NR prepared under optimal processing conditions showed a significant improvement in the elongation at break with the value of 200%, compared to 3.3% of neat PLA. The

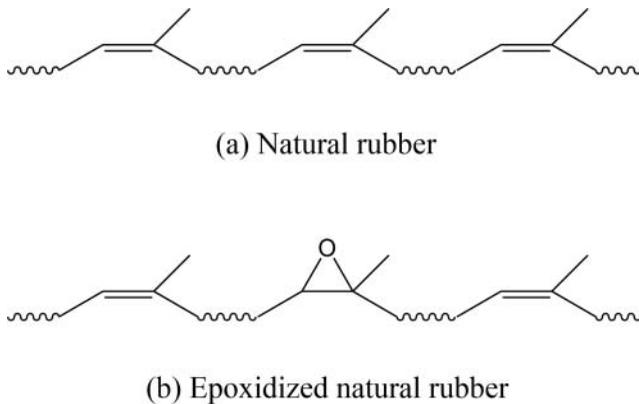


Figure 14. Chemical structure of natural rubber (a) and epoxidized natural rubber (b).

other work by Jaratrokajorn et al.¹⁶¹ indicated that melt blending PLA with 10 wt% NR only increased the elongation at break to 7.26% from 5.44%, and the notched Izod impact strength increased obviously from 2.85 to 6.36 kJ/m².

The compatibility between PLA and NR could be improved by addition of free radical initiators, which would cause interfacial reaction to form PLA-NR copolymer located at the interface of the phase-separated blends to refine the phase morphology and improve the interfacial adhesion. The study by Huang et al.¹⁵⁹ indicated that crosslinking between PLA and NR occurred at the interface by addition of a free radical initiator dicumyl peroxide (DCP). As a result, both elongation at break and impact strength were improved obviously. For example, the elongation at break of a PLA/NR (95/5) blend with 0.2 wt% DCP was enhanced by 2.5 times to 26.21% from 10.7% of neat PLA, and the Charpy impact strength was increased by 1.8 times to 7.36 kJ/m² with 2 wt% DCP, compared to 4.18 kJ/m² for neat PLA.

To improve compatibility between PLA and NR, Zhang et al.¹⁶² incorporated poly(butyl acrylate) (PBA) into NR by preparing NR-g-PBA copolymer to improve polarity of NR, hence the compatibility with PLA, which was proved by the disappearance of spherical-particle-dispersed phase for PLA/NR-g-PBA blends. Consequently, the elongation at break and impact strength of the PLA/NR-g-PBA blends were enhanced significantly compared to those of homologous PLA/NR blends. The same group has recently reported another way of enhancing polarity of NR by incorporation of carbonyl or epoxy groups via pre-hot shearing NR. Through this way, the elongation at break and tensile toughness of a PLA blend containing 10 wt% pre-hot sheared NR increased to 196.2% and 77.5 MJ/m³, respectively, compared to 13.6% and 8.8 MJ/m³ of pure PLA.¹⁶⁰

Chumeka et al.¹⁶³ synthesized PLA-NR-PLA triblock copolymer by condensation of hydroxyl telechelic natural rubber (HTNR) and PLA prepolymer in the presence of tin (II) ethylhexanoate as a catalyst, and used the triblock copolymer as a compatibilizer for PLA/NR blends. The addition of triblock copolymer apparently reduced the particle size of the dispersed NR phase. The impact strength and elongation at break of the PLA/NR (90/10) blends increased by more than 90% and 80%, respectively, with the addition of only 2.5 wt% copolymer.

A combination of dynamic vulcanization and interfacial compatibilization provides a powerful way of enhancing compatibility, interfacial adhesion, and toughening efficiency of rubbery polymer toughened PLA blends.^{8,46,47,53,73,122} Dynamic vulcanization and interfacial compatibilization involve a process where the rubber molecules are selectively crosslinked during melt blending with thermoplastics. Meanwhile the compatibilization reaction occurs at the interface of the immiscible blends to improve compatibility.⁴⁶ Plenty of double bonds with NR make it very suitable for dynamic vulcanization through traditional free radical initiation. Chen et al.^{53,96,122} selectively vulcanized NR phase during blending with PLA via free radical initiation procedure, where interfacial reaction between PLA and NR occurred. Consequently, the compatibility of the PLA/NR blends was improved significantly. Furthermore, a unique co-continuous “net-like” phase morphology (Figs. 15a–15b) was obtained when the content of NR was \geq 30 wt%. As a result, dynamic vulcanization of PLA with 35 wt% resulted in a super-toughened and fully biobased PLA blend with notched impact strength increased to 58.3 kJ/m² from 2.75 kJ/m² of neat PLA. As the vulcanized NR phase was also a continuous phase, it underwent considerable deformation during loading of the outside force and thus absorbed a large amount of energy (Figs. 15c–15d) exhibiting super toughness.^{53,96,122}

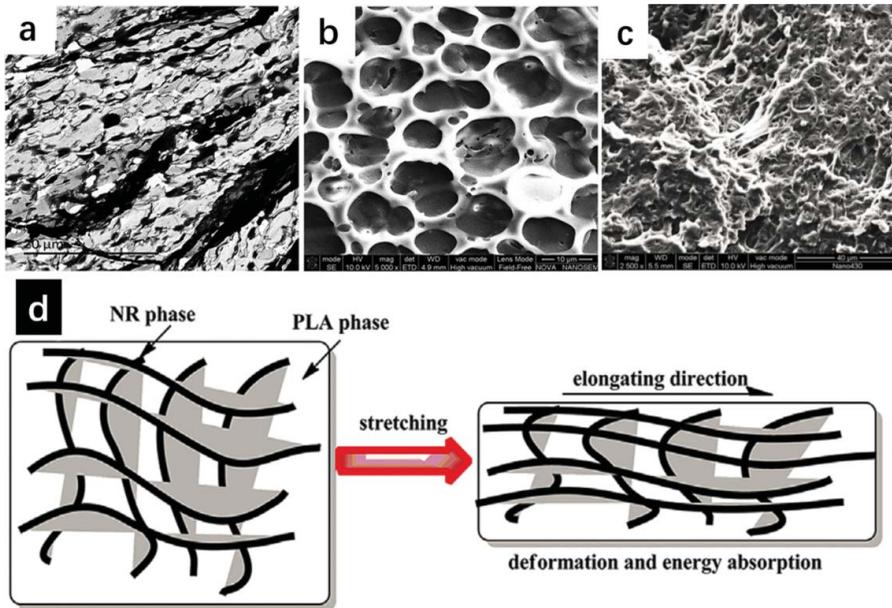


Figure 15. (a) TEM and (b) SEM images for co-continuous morphology for PLA/NR (65/35), (c) SEM image of the fractured surface of PLA/NR (65/35) without complete cryogenically frozen, and (d) Illustration of the deformation of crosslinked NR phase with net-like structure during stretching.¹²² © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholder.

Epoxidized natural rubber (ENR). ENR is a commercialized NR derivative prepared by reacting NR with peroxide.⁹⁷ Plenty of epoxy groups would improve polarity of NR and hence promote compatibility with PLA. Furthermore, the epoxy groups are able to react with ester or terminal groups of PLA to further enhance compatibility and interfacial adhesion of the blends.^{164,165} Zhang et al.⁹⁷ observed that melt blended PLA/ENR blends showed a good interfacial adhesion, and found that the impact strength of PLA with addition of 20 wt% ENR increased by 6-fold compared to neat PLA. Chen et al.^{51,166} have recently introduced dynamic vulcanization and interfacial compatibilization technique in preparation of PLA/ENR blends with DCP as an initiator. A co-continuous phase morphology with super toughness was also observed for the prepared PLA blend containing 40 wt% ENR. The elongation at break and notched impact strength increased by ~ 16 and ~ 15 times to 150% and 47 kJ/m² compared to 9.5% and 3 kJ/m² of neat PLA, respectively. Tham et al.¹⁶⁷ have recently toughened PLA/halloysite (HNT) nanocomposites with ENR through melt blending, and found that HNT has good affinity with both PLA and ENR, thus tending to form “bridge-like” linkages with each other at the interface to improve their interfacial adhesion. The Charpy impact strength of PLA/HNT (94/6) increased from 11.4 kJ/m² to 45 kJ/m² by replacing 15 wt% PLA with ENR.

4.6 Plant oils and derivatives toughened PLA

Soybean oil and derivatives. Plant oils are triglycerides obtained from annually renewable plants or crops and are used as important resources for biopolymers such as polyesters, polyurethanes, polyamides, epoxy resins, etc.¹⁶⁸ Soybean oil (SOY) is an abundant plant oil

which can be used directly to blend with PLA. Although SOY is immiscible with PLA, PLA/SOY blends can be compatibilized with poly(isoprene-*b*-lactide) block copolymer.⁹¹ Due to the large difference in viscosity, only very limited content of SOY (< 6.0 wt%) can be incorporated into the PLA matrix, while after compatibilization with the block copolymer, a higher content of SOY (20 wt%) could be incorporated into the PLA matrix. However, the mechanical properties of the blends were not reported.

Robertson et al.¹⁶⁹ prepared polymerized soybean oil (polySOY) by crosslinking soybean oil with a free radical crosslinking agent or oxygen via heating, and then blended polySOY with PLA in the presence of poly(isopropene-*b*-lactide) (PI-PLLA) block copolymer as a compatibilizer. The gel fraction of polySOY played an important role in particle size of the dispersed phase in PLA/polySOY (85/15) binary blends, small particle size with 1.0~1.5 μm generated at gel fraction range of 0.23–0.41. The particle size was further reduced to $\sim 0.5 \mu\text{m}$ for the PLA/polySOYA/PI-PLLA (81/14/5) ternary blends. The elongation at break and tensile toughness of PLA were enhanced by 6 and 4 times, respectively, compared to neat PLA.

To improve compatibility between PLA and SOY, Gramlich et al.⁹² first incorporated maleimide unit into PLA (HEMI-PLLA), meanwhile changing SOY to conjugated SOY (CS) containing conjugated dienes, and then reactively blended HEMI-PLA with CS. The compatibility was improved by Diels-Alder reaction (as shown in Fig. 16) between HEMI-PLA and CS during blending. Consequently, HEMI-PLA/CS (95/5, W/W) blend showed a greater than 17-fold increase in elongation at break compared to neat PLA and more than doubled the elongation at break compared to unreactive blend of PLA with 5 wt% CS.

Mauck et al.⁵⁵ have recently toughened PLA by reactive blending with acrylated epoxidized soybean oil (AESO). The compatibility between PLA and AESO was improved compared to the PLA/SOY blend, as evidenced by the apparent reduction in droplet size and inter-particle distance. The improved compatibility was attributed to the prevention of coarsening by crosslinking and transesterification between PLA and AESO. The elongation at break of prepared PLA/AESO (95/5) blends increased to 31% from 4.1% of neat PLA, meanwhile the tensile strength remained at a high level, 62 MPa of the blends versus 64 MPa of neat PLA.

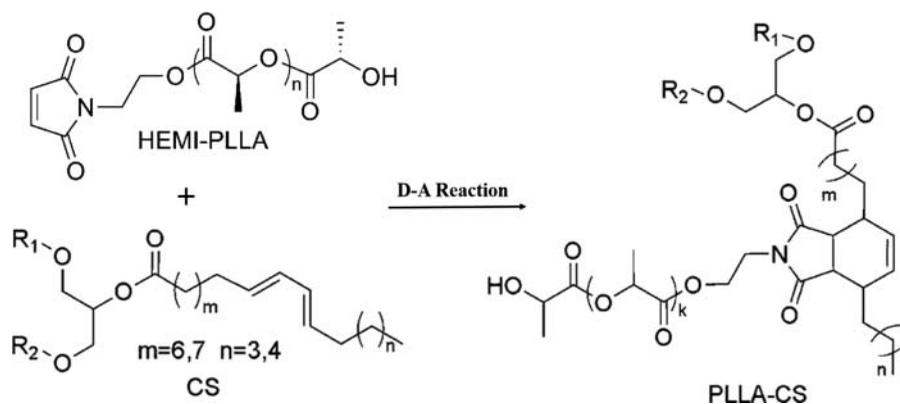


Figure 16. Diels-Alder reaction CS and HEMI-PLLA.⁹² © The American Chemical Society. Reproduced by permission of The American Chemical Society. Permission to reuse must be obtained from the rightsholder.

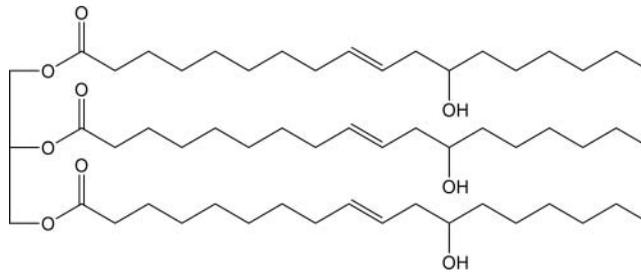


Figure 17. Chemical structures of castor oil.

Castor oil and derivatives. Castor oil is a triglyceride that contains reactive hydroxyl groups within the fatty acid, as shown in Fig. 17. Robertson et al.¹⁷⁰ tried to toughen PLA with castor oil directly, and found that the elongation at break of PLA increased from 5% to 40% with the addition of 5 wt% castor oil, although they were immiscible. The elongation at break could be further increased to 60% when compatibilized with 5 wt% poly(ricinoleic acid)-PLLA diblock copolymer.

The presence of hydroxyl group of castor oil makes it possible to design and synthesize some new biobased polymers to show good compatibility with PLA. Gurunathan et al.¹⁷¹ toughened PLA with castor oil-based polyurethane prepolymer (COPUP). Phase-separated morphology occurred for the blends and their compatibility was enhanced by the reaction of -NCO groups with terminal hydroxyl groups of PLA. Addition of 30 wt% COPUP increased elongation at break and impact strength to 377% and 269 J/m from 3.56% and 24.98 J/m of PLA, respectively. The tensile strength and Young's Modulus decreased from 61.19 MPa and 2.60 GPa of PLA to 37.28 MPa and 1.52 GPa, respectively.

Huang et al.¹⁷² toughened PLA with a PLA grafted poly(castor oil) copolymers (PCO-g-PLA), which was prepared by ring-opening polymerization of L-lactide in the presence of branched poly(castor oil), and showed good compatibility with PLA matrix, due to the presence of long PLA chains in the copolymer. As a result, the tensile toughness and elongation at break were improved by more than 10 times and 30 times, respectively, compared to PLA, with minimal reduction in tensile strength.

Our group has recently reported toughening PLA by dynamic vulcanization with castor oil and 4,4'-diphenylmethane diisocyanate (MDI). Dynamic vulcanization of castor oil and MDI occurred quickly during melt blending and formed a phase-separated morphology with castor oil-based polyurethane (COP) particles dispersed in PLA matrix. The particle size of COP increased with the feeding content of castor oil and MDI. It was interesting to find that the elongation at break of PLA was drastically increased to more than 330% with incorporation of only 5 wt% COP. The mechanical strength and Young's modulus were kept at a high level. When the content of COP increased to more than 10 wt%, the elongation at break decreased to ~200%, due the large-sized COP particles. Debonding cavitation induced matrix shear yielding was the toughening mechanism for the PLA/COP blends. Unfortunately it was found that the improvement in impact strength was limited possibly due to the poor interfacial adhesion between COP and PLA.⁵⁷

Plant oil derived flexible polymers. Fatty acids from plant oils represent promising feedstock for flexible polyesters and polyamides,¹⁶⁸ which may be used as biobased toughening agents for PLA. Lebarbé et al.⁴⁸ directly melt blended PLA with a biobased rubbery poly

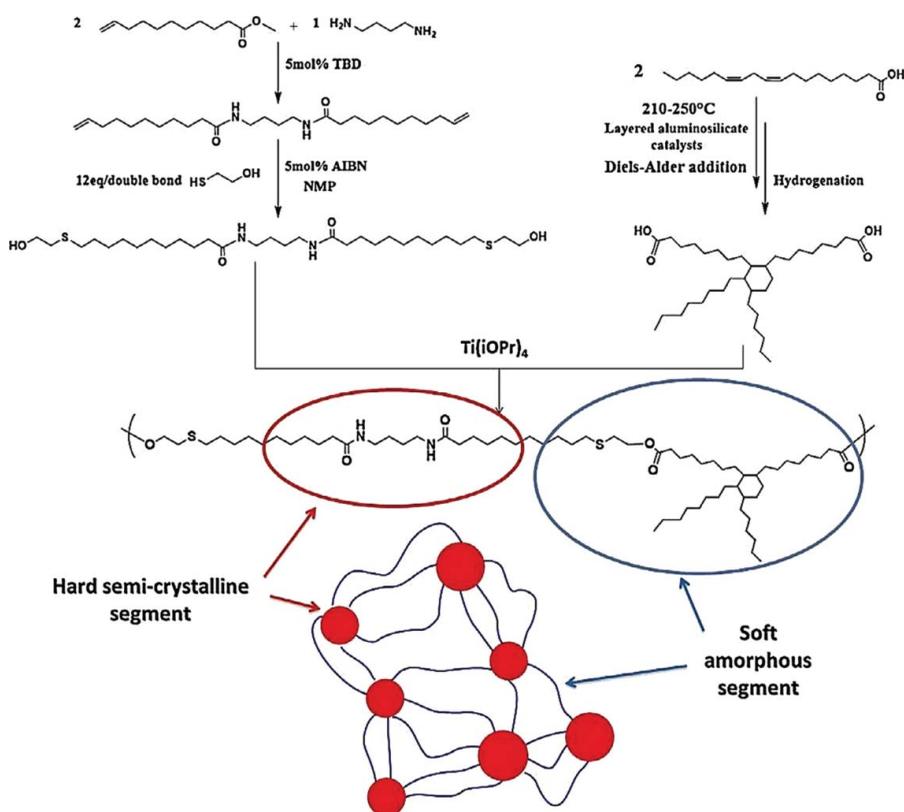


Figure 18. Synthesis of PEA rubber by polycondensation of UndBdA-diol and DFA.⁴⁸ © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholder.

(ester-amide) (PEA), which was synthesized by polycondensation of undecenoate butylene diamide diol (UndBdA-diol) with a hydrogenated dimer fatty acid (DFA), as shown in Fig. 18. The PLA/PEA showed poor interfacial adhesion and phase-separated morphology with spherical PEA particle dispersed in PLA matrix. The particle size increased with PEA content. The addition of 10 wt% PEA showed a good balance between particle size and volume fraction of rubbery phase and thus exhibited the best toughening efficiency with the elongation at break and impact strength increased from 3.8% and 2.45 kJ/m² of neat PLA to 155.2% and 3.37 kJ/m², respectively.

The same group synthesized another polyester rubber from polycondensation of plant oil derived monomers, that is, sebacic acid, 1,10-decanediol, and a dimer fatty acid, and evaluated the toughening efficiency of the polyester rubbers on PLA. Their blends also showed phase-separated morphology. The particle size of the dispersed polyester phase was tunable through the feeding content and the structure of polyesters by varying diacid's ratio. The particle size can be in the optimum range for high toughening efficiency in some specific blends. The elongation at break and impact strength of PLA increased from 3.8% and 2.45 kJ/m² to 385% and 10.34 kJ/m², respectively, when a suitable blend composition and polyester rubber structure were employed.⁴⁹ The improvement in impact strength is smaller than in tensile ductility, possible due to the poor interfacial adhesion resulted from the poor compatibility.

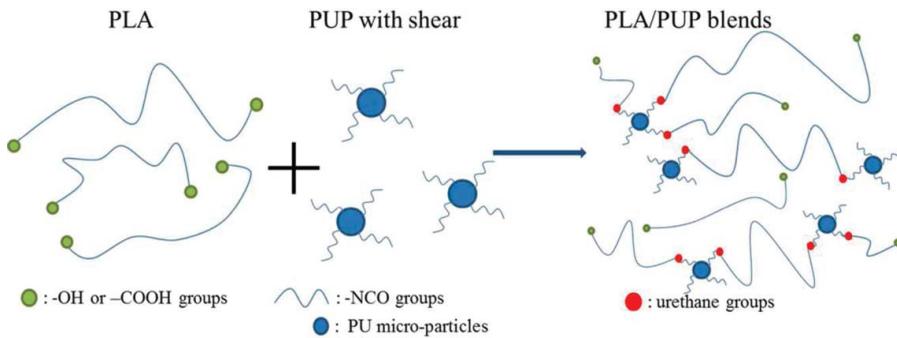


Figure 19. Compatibilization reaction between PLA and PUP.¹⁷⁷ © John Wiley and Sons. Reproduced by permission of John Wiley and Sons. Permission to reuse must be obtained from the rightsholder.

4.7 Other biobased polymers toughened PLA

Biobased polyamide. Polyamide 11 (PA11) is a biobased polymer derived from vegetable oil and displays high impact strength, excellent resilience, and acceptable tensile strength.¹⁷³ Those mechanical properties make PA11 suitable to toughen PLA. Unfortunately, PA11 is immiscible with PLA and hence their blends showed brittle behavior, although the content of flexible PA11 was as high as 40 wt%.⁹³ When PLA/PA11 blends were compatibilized by ethylene glycidyl methacrylate-graft-styrene-co-acrylonitrile (EGMA-g-AS), both tensile toughness and impact toughness could obviously be improved. The PLA/PA11 (55/45) blend compatibilized by 9 wt% EGMA-g-AS showed a 78-fold and 5.2-fold improvement in elongation at break and impact strength, respectively, compared to neat PLA.¹⁷⁴

Biobased polyurethanes. Yu et al.¹⁷⁵ prepared a biobased polyurethane (bio-PU) containing a soft segment renewable aliphatic polyester, which was synthesized from condensation polymerization of adipic acid, itaconic acid, 1,10-decanediol, and 1,4-butanediol, and melt blended the bio-PU with PLA for toughening. Addition of 15 wt% polyurethane increased the elongation at break of PLA from 7% to 230% and the notched impact strength from 3.77 kJ/m² to 9.5 kJ/m², respectively. It is noted that double bonds exist in the soft segments of the bio-PU, which facilitate compatibilization of the PLA/bio-PU blends via peroxide induced free radical crosslinking. After compatibilization, the interfacial adhesion between PLA and the polyurethane was enhanced as evidenced by the absence of pulling out of dispersed bio-PU particles. The compatibilized blends showed improved ductility with the elongation at break of a PLA/polyurethane (90/10) blend increased from 38.6% to 162% when compatibilized with 0.1 wt% L 101, while impact strength almost kept unchanged, as reported in their recent study.¹⁷⁶

Zhang et al.¹⁷⁷ prepared a biobased polyurethane prepolymer (PUP) from the reaction of poly(1,4-butylene glycol adipate) diol and 4,4'-Methylenedi-*p*-phenyl diisocyanate, and blended the PUP with PLA for toughening. Compatibilization through reaction between terminal isocyanate groups of PUP and hydroxyl or carboxyl groups of PLA occurred during melt blending, as shown in Fig. 19, which significantly improved mechanical properties of the resulting blends. For example, the elongation at break of PLA increased from 2.9% to 231.5% by blending with 5 wt% PUP.

5. Conclusions

To improve the toughness of brittle PLA without compromising sustainability, various commercial or purposely designed/synthesized flexible/elastic sustainable polymers have been used to toughen PLA. It is relatively simpler to improve tensile toughness than to enhance impact toughness, since it is easy to increase the elongation at break of PLA to more than 200% by directly blending with some biobased polymers. Whereas, direct blending was usually unable to endow PLA blends with high impact toughness, due to the low interfacial adhesion and poor phase morphology resulting from the immiscibility between various polymers and PLA. However, fully sustainable super-toughened PLA blends with impact strength of higher than 530 J/m (or 53 kJ/m²) were also obtainable for some specific blend systems after suitable compatibilization.^{56,73,98,122}

Interfacial adhesion and phase morphology are the two dominating factors for the final toughness of a given polymer blend, as they determine the toughening mechanism of the blends. Matrix shear yielding induced by cavitation or debonding is believed to be the most efficient way of energy dissipation with respect to toughening mechanisms in plastic/rubber phase-separated blends. Therefore, the most important thing for renewable polymer toughened PLA blends to exhibit high toughness is to make the PLA matrix to undergo shear yielding, which is a complicated process that is affected by many factors including inherent property of dispersed phase, interfacial adhesion, and various morphological parameters such as phase structure, dispersed particle size and distribution, and inter-particle distance, while for a given renewable polymer toughened PLA blends, the optimal interfacial adhesion and phase morphology are available via a suitable compatibilization technique to make the blends show the highest toughening efficiency. After carefully tailoring the interfacial adhesion and phase morphology, several super-toughened PLA materials were obtained by blending with some renewable polymers, such as poly(butylene succinate),⁵⁶ natural rubber,¹²² and bioelastomer.⁷³

The toughening modification of PLA with renewable polymers has reached a series of important achievements. However, it should be noted that the inherent high mechanical strength and elastic modulus obviously reduced during toughening. In addition, the other significant issues of slow crystallization rate and low HDT remained for the toughened PLA blends. Although toughening PLA without compromising sustainability is well realized, the slow crystallization rate and low HDT deflections would still restrict the wide application of PLA, from the viewpoints of processing and heat resistance applications. Therefore, the future investigation on toughening PLA with renewable polymers is suggested to consider accelerating crystallization rate, improving HDT, and supplementing strength as well. If all those problems are well addressed, the PLA-based sustainable materials will play more important roles in the sustainable development of our society.

Funding

This work was supported by the Natural Science Foundation of China (51673158), the Opening Project of State Key Laboratory of Polymer Materials Engineering (Sichuan University) (Grant No. sklpm2015-4-26), and Fundamental Research Funds for the Central Universities (SWU115006).

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