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Title page

Compatibilization strategies in poly(lactic acid)-based blends

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Abstract:

Poly(lactic acid) (PLA) is regarded as one of the most promising bio-based and biodegradable polymers, due to its excellent biodegradability, biocompatibility, renewability, high strength, and easy processibility. However, the disadvantages such as brittleness and relatively high cost have restricted its applications significantly. Polymer blending provides an economic and efficient way to modify the properties of PLA. Most shortcomings of PLA are theoretically surmountable by blending with abundant of polymers with various properties. But, unfortunately, PLA is thermodynamically immiscible with most existing polymers. High performance PLA-based blends are usually unanticipated by direct blending. In order to obtain PLA-based blends with excellent overall properties, compatibilization is required during polymer blending. Various strategies have been employed or developed to compatibilize PLA blends with different polymers, as reported in recent studies. This article is aim to review the development in compatibilization strategies employed in PLA-based blends.

1. Introduction

Biodegradable Polymers especially those derived from renewable resources have attracted great attention due to the increasing environmental concerns and resources crisis associated with traditional petroleum-based polymers [1-3]. Poly(lactic acid) or polylactide (PLA) is one of the most extensively investigated biobased and biodegradable polymers due to its attractive mechanical strength, high melting temperature, excellent biodegradability, sustainability, and relatively low cost [4]. The monomer for PLA is lactic acid, which was first isolated from sour milk by Scheele in 1780 and first commercially available in 1881 [5]. The majority of the world's commercial lactic acid is now made by bacterial fermentation of saccharides, and various technologies for purification of lactic acid were reported in a review by Datta and Henry [6]. In 1845, Pelouze for the first time synthesized PLA by condensation of lactic acid under continuous removal of water [7]. However, applicable PLA with high molecular weight is difficult to be produced by this method due to the low reactivity of lactic acid and the reversibility of the polymerization technique.

The commercialized PLA is often produced by ring-opening polymerization (ROP) of lactide, the dimer of lactic acid, prepared by depolymerization of low molecular weight PLA oligomer [4], as shown in Fig. 1. The purity of lactide is very important for synthesizing high molecular weight PLA. Carothers and coworkers for the first time prepared PLA by ROP of lactide [7], but the high molecular weight PLA was only obtained after DuPont developed purification techniques in 1954 [4]. Recently, Cargill Dow LLC has commercialized PLA under the trade name NatureWorks at a capacity of 140,000 tons/year with starch as the starting material in 2002 [8]. Fermentation of starch gives rise to lactic acid, condensation of lactic acid leads to PLA oligomer, and the catalytic depolymerization of the oligomer under vacuum produces lactide. After purification, high molecular weight PLA could then be synthesized by ROP of lactide in the presence of a catalyst such as $Sn(Oct)_2$ [4]. Besides ring-opening polymerization, some other techniques such as chain-extension reaction [9-11], azeotropic dehydration condensation [12, 13], and melt/solid state polymerization[14, 15] could also be used to prepare high molecular weight PLA with the values of more than 100000 g/mol. The various synthetic routes for preparation of HMW PLA are schematically shown in Fig. 1.

Due to the presence of two chiral carbon centers, lactide has three stereoisomers: D,D-lactide (D-LA), L, L-lactide (L-LA), and D,L-lactide (*meso*-LA), as shown in Fig. 2. The physical properties including melting temperature, crystallization behaviors, and mechanical properties of PLA depend strongly on the stereochemical compositions. PLA homopolymer polymerized from pure L-LA or D-LA has an equilibrium crystalline melting point of 207 °C [8]. However, the commercially available PLA usually shows a melting point of 170-180 °C due to the slight racemization, imperfect crystallites, and impurities [4]. A 1:1 mixture of poly(L-lactide) and poly(D-lactide) presents a higher melting temperature of 230 °C and better mechanical properties than either homopolymer due to the formation of a stereocomplex structure [16, 17]. The effect of stereochemical composition on the glass transition temperature is much less significantly than on the melting temperature as the crystalline PLA and amorphous PLA showed similar glass transition temperature with the value of 55-63 °C [4]. Although there are three types of PLA, the commercial PLA is the copolymers of poly(L-lactide) with small amount of poly(D,L-lactide), since the lactic acid derived from biological sources is composed of major L-lactic acid and minor D-lactic acid [13]. In the following sections, for brevity, the stereo structure of PLA was not discriminated since the compatibilization techniques in PLA blends are almost the same regardless of the stereo structure.

PLA shows many advantages which make it to be widely used in many fields. Besides being derived from annually renewable resources (e.g., corn, sugar, potato), PLA is recyclable [18, 19], biodegradable and compostable with the final degradation products of carbon dioxide [20-22], and easily processible to form applicable products with traditional processing equipments [13, 23]. These characteristics make PLA very attractive to replace non-degradable petroleum-based plastics in commodity plastic applications, such as mulch film, disposable cutlery, shopping bags, trash bags, food containers, and packaging materials [13, 23-25]. The good biocompatibility and bioresorbability enable PLA to find extensive applications in biomedical and pharmaceutical fields including surgical sutures, tissue engineering materials, and drug delivery systems[26]. The high strength and melting temperature is helpful for PLA to find potential application in engineering plastics [27]. The tensile strength of PLA is usually in the range of 50-70 MPa depending on the molecular weight and stereochemical composition, and the Young's modulus can be as high as 3 GPa [28].

However, there are still some drawbacks that restrict the wide application of PLA. For example, PLA is lacking of toughness with very low impact strength and short extensibility, which is one of the biggest problems that hindered the use of PLA in many areas, where good impact resistance is required. The elongation at break is usually less than 10% and the impact strength is only ~2.5 kJ/m^2 [28, 29]. In addition, the poor crystallizability, slow biodegradation rate, low heat distortion temperature are the other shortcomings for wide application of PLA [8]. In order to extend the application of PLA, modifications have to be done to improve the properties.

2. PLA modifications

The most widely used methods to modify properties of polymers include chemical copolymerization, polymer blending, and nanocomposite technology. Chemical copolymerization is a very important way of modifying properties of homopolymers, and a variety of commercially important copolymers have been achieved via macromolecular design and chemical copolymerization. With respect to structure-properties relationships, new materials with tunable properties can be prepared by judicious selective of commoners and the variation of copolymer compositions. Physical blending is a convenient route for developing new polymeric materials, which combine the advantages of more than one existing polymers. The properties of the resulting polymer blends are also tunable through the choice of blending partners and the change of blend compositions. Nanocomposite technology involves the nanoscale dispersion of nanosized fillers into a polymer matrix. The nanofillers have very high surface areas. With good dispersion, their high surface area could potentially lead to reinforced properties of the nanocomposites. The reinforcing efficiency is usually better than that of conventional micro- and macro-composites for the same quantity of fillers. We would not like to introduce this technique in property modification of PLA, although this method provides an efficient way of reinforcing physical properties without sacrificing advantages of polymer matrix. The detailed information for property modification of PLA through nanocomposite technology could be found in a recent review by Raquez et al[30]. However, the use of nanoparticles as compatibilizers for PLA-based blends is included in the review. In the following text, we would like to briefly introduce the modification of PLA via chemical copolymerization and physical blending.

2.1. Chemical copolymerization

For property modification or developing new materials, PLA has been copolymerized with a variety of polymers including polyesters, polyolefin, and natural polymers through several polymerization techniques such as condensation polymerization [31, 32], ring-opening polymerization [33-35], and chain-extension reaction [10, 11, 36]. Herein, we would not like to review this technique in detail but briefly summarize its advantages and disadvantages. The detailed information for properties modification of PLA via chemical copolymerization could be found in a recent review paper by Rasal et al [37]. The greatest advantages of chemical copolymerization should be that there are abundant of species with various properties can be selected to copolymerize with PLA to generate a variety of new materials with tunable properties thus versatile applications. The species from biobased to petroleum-based, biodegradable to non-degradable, crystalline to amorphous, can be used to copolymerize with PLA to produce novel materials with various properties. However, the disadvantages of chemical copolymerization for modification of PLA are also conspicuous. The improvement in certain properties of one polymer achieved by chemical copolymerization is always accompanied by the deterioration of other properties. Taking toughening PLA by copolymerization with poly(ε-caprolactone) (PCL) for an example, the elongation at break of PLA-PCL multiblock copolymer could reach 600%, depending on the composition, however, the tensile strength and Young's modulus dropped dramatically to 32 MPa and 30 MPa, respectively, and the melting temperature and degree of crystallinity were also apparently decreased [38]. The lengthy period, rigorous copolymerization condition and high cost constitute the other disadvantages with respect to modification of PLA via chemical copolymerization especially through ring-opening polymerization. In a word, chemical copolymerization is a powerful technique to developing new materials with novel properties and applications but not a convenient and economic method of modifying properties of PLA without significant loss of other properties.

2.2. Polymer blending

In contrast to chemical copolymerization, physical blending with a carefully selected component represents an economic and convenient way of modifying properties of homopolymers [39-41]. To develop new materials with desired properties, PLA has been blended with various plasticizers and polymers [8, 28, 29]. The introduction of small molecular or macromolecular plasticizers would significantly improve the toughness especially the elongation at break of PLA due to the plasticization effect, which could reduce the glass transition temperature thus increase the ductility of PLA [28, 29]. More importantly, physical blending with other polymers provides the most promising way to modify properties of PLA. The PLA based materials with wide range of properties are theoretically obtainable by blending since a great number of polymers with various properties can be selected to blend with PLA. However, it does not mean that excellent properties of PLA blends are easily obtainable by simple blending. On the contrary, it is difficult to prepare high performance PLA blends through simple blending in most cases since most of the existing polymers are incompatible with PLA [42-48]. Compabilization is usually required for the incompatible polymer blends to exhibit excellent properties.

3. Compatibilization strategies

3.1. Generalities of compatibilization

Before going to describe compatibilization, it is necessary to talk about miscibility. Miscibility is a thermodynamic term that describes the behavior of a polymer pair by specifying the number of phases and their composition forming upon blending [41]. There are three types of blends in terms of miscibility: (1) completely miscible, (2) partially miscible, and (3) fully immiscible. The miscibility of a polymer blend can be distinguished from the morphology and the glass transition temperature (T_g) of the blend. Two types of morphologies, i.e., homogeneous and heterogeneous, exist for polymer blends. Completely miscible blend exhibits a homogeneous morphology with a single T_g, which is between the T_gs of both components and changes with the composition. Partially miscible blend, usually presenting a fine phase morphology with improved properties, is referred to as compatible blend [41]. Two phases exist in partially miscible blend and each phase is homogeneous with a part of one polymer dissolved in the other. This blend has two T_gs corresponding to the two phases, and each T_g shifts from the value of one component towards that of the other. A fully immiscible blend usually exhibits a macrophase-separated morphology with coarse interface boundary, large dispersed phase size, poor phase adhesion, and two T_gs, which are independent of blend compositions.

The state of miscibility of two polymers is governed by the free energy of mixing, $\triangle G_{mix}$, which is defined as

$$\triangle G_{mix}=\triangle H_{mix}-T\triangle S_{mix}$$

where $\triangle H_{mix}$ and $\triangle S_{mix}$ are the enthalpy change and entropy change by mixing, respectively [49]. The two polymers are miscible if $\triangle G_{mix}$ is negative, while immiscible if not. It is acknowledged that $\triangle S_{mix}$ is negligible when two high molecular weight polymers are blended. So, the $\triangle G_{mix}$ can only be negative when $\triangle H_{mix}$ is negative. That is to say, the mixing has to be exothermic, which requires special interactions between the blend components. The special interactions may be the strong ionic interaction or the relatively weak hydrogen bonding, ion-dipole, dipole-dipole, and donor and acceptor interactions. However, usually only very weak Van der Waals interactions exist between most of polymers, which explains why most existing polymers are fully immiscible. There blends are usually useless unless compatibilized.

Compatibility is a technical term defining the phase morphology and property profile of the blend in view of a certain application [50]. If blending partially miscible or immiscible two polymers generates a fine phase morphology and combines advantageous properties of the blend components, the compatibility between the two polymers is good, while they are incompatible if resulting in coarse phase morphology and poor properties. For the incompatible polymer blends, their compatibility can be improved via proper method, which is usually referred to as compatibilization. We call that the compatibility of the incompatible blend is changed to compatible if the phase morphology transfers from coarse to fine and the properties changes from poor to good after compatibilization.

Compatibilization is a technique to improve compatibility and enhance properties of immiscible polymer blends. The most important roles of compatibilization are first to reduce the size of the dispersed phase through the reduction of interfacial tension and second to prevent the dispersed phase from coalescence thus to stabilize the formed fine phase morphology [41]. In addition, compatibilization can improve the interfacial interactions between dispersed phase and the matrix as a result of using compatibilizers, which are usually macromolecular species showing interfacial activities in heterogeneous blends [50]. With formation of the fine phase morphology and improved interfacial interaction, the useless incompatible blends can be changed to useful compatible materials which combined the excellent properties of the blend components. Taking immiscible poly(lactic acid)/low density polyethylene (PLLA/LDPE) blend as an example, Fig. 3 shows the morphologies of cryofractured surfaces for immiscible PLLA/LDPE before and after compatibilized by block copolymer PLLA-b-LDPE, as reported by Wang and Hillmyer [42]. The uncompatibilized blend showed coarse morphology with large LDPE dispersed particle and obvious phase boundary, indicating poor compatibility and interfacial adhesion, while the size of dispersed LDPE particle decreased gradually and the phase boundary became less distinct with increase in the content of compatibilizer. The compatibilized blends showed significantly improved mechanical properties over the pristine blend. Except for addition of block copolymers, there are several other approaches that can compatibilize PLA-based blends, as described in the following section.

3.2. Addition of premade copolymers

3.2.1. General principles

Although random copolymers were occasionally used to compatibilize some specific blends, the most widely used copolymers are those which have blocky structures with one constitutive block miscible with one component and a second block miscible with the other component [41]. Those copolymers usually have blocky or grafting structures. Emulsification occurs to result in fine phase morphology and good mechanical properties when blocky structured copolymers are incorporated and located at the interface of the immiscible blends. The widely employed copolymers are diblock, triblock, and grafted copolymers. Fig. 4 shows a schematic picture of the supposed conformation of some copolymers at the interface of an immiscible blend. Diblock copolymer C-b-D can be used to compatiblize an immiscible A/B polymer blend if block C is miscible with polymer A and block D is miscible with polymer B. Therefore, block C can also be polymer A and block D can also be polymer B. Similarly, triblock copolymer C-b-D-b-C or D-b-C-b-D and grafted copolymer C-g-D or D-g-C can also be used to compatibilize the immiscible A/B polymer blend.

The presence of the block or grafted copolymers at the interface can decrease the interfacial tension of the immiscible blends thus reduce the size of the droplets of dispersed phase during melt processing [41]. Usually, the minor phase exhibit an average particle size in the sub-micron range when dispersed in the other polymer matrix. In addition, the existence of the blocky structured copolymer at the surface could prevent coalescence of the generated dispersed particles during subsequent processing or storage. Therefore, the addition of blocky structured copolymers as compatibilizers is able to form and stabilize a fine phase morphology in phase separated polymer blends. It is worth noting that the presence of the blocky structured copolymers can enhance the interfacial adhesion of the immiscible blends due to the entanglement of each block with the corresponding blend component. Sufficient interfacial adhesion is essential for stress transfer from one phase to the other, which is efficient to stop the cracks initiated at the interface from growth to catastrophic failure. The formation and stabilization of a fine phase morphology and the improvement in the interfacial adhesion usually change a useless immiscible blend to a useful material in which the advantages of each blend component are combined [41].

3.2.2. Addition of random copolymers

Random copolymers usually have sequential comonomer units although they distributed randomly. The sequential comonomer units can be regarded as short blocks which are miscible with corresponding blend components. Therefore, the addition of random copolymers can improve compatibility of immiscible blends. The copolymer P(LA-*co*-CL) synthesized by one-step ring-opening polymerization of *L*-lactide and *ε*-caprolactone have been reported to have blocky structure and therefore have been used a compatibilizer in immiscible PLA/PCL blends [51-53]. Kim et al [51] improved the compatibility between PLA and PCL by addition of P(LA-*co*-CL) random copolymer consisting of 50/50 mol ratio of *L*-lactide and *ε*-caprolactone, and the sequential comonomer units of LA and *ε*-CL unit per copolymer chain were 3.4 and 2.0, respectively. Tsuji et al [52] investigated the effect of P(LA-*co*-CL) containing 68.2 mol% LA on the morphology, phase structure, crystallization, and mechanical properties PLA/PCL blend, and found that the addition of P(LA-*co*-CL) decreased number densities of spherulites in PLLA/PCL blend, improved the tensile strength and the Young's modulus of PLLA/PCL blends at some compositions, and enhanced elongation at break of the blends with all the PLLA contents. The improvement in mechanical properties of PLLA/PCL blend by addition of P(LA-*co*-CL) was ascribed to the improved compatibility between the two polymers. Choi et al [53] investigated the effect of P(LA-*co*-CL) on the phase morphology of PLLA/PCL (70/30 W/W) blend, and found that the size of dispersed PCL domains decreased significantly from ~10 um to ~3 um with addition of 5 phr P(LA-*co*-CL), which indicated that the use of P(LA-*co*-CL) as a compatibilizer can efficiently enhance the compatibility between the dispersed PCL domains and the PLLA matrix.

Bai et al [54] reported the use of poly(D,L-lactide-*co*-*p*-dioxanone) (PLADO) random copolymer to compatibilize poly(*p*-dioxanone)/poly(D,L-lactide) (PPDO/PLA, 80/20 W/W) blend, and found that the addition of PLADO could obscure phase boundary between PPDO and PLA phase and increase compatibility between the two component although the average number of sequential comonomeric units of PDO unit was only 1.0. Recently, they used poly(*p*-dioxanone-co-*L*-lactide) (PDOLLA) to compatibilize poly(L-lactide)/poly(*p*-dioxanone) (PLLA/PPDO, 85/15 W/W) blend, and found that the compatibility and mechanical properties of the blend was much improved with addition of 3.0 wt% PDOLLA [55]. In order to improve compatibility of poly(D, L-lactic acid)/poly(glycolic acid) (PLA/PGA) blend, Ma at al [56] added poly(D, L-lactic-co-glycolic acid) (PLAGA) as a compatibilizer to the mixed solution of PLA and PGA during film preparation, and found that when 5% PLAGA was added the blend showed smooth and homogeneous morphology which was similar to that of neat PGA film.

3.2.3. Addition of block copolymers

Many efforts were focused on the compatibilization of PLA blends by adding block copolymers possessing one block identical to PLA and the other block identical to the other component. This type of blend will be denoted as "A/B/A-B" system, where A is PLA, B is the blend component, and A-B is the block copolymer of PLA and B. The compatiblization of PLA and different types of PE blends by PLA-PE diblock copolymers has been extensively investigated by Hillmyer and coworkers [42,57], and they found that the tensile and impact toughness of PLA/PE blends could be significantly improved by the addition of PLA-PE block copolymers.

PLA-PCL diblock or triblock copolymers have been widely used to compatibilize immiscible PLA/PCL blends. Choi et al [53] synthesized a PLA-PCL diblock copolymer and used it to compatiblize PLA/PCL blends and found that the size of PCL domains in PLA matrix can be reduced upon addition of PLA-PCL diblock copolymer, however, the reducing extent was poorer than the addition of PLA-PCL random copolymer. Maglio et al [58-60] and Wu et al [61] used the PLA-PCL-PLA triblock copolymer to compatiblize PLA/PCL blends. The good emulsifying effect was evidenced by the strong reduction in particle size of dispersed PCL phase upon addition of the triblock copolymer. For example, the dimension of dispersed PCL domains in PLA/PCL (70/30, W/W) drastically decreases from about 10-15 um to about 3-4 um after adding 4 wt% of the triblock copolymer [59].

To improve the compatibility of PLA with natural rubber, Chumeka et al [62] synthesized a diblock copolymer from hydroxyl telechelic natural rubber (NR) oligomers and poly(lactic acid) (PLA) and used it as a compatibilizer for PLA/NR blend. The results showed that the size of dispersed particles was reduced by the addition of the diblock copolymer.

Na et al [48] have extended this approach to C-B block copolymers, where the C block was miscible with PLA. They blended PLA with PEG-b-PCL block copolymer and found that PLA was miscible with PEG block while immiscible with PCL block although it was block-copolymerized with PEG, then they employed this block copolymer to compatibilize PLA/PCL blends and achieved improved mechanical properties upon addition of the copolymer. Considering poly(oxyethylene) (PEO) was miscible with both PLA and PCL, the diblock copolymer PLA-b-PEO “A-C” type was employed by Maglio et al to compatabilize PLA/PCL blend and it exhibited similar behavior to PLA-b-PCL-b-PLA triblock copolymer [60]. Chang et al [63] improved compatibility between PLLA and soybean oil (SOY) by addition of poly(isoprene-b-lactide) (A-C type) in which polyisoprene is miscible with SOY due to the small Flory-Huggins interaction parameter. With the aids of poly(isoprene-b-lactide), the incorporated content of SOY could be increased from 6 wt% to 20 wt%, and a phase inversion occurred with the minor SOY changed to matrix surrounding PLLA particles to provide improved toughness.

Another type of copolymer (C-D type) such as polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) triblock copolymer was sometimes used to compatibilize PLLA blends. For example, PEO-PPO-PEO was employed as a compatibilizer in PLLA/PCL [64] and PLLA/PBSL [65] blends. In those systems, PEO-PPO-PEO worked like a third homopolymer such as PEG which was miscible with both blend components thus could emulsify the phase interface to improve compatibility. Real C-D type block copolymer, of which one block (C block) is miscible with A component and the other block (D block) is miscible with B component, has seldom been used in compatibilization of PLLA blends, possibly due to the difficulty of finding such specific block copolymers.

3.2.4. Addition of grafting copolymers

Grafting copolymers consisting of blocky structures can also work as a good compatibilizer for immiscible polymer blends. However, there were very less studies that used grafting copolymers to compatibilize PLA-based blends, compared to block copolymers, which should be attributed to the more difficulty in preparation of PLA-based grafting copolymers than the block copolymers. The grafting copolymers were usually used in those PLA-based blends containing natural polymers, since the grafting copolymers of PLA grafted natural polymers are relatively easier synthesized via the functional groups initiated ring-opening-polymerization procedure [66]. Wootthikanokkhan et al [67] prepared and added modified starch-grafted poly(lactic acid) (PLA-g-MTPS) to poly(lactic acid)/thermoplastic starch (PLA/TPS) blends, and found that PLA-g-MTPS was capable of acting as a compatibilizer by reducing coalescence and surface tension of TPS phase during blending. Yang et al [66] compatibilized PLA/starch composites by the introduction of starch-g-PLA copolymer which could improve the interfacial adhesion between starch granules and PLA matrix.

From the above description, we can find that addition of premade copolymers is an efficient way to compatibilize PLA blends with various polymers. Besides the powerful compatibilization efficiency, the best advantage of this technique is its universality. Theoretically, this method can be used to compatibilize various immiscible blends by careful design and synthesis of suitable copolymers. The literatures that focused on the use of this method to compatibilize immiscible blends grow rapidly. However, this technique seems not suitable in large scale production due to the commercial unavailability and high cost of the specific copolymers.

3.3. Addition of reactive polymers

3.3.1. General principles

Addition of reactive polymer could compatibilize immiscible blends if the reactive polymer is miscible with one component and reactive towards functional groups of the other component. The real compatibilizer, i.e., block or graft copolymer is *in-situ* formed through reaction of reactive polymer with the blend component during thermal processing. Fig. 5 shows the types of reactive polymer that can be added to an immiscible A/B blend, and the types of copolymer formed. The added reactive polymer can be either an X-functionalized polymer A or an X-functionalized polymer C, provided that polymer C is miscible with polymer A. The X functional group may be either terminal or pendent groups. Polymer B should have either end-reactive or pendent-reactive Y functional groups. In the case of PLA-based blends, PLA has terminal reactive groups of hydroxyl and carboxyl.

There are many advantages of addition of reactive polymer over addition of premade copolymer. Firstly, the reactive polymers only give rise to block or grafted copolymers at the location where they are needed, always at the interface of immiscible blends, which should display more efficient in compatibilization than the addition of premade copolymer. Secondly, reactive polymers usually show lower melt viscosity than the premade copolymer, at least if the blocks of premade copolymer possess similar molecular weight with the reactive "blocks", which makes the reactive polymer to diffuse towards the interface of immiscible blends much faster than the premade copolymer. This is extremely important with respect to the short processing time during reactive blending which is usually on the order of a minute or even less. In some cases, the reactive polymers may be not miscible with either component of the blends, but they can also be used as compatibilizer if they are reactive towards the functional groups of both blend components. Copolymers, working as the compatibilizers, could also be formed at the interface of the immiscible blends through the reaction between the components in the presence of the reactive polymers [68].

In order to successfully compatibilize immiscible blends with reactive polymers, they must have a suitable reactivity with the functional groups of blend components so as to accomplish reaction to form block or graft copolymers during the short blending time. Furthermore, the formed covalent bonds must be stable enough to suffer from the subsequent processing conditions. PLA is an aliphatic polyester with terminal groups of carboxyl and hydroxyl, which are reactive with many functional groups such as epoxy, anhydride, isocyanate, and oxazoline groups. Fig. 6 shows the reactions between terminal groups of PLA and reactive polymers with those functional groups.

Addition of reactive polymers to compatibilize immiscible blends also has some other advantages. Compared to grafted and block copolymers, reactive polymers with various functional groups are relatively easier to be produced with simple techniques and some reactive polymers even have been commercialized. However, this technique would also have some disadvantages. The reactive polymers with functional groups may be poisonous, which would cause some potential injuries to operators. The inevitable residue of some poisonous functional groups if contained would cause some safety problems to the resulting blends. Nevertheless, this method has been widely used in PLA-based blends. Many reactive polymers with various functional groups that were used in compatibilization of PLA-based blends have been described in the following text.

3.3.2. Addition of reactive polymers with epoxy groups

In order to improve the mechanical properties of immiscible PLA/LDPE blends, Kim et al [69] compatibilized the blends with glycidyl methacrylate containing PE (PE-GMA), and found that the domain size of the dispersed phase was reduced and the mechanical properties were improved due to the formation of a compatibilizer through the reaction between terminal groups of PLA and the epoxy group of PE-GMA. Lai et al [70] compatibilized immiscible blends composed of major metallocene polyethylene (mPE) and minor PLA with ethylene-glycidyl methacrylate-vinyl acetate (EGMA-VA) as a compatibilizer, and found that the dispersed PLA domain size tended to decrease with addition of compatibilizer due to the increased interfacial interaction. Acrylonitrile-butadiene-styrene copolymer (ABS) can be used as a toughening agent for brittle PLA due to it has a structure with a rubbery polybutadiene (PB) dispersed in a rigid styrene-acrylonitrile copolymer (SAN) matrix. However, blends with improved toughness are not obtainable through simple blending since PLA is thermodynamically immiscible with ABS. To successfully toughening PLA with ABS, Li et al [43] applied a reactive copolymer consisting of styrene, acrylonitrile, and glycidyl methacrylate (SAN-GMA) to compatibilize PLA/ABS blends, and found that the domain size of ABS was significantly reduced and the size distribution became much narrower compared to the blends without SAN-GMA. Jo et al [71] also compatibilized PLA/ABS blends with SAN-GMA for automobile console boxes application. The compatibilized blends showed a very nice stiffness-toughness balance, i.e., the improvement in impact strength and elongation at break with a slightly loss in the modulus.

Poly(butylene adipate-*co*-terephthalate) (PBAT) is a flexible biodegradable polyester thus can be used to toughen PLA without compromising the biodegradability. Zhang et al [68] improved the compatibility between PLA and PBAT by adding a polymer containing 8% glycidyl methacrylate (T-GMA), which containing epoxy groups can react with both PLA and PBAT to form copolymers of PLA and PBAT thus to compatibilize the blends. Al-Itry et al [72] also compatibilized PLA/PBAT blends with a reactive polymer named Joncryl containing nine Glycidyl methacrylate (GMA) functions.

Natural rubber (NR) is a biobased polymer with high resilience and high elongation at break thus can be used as an impact modifier for PLA without sacrificing sustainability. But NR is also immiscible with PLA. The compatibility of PLA/NR blends was improved by the addition of glycidyl methacrylate-grafted natural rubber (NR-g-GMA), and the impact strength and elongation at break of PLA/NR blend increased about 2.5 times and 2 times, respectively, when 1 wt% NG-g-GMA was introduced, as reported by Punmanee et al [73]. Polyamide 610 (PA610) is also a biobased polymer and not miscible with PLA. In order to obtain a fully biobased blends with improved mechanical properties, Pai et al [74] compatibilized PLA/PA610 blends with a low molecular weight bisphenol-A type epoxy resin, and found that PA610 could toughen PLA and no-break untorched impact products was obtainable with suitable content of epoxy resin, due to the formation of copolymers at the interface of the blends via reaction of PLA and PA610 in the presence of the epoxy resin. Shi et al [75] compatibilized the blends of PLA and thermoplastic starch (TPS) with addition of glycidyl methacrylate grafted poly (ethylene octane) (GPEO), which is able to react with both PLA and TPS. Wu et al [76] compatibilized a blend of PLA and olefin block copolymer (OBC) with a random terpolymer of ethylene, methyl acrylate and glycidyl methacrylate (EMA-GMA). The compatibilization was evidenced from the reduced particle size of dispersed OBC and the narrowed particle size distribution.

3.3.3. Addition of reactive polymers with anhydride groups

Bhardwaj et al [77] compatibilized PLA blends containing a hydroxyl functional hyperbranched polymer (HBP) with a polyanhydride. Crosslinking between PLA and HBP, which could enhance interfacial interaction and compatibility of the blends, occurred through reaction of their hydroxyl groups with anhydride groups of the polyanhydride. After blended with HBP and compatibilized by the polyanhydride, PLA/HBP blends showed significantly improved mechanical properties with the toughness and elongation at break increased by ~570% and ~847%, respectively, as compared to the unmodified PLA. In order to improve the compatibility and mechanical properties of blends of PLA and thermoplastic starch (TPS), Huneault et at [78] prepared maleic anhydride (MA) grafted PLA and used it as a reactive compatibilizer for the blends. They found that the dispersed TPS domain size decreased apparently from 5~30 um to 1~3 um after compatibilization, and the ductility of the blends was increased significantly. Zhang et al [79] reported a compatibilization strategy for PLA/starch composites through a one-step procedure, where the formation of PLA-g-MAH and the compatibilization reaction took place simultaneously by thermal extrusion of PLA, starch, and MA in the presence of an initiator 2,5-bis(tert-butylperoxy)-2,5 dimethylhexane (L101). Hwang et al [80] also used a similar technique to compatibilize PLA/Starch blends, in which the dicumyl peroxide (DCP was used as an initiator for the formation of PLA-g-MAH. This procedure was extended to the compatibilization of PLA/TPS blends by Wang et al [81], and good compatibility between PLA and TPS was also obtained as homogeneous phase morphology was observed for the compatibilized PLA/TPS blends. Recently, this one-step procedure has been successfully applied to a PLA blend with the other biobased polyester PHB, as reported by Jandas et al [82]. They compatibilized PLA/PHB blends by the addition of MA as a reactive compatibilizer and benzoil peroxide (BPO) as an initiator. In this blend, MA could be grafted onto the polymer chains of both PLA and PHB, the MA-grafted polymer chains could then react with other PLA or PHB molecules to form copolymer to cause compatibilization.

Singh et al [83] enhanced the compatibility of a blend containing major low-density polyethylene (80 wt%) and minor PLA (20 wt%) with a grafted low-density polyethylene maleic anhydride (MA-grafted LDPE). When 4 phr MA-grafted LDPE was added, PLA dispersed uniformly in LDPE matrix, and optimum mechanical properties were obtained. Yoo et al [84] compatibilized immiscible blend containing major polypropylene (PP) and minor PLA with a polypropylene-g-maleic anhydride (PP-g-MAH), and found that the maximum tensile strength and minimum interfacial tension were obtained when 3 phr PP-g-MAH was added for a PP/PLA (80/20, w/w) blend. In PP/PLA blend consisting of major PLA and minor PP, PP-g-MAH could also be used as a reactive compatibilizer, as reported by Choudhary et al [85]. The mechanical properties especially the toughness of PP/PLA blend may be improved if ethylene-propylene-diene monomer rubber (EPDM) is added and proper compatibilization occurred for the PP/EPDM/PLA ternary blends. PP-g-MAH alone could not successfully compatibilize the blends in this case, since PP is not miscible with EPDM. While if EPDM-g-MAH was used as a mixing compatibilizer with PP-g-MAH, PP/EPDM/PLA ternary blends with good compatibilization and excellent mechanical properties were obtained, as reported by Park et al [86]. Since PP-g-MAH can only react with hydroxyl groups of PLA, the carboxyl groups remained after processing. The compatibilization could be further improved if a co-compatibilizer, which is able to react with carboxyl groups of PLA, was added in the PP/PLA blends. In this regard, Lee et al [87] evaluated the use of PP-g-MAH and PE-g-GMA as a hybrid compatibilizer for PP/PLA blends containing a toughening modifier and compared with using PP-g-MAH or PE-g-GMA as a single compatibilizer. They found that the hybrid compatibilizer has much better compatibilization efficiency than either PP-g-MAH or PE-g-GMA. In addition, the PP-g-MAH was also used as an efficient compatibilizer for PLA/PP/sepiolite nanocomposites as reported by Nunez et al [88]. Polycarbonate (PC) is an important engineering plastic with excellent comprehensive performance. To blend with the renewable PLA could endow PC with sustainability. However, PLA and PC are immiscible. In order to improve compatibility of PLA/PC blend, Lee et al [89] employed three types of maleic anhydride containing reactive polymers, i.e., poly(styrene-g-acrylonitrile)-maleic anhydride (SAN-g-MAH), poly(ethylene-co-octene) rubber-maleic anhydride (EOR-MAH) and poly(ethylene-co-glycidyl methacrylate) (EGMA), to compatibilize PC/PLA blends. They found that SAN-g-MAH was the most efficient compatibilizer for the blends since the maximum impact and tensile strengths and the minimum interfacial tension were achieved for a PC/PLA (70/0, w/w) blend when 5 phr SAN-g-MAH was added. The best compatibilization efficiency of SAN-g-MAH to PC/PLA blends was ascribed to the partial miscibility between SAN and PC [90] and the reaction between MAH and hydroxyl groups of PLA. Teamsinsungvon et al [91] prepared maleic anhydride grafted PLA (PLA-g-MA) and evaluated the effect of PLA-g-MA on the compatibility of PLA/PBAT blend, and found that the tensile properties of PLA/PBAT with incorporation of PLA-g-MA were much better than the uncompatibilized PLA/PBAT blends. Jiang et al [92] also prepared maleic anhydride grafted PLA (PLA-g-MAH) and used it as a compatibilizer in another immiscible blend containing PLA and poly(ethylene terephthalate glycol) (PETG), and found that the phase morphology of the blends were fined with addition of PLA-g-MAH and optimum content of

PLA-g-MAH was 3 phr for a PLA/PETG (80/20, w/w) blend, because it showed the finest phase morphology and the largest elongation at break.

3.3.4. Addition of reactive polymers with other functional groups

Some polymers that contain other reactive functional groups such as oxazoline and isocyanate could also be used to compatibilize PLA blends, since oxazoline is highly reactive towards carboxyl and isocyanate is highly reactive to hydroxyl. Due to the shortage and high cost of such kind polymers, they were not frequently used in compatibilization of immiscible PLA blends. There was an example of using poly(2-ethyl-2-oxazoline) (PEOX) and polymeric methylene diphenyl diisocyanate (pMDI) as synergetic compatibilizers for PLA/soy protein concentrate (PLA/SPC) blends, as reported by Liu et al [93]. The compatibilization included two steps: in the first step, PLA/SPC was compatibilized by extrusion with PEOX which could react with carboxyl groups of both PLA and SPC; and in the second step, pPDI was used to further compatibilize PLA/SPC/PEOX through reaction with hydroxyl groups of both PLA and SPC during injection molding. The tensile strength of PLA/SPC could be increased by ~24 MPa when pPDI and PEOX were used as the synergetic compatibilizers.

3.4. Addition of low molecular weight chemicals

3.4.1. General principles

Some low molecular weight chemicals with reactivity can be used to compatibilize polymer blends. In fact, the actual compatibilizer is not the low molecular weight chemical but the block, grafted or branched copolymer, which is formed during blending process. Bifunctional or multi-functional chemicals, such as isocyanates, oxazolines, and anhydrides, were usually employed to compatibilize PLA blends with other polyesters or carbohydrate polymers, since those functional groups are highly reactive towards hydroxyl or carboxyl groups of the mentioned polymers. Grafted, block, or branched copolymers could be formed through coupling reaction of the blend components in the presence of the bifunctional or multi-fucntional chemicals. Free radical initiator, which is able to activate the polymer chains of polyolefin, polyesters, and unsaturated polymers thus leads to the formation of branched copolymers, could be used to compatibilize PLA blends with polyolefin, polyesters, and unsaturated polymers.

The most advantages of this method would be the high reactivity of the low molecular weight chemicals, which would react with blending components quickly during melt blending. The fast reaction makes it very suitable to be used in the preparation polymer blends through extrusion, which usually occurred in several minutes. The challenges of this method should be the unmatched viscosity between the low molecular weight chemicals and blend components. It is hard to mix them uniformly due to the rather low viscosity of the low molecular weight chemicals. In addition, the volatility of some low molecular weight chemicals would result in greater harm to operators.

3.4.2. Addition of isocyanates

Organic compounds that contain an isocyanate group are referred to as isocyanates. Isocyanate group is highly reactive towards many functional groups such as hydroxyl and amino groups. An isocyanate contains two isocyanate groups is known as a diisocyanate, which is usually used to produce polyurethane in industry. Due to the high reactivity, isocyanates containing more than one isocyanate groups can be used to compatibilize immiscible blends of PLA with other polymers that contain hydroxyl groups or amino groups such as other biodegradable polyesters, polyamide, and natural polymers, because the reaction of the isocyanates with the functional groups of the blend components would form block or grafted copolymers at the interface of the immiscible blends to improve compatibility of the blends. The isocyanates which were usually used as reactive compatibilizers in PLA-based blends include lysine triisocyanate (LTI), lysine diisocyanate (LDI), 1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione (Duranate TPA-100), 1,3,5-tris(6-isocyanatohexyl)biuret (Duranate 24A-100), methylene diphenyl diisocyanate (MDI), and 1,4-phenylene diisocyanate (PDI). The chemical structures of those isocyanates are shown in Fig. 7.

Poly(butylene succinate) (PBS) is another biodegradable polyester can be obtained from renewable resources and shows excellent mechanical properties with good flexibility. It can be used to toughen PLA without sacrificing both sustainability and biodegradability if their compatibility can be improved. Isocyanates should be a good reactive compatibilizer for PLA/PBS blend, since the two components contain hydroxyl groups. Harada et al [94] reported the use of lysine triisocyanate (LTI) to compatibilize PLA/PBS blends during melt extrusion, and found that the impact strength of a PLA/PBS (90/10, w/w) blend was significantly increased from 18 kJ/m^2 to 50-70 kJ/m^2 when only 0.5 wt% LDI was added, indicating an improvement in compatibility. LTI also succeeded in compatibilizing immiscible blends of PLA and poly(butylenes succinate-*co*-L-lactate) (PBSL) or poly(butylene succinate-*co*-ε-caprolactone) (PBSC), as evidenced by the changed phase morphologies reported by Vannaladsaysy et al [95, 96]. Harada et al [97] compared the compatibilization efficiency of four isocyanates, i.e., lysine triisocyanate (LTI), lysine diisocyanate (LDI), 1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione (Duranate TPA-100), and

1,3,5-tris(6-isocyanatohexyl)biuret (Duranate 24A-100), towards immiscible PLLA/PCL blends, and found that the highest impact strength was obtained when LTI was used, but the authors did not explain the reason for the result. The reason might be that the isocynante group of LTI is more reactive than that of other isocyanates, thus could react with the both blend components sufficiently to compatibilize the blends.

Fang et al [98] compatibilized immiscible blends of PLA and soy protein isolate (SPI) with methylene diphenyl diisocyanate (MDI). The PLA/SPI blends showed a more uniform morphology in the presence of MDI, due to the formation of block or grafted copolymers of PLA and SPI through urethane linkage generated by reaction of isocyanate group of MDI and hydroxyls of blend components. Phetwarotai et al [99, 100] investigated the effect of MDI on the properties of PLA/gelatinized starch (GS) blends, and found that the interfacial adhesion between the two phases was improved and the tensile properties was increased by addition of 1.25 wt% MDI. Karagoz et al [101] enhanced compatibility and improved mechanical properties of immiscible blends of PLA and citric acid modified TPS with MDI, both the tensile and impact strengths of the blends were apparently improved by compatibilized with only 1 wt% MDI. MDI was also reported to be efficient in compatibilization of PLA/chitosan blends [102].

With the aim of toughening PLA without significant loss in modulus and ultimate tensile strength, Zaman et al [103] blended PLA with a thermoplastic polyester elastomer (TPEE) in the presence of MDI as a reactive compatibilizer, and investigated the effect of MDI content on the mechanical properties and morphologies of PLA/TPEE blends. The results suggested that the dispersed TPEE particle size decreased with increasing MDI content, and the elongation at break of PLA/TPEE (80/20, w/w) increased to more than 200% with only 1 wt% MDI compared to 80% of the control blend and the tensile strength was also improved slightly by the addition of MDI.

Thermoplastic polyurethane (TPU) with good flexibility can be used to toughen PLA if their immiscible issue could be resolved. To improve compatibility of immiscible PLA/TPU blends, Dogan et al [104] introduced 1,4-phenylene diisocyanate (PDI) into PLA/TPU blends during thermal processing, where reactive compatibilization occurred through reactions between isocyanate group of PDI and hydroxyl/carboxyl groups of PLA and hydroxyl or urethane groups of TPU. The particle size of TPU in a PLA/TPU (80/20, w/w) blend reduced from 1-2 microns to 0.4-1 microns on average with the addition of 1 wt% PDI, and the optimum PDI content for mechanical properties was only 0.5 wt%.

3.4.3. Addition of free radical initiators

Free radical initiators can be used in immiscible PLA blends containing either polyester or vinyl polymer. During thermal processing, initiators decomposed to free radicals which could react with PLA or the blend component to from macromolecular free radicals, which then reacted with the blend component or PLA to generate the real compatibilizers to improve compatibility of the blends. The reaction mechanism is presented in Fig. 8. Dicumyl peroxide (DCP) and 2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane (perox) with decomposition temperature matching with thermal processing temperature of PLA were usually used.

Wang et al [105] improved compatibility of PLA/PBS blends via an *in-situ* compatibilization procedure in the presence of dicumyl peroxide (DCP), and found that when only 0.1 wt% DCP was added, the particle size of dispersed PBS reduced significantly to 0.2-1.0 *um* and the blend showed a uniform morphology, which were very beneficial for obtaining excellent mechanical properties. The notched impact strength of a PLA/PBS (80/20, w/w) blend with addition of 0.1 wt% DCP showed the highest impact strength of 30 kJ/m^2, compared to 3.7 kJ/m^2 for the blend without DCP. Ji et al [106] also studied the effect of DCP on the morphology and properties of PLA/PBS blends, and found that the compatibility of PLA/PBS was increased significantly as evidenced by the decreased dispersed PBS particle size and the fined phase morphology with increasing DCP content, which resulted in significant improvement in mechanical properties, and the addition of DCP could cause branched and crosslinked structure, which could work as nucleation site to accelerate the crystallization rate of PLA. DCP was also applicable in compatibilization of PLA/PBAT blends, as reported by Ma et al [107]. They found that the introduction of DCP during thermal blending of PLA and PBAT could lead to a reduction in PBAT domain size and an enhancement in their interfacial adhesion. The elongation at break and impact strength of the PLA were increased to 300% and 110 J/m, respectively, after blending with PBAT in the presence of DCP. Branched/crosslinked structure also formed as evidenced by the solid-like behavior in the low frequency zone. Another peroxide, 2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane was also reported to improve compatibility of PLA/PBAT blends as reported by Coltelli et al [108]. The best compatibilization efficiency was obtained by the addition of 0.2 wt% peroxide for a PLA/PBAT (75/25, w/w) blend, which showed the largest elongation at break and the best phase morphology with smallest PBAT particles dispersed uniformly in PLA matrix. The compatibilization mechanism was proposed by the formation of copolymers consisting of PLA and PBAT through the reaction of macro-radicals PBAT· or PBAT-O-O· with PLA· or PLA-O-O· generated in the presence of the peroxide. Dong et al [109] investigated the effect of DCP on the morphology and properties of a fully biobased polymer blends of PLA and poly(β-hydroxybutyrate) (PHB), and found that the size of dispersed PLA phase was reduced obviously and the phase boundary became unclear by the addition of DCP and the mechanical properties of PLA/PHB blends were significantly improved, indicating improved compatibility, which was ascribed to the formation of PHB-g-PLA copolymers and/or PHB-crosslink-PLA network at the interfaces. The compatibility of immiscible PLA/NR blends could be also significantly enhanced by addition of DCP through the formation of cosslinking copolymers containing both PLA and NR, as reported by Huang et al [110].

3.4.4. Addition of other reactive chemicals

Some other reactive chemicals were occasionally used in compatibilization of immiscible PLA blends. Dong et al [111] prepared PLA/PBAT blends with improved compatibility and mechanical properties by addition of 2,2’-(1,3-phenylene)bis(2-oxazoline) (BOZ) and phthalic anhydride (PA) as the reactive compatibilizers during melt blending. BOZ could react with the carboxyl groups while PA could react with hydroxyl groups of the components, which would lead not only to the formation of block copolymers of PLA and PBAT to enhance compatibility but also to the increase in molecular weight of the blend components through coupling reaction. After compatibilization, both the elongation at break and the tensile strength were apparently improved. For example, a pristine PLA/PBAT (80/20, w/w) blend showed the elongation at break and tensile strength of 212.4% and 38.8 MPa, respectively; while with addition of 1phr BOZ and 1 phr PA, the compatibilized blend showed significant improved mechanical properties with the elongation at break and tensile strength of 515.7% and 45.3 MPa, respectively.

Shin et al [112] compatibilized PLA/PCL blends through addition of glycidyl methacrylate (GMA) monomer with the help of electron-beam irradiation. Two steps were involved in this technique. In the first step, melt blending of PLA, PCL and GMA was carried out in a twin-screw co-rotating extruder, which caused the formation of PLA/PCL blends with GMA located at the interface. The existence of GMA could result in fine dispersion of minor PCL in PLA matrix. In the second step, electron-beam irradiation was used to initiate the cross-copolymerization of GMA at the interface to enhance interfacial adhesion between PLA and PCL phases. The combination of the two steps could result in a significant improvement in compatibility between PLA and PCL.

Xiong et al [113] compatibilized immiscible PLA/starch blends with epoxidized soybean oil (ESO), which is usually used as an eco-friendly plasticizer for PVC and chlorinated rubber and contains several epoxy groups available for the reaction with carboxyl and hydroxyl groups of polymers. Limited improvement in compatibility was obtained by direct blending of PLA with starch and ESO, due to the relatively low reactivity between hydroxyl towards epoxy group of ESO, while sufficient compatibilization occurred if MA grafted native starch (MGAT) was used to replace native starch to blend with PLA and ESO, owning to the increased reaction possibility between ESO and MGAT. The formation of the real compatibilizer, i.e., copolymer of starch and PLA, is shown in Fig. 9.

Jariyasakoolroj et al [114] reported the compatibilization of PLA and starch by the use of chloropropyl trimethoxysilane (CPMS), which was first grafted onto the surface of starch through formation of covalent bonds to modify starch. The CPMS-grafted starch would then react with PLA during blending to generate copolymers of PLA and starch, which provided the compatibility between PLA and starch and also worked as nucleating agent to significantly increase degree of crystallinity.

3.5. Incorporation of reactive groups on the polymer chains of one component

This approach is similar to addition of reactive polymers with the respect to the compatibilization mechanism. The both techniques involve the formation of copolymers through the reaction between the reactive group of reactive polymer and the terminal/pendent groups of the other component. The difference is that the blending component in this case was the reactive polymer. This technique may have better compatibilization efficiency since there are direct covalent bonds between PLA and blend components through functional groups reaction.

Epoxy was the most wide reported reactive group that was incorporated into polymer to prepare compatible PLA blends, which should be ascribed to the high reactivity towards terminal groups of PLA and easy introduction of epoxy to polymers through copolymerization of GMA with other vinyl monomers. In order to improve the compatibility between liquid natural rubber with PLA, Nghia et al [115] modified the liquid natural rubber by incorporation of epoxy groups, which would react with the terminal carboxyl groups of PLA to form covalent bonding at the interface to enhance the interfacial adhesion and improve the compatibility. Oyama [116] prepared a super-tough PLA blend by reactive blending of PLA with an ethylene copolymer, poly(ethylene-glycidyl methacrylate) (EGMA), which contains 3 wt% glycidyl methacrylate. The epoxy groups could react with the terminal carboxyl and hydroxyl groups of PLA leading to sufficient compatibility between the two components. The super-tough PLA/EGMA blends with impact strength of 72 kJ/m^2 could be obtained when the dispersed EGMA particle size was reduced to 100-300 nm under suitable processing condition. Su et al [117] prepared compatibilized PLA binary blends by blending with a glycidyl methacrylate grafted poly(ethylene octane) (GMA-g-POE). The good compatibility was also ascribed to the reaction between epoxy group of GMA-g-POE and terminal groups of PLA. In order to toughen PLA with acrylonitrile-butadiene-styrene (ABS) and improve compatibility of PLA/ABS blends, Su et al [118] prepared glycidyl methacrylate functionalized ABS (ABS-g-GMA) and used it as a component to blend with PLA. They found that compatibilization and crosslinking took place simultaneously between the epoxy groups of ABS-g-GMA and the end carboxyl or hydroxyl groups of PLA. Super toughness of the blend was obtained, as evidenced by the impact strength of 540 J/m when only 1 wt% GMA was grafted to ABS. When some other polymers such as poly(butyl acrylate-co-ethyl acrylate) and poly(methyl methacrylate-co-butadiene) was modified by GMA, they also showed good compatibility with PLA, and their blends showed excellent mechanical properties, as reported by Hao et al [119, 120].

Anhydride group could be incorporated into polymer chains with the aid of free radicals, thus was sometimes introduced into the blending component of PLA based blends to improve compatibility. Orozco et al [121] prepared maleic anhydride (MA)-grafted PLA (PLA-g-MAH) and used it as a component to blend with starch so as to obtain a PLA/starch blend with improved compatibility and mechanical properties. The compatibilization happened by the reaction between anhydride groups of PLA and the side hydroxyl groups of starch.

3.6. Interchange reactions

When two polyesters are blended in melt state, several interchange reactions, as shown in Fig. 10, can take place to a certain level that depends on the structures of the polymers, the nature and concentration of exchangeable functional groups, blending time and temperature, and the presence and concentration of catalyst. The level of interchange reaction plays a very important role in determining the properties of the final products. Sometimes, complete interchange reaction with formation of a random copolymer can occur if the blending temperature is high enough, or the blending time is sufficiently long, and or an efficient catalyst is used. Such a level of interchange reaction is usually not preferable, because the random copolymer lose the beneficial properties of both blend components. What we need should be a suitable level of interchange reaction, i.e., to an extent where suitable amount of block copolymers is formed at the interface of the two immiscible blends. Thus, the advantageous properties of both components are kept. To get such a level of interchange reaction, carful choice of blending temperature, residence times in melt and suitable content of catalyst if any is required.

Yoon et al [122] studied the effects of blend composition and blending time on the interchange reaction and tensile properties of PLA blends with low and high molecular PCL (PLA/LPCL/HPCL), and found that copolymer of PLA and PCL was formed by the ester interchange reaction at 220 °C for 30-60 minutes, and the tensile strength and modulus of blends increased with increasing HPCL (high molecular weight PCL) content, while the elongation at break of the blend increased with increasing LPCL (low molecular weight PCL) content.

Coltelli et al [123] investigated the interchange reaction between PLA and PBAT in an discontinuous mixer with tetrabutyl titanate [$Ti(OBu)_4$] as a catalyst, and found that the dispersed PBAT particle size decreased and interfacial adhesion increased with increasing blending time, and that good compatibility could be obtained when the blending was performed at 200 °C for more than 20 min with the $Ti(OBu)_4$ content of 0.07 wt%. Lin et al [124] carried out interchange esterification between PLA and PBAT at 165~175 °C through melt extrusion under the screw speed at 90 rpm. They studied the effect of addition content of the catalyst $Ti(OBu)_4$ on the compatibility and mechanical properties of PLA/PBAT blends, and found that large PBAT particle dispersed non-uniformly in PLA matrix in pristine PLA/PBAT blend and distinct interface can be observed, while when $Ti(OBu)_4$ was added, the size of PBAT decreased and the interface became obscure, indicating improved compatibility. The particle size of PBAT was reduced to 0.5 um when 0.5 wt% $Ti(OBu)_4$ was added and the blends showed tensile strength, elongation at break and impact strength of 45 MPa, 298% and 9 kJ/m^2, respectively, compared to 35 MPa, 46% and 5 kJ/m^2 for the pristine PLA/PBAT blend.

Sadik et al [125] studied interchange reaction between PLA and poly(ethylene-co-vinylalcohol) (EVOH) in the absence and presence of different catalysts, i.e., 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) and Tin(II) bis(2-ethylhexanoate) [$Sn(Oct)_2$]. The reaction was accelerated by the addition of both catalysts, but $Sn(Oct)_2$ showed higher catalytic efficiency than TBD. The reaction finished in only a few minutes if $Sn(Oct)_2$ was used as the catalyst at 200 °C. PLA-grafted EVOH (EVOH-g-PLA) was formed through the reaction as confirmed by thermal, thermo-mechanical and ^{1}H NMR analysis.

To improve compatibility and physical properties of PLA blends with polycarbonate (PC), Phuong et al [126] added tetrabutylammonium tetraphenylborate (TBATPB) and triacetin (TA) into the blends during melt processing. Interchange reaction between PLA and PC occurred when TBATPB and TA were used as catalysts, and thus PLA-PC copolymers were formed in the blend. Consequently, the compatibility between PLA and PC was improved significantly with co-continuous phase morphology formed, and mechanical strength of the compatibilized blends was improved significantly.

Recently, Thurber et al [127] improved compatibility of PLA/PE blends by addition of interfacially localized catalysts. In the study, the compatibilization occurred through interchange reaction between telechelic hydroxyl functional PE and PLA. Interfacially localized catalyst (stannous octoate) accelerated the interchange reaction and resulted in improved compatibility. The size of dispersed PLA domain decreased while the number of dispersed PLA particles increased considerably.

Interchange reaction is a simple, efficient, and eco-friendly method to compatibilize PLA-based blends. However, the method has some limitations, as it could only be applicable when the blend components have exchangeable functional groups. It could not happen between PLA and some vinyl polymers. In addition, interchange reaction usually occurred at high temperatures, where thermal degradation of the components could not be avoided, which would lead to deteriorated properties, undesirable color and appearance.

3.7. Dynamic vulcanization and interfacial compatibilization

Dynamic vulcanization involves a process of selective crosslinking of a rubber phase during melt blending with a thermoplastic polymer, resulting in a two-phase material in which the crosslinked rubber phase dispersed in the thermoplastic matrix. Dynamic vulcanization could prevent the dispersed rubber phase from undergoing coalescence, thus affect the final morphology and properties of the resulting materials. When two polymers with similar polarities are blended, a fine morphology can be frozen through dynamic vulcanization and no extra compatibilizer is required. But dynamic vulcanization of two incompatible polymers usually leads to coarse morphology, where *in-situ* compatibilization is still required to increase the interfacial adhesion, and then a blend with high performance is obtainable. The process involving both dynamic vulcanization and *in-situ* compatibilization is referred to as dynamic vulcanization and interfacial compatibilization. This technique is very useful to compatibilize PLA blends with curable elastic polymers with the aim of improving toughness. The most advantage of this technique is the ability to control the phase morphology and therefore the properties of the resulting blends through the extent of vulcanization and interfacial reaction. This method is usually limited to the blends which contain curable polymers, but cannot be applicable in other systems without curable polymers.

The dispersed phase in this technique is a rubber, which is a very efficient toughening agent for brittle polymer. Therefore, this technique is very powerful to toughen PLA. Liu et al [128-130] for the first time employed this technique to prepare PLA based materials with super toughness. The rubber phase what they used is an ethylene-butyl acrylate-glycidyl methacrylate terpolymer (EBA-GMA), and a zinc ionomers of ethylene methyacrylic acid copolymer (EMAA-Zn) was used as a catalyst, of which the carboxyl group initiated the crosslinking of epoxy groups in the EBA-GMA phase, and zinc ions catalyzed the reaction between the epoxy groups of EBA-GMA and the terminal groups of PLA to improve interfacial adhesion between the dispersed rubber phase and the PLA matrix. The morphological analysis indicated that the binary blend of PLA/EBA-GMA (80/20, w/w) showed very fine morphology with EBA-GMA dispersed uniformly in PLA matrix at the size of ~0.3 *um* due to the good compatibility of the blend resulted from the reaction of epoxy of EBA-GMA and hydroxyl of PLA; the vulcanization of EBA-GMA after introduction of EMAA-Zn led to an increasing size of dispersed phase in the PLA/EBA-GMA/EMAA-Zn (80/10/10, w/w/w) to ~0.83 um, which is in the optimum range in highly toughening efficiency in rubber toughened PLLA blend. Through dynamic vulcanization and interfacial compatibilization, the ternary blends showed the elongation at break and notched impact strength of 229.1% and 777.2 J/m, respectively, compared to 10.2% and 101.9 J/m for the binary PLA/EBA-GMA blend.

Chen et al [131] employed dynamic vulcanization and interfacial compatibilization to improve compatibility between PLA and NR by melt blending in the presence of dicumyl peroxide (DCP) as an initiator. The thermal decomposition of DCP led to the formation of free radicals, which then initiated vulcanization of NR and also caused the formation of PLA macroradicals that reacted with NR to generate copolymers to enhance interfacial adhesion between PLA and vulcanized NR. A super-tough blend with notched impact strength of 58.3 kJ/m^2 was obtained when 35 wt% NR was blended with 65 wt% PLA. It is interesting that they found in such a system, the minor phase of NR changed to the continuous phase while the major PLA became the dispersed phase after dynamic vulcanization and interfacial compatibilization. But the mechanism for the formation of continuous vulcanized NR phase was unclear.

Fang et al [132] reported a super-tough PLA blends with poly(ethylene glycol) diacylate (PEGDA) monomer via dynamic vulcanization and interfacial compatibilization without an additional radical initiators. Rheological measurement suggested that thermally induced crosslinking of PEGDA occurred when the temperature was increased to higher than 116 °C in the absence of additional initiator. They thought that the polymerization may be initiated by free radical species such as radical impurities, peroxides, and oxygen plasma. When PEGDA was melt blended with PLA, the crosslinking of PEGDA finished within the blending period of 10 min, as evidenced by the change of melt torque of the blend. The FT-IR analysis indicated that *in-situ* compatibilization took place by interchange esterification of PLA and PEGDA during melt blending. The blends after dynamic vulcanization and interfacial compatibilization showed notched impact strength up to 50 kJ/m^2 when 15 wt% PEGDA was introduced.

Recently, we have introduced two different crosslinked polyurethanes (CPUs), which were obtained via *in-situ* polymerization, as the rubber phases to toughen PLA through dynamic vulcanization and interfacial compatibilization [133, 134]. In one case, the CPU was composed of poly(ethylene glycol) (PEG) and polymeric methylene diphenylene diisocyanate (PMDI). During blends preparation, PLA was first premixed with PEG in an internal mixer at 190 °C for 4 min, the blending was finished when the melt torque leveled off after the addition of PMDI. The CPU was *in-situ* formed through polymerization of PEG with PMDI, and the interfacial compatibilization occurred by the reaction of isocyanate groups with the terminal groups of PLA, as evidenced by the FT-IR analysis. Super-tough PLA blend was obtained when the content of the incorporated CPU was 30% with the elongation at break and notched impact strength of ~250% and 546 J/m, respectively. In order to further investigate the effect of crosslinking density of CPU on the properties of CPU toughened PLA blend, PMDI was replaced by methylene diphenylene diisocyanate (MDI) and glycerol in the other system. The crosslinking density, which was proved to be very important in determination of phase morphology and mechanical properties of PLA/CPU blends, could be tuned by the content of the tri-functional monomer glycerol. The particle size of CPU in PLA matrix increased gradually while the notched impact strength increased first and then decreased with increasing CPU crosslinking density. The highest notched impact strength of 407.6 J/m was achieved for a PLA/CPU (80/20, w/w) blend that contained 10 wt% glycerol (based on PEG weight), and the particle size of CPU in this blend was ~0.76 um, which was just in the optimum range for rubber toughened PLA blends.

In order to produce super-tough PLA materials without compromising sustainability, we prepared an unsaturated aliphatic polyester elastomer (UPE) from biobased monomers and melt blended it with PLA in the presence of DCP as a free radical initiator via a dynamic vulcanization and interfacial compatibilization technique [135]. During melt processing, dynamic vulcanization of UPE occurred by the initiation of free radicals formed via thermal decomposition of DCP. Meanwhile free radicals could abstract hydrogen from PLA polymer chain to generate PLA macroradicals, which then grafted onto the vulcanized UPE dispersed phases via attacking the double bonds of the UPE to form grafting copolymers, which located at the interface to significantly improve the interfacial adhesion between the two phases. Fig. 11 shows the proposed reactions for the preparation of PLA blends with UPE through dynamic vulcanization and interfacial compatibilization. The blend was named by thermoplastic vulcanizate (TPV) which referred to a polymer blend with a crosslinked rubber phase dispersed finely in a thermoplastic matrix. Super-tough TPV with elongation at break and notched impact strength of 259.9% and 586.6 J/m was obtained by blending PLA with 20 wt% UPE in the presence of 0.2 phr DCP at 180 °C and 50 rpm for about 10 min.

3.8. Addition of nanoparticles

Addition of nanoparticles to an immiscible blend provides an alternative way of improving compatibility of the blend. Nanoparticles usually locate at the interface of the components, acting as interfacial modifiers to strengthen the interfacial adhesion and therefore the performance of the blend. Nanoparticles can prevent preformed fine dispersed phase particles from coalescence during melt processing thus to stabilize the fine morphology and therefore keep properties of the blend. Unlike polymer compatibilizers, nanoparticles are unspecific to the nature of immiscible blend components, and easily incorporated via blending. Except for improving compatibility, the incorporation of nanoparticles can generate high performance material that combines the advantages of polymer blends and the merits of polymer nanocomposites. Therefore, tailoring phase morphology of immiscible blends by addition of nanoparticles represents a universal way of preparing compatible polymer blend nanocomposites with improved physical properties.

Chen et al [47] evaluated the effect of twice functionalized organoclay (TFC) on the compatibility between PLA and PBS, and found that the content of TFC played an important role in the morphology of the blend. TFC exfoliated fully and dispersed almost exclusively in PLA matrix and the domain size of dispersed PBS did not change considerably when the content of TFC was less than 0.5 wt%; while as the TFC content increased, the clay layers dispersed in both PLA and PBS phases and the domain size of PBS became much smaller and increased gradually with further increasing TFC content. This change was attributed to two factors by increasing TFC content. On one hand, TFC with functional groups could react with both PLA and PBS thus act like a reactive compatibilizer. On the other hand, some clay layers that located at the interface of PLA/PBS blend could prevent coalescence of the dispersed domains and contribute to the reduction in the domain size. Hoidy et al [136] compatibilized PLA/PCL blends with organoclay (OMMT), and found that the presence of OMMT as a filler not only enhanced the dispersion and interfacial adhesion of polymer matrix but also improved mechanical properties and thermal stability of PLA/PCL blends. Ojijo et al [137] compatibilized PLA/PBSA blends with organoclay (C20A) and investigated the effect of the content of C20A on the properties of the blends, and they found that the optimum property for a PLA/PBSA (70/30, w/w) blend was obtained when the content of C20A was 2 wt%. Risse et al [138] tailored the morphology and properties of PLA/PBS blend by addition of an organoclay (Cl30B). They found that Cl30B exfoliated partially in the blend and its content played an important role in the morphology and properties of the blend. Co-continuous morphology of a PLA/PBS (50/50, w/w) blend with a ductile behavior was achieved when 3 wt% Cl30B was added, while lamellar morphology accompanied by brittleness was obtained with further increasing Cl30B content. A recent study by Ferreira et al [139] suggested that the addition of Cloisite® 30B(C30B) into thermoplastic starch/PLA blends would improve adhesion between two phases, compared to the blank binary blends.

Carbon nanotube (CNT) is a new anisotropic one-dimensional nanoparticle, which has attracted considerable attentions in reinforcing physical properties of polymer matrix through nanocomposite technology, due to its extraordinarily high elastic modulus, strength, and resilience. It could also be used in improving compatibility of immiscible blend via selective localization, as reported by Wu et al [140]. They functionalized multiwalled carbon nanotube (MWCNT) with carboxyl groups, and added the functionalized MWCNT into melts of immiscible PCL/PLA blend during mixing with a HAAKE polylab rheometer. The compatibility between PCL and PLA was improved obviously by the addition of functionalized MWCNT, as evidenced by the significant reduction of dispersed PLA domain size and the enhanced interfacial adhesion. The dispersed PLA particle size in a PCL/PLA (70/30, w/w) blend decreased apparently from 21.5 to 6.3 *u*m as the MWCNT loadings increased up to 1 phr. The improved compatibility was attributed to the formed special morphological structure in which carboxylic MWCNTs mainly dispersed in PCL matrix and at the phase interface. The compatibilized PCL/PLA blends then showed highly improved performance with respect to rheological, conductive, and mechanical properties as compared with those of blank PCL/PLA blend.

Another nanoparticle that has been used to compatibilize immiscible PLA blends was silica, as reported by Odent et al [141] in PLA blend with a rubbery ε-caprolactone-based copolyester (P[CL-*co*-LA]). They found that P[CL-*co*-LA] with round-like nodules dispersed regularly in PLA matrix in a blank blend containing 10 wt% P[CL-*co*-LA], while the spherical nodules disappeared when 5 wt% hexamethyldisilazane surface-treated fumed silica nanoparticles were added and oblong microstructures began to appear, and more interestingly co-continuous morphology was observed with further increasing silica nanoparticle content up to 10 wt%, as shown in Fig. 12. Such a morphological change was ascribed to the presence of large surface silica nanoparticles at the interface of the blend components. The impact strength of the blend by addition of silica was significantly increased from 11.4 kJ/m^2 for the blank blend to 27.3 and 39.7 kJ/m^2 for the blends containing 5 and 10 wt% silica, respectively.

Recently, Monticelli et al [142] evaluated the effects of different types of modified polyhedral oligomeric silsesquioxane (POSS) on the compatibility of PLA/PCL blends. Addition of unmodified POSS reduced the size of PCL domains; addition of hydroxyl group functionalized POSS (POSS-OH) increased the adhesion between PLA and PCL; and addition of poly(ε-caprolactone)-b-poly(L-lactide) diblock copolymer grafted POSS (POSS-PCL-b-PLLA) led to the formation of an almost homogenous microstructure. All the characteristics indicated the improved compatibility of the blends.

3.9. Other strategies

Some sporadic techniques have been reported in compatibilization of some specific immiscible PLA blends. Addition of a third polymer that is miscible with both PLA and the other component could improve compatibility of PLA based blends. But due to the lack of such polymers, this technique can only be used in very special blend pairs. Poly(vinyl acetate) (PVAc) is miscible with both PLA and PHB, thus can be used to improve compatibility of PLA/PHB blends [143]. Poly(ethylene oxide) (PEO) is miscible PLA and PCL and the presence of PEO in PLA/PCL blend could result in a single phase completely miscible blend under suitable conditions, as reported by Buddhiranon et al [144].

Introducing some special interactions such as hydrogen bonding between PLA and the blending component is also able to improve compatibility. The work by Kuo et al [145] indicated that addition of bisphenol A (BPA) was able to improve compatibility between PLA and PCL since the both polymers were miscible with BPA. In order to improve compatibility between PLA and polystyrene (PS), Zuza et al [44] incorporated hydroxyl groups into PS by copolymerization of styrene with hydroxystyrene (HS) and then blended the modified PS with PLA. The introduction of hydroxyl groups to PS leaded to the formation of hydrogen bonding with carbonyl group of PLA, resulting in significant improvement in compatibility between the two polymers. A completely miscible blend was even achieved when the molar content of HS was increased to 16%.

4. Conclusions

Polymer blending provides a simple and economic way to modify properties and thus expand applications of PLA. In this sense, a variety of polymers have been blended with PLA. Unfortunately, most of the polymers are thermodynamically immiscible with PLA. High performance blends are unanticipated without compatibilization. Various compatibilization strategies, including addition of copolymers, addition of reactive polymers, addition of low molecular weight chemicals, addition of nanoparticles, interchange reactions, dynamic vulcanization and interfacial compatibilization, etc, have been applied to improve compatibility between PLA and different blend components. The addition of copolymers is the conventional and efficient way to compatibilize polymer blends. This technique showed very good compatibilization efficiency. However, due to the commercial unavailability of the specific copolymers, which have to be synthesized prior to blending. This method seems undesirable especially for industrial application due to the additional investment regarding preparation of the specific copolymers. Interchange reaction represents an economic way by melt blending PLA and other polymers with exchangeable functional groups. But thermal degradation usually occurred during interchange reaction, which would cause deteriorated properties combining with undesirable color and appearance. The other techniques such as addition of reactive substances and dynamic vulcanization and interfacial compatibilization involving chemical reactions between PLA and blend components or compatibilizers can be called as reactive compatibilizations, which are much more applicable not only for laboratory study but also for industrial application, due to the existence of various reactive substances and high compatibilization efficiency of the techniques. In addition, the introduction of nanoparticles to modify the interfacial properties and phase morphologies should be a very promising technique to compatibilize PLA-based blends, as the presence of nanoparticles would not only improve the compatibility between PLA and blend components, but also reinforce the mechanical strength or impart some novel functionalities to the resulting composites. Therefore, more efforts should focus on the compatibilization of PLA-based blends with various nanoparitcles thus to develop novel properties and expand applications of PLA-based materials.

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Figures

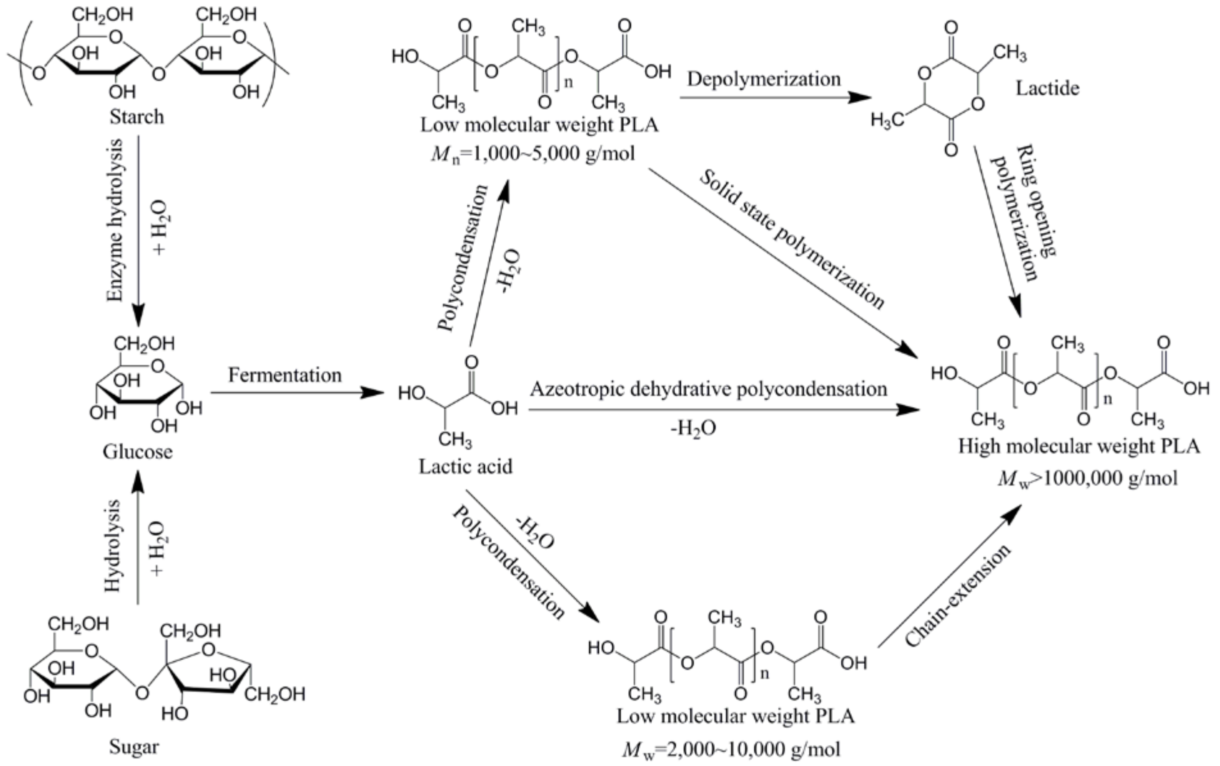
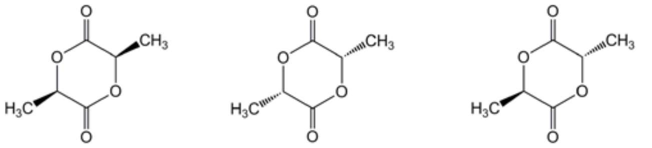


Fig. 1. Synthetic routes of poly(lactic acid).



D,D-Lactide (D-LA) L,L-Lactide (L-LA) D,L-Lactide (*meso*-LA)

Fig. 2. Chemical structures of three stereoisomers of lactide.

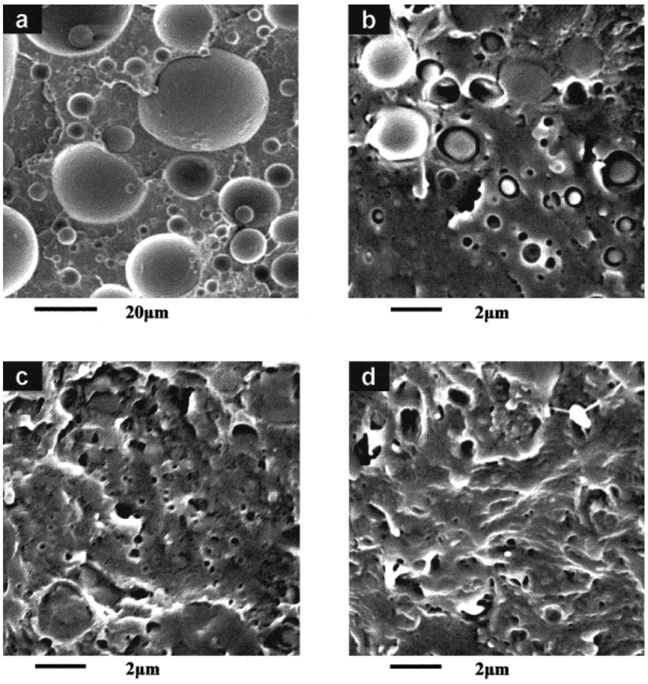


Fig. 3. Morphologies for cryofractured surfaces of (a) 80:20 PLLA/LDPE and (b) 80:20:2, (c) 80:20:5, and (d) 80:20:10 PLLA/LDPE/PE-*b*-PLLA blends. Reprinted with permission from ref. 42 Copyright 2001 John Wiley.

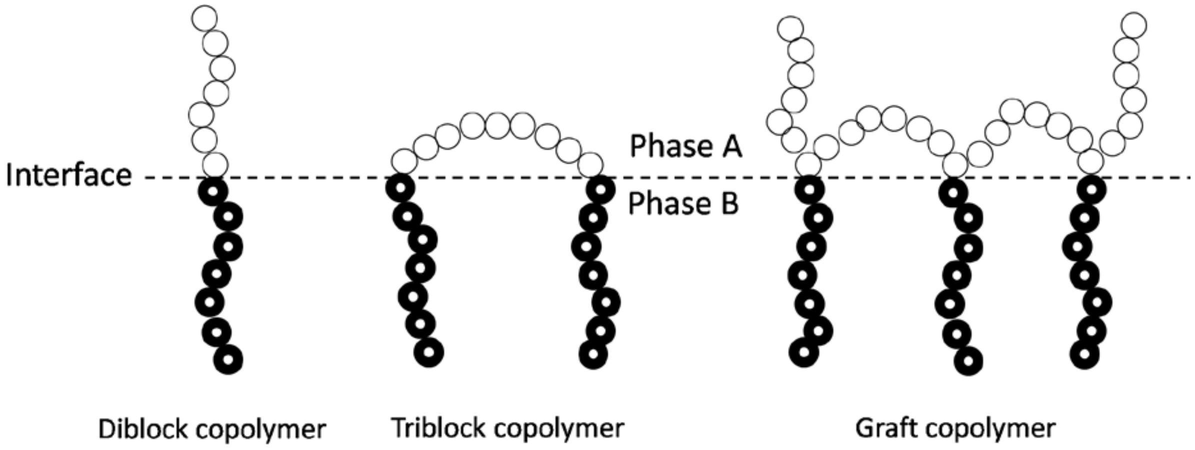


Fig. 4. Ideal location of diblock, triblock, and graft copolymers at the interface of an immiscible A/B polymer blend.

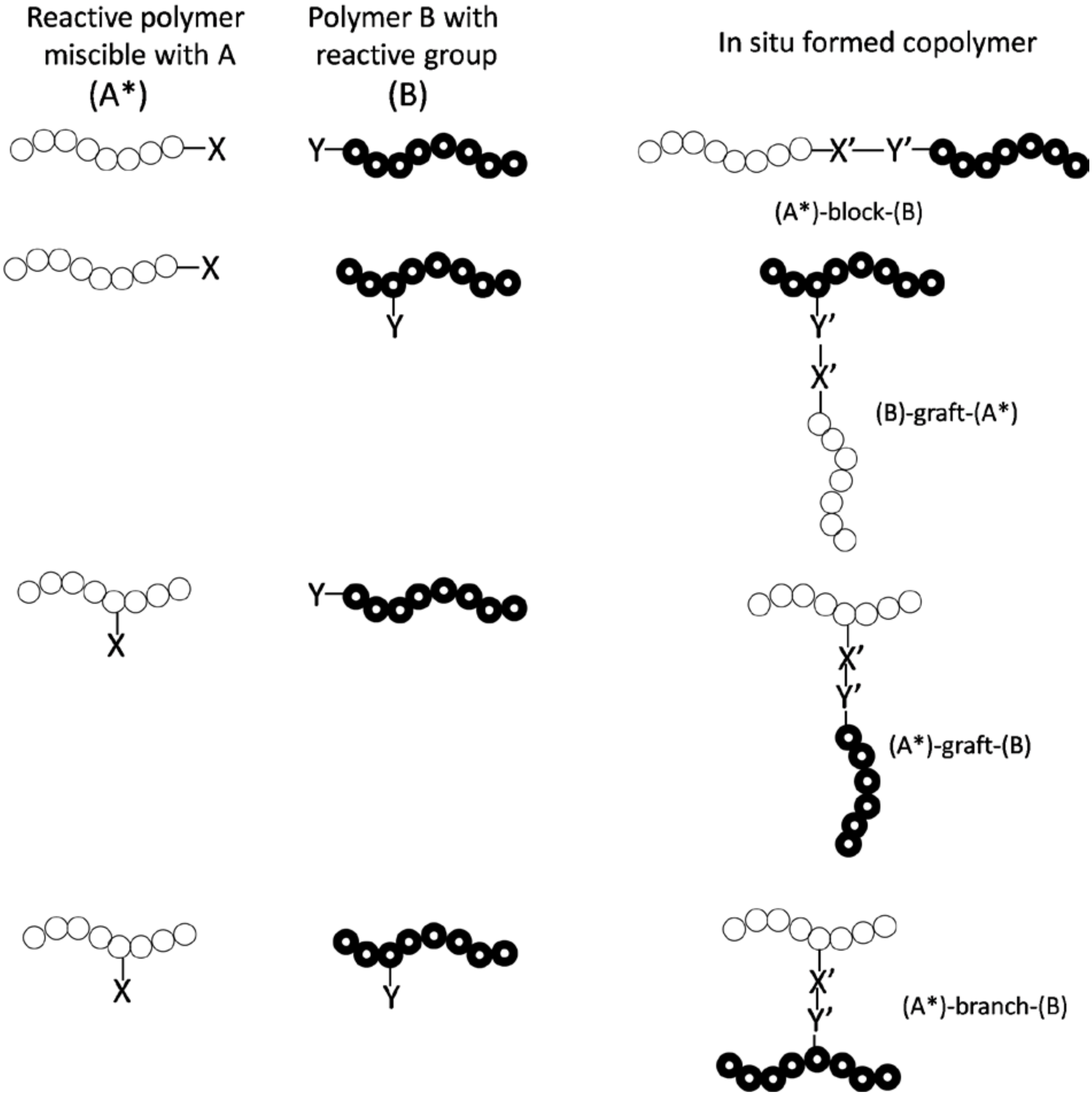


Fig. 5. Reactive polymer and the type of copolymer formed during processing.

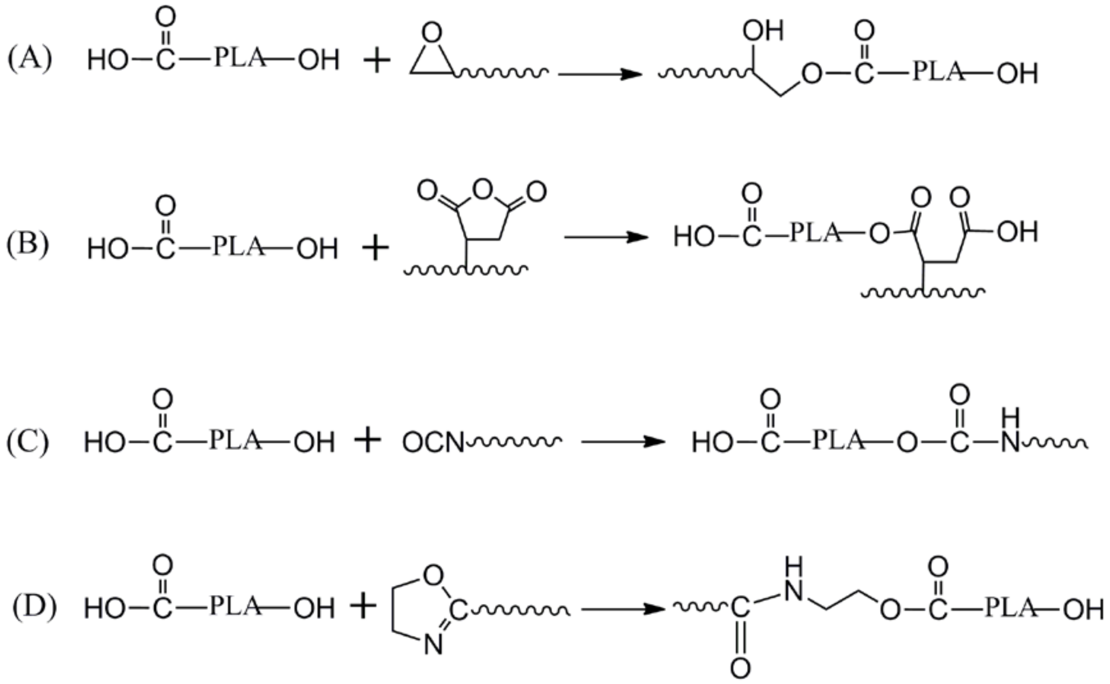
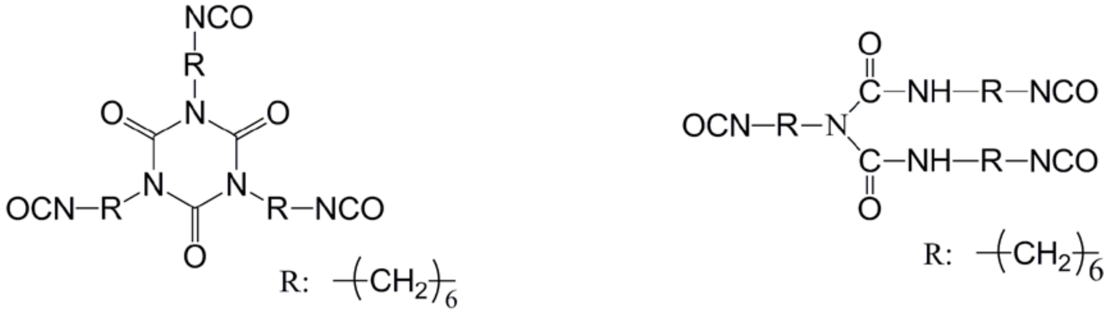


Fig. 6. Reactions between functional groups of reactive polymers and terminal groups of PLA.

Lysine triisocyanate (LTI) Lysine diisocyanate (LDI)

1,4-Phenylene diisocyanate (PDI) Methylene diphenyl diisocyanate (MDI)



1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione (Duranate TPA-100)

1,3,5-tris(6-isocyanatohexyl)biuret (Duranate 24A-100)

Fig. 7. Chemical structures of isocyanates used in compatibilization of PLA-based blends.

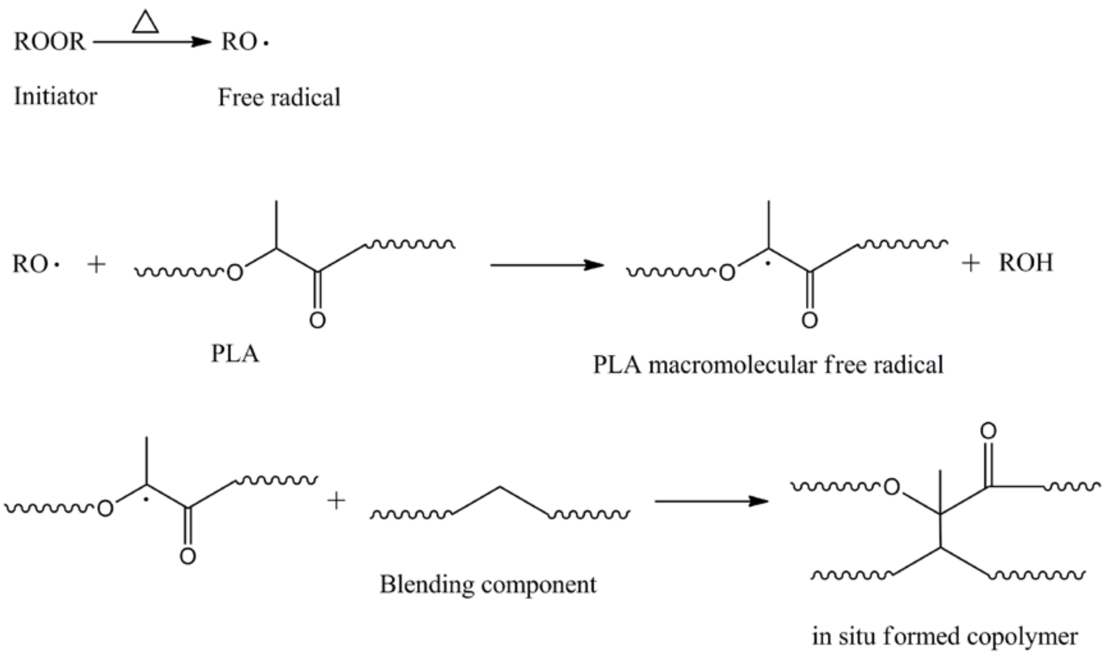


Fig. 8. Proposed reactions in compatibilization of PLA-based blends with free radical initiator.

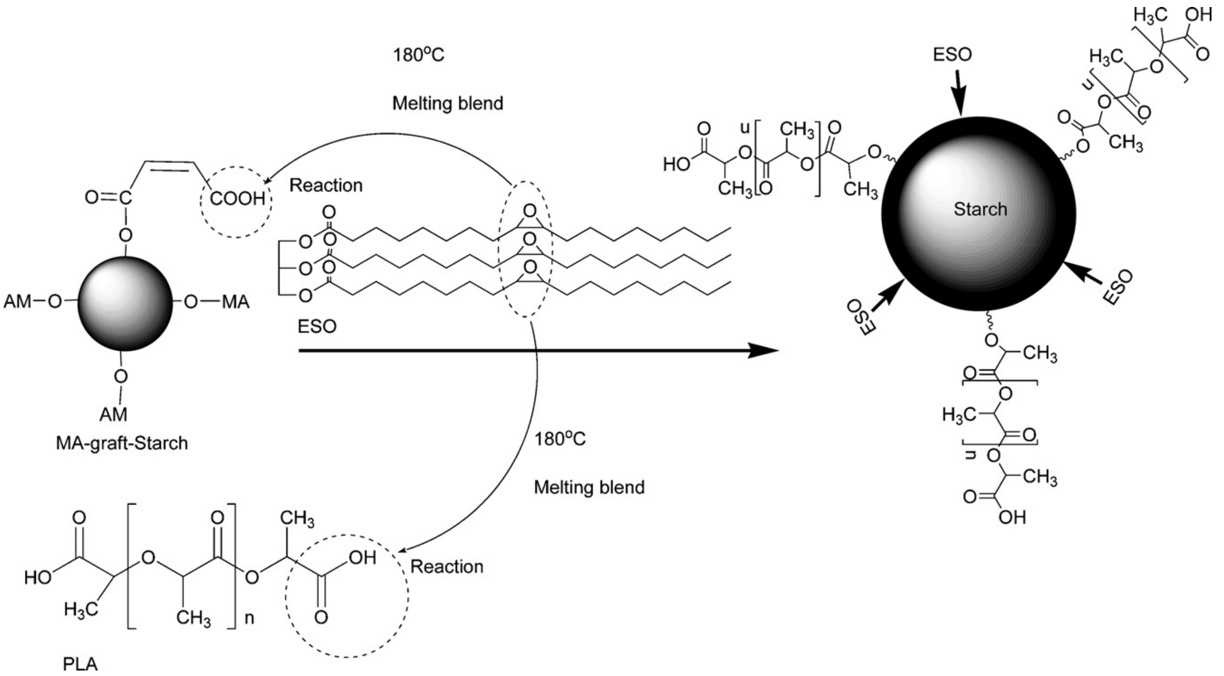


Fig. 9. Possible reaction in PLA/MGST blends compatibilized by ESO during melting blend process.

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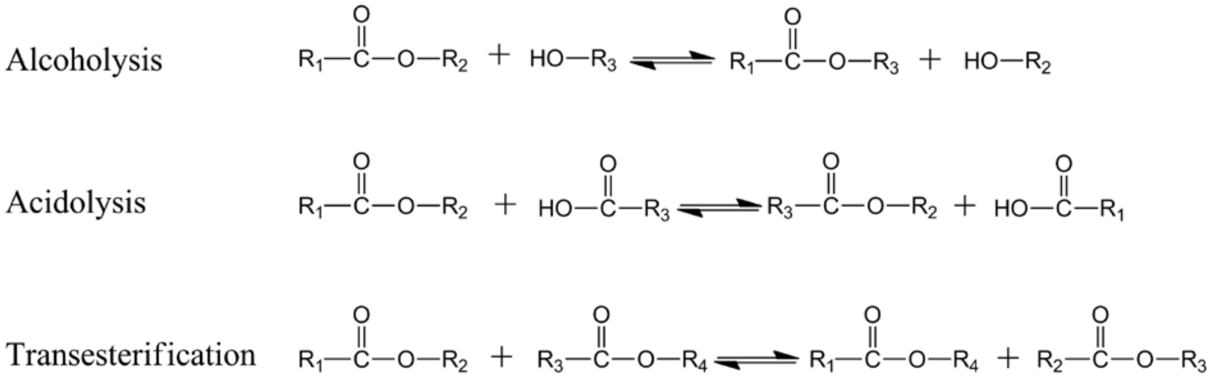


Fig. 10. Interchange reactions for compatibilization of two polyesters.

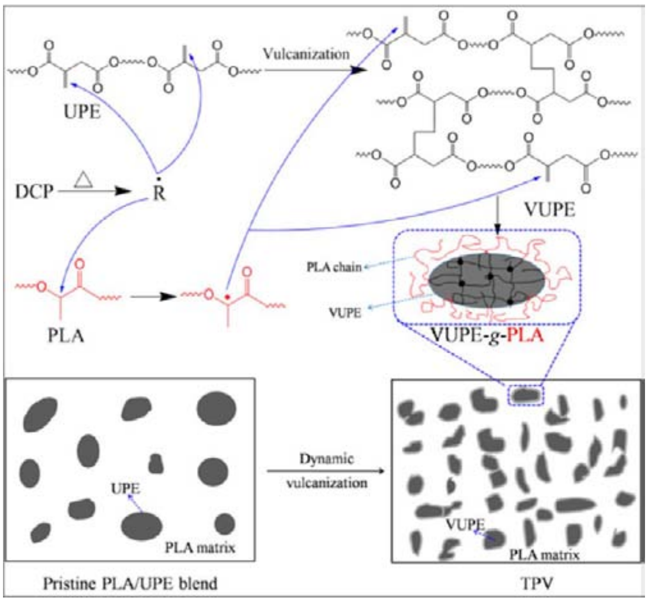


Fig. 11. Possible reactions in preparation of super-tough PLA blends with unsaturated aliphatic polyester elastomer through dynamic vulcanization and interfacial compatibilization. Reprinted with permission from ref. 135 Copyright 2014 American Chemical Society.

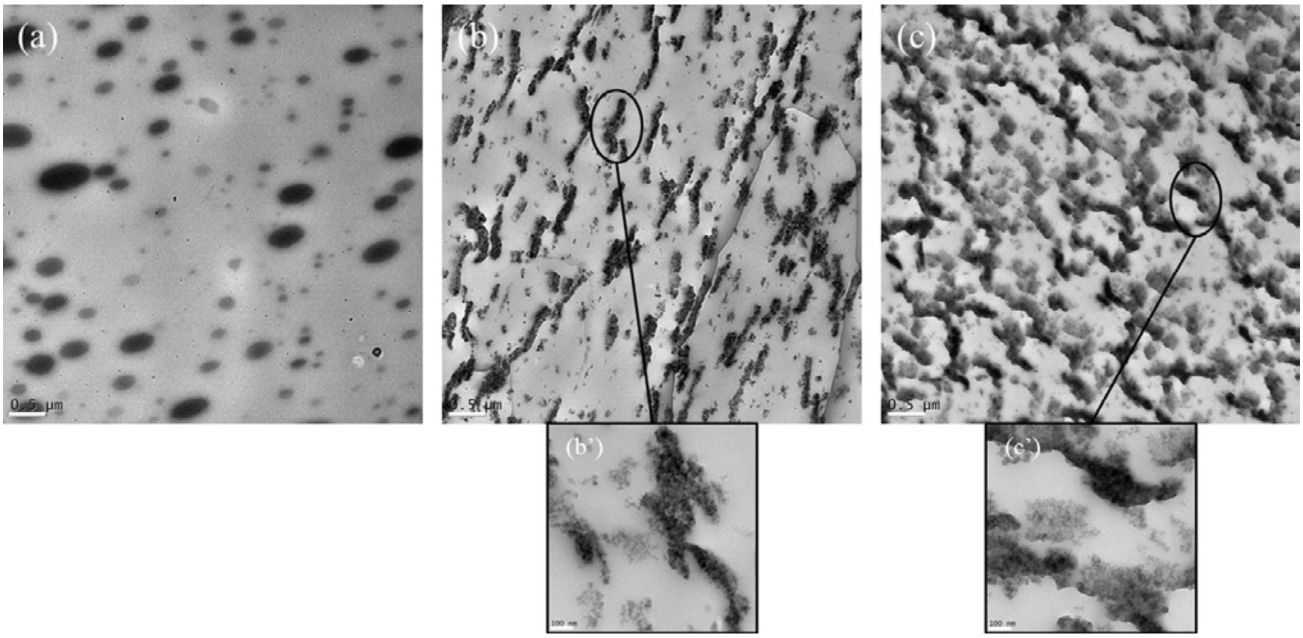
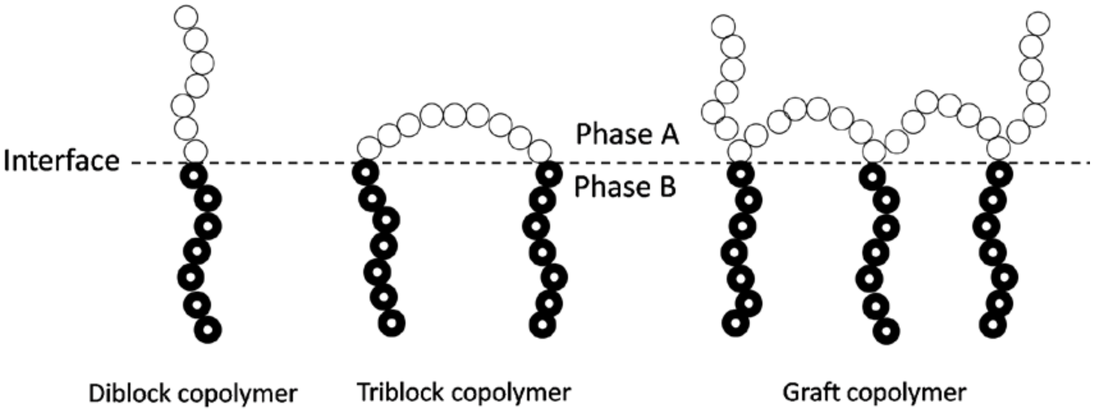


Fig. 12. TEM images of room-temperature notched surfaces of PLA-based materials containing 10 wt% of P[CL-co-LA] copolyester without silica nanoparticles (a), with 5 wt% (b and b’) and 10 wt% of silica nanoparticles (c and c’). Reprinted with permission from ref. 141 Copyright 2013 Elsevier.

Graphical Abstract



Recent compatibilization strategies in poly(lactic acid)-based blends have been reviewed in the present paper.