

# Polyblends and Composites of Poly (Lactic Acid) (PLA): A Review on the State of the Art

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## ABSTRACT

Polymers obtained from renewable sources are gaining popularity over their petroleum based counterparts in recent years due to their capability to address the environmental pollution related concerns emanating from the widespread usage of synthetic polymers. Even though the polymers from renewable sources are attractive in an environmental point of view, some of the property limitations and the high cost of these materials pose limitations for their extensive commercial applications. These aspects opened the door for a large chunk of research activities in development of polyblends and composites containing polymers from renewable sources as one of the components. Poly (lactic acid) (PLA) is one of the most discussed and commercialized polymer originated from renewable resources. Even though it has many useful properties, certain disadvantages like high brittleness, low impact resistance etc. limit the wide spread commercialization of PLA. In this review article, the recent research activities which are aimed to fill this gap by various modifications of PLA are discussed with special emphasis on the latest research advancements in the field of biodegradable and non biodegradable systems containing PLA.

**Keywords:** Poly (lactic acid); Polyblends; Composites; Modifications

## 1. Introduction

Poly (lactic acid) (PLA) is a biodegradable biopolymer produced from natural resources. It is considered as one of the most promising bio-based polymers and hence attracted the interest of researchers over the last two decades. **Figure 1** shows the tremendous increase in publications reported on PLA since year 1996.

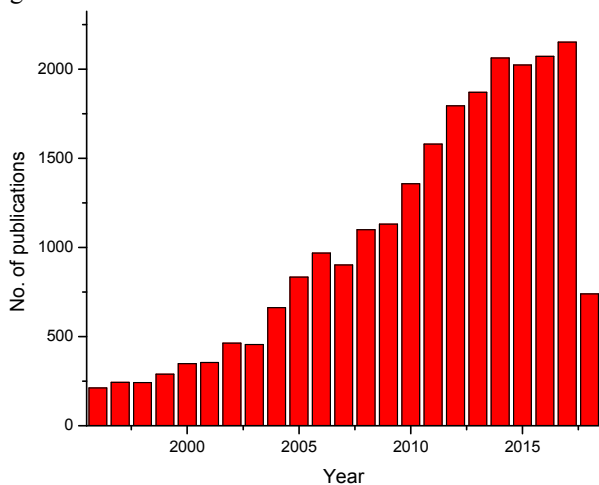
The research on PLA is truly interdisciplinary in nature with the involvement of all branches of science and technology. Scarcely an area is untouched. **Figure 2** shows the distribution of reported literatures in figure 1 into various subject areas.

PLA belongs to the family of aliphatic polyesters, for which the starting materials are  $\alpha$ -hydroxy acids. The main feedstock for PLA synthesis is lactic acid. The commercial production of lactic acid started in Japan during 1950<sup>[1]</sup>. Chemically, lactic acid is

2-hydroxypropanoic acid. Due to the presence of a chiral carbon atom in its structure, it exists in two enantiomeric forms, widely known as L-lactic acid and D-lactic acid (**Figure 3**).

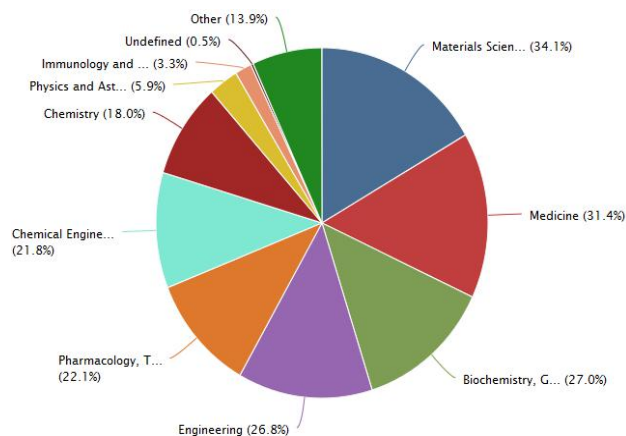
Majority of the lactic acid available in the market today is produced by bacterial fermentation of carbohydrates such as corn, sugarcane, or tapioca<sup>[2]</sup>. Other carbohydrate feedstock for the production of lactic acid includes cassava starch, lignocellulose/hemicellulose hydrolysates, cottonseed hulls, corn cobs, corn stalks, beetmolasses, wheat bran, rye flour, sweet sorghum, sugarcane pressmud, cassava, barley starch, cellulose, carrot processing waste, molasses spent wash, corn fiber hydrolysates, and potato starch<sup>[3]</sup>. Abdel-Rahman *et al*, reviewed the recent developments of fermentation processes for lactic acid production<sup>[4]</sup>.

PLA can be synthesized from lactic acid by polycondensation of lactic acid or ring-opening polymerization of lactide. The stereo chemical structure, molecular weight and crystallinity of the resulting polymer can easily be controlled by polymerizing a mixture of l and d isomers of lactic acid. Large number of literatures is available describing the synthesis of PLA from lactic acid<sup>[5-12]</sup>. The major producers of PLA include NatureWorks® LLC, Mitsui Chemicals, Dai Nippon Printing Co., Shimadzu, NEC, Toyobo, Toyota (Japan), PURAC Biomaterials, Hycail (The Netherlands), Galactic (Belgium), Cereplast (U.S.A.), FkuR, Stanelco, Biomer, Inventa-Fischer (Germany), and Snamprogetti (China)<sup>[13]</sup>. PLA can be processed by conventional plastic processing techniques such as injection molding, extrusion, blow molding, thermoforming, foaming and fiber spinning process into various articles. In addition to its biodegradability and biocompatibility, PLA exhibits good transparency and processability, which makes it a versatile polymer for several commercial as well as medical applications<sup>[10]</sup>. PLA exhibits major functional properties such as, high gloss and clarity, crimp (ability to hold a crease or fold), low temperature heat seal, low coefficient of friction and resistance to oils, which makes it a suitable candidate for packaging applications<sup>[14]</sup>. Other applications include automotive interiors, consumer electronics, sportswear, boots, coffee cups and lids, game consoles and personal protection equipments. The properties of some of the commercial grades of Corbion PLA are summarized in **Table 1**.

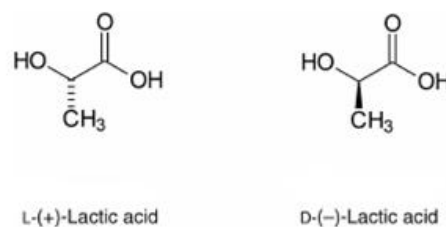


**Figure 1;** Number of articles published since 1996 based on Scopus search (accessed on 13<sup>th</sup> April 2018) using keyword

“polylactic acid”.



**Figure 2;** Distribution of reported publications in figure 1 into various fields of research (source: scopus, accessed on 13<sup>th</sup> April, 2018).



**Figure 3;** Isomers of Lactic acid (L-lactic acid and D-Lactic acid).

Properties /Grades	L 105 (Thin wall injection molding grade)	L 130 (General purpose injection molding, fibers)	L 175 (Thermoforming, fibers, films, L 175)	LX 175 (Thermoforming, fibers, films, L 175)
Density, g/cm <sup>3</sup>	1.24	1.24	1.24	1.24
Optical purity, %	>99	>99	>99	96
MFI (210°C, 2.16 kg), g/10 min	50	16	6	6
Melting temperature (T <sub>m</sub> ), °C	175	175	175	155
Glass transition temperature	57	57	57	55

re (Tm), °C				
Tensile modulus, MPa	3500	3500	3500	3500
Tensile strength, MPa	50	50	50	45
Elongation at break, %	<5	<5	<5	<5
Charpy impact strength, kJ/m <sup>2</sup>	<5	<5	<5	<5
HDT (amorphous) °C	B 55-60	55-60	55-60	55-60
HDT (crystalline) °C	B 100-110	100-110	100-110	-

**Table 1.** Properties of Corbion PLA grades (Source: <http://www.corbion.com>)

## 2. Modifications of PLA

Even though PLA exhibits several useful properties, its brittleness, susceptibility to hydrolysis, low impact resistance and low elongation at break are some of the limiting factors for widespread commercial application of this material. In order to overcome these deficiencies, several methods were developed by various researchers in this field and some of them are: i) blending with plasticizers, ii) copolymerization, iii) blending with other polymers, iv) preparing nanocomposites and v) surface modifications<sup>[15]</sup>. Preparation of blends and composites of PLA as a performance improvement technique for PLA is reviewed in detail in this article, with more emphasis on the recent developments.

## 3. Blends and composites of PLA with polyolefins

The blending of PLA with polyolefins is carried out by several researchers as a method to improve the resistance to hydrolysis and biodegradation, and also to

toughen PLA. But the main barrier in blending polyolefins with PLA is the formation of an immiscible blend due to the lack of chemical interactions between the blend components. Wang *et al.*<sup>[16]</sup> prepared solution blend of LDPE and PLA using a diblock copolymer (PE-b-PLLA) as the compatibilizer. The particle size and distribution of the dispersed phase (LDPE) was observed to decrease sharply and the mechanical properties were significantly improved with the incorporation of the diblock copolymer. Anderson *et al.*<sup>[17]</sup> carried out melt blending of linear low-density polyethylene (LLDPE) with PLA. Poly(lactide-polyethylene (PLLA-PE) block copolymers were used as compatibilizers for the blend. Young *et al.*<sup>[18]</sup> used PE-g-GMA as a reactive compatibilizer for the immiscible blend system consisting of LLDPE and PLA. For PLA matrix blends, the reactive compatibilizer reduced the domain size of the dispersed phase (LLDPE) and enhanced the tensile properties of the blend. In an attempt to improve the dyeability and resistance to biodegradation and hydrolysis of PLA, Reddy *et al.*<sup>[19]</sup> prepared polyblend fibres of PP and PLA. Polypropylene-graft-poly(methylmethacrylate)(PP-g-PMMA) graft copolymers were synthesised as effective compatibilizers for PP/PLA blends by Kaneko *et al.*<sup>[20]</sup>. Tensile and flexural strength and modulus of the PP/PLA blends were significantly improved by adding PP-g-PMMA, whereas, the compatibilizer could not succeed in improving the izod impact strength and elongation at break of the blends. Choudhary *et al.* also used Maleic anhydride grafted PP (MAH-g-PP) and glycidyl methacrylate in PLA/PP blends as reactive compatibilizers<sup>[21]</sup>. Recently, Zuzanna Donnelly patented the technology related to the blends of PLA with polyolefins<sup>[22]</sup>. Hong *et al.*<sup>[23]</sup> patented the process for the preparation of eco-friendly PP/PLA composite composition containing a compatibilizer. Rheological and mechanical properties of PP/PLA blends were characterised by Hamad *et al.*<sup>[24]</sup>. The rheological measurements showed that the true viscosity of the blends was in between the viscosity of neat PP and PLA, whereas, the mechanical properties clearly indicated the incompatibility between PP and PLA.

Polyblends of PP and PLA in the ratio 80:20 were prepared by Yoo *et al.*<sup>[25]</sup> Polypropylene-g-maleic

anhydride (PP-g-MAH). And styrene-ethylene-butylene-styrene-g-maleic anhydride (SEBS-g-MAH) were used as compatibilizers. It was reported that at 3 wt% of PP-g-MAH content, the tensile strength reached a maximum value and the tensile strength did not change appreciably even after hydrolysis. Ternary blends of PP, PLA and a toughening modifier in the ratio 60:30:10 were prepared by Lee *et al.*<sup>[26]</sup> PP-g-MAH and polyethylene-g- glycidyl methacrylate (PE-g-GMA). And a hybrid compatibilizer composed of these two were incorporated into the ternary blends in various ratios. It was reported that 3 wt% of the hybrid compatibilizer enhanced the mechanical properties of the ternary blend before and after hydrolysis. Recently, the effectiveness of ethylene-glycidyl methacrylate-methyl acrylate terpolymer(PEGMMA) as a reactive compatibilizer for PLA and PP blends (in the ratio 90:10) was reported by Xu *et al.*<sup>[27]</sup>. This compatibilization strategy resulted in reduced interfacial tension, enhancement of tensile toughness and elongation at break of the resulting polyblend system. The isothermal crystallisation process of PLA and PP blends with and without MA-g-PP was studied by Bai *et al.*<sup>[28]</sup>. It was shown that blending PLA with PP resulted in a reduction in the size of spherulites and the presence of MA-g-PP in blends of PLA with PP promoted the growth of spherulites during the crystallisation process. The effect of ethylene-butyl acrylate glycidyl methacrylate terpolymer (EBA-GMA) as a compatibilizer for 70:30 blend of PLA and PP was investigated by Kang *et al.*<sup>[29]</sup>. Based on the mechanical properties, it was shown that at 2.5 wt% of EBA-GMA, the tensile strength of the blend reached a maximum, whereas, the impact strength showed a steady increase with an increase in compatibilizer content.

Kim *et al.*<sup>[30]</sup> prepared natural-flour-filled PP/PLA bio-composites. Bamboo flour and wood flour were used as the reinforcing filler. Modifications of these natural flours were carried out by treating them with maleic anhydride-grafted PP and acrylic acid-grafted PP. Tensile and flexural strengths of biocomposites were found to improve as a result of the modification. In a similar investigation, oat hull fibre was used as reinforcement for PP/PLA based biocomposites by

Reddy *et al.*<sup>[31]</sup> They have prepared a PP/PLA (90/10) blend reinforced with 30 wt% oat hull and investigated the effect of ethylene propylene-g-maleic anhydride (EP-g-Ma) as a compatibilizer for this biocomposite. Nunez *et al.*<sup>[32]</sup> prepared PLA/PP blends compatibilized by four different grafted polymers and subsequently prepared their nanocomposites with Sepiolite. The blend containing grafted metallocene polyethylene as the compatibilizer exhibited the highest tensile toughness. The incorporation of Sepiolite into the compatibilized blend resulted in an improvement in mechanical properties, complex viscosity and storage modulus compared with similar nanocomposites containing only PLA as the matrix. Gallego *et al* synthesised three random copolymers of PLA and PE and studied their effectiveness as compatibilizers for PLA-HDPE blends<sup>[33]</sup>. The compatibilizers were prepared by three different methods: reactive extrusion, ring-opening polymerization and polycondensation of lactide with PE. The PLA-HDPE blends containing the compatibilizer prepared by ring opening polymerization of lactide with PE exhibited the highest tensile toughness. Light weight semicrystalline micro cellular plastics based on PLA/polyolefin hybrids by cold drawing technique were prepared by Xu *et al.*<sup>[34]</sup>. Rheological studies, morphological investigations using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and wide angle x-ray scattering (WAXS) techniques along with theoretical models were used by Aghjeh *et al.*<sup>[35]</sup> to quantitatively assess the microstructure of PLA/PP/organoclay nanocomposites. The investigations also revealed that the organoclay has a tendency to localize near the PLA phase. Some recent developments in the blends and composites of PLA with polyolefins, especially with PP are given in **Table 2**.

S. No.	Description of the investigation	Result	Reference
1.	Preparation of polyblend fibres of PP and PLA.	The inclusion of PP to PLA resulted in an improvement in the dyeability and resistance to biodegradation and hydrolysis of PLA.	Reddy <i>et al.</i> <sup>[19]</sup>
2.	Polypropylene-graft-poly (methyl methacrylate) (PP-g-PMMA) graft copolymers as effective compatibilizers for PP/PLA blends	Tensile and flexural strength and modulus of the PP/PLA blends were significantly improved by adding PP-g-PMMA, whereas, the compatibilizer could not succeed in improving the Izod impact strength and elongation at break of the blends.	Kaneko <i>et al.</i> <sup>[20]</sup> .
3.	Maleic anhydride grafted PP (MAH-g-PP) and glycidyl methacrylate in PLA/PP blends as reactive compatibilizers	Improved the compatibility between PP and PLA	Choudhary <i>et al.</i> <sup>[21]</sup> .
4.	The technology related to the blends of PLA with polyolefines	Patent	Zuzanna Donnelly <sup>[22]</sup> .
5.	The process for the preparation of eco-friendly PP/PLA composite composition containing a compatibilizer.	Patent	Hong <i>et al.</i> <sup>[23]</sup>
6.	Characterization of rheological and mechanical properties of PP/PLA blends.	The rheological measurements showed that the true viscosity of the blends was in between the viscosity of neat PP and PLA, whereas, the mechanical properties clearly indicated the incompatibility between PP and PLA.	Hamad <i>et al.</i> <sup>[24]</sup> .
7.	Polyblends of PP and PLA in the ratio 80:20. Polypropylene-g-maleic anhydride (PP-g-MAH) and styrene-ethylene-butylene-styrene-g-maleic anhydride (SEBS-g-MAH) were used as compatibilizers.	At 3 wt% of PP-g-MAH content, the tensile strength reached a maximum value and the tensile strength did not change appreciably even after hydrolysis.	Yoo <i>et al.</i> <sup>[25]</sup> .
8.	Ternary blends of PP, PLA and a toughening modifier in the ratio 60:30:10 PP-g-MAH and polyethylene-g-glycidyl methacrylate (PE-g-GMA) and a hybrid compatibilizer composed of these two were incorporated into the ternary blends in various ratios.	3 wt% of the hybrid compatibilizer enhanced the mechanical properties of the ternary blend before and after hydrolysis.	Lee <i>et al.</i> <sup>[26]</sup> .
9.	The effectiveness of ethylene-glycidyl methacrylate-methyl acrylate terpolymer (PEGMMA) as a reactive compatibilizer for PLA and PP blends (in the ratio 90:10)	This compatibilization strategy resulted in reduced interfacial tension, enhancement of tensile toughness and elongation at break of the resulting polyblend system	Xu <i>et al.</i> <sup>[27]</sup> .

10.	Investigation of the isothermal crystallisation process of PLA and PP blends with and without MA-g-PP	Blending PLA with PP resulted in a reduction in the size of spherulites and the presence of MA-g-PP in blends of PLA with PP promoted the growth of spherulites during the crystallisation process.	Bai <i>et al.</i> <sup>[28]</sup> .
11.	The effect of ethylene-butyl acrylate glycidyl methacrylate terpolymer (EBA-GMA) as a compatibilizer for 70:30 blend of PLA and PP	Based on the mechanical properties, it was shown that at 2.5 wt% of EBA-GMA, the tensile strength of the blend reached a maximum, whereas, the impact strength showed a steady increase with an increase in compatibilizer content.	Kang <i>et al.</i> <sup>[29]</sup> .
12.	Preparation of natural-flour-filled PP/PLA bio-composites. Bamboo flour and wood flour were used as the reinforcing filler. Modifications of these natural flours were carried out by treating them with maleic anhydride-grafted PP and acrylic acid-grafted PP.	Tensile and flexural strengths of biocomposites were found to improve as a result of the modification.	Kim <i>et al.</i> <sup>[30]</sup>
13.	Oat hull fibre as a reinforcement for PP/PLA based biocomposites. PP/PLA (90/10) blend reinforced with 30 wt% oat hull.	Investigated the effect of ethylene propylene-g-maleic anhydride (EP-g-Ma) as a compatibilizer for this biocomposite.	Reddy <i>et al.</i> <sup>[31]</sup> .
14.	PLA/PP blends compatibilized by four different grafted polymers and subsequently prepared their nanocomposites with Sepiolite.	The blend containing grafted metallocenopolyethylene as the compatibilizer exhibited the highest tensile toughness. Incorporation of Sepiolite into the compatibilized blend resulted in improvement in mechanical properties, complex viscosity and storage modulus compared with similar nanocomposites containing only PLA as a matrix.	Nunez <i>et al.</i> <sup>[32]</sup>
15.	PP/PLA blends (80/20) compatibilized by maleic anhydride-grafted PP and subsequent preparation of their nanocomposites with Halloysite nanotubes.	Dielectric analysis showed that consistent properties were shown by addition of 6 wt% of HNT to the compatibilized base blend, similar to static and dynamic mechanical properties	Rajan <i>et al.</i> <sup>[36,37]</sup>
16.	Ternary blend of PLA, liquid natural rubber (LNR) and linear low density polyethylene (LLDPE).	LNR acted as an effective compatibilizer for PLA and LLDPE and resulted in improved mechanical and thermal properties.	Bijarimi <i>et al.</i> <sup>[38]</sup>

**Table 2.** Recent literature on blends and composites of PLA with polyolefins

## 4. Blends and composites of PLA with other biodegradable materials

The main attraction for the development of blends of PLA with other biodegradable materials is the improvement of properties of PLA without compromising the biodegradability of the resulting blend system. Blends of amorphous poly(D,L-lactic acid) (PDLLA) and crystalline poly (L-lactic acid) (PLLA) was prepared by Essawy and group<sup>[39]</sup>. The preparation

was carried out in one step by melt/solid polycondensation.

### 4.1 PLA with starch

Starch is blended with PLA by various research groups in order to improve the properties of PLA. Wang *et al.*<sup>[40]</sup> prepared a blend of thermoplastic dry starch (DTPS) and PLA using maleic anhydride (MA) as a compatibilizer in presence of dicumyl peroxide using a twin screw extruder. The blend showed an improvement

in tensile properties and thermal degradation behavior compared with the individual components. Compatibility between starch and PLA is the major factor affecting the performance of the resulting blend. The various strategies adopted for compatibilizing starch/PLA blends were investigated by Schwachand and co-workers<sup>[41]</sup>. The different compatibilization routes: (i) formation of urethane linkages in situ; (ii) peroxide coupling between starch and PLA, and (iii) the addition of PLA-grafted amylose (A-g-PLA). The compatibilization efficiency was analyzed by measuring the mechanical and thermal properties of the blends. Based on the results, it was concluded that peroxide reticulation and the addition of a copolymercompatibilizer (PLA-grafted amylose) gave the best results. But the best compatibilization effect, with a significant increase (up to 60%) of the tensile strength without decrease in the elongation at break, was obtained with the copolymer (A-g-PLA). The crystallization of PLA in a PLA/starch blend system was studied by Li *et al*<sup>[42]</sup> and it was reported that crystallinity was more than 50% even at cooling rate of 80°C/minute. Thermal and physical degradation of PLA and its blends with starch and methylene diphenyl diisocyanate (MDI) was investigated by Acioli and co-workers<sup>[43]</sup>. Nanocomposite foams containing tapioca starch, PLA and nanoclay (Cloisite 30B) were prepared by Lee *et al*<sup>[44]</sup> using melt intercalation technique. Nanocomposites of thermoplastic starch (TPS) and PLA with natural montmorillonite (MMT) were prepared by Arroyo and coworkers<sup>[45]</sup> using a twin-screw extruder and the structure-property relationship of the nanocomposite was characterized to examine the use of water to enhance clay exfoliation. It was observed that the TPS can intercalate the clay structure and the clay was preferentially located in the TPS phase or at the blend interface, leading to an improvement in tensile modulus and strength and to a reduction in fracture toughness.

In another study, TPS/PLA composites were prepared by melt blending with glycerol plasticized-starch and the isothermal crystallization kinetics of TPS/PLA composites was performed by differential scanning calorimetry (DSC) at different crystallization temperatures<sup>[46]</sup>. Avrami theory, which was applied to describe the process of isothermal

crystallization, indicated that TPS acted as a nucleating agent, improving the spherulite growth rate, overall crystallization rate, and activation energy of TPS/PLA composites. Biodegradation of starch/poly(lactic acid)/poly(hydroxyester-ether) composite bars in soil was reported by Shogren and co-workers<sup>[47]</sup>, whereas, water absorption and enzymatic degradation of poly(lactic acid)/rice starch composites were investigated by research group of Yew<sup>[48]</sup>. Recently, sea water degradation of starch/PLA composite was studied by Chen *et al*<sup>[49]</sup>. Their one year long observation showed that starch particles were lost from the composite material due to microbial action and the water was acting as a plasticizer. The observed degradation rate was very slow. Biodegradation of thermoplastic starch and its blends with PLA and polyethylenewas investigated by Li *et al*<sup>[50]</sup>.

Mechanical, thermal and biodegradability properties of PLA/modified starch blends were investigated by Gao *et al* and observed that addition of 15 wt% of modified starch resulted in a decrease of melting temperature and vicat softening temperature (VST) of the blend<sup>[51]</sup>. But similar blends of PLA with maleic anhydride grafted starch (MA-g-ST) exhibited slightly improved thermal stability. Blend of PLA with MA-g-ST showed improvements in notched impact strength, elongation at break, and tensile strength and biodegradability compared with the unmodified blend system, which means MA-g-ST is suitable filler for improving the toughness of PLA. Blends of TPS and PLA with and without addition of glycidyl methacrylate grafted poly(ethylene octane) (GPOE) were prepared using Haake Mixer by Shi and co-workers<sup>[52]</sup>. They have investigated mechanical properties, morphology, thermal properties, water absorption and degradation of these binary and ternary blends. The blends showed excellent biodegradability too. Shin *et al* blended PLA with chemically modified thermoplastic starch (CMPS) using a twin-screw extruder<sup>[53]</sup>. Morphology, thermal, and mechanical properties, and biodegradability of the resulting blend was investigated. Scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) studies revealed the formation of PLA-g-starch copolymer that were formed at the interface through a transesterification reaction between PLA and CMPS,

which improved the interfacial adhesion between the blend components. It was also observed that the biodegradability of the blends increased with increasing CMPS content. Shogren *et al* studied the effect of fiber orientation on the morphology and mechanical properties of PLA/starch composite filaments<sup>[54]</sup>. It was reported that tensile strength and moduli increased with increasing draw ratio but decreased with increasing starch content. They have concluded that fiber orientation greatly increased the flexibility of PLA/starch composites.

Silva *et al*<sup>[55]</sup> incorporated wheat starch and coupling agents into poly(lactic acid) in an attempt to develop biodegradable composites. They have studied the effects of incorporating different coupling agents on the physical properties and morphology of the composites. They have observed that with the addition of 10% wheat starch and 2% MDI, blends of wheat starch/PLA exhibit tensile strength, elongation at break and impact strength properties similar to that of raw PLA and in the presence of 2% MDI and 10% glycerol, blends of PLA and starch exhibits enhanced flexibility. The role of polylactide modified with reactive anhydride groups (PLA(m)) as a compatibilizer for PLA and TPS was investigated by Swierz *et al*<sup>[56]</sup>. It was reported that the blends with the compatibilizer showed improved tensile, flexural and impact properties as compared to the composites without compatibilizer. The authors reported that the interphase interactions between the hydrogen atoms of the anhydride groups in the compatibilizer and the hydroxyl groups of the starch during the reactive extrusion process are the reason behind this property enhancement. As a result of this improved interaction between the blend components, the rate of biodegradation of the blends decreases with an increase in the content of compatibilizer.

There are various strategies to improve the compatibility of PLA with various other polymers. A detailed report on these strategies are available in the recent review article authored by Zeng *et al*<sup>[57]</sup>. In an attempt to increase the compatibility between PLA and starch, Wu *et al*<sup>[58]</sup> added glycerine into the blend system and found that the higher the glycerine content, the better the compatibility between PLA and starch. They have also tried to crosslink the starch as a strategy to improve

its compatibility with PLA and found that crosslinking greatly improved the compatibility. Yokesahachart *et al*<sup>[59]</sup> modified the thermoplastic starch by adding three different types of amphiphilic molecules and prepared binary blends of modified starch with PLA. It was found that the amphiphiles improved the processability, flowability and extensibility of the blends. Chabrat and co-workers<sup>[60]</sup> plasticized wheat flour with glycerol and blended with PLA using a twin screw extruder in presence of citric acid and water. Here, citric acid acted as a compatibilizer by promoting depolymerization of both starch and PLA. Hence its dosage has to be limited to a maximum of 2%, in order to avoid decrease in mechanical properties. Here the role of water is to minimize PLA depolymerization and to favor starch plasticization by citric acid and thus improve phase repartition. PLA was grafted onto starch nanoparticles by Garcia *et al*<sup>[61]</sup>. The reactions include three steps and the first step is protection of hydroxyl groups of PLA by benzoylation. This step is followed by activation of carboxyl groups using thionyl chloride and at last the modified PLA was grafted onto starch nanoparticles. The benzoylation step helped in decreasing the glass transition temperature ( $T_g$ ). The nano grafted PLA exhibited a slightly lower degradation temperature than that of pure PLA.

Poly(lactide)-graft-glycidyl methacrylate (PLA-g-GMA) copolymer was prepared by Liu *et al*<sup>[62]</sup> by grafting GMA onto PLA using benzoyl peroxide as an initiator. PLA-g-GMA copolymer was used as a compatibilizer for PLA/starch blends. The structure and properties of PLA/starch blends with and without PLA-g-GMA copolymer were characterized by SEM, DSC, tensile test and medium resistance test. The blend system with the compatibilizer exhibited an improvement in properties. Ouyang *et al*<sup>[63]</sup> did pre-treatment of PLA as a method to improve the compatibility between PLA and modified starch. DSC and SEM analysis were done to find the effectiveness of pretreatment and found that the pretreatment improved the compatibility of the composites. Phetwarotai and group<sup>[64]</sup> polylactide/gelatinized starch films by blending PLA with gelatinized starch in the presence of plasticizers and compatibilizer for improving interfacial bonding between two phases. Two types of



starch (corn and tapioca) were used for blending with PLA. Polyethylene glycol (PEG400) and propylene glycol (PG) were used as plasticizers and methylenediphenyldiisocyanate was used as a compatibilizer. The role of poly(ethylene glycol) (PEG) as a compatibilizer for PLA/TPS blend was studied by Favaro *et al*<sup>[65]</sup>. They have reported that incorporation of PEG resulted in the increase of PLA crystallization, improved the interfacial interaction between TPS and PLA matrix, increased the impact strength of the ternary blend whereas the elastic modulus remained similar to the PLA/TPS blend. Xue *et al*<sup>[66]</sup> also studied the effect of adding PEG into TPS/PLA blends. The addition of PEG resulted in lower  $T_g$  and  $T_m$  as well as higher MFI for the blends. It was observed that the optimum mechanical properties can be obtained for the blend system with addition of 3 wt % PEG. Li *et al*<sup>[67]</sup> studied the non isothermal crystallization kinetics of pure PLA and TPS/PLA composites by DSC. It was observed that TPS acted as a nucleating agent and improved the crystallinity of the PLA and restricted the mobility of the PLA chains. They have also used theoretical models to describe the process of non isothermal crystallization.

The effect of nanoclay on the properties of thermoplastic Starch/PLA blends were investigated in detail by Paglicawan and group<sup>[68]</sup>. Thermoplastic starch nanocomposites with different amounts of nanoclay were prepared initially and these nanocomposites were blended with PLA in presence of maleic anhydride. The mechanical properties, thermal characteristics, microstructure and water resistance of the biodegradable nanocomposite blends were studied in detail. Biodegradable films from blends of TPS and PLA plasticized with different adipate or citrate esters were prepared by Shirai and group<sup>[69]</sup>. The films were prepared by blown film extrusion process and it was concluded that adipate esters were the most effective plasticizers based on the desired mechanical properties of the films. In another study, sheets were prepared from a blend of TPS/PLA (70:30 wt/wt) by thermopressing<sup>[70]</sup>. The sheets so prepared were coated with cross-linked chitosan by two different methods: spraying and immersion. The chitosan coating reduced the water solubility and water vapor permeability of the sheets due to the hydrophobic nature of chitosan. The coated sheets

exhibited higher tensile strength than the uncoated sheets. It was concluded that coating by spraying was more effective at changing the sheet properties than coating by immersion. Xiong *et al* used tung oil anhydride (TOA) as a plasticizer for PLA/starch blends<sup>[71]</sup>. The addition of TOA improved the compatibility between starch and PLA and resulted in an enhancement of mechanical properties of the resulting blend. Epoxidised soybean oil (ESO) was used as a reactive compatibilizer for PLA and starch blend by Xiong *et al*<sup>[72]</sup>. In the beginning, starch granules were grafted with maleic anhydride to improve its reactivity with ESO. The same research group has studied the effect of castor oil (CO) on the properties of starch/PLA blend<sup>[73]</sup>. They have tried to graft hexamethylene diisocyanate (HDI) with starch in order to accumulate the CO on starch surface. The accumulation of CO on starch greatly improved the toughness and impact strength of PLA/starch blends. Zhang *et al*<sup>[74]</sup> investigated pressure-induced flow (PIF) processing as a method to produce a layer-like microstructure along the flow direction in PLA/starch blends. It was observed that impact and tensile strength can be improved by 200% and 40% respectively with the formation of layer-like microstructure. Composites of PLA with chitin nanowhiskers were prepared by Rizvi<sup>[75]</sup> and group adopting melt blending technique. The incorporation of chitin resulted in a decrease in viscosity and thermal stability of the composites. The stiffness of the composites increased with an increase in chitin content. They have also prepared a porous composite structure of these composite materials by two stage batch foaming technique. The production of microfibrillated cellulose-reinforced polylactide cellular biocomposites was described by Boissard *et al*<sup>[76]</sup>. They have used a wet mixing technique combined with supercritical carbon dioxide foaming to achieve the cellular composites. A comprehensive review by Koh *et al*<sup>[77]</sup> describes various toughening strategies for PLA/starch blends.

## 5. PLA and natural fibers

The incorporation of natural fiber to a PLA matrix leads to the development of a completely bio-based composite material. The study conducted by Graupner *et al*<sup>[78]</sup> showed that incorporation of kenaf and hemp

fibers in to PLA resulted in an improvement in tensile strength and Young's modulus values of the resulting composites. Cotton/PLA composites exhibited excellent impact properties, whereas, Lyocell/PLA composites possess improved tensile strength, Young's modulus and impact properties. Nettle fibers were used as a reinforcement for PLA by Fischer *et al*<sup>[79]</sup>. They have also compiled the effect of other fibers such as hemp, flax, jute, bamboo, kenaf and ramie as reinforcements for PLA reported by other research groups. A detailed description on the developments in the field of natural fiber reinforced PLA is available in the review article of Faruk *et al*<sup>[80]</sup>. In addition to the above mentioned fibers, they have also mentioned the use of natural and man-made cellulose fibers, coir fibers and recycled newspapers as reinforcements for PLA matrix

The influence of various natural fibers on mechanical properties and biodegradation of PLA was reviewed by Wahit and co-workers<sup>[81]</sup>. Hu *et al*<sup>[82]</sup> prepared completely biodegradable composites of PLA with hemp fibers. Effect of fiber surface treatment with alkali on the properties of the composites was also investigated. It was observed that incorporation of 40 vol% of treated fibers into PLA resulted in optimum mechanical properties of the composites. Alkali treated kenafbast fiber (KBF) was used as a reinforcement for plasticized PLA by Nor Azowa Ibrahim<sup>[83]</sup> and group. The effect of KBF surface treatment on the static and dynamic mechanical properties of the composites was studied in detail. It was observed that 4% of NaOH-treated KBF produced composites with optimum properties. Biocomposites of PLA with banana fibers were prepared by Jandas and group<sup>[84]</sup>. The surface treatment of banana fiber was carried out by NaOH and various silanes and the effect of these treatments on the properties of the composites were also investigated. Jute fiber reinforced PLA was prepared by Hongwei<sup>[85]</sup> and co-workers. They have investigated the effect of jute fiber content, processing temperature and alkali treatment on the structure and mechanical properties of jute/PLA composites. The morphology of the composite was analyzed using SEM. It was found that a fiber content of 15 wt% and a processing temperature of 210°C resulted in optimum tensile properties of the composites. Recently, Smithipong *et al.* studied the role

of pineapple leaf fiber (PALF) as reinforcement along with TPS and TPS/PLA blend as the matrices<sup>[86]</sup>. They have reported that the optimum fiber volume fraction of PALF for tensile strength improvement for TPS based composites is 8%. They have also observed that the tensile strength of TPS with PALF/PLA composite was higher than that of the TPS/PLA blend until 60 wt% of TPS. Beyond this concentration, phase reversion was observed between TPS and PLA. TPS with PALF/PLA composite gave better mechanical properties and water resistance than the TPS/PLA blend. The effect of surface treatment of sisal fibers on the properties of PLA/sisal fiber composites was studied by Jiang *et al*<sup>[87]</sup>. It was found that the mechanical properties of the fibers as well as the composites were greatly influenced by the fiber surface treatment methods. Similar studies were carried out by Zou *et al*<sup>[88]</sup> for short sisal fiber reinforced PLA. Akos *et al*<sup>[89,90]</sup> prepared blends of poly( $\epsilon$ -caprolactone) (PCL) and PLA reinforced with Dura and Tenera palm press fibers. Dicumyl peroxide (DCP) was used as compatibilizer for the blend system and resulted in good interfacial adhesion between the matrix and the reinforcements and thereby increased the mechanical properties of the composites. Flax fiber was used as a reinforcement for PLA by Oksman *et al*<sup>[91]</sup>. The composite was prepared by extrusion followed by compression molding. The properties of the composites were compared with that of PP/flax composites, which are widely used in making automobile components. The PLA/flax fiber composites showed 50% better strength compared with the PP counterpart. The SEM micrographs of the fractured surface showed that the fiber-matrix adhesion needs to be improved in order to improve the performance properties of PLA/natural fiber composites.

Flax fiber reinforced PLA composites were prepared by Alimuzzaman *et al*<sup>[92]</sup>. They have prepared fiber webs of flax and PLA fibers using an air-laying process. Prepregs were prepared from these fiber webs and subsequently these prepregs were converted to composites by compression molding. It was reported that mechanical properties of the composites were increased as the flax fiber content was increased. Also, the mechanical properties of the composites were decreased with an increase in the molding time and molding

temperature. Siengchin *et al*<sup>[93]</sup> prepared nanocomposites of PLA and woven flax fiber textiles containing nano alumina. TiO<sub>2</sub> grafted flax fibers were used as a reinforcement for PLA by Foruzanmehr *et al*<sup>[94]</sup>. The modified fibers exhibited better adhesion and bonding towards PLA and thereby resulted in a threefold improvement in the impact resistance of PLA. Also the water absorption of PLA was reduced by 18% due to the incorporation of modified flax fibers. Wu *et al*<sup>[95]</sup> prepared  $\alpha$ -cellulose short-fiber reinforced PLA composites and investigated the isothermal crystallization behavior of these composites. The crystallinity of the composites was greatly improved due to the presence of cellulose fibers. Sugarcane bagasse residues from bio-refinery processes were used as a reinforcement for the production of PLA based green composites by Wang *et al*<sup>[96]</sup>. The results proved that PLA composite with pretreated residue, in the presence of 2 % coupling agent, exhibited the optimum strength properties. The effect of fiber surface treatments on the performance properties of PLA/jute fiber composites was studied by Goriparthi *et al*<sup>[97]</sup>. In this study, Jute fibers treated with NaOH solution, permanganate acetone, benzoyl peroxideacetone solution, 3-amino propyl trimethoxysilane (silane 1) and trimethoxy methyl silane (silane 2). The tensile and flexural properties of the treated composites showed improvements compared with the un treated composites. The thermal stability of the silane treated fiber composites were higher than the un-treated fiber composites whereas, all other treatments resulted in lower thermal stability for the composites. They have shown that the fiber-matrix adhesion was better in silane 2 treated fiber composites. By comparing the SEM images of the un treated composites and silane treated composites, they have shown that the silane 2 treatment improved the fiber-matrix adhesion, and thereby resulted in an improvement of the properties of the resulting composites. A recent study by Zafar *et al*<sup>[98]</sup> describe in detail about various surface treatments and their effects on the interfacial adhesion between jute fiber and PLA.

## 6. PLA with Poly ( $\epsilon$ -caprolactone) (PCL)

Poly ( $\epsilon$ -caprolactone) (PCL) is a

completely biodegradable polyester. Combining the properties of PCL with PLA attracted interest of researchers in recent years. Reasonably good number of publications is available in this area<sup>[99-114]</sup>. Composites of poly( $\epsilon$ -caprolactone) (PCL) with PLA fibers were prepared by research group of Ju *et al*<sup>[115]</sup>. They have investigated the influence of PLA fibers on the crystallization, mechanical properties and enzymatic degradation of its composites with PCL. Salehiyan *et al.* prepared nanocomposites of PLA/PCL/montmorillonite (MMT) toughened with metallocene-catalyzed linear low-density polyethylene (mLLDPE)<sup>[116]</sup>. It was proved that 2 phr MMT resulted in improvement of properties owing to the intercalated structure of the clays. Jiao *et al*<sup>[117]</sup> designed a series of PCL/PLA multiblock copolymers by a two-step process and characterized. A block copolymer of poly(ethylene glycol) and poly(propylene glycol) was used as a compatibilizer for PLA/PCL blends by Chavalitpanya *et al*<sup>[118]</sup>. An 80:20 blend of PLA/PCL was prepared by melt blending and the block copolymer content was varied from 1-10 phr. The blend system was characterized in for morphology, mechanical and thermal properties. It was concluded that 7.5 phr of block copolymer provided a notable improvement in tensile strain at break compared to that of the neat PLA/PCL blend. Gloria *et al* describe the use of PCL/PLA blends as scaffolds for bone tissue regeneration<sup>[119]</sup>. The effect of MMT on the non-linear viscoelastic properties of PLA/PCL blends was investigated by Salehiyan *et al*<sup>[120]</sup>. Finotti *et al*<sup>[121]</sup> investigated the use of two different compatibilizers for immiscible PLA/PCL blends. The compatibilizer-1 was prepared from  $\epsilon$ -caprolactone and 1,4butanediol and compatibilizer-2 was based on  $\epsilon$ -caprolactone and an aliphatic polycarbonate. The compatibilization resulted in a marked improvement in elongation at break of the immiscible blends in comparison with the uncompatibilized blend. It was also shown that the melting temperature of PLA was not affected by the chemical structure of the compatibilizer.

## 7. PLA with Poly hydroxy butyrate (PHB)

Like PLA, PHB also belongs to the family of biodegradable polyesters and finds its application in

various areas due to its biodegradability, biocompatibility and sustainability. It is reported that both PLA and PHB are brittle at room temperature and process poor processing properties<sup>[122]</sup>. As part of improving their mechanical properties and processing characteristics, several strategies have been tried by researchers, and blending PLA with PHB is one among them. Blending of PLA with PHB has been carried out by several research groups<sup>[122-132]</sup>. These studies proved that the miscibility between PLA and PHB depends on the molecular weight of the minor component in the blend system. In case of high molecular weight blend components, PLA is immiscible with PHB in all compositions. Also it was concluded that the mechanical properties of the blends are intermediate between those of the individual blend components. The effect of processing conditions on the miscibility, crystallization, melting behavior and morphology of blends of PHB and PLA with and without poly(vinyl acetate) (PVAc) was studied by El-Hadi<sup>[133]</sup>. The results showed that PVAc can be used as an effective compatibilizer for immiscible polymer blends of PHB and PLA. Morphology, thermal properties, mechanical properties, and biodegradation behavior of PLA/PHB blends were investigated by Zhang *et al.*<sup>[134]</sup>. The results showed that blending PHB with PLA is a cost effective method to improve the mechanical properties of PLA as the 75/25 blend of PLA/PHB showed significant improvement in mechanical properties compared with pure PLA. The authors correlate this to the observation that finely dispersed PHB crystals acted as a filler and nucleating agent in PLA. A polyester plasticizer was used for PLA/PHB blend by Abdelwahab *et al.*<sup>[135]</sup> and the blend system was characterized by TGA, DSC, XRD, SEM, mechanical testing and biodegradation studies. The rheological properties and the morphology of PLA/poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) blends were studied by Gerard *et al.*<sup>[136]</sup>. Zhao *et al.* also<sup>[137]</sup> blended PHBV with PLA. They have also prepared PLA/PHBV/clay nanocomposites and applied conventional and microcellular injection-molding processes to produce solid and microcellular specimens. Bartczak *et al.*<sup>[138]</sup> prepared blends of Poly(lactide) and amorphous poly ([R,S]-3-hydroxy butyrate) for packaging applications and characterized by DSC, TGA,

SEM, WAXS, DMTA and tensile tests. The effects of PHB and talc on the non isothermal cold crystallization kinetics of PLA were investigated by Tri *et al.*<sup>[139]</sup>. They have reported a synergistic nucleating effect of PHB and talc on isothermal crystallization of PLA from the melt. The effect of plasticizer triacetine on the structure and properties of a polymer blend of PLA and PHB (85:15 blend) was investigated by Baran *et al.*<sup>[140]</sup> using high - resolution solid - state <sup>13</sup>C nuclear magnetic resonance spectra and <sup>13</sup>C spin-lattice relaxation times T<sub>1</sub>(<sup>13</sup>C).

## 8. PLA with Polyvinyl alcohol (PVOH)

Polyvinyl alcohol (PVOH) is a water soluble and biodegradable synthetic polymer. Melt blending of PLA with PVOH can give rise to a partially miscible biodegradable blend system with improved flexibility than virgin PLA<sup>[141]</sup>. However, solution blending of PVOH with PLA leads to an immiscible blend when the PLA content in the blend system is more than 60 wt%<sup>[142,143]</sup>. Molecular modeling simulations and thermodynamic approaches were utilized for predicting the compatibility of PLA/PVOH blend system by Jawalkar *et al.*<sup>[144]</sup>. Enzymatic and non-enzymatic hydrolysis of blends of PLA and PVOH were investigated by Tsuji *et al.*<sup>[145]</sup>. Use of PVOH as a compatibilizer for starch/PLA blend system was investigated by Tianyi *et al.*<sup>[146]</sup>. It was observed that above 30wt%, PVOH formed a continuous phase with starch. The optimum tensile strength of starch/PLA blends was obtained at a PVOH addition of 40 wt%. 70/30 blends of PVOH and PLA were melt spun into continuous nanofibrils of average diameter 60 nm by An Tran *et al.*<sup>[147]</sup>. The PVOH was subsequently removed from the fiber. This process produced 2D and 3D PLA textile structures suitable for scaffolds in tissue engineering. Hu *et al.*<sup>[148]</sup> prepared composite films from starch-g-PLA/PVOH. In the first step, starch-g-PLA was prepared by in situ copolymerization of starch grafted with lactic acid catalyzed with sodium hydroxide. This was then mixed with PVOH to get composite films. It was observed that the compatibility, mechanical properties and thermal stability of the composite film was improved compared with Starch/PVA film.

## 9. Conclusion

Development of sustainable materials and products from renewable resources is one of the key focus areas of global research and development. Hence modifications of presently available commercial polymers from renewable resources become one of the hot topics of research worldwide. The main aim of preparation of polyblends and composites containing PLA is to address the current drawbacks associated with processing problems and some of the performance properties of PLA. The large volume of research works focused towards the modifications of PLA by preparing blends and composites suggest that there is still scope for further studies in this area to develop more feasible methods to address the issue.

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