RECENT DEVELOPMENTS IN POLY LACTIC ACID BASED BIODEGRADABLE COMPOSITES, APPLICATIONS AND ITS LIMITATIONS

Abstract

Demand for biodegradable polymers are increasing as a result of the havocs caused by the plastics in the present environment. A shift of trend towards the bioplastics is seen in recent years, which has less impact on the environment as it can be a suitable alternative to petroleum based synthetic polymers. Poly lactic acid one of the biodegradable alternative that can be used in a wider application range. PLA based blends and composites have been developed which was found to have better properties. More innovative materials with better properties can be synthesized through nanocomposite concepts. There is a huge potential for use of these materials as carriers of drugs, additives and antimicrobials whose release can be in controlled manner, making it an active packaging. Various modern blending techniques, production of micro and nanocomposites of PLA can overcome most of the inherent drawbacks associated with the base PLA polymer. More research is yet to be focused in this field to develop cost effective PLA based alternatives having better mechanical and physical properties for complete replacement of the petroleum based polymers.

Keywords: Poly Lactic Acid, Biodegradable Composites

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I. INTRODUCTION

Packaging materials are essential to contain and protect the product from external environment. Packaging industry is mainly contributed by materials such as glass, petrochemical-based polymers, paper, metals and combinations of the above items. Among them, Plastic has dominated in all the fields due to its better properties and handling conveniences. Increased consumption of plastics made from synthetic polymers (petrochemical derived), lead to wide scale accumulation of the plastic wastes and landfill which finally ended towards so called White pollution. Most of the countries are in the verge of banning plastics, as a result of the havoc caused due to non-degradability of plastic polymers. Present trend is towards the use of bio degradable packaging materials which include Bioplastics that has less impact on the environment. It can be a suitable alternative to petroleum based synthetic polymers. These materials are biodegradable and compostable and most of them are derived of renewable sources such as starch (potato, tapioca, corn etc.), cellulose, soy protein, lactic acid etc. by the microbial fermentation process. Even though commonly known as biodegradable polymers, the degradability may be by different ways: Bioerodable (erosion due to biological activity), Photo-biodegradable (Due to light) and Hydro biodegradable (Water). Chemical structure and the composition of the developed polymer mainly decides the biodegradable nature of the polymer. Biopolymers mainly undergo degradation through on interactions with the environment, resulting in structural degradation, loss of structural and mechanical properties and production of final degraded by-products such as CO_2, water, biomass, humic materials, minerals etc. Rate of biodegradation is largely affected by the factors such as pH, humidity, temperature, oxygen concentration of the environment in contact (Zee, 2005). Poly Lactic acid is one of the widely used biodegradable polymer in the present era. This material possesses wide application range and is having comparable properties with the plastic alternatives. United States Food and Drug Administration (USFDA) has approved PLA for food packaging applications with Generally Recognized as Safe (GRAS) status. In addition to food packaging, PLA polymers are widely employed in the medical fields for developing medical implants, medical devices due to its high compatibility with the human body. Applications are growing to other fields also including environmental remediation films, service wares, plasticulture, textiles and other fibres. Various blends of PLA with both bio-degradable and non-biodegradable polymers are developed to improve the mechanical, barrier and thermal properties of the PLA.

This chapter deals with various processing and production methods used to develop the PLA based polymers and composites, biodegradability, general properties associated with the same. Applications and stability of the PLA are also reviewed in this chapter.

II. LACTIC ACID

Lactic acid is the monomer for the production of PLA, which is a low molecular weight component, with Melting and Glass transition temperatures of 175 ^{o}C and 55 ^{o}C respectively. Lactic acid (CH_3-CHOHCOOH), the base material for PLA, which is basically 2-hydroxypropionic acid is a largely available naturally occurring hydrocarboxylic acid which is water soluble (Vickroy, 1985). It can be produced either by natural fermentation or by chemical synthesis. Strong acids are used to hydrolyse lactonitrile to yield the end product by chemical synthesis which is a racemic mixture (isomers) of L and D-Lactic acid (Fig 1). Other chemical methods used for PLA synthesis include sugar degradation in presence of catalysts, propylene oxidation using nitric acid, propylene glycol oxidation, combined reaction of carbon monoxide, acetaldehyde, water conducted at high pressure and temperature (Nampoothiri et al., 2010). Interest towards natural fermentative production of Lactic acid is gaining nowadays, due to various benefits such as eco-friendliness, low production temperature, less energy consumption, cheaper, use of renewable substrates and higher product specificity (John et al., 2007). Various bacterial strains used for production of Lactic acid is given in Table 1.

Table 1: Bacterial Strains used for Lactic Acid Production

Isomer	**Prominent Yielding Bacterial Strains**
L-isomer	*Lactobacillus casei, Lactobacillus amylophilus, Lactobacillus salivarius, Lactobacilli bavaricus, Lactobacilli maltaromicus*
D-isomer	*Lactobacillus delbrueckii, Lactobacillis jensenii. Lactobacillus acidophilus*
Mixture of L and D isomer	*Lactobacillus acidophilus, Lactobacillis jensenii*

Carbon sources are essential requirement for bacterial fermentation and the selection is mostly based on cost of raw material. Sucrose, glucose, lactose, starches (potato, wheat, corn), molasses, sugar cane bagasse are commonly used as carbon sources. Various agriculture by-products such as rye flour, corn stalks, cellulose and hemicelluloses hydrolysates, beet molasses, barley starch, spent wash from molasses are also used in cost-effective production of PLA.

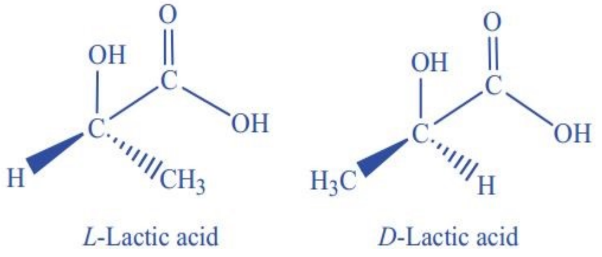


Figure 1: Stereoisomers of Lactic Acid
(Source: Xiao et al. 2012)

III. POLYLACTIC ACID (PLA)

Polylactic acid, also known by the name polylactide is a commonly used biodegradable polymer which resembles to polyolefins in their properties. It is the second most widely used bioplastic of the world. It has gained a wide attention in the recent years due to ease of processability. PLA is basically a thermoplastic, aliphatic polyester, made by condensation polymerization reaction resulting in formation of polymers with low molecular weight. Major physical properties of PLA are explained in Table 2. Credit of first PLA synthesis goes to scientists of Du Pont who made it by polymerization of lactic acid in presence of p-toluenesulfonic acid. Final PLA synthesis requires either D or L or a mixture of both components and these can form three different PLAs and a PLA mixture (Fig 2).

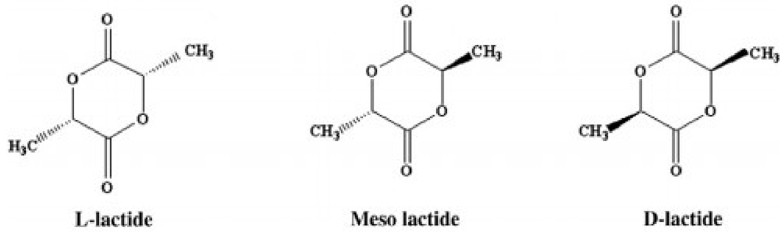


Figure 2: Different Stereoforms of PLA
(Source: Nampoothiri et al., 2010)

1. **PDLA:** Poly (D- Lactic acid): Crystalline in nature with T_g and T_m of 50-60 and 180 ^oC respectively. Chain structure is regular and remains as white powder at room temperature

2. **PLLA:** Poly (L- Lactic acid): Has a hemi crystalline structure and is having regular chain structure similar to PDLA with T_g and T_m of 55-60 and 180 ^oC. It is more biocompatible

3. **PDLLA:** PLA with both D and L isomer, amorphous structure with variable T_g and T_m

4. **Meso-PLA:** Made from the meso-lactide polymerization

All these forms of PLA are soluble in most of the organic solvents. PLA has a continuous life cycle and is explained in Figure 3.

Table 2: Physical Properties of PLA

Properties	**Values**
Glass Transition Temperature (Tg)	55-75 ^oC
Melting Temperature	164-178 ^oC. 180-184 (L-PLA)
Decomposition temperature	> 200 ^oC
Crystallinity (%)	37%
Density (g/cm^3)	1.21-1.29
Transmittance (%)	2.5
Refractive Index (20 ^oC)	1.35-1.45
Specific heat capacity (J K^{-1}Kg^{-1})	540-600
Heat of fusion (kJ mol^{-1})	146
Enthalpy of fusion (J g^{-1})	21.9-43.8
Number average molecular weight (M_n) (Dalton)	74,000-660,000
Mass average molecular weight (M_w) (Dalton)	80,000- 380,000
Polydispersity, (M_w/M_n)	1.5-3.79
Young's Modulus (MPa)	3600
Moisture absorption (%)	0.3
Melt Flow Index (MFI) (g/10 min)	3-6

Elongation at break (%)	2.4
Impact strength (kJ/m^2)	16.5
Tensile strength (MPa)	21-60
Elastic Modulus (GPa)	0.35-0.50
Ultimate strain (%)	2.5-6.0

(Source: Bastioli et al., 2005; Farah et al., 2016)

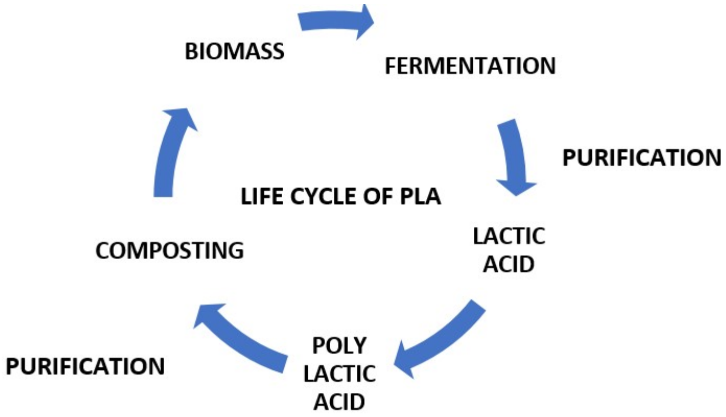
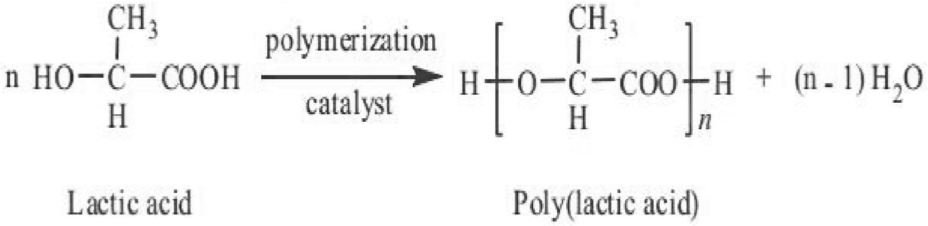


Figure 3: Life Cycle Of PLA

IV. PLA SYNTHESIS METHODS

1. **Direct Polymerization:** Polymerization occurs by self-condensation reaction which is given in Fig 4. Lactic acid is polymerized in presence of a catalyst to yield PLA.



$$n\ \mathrm{HO-\overset{\overset{\textstyle CH_3}{|}}{\underset{H}{C}}-COOH} \xrightarrow[\text{catalyst}]{\text{polymerization}} \mathrm{H}\left[\mathrm{O-\overset{\overset{\textstyle CH_3}{|}}{\underset{H}{C}}-COO}\right]_n\mathrm{H} + (n-1)\,H_2O$$

Figure 4: Direct Polymerization Synthesis
(Source: Xiao et al. 2012)

- **Solution Polycondensation:** This method involves the use of a solvent (organic) to dissolve PLA with no effect on the proceeding reaction. Major advantage by this process is the production of PLA having high molecular weight which is obtained by refluxing the reaction mixture with water (Ohta et al*.,* 1995). PLA's with MW greater than 200,000 can be yielded by this process. MW can be varied by coupling with various compounds such as peroxides, isocyanates and epoxides (Lunt et al*.,* 1998). Major drawbacks of this process are:
  - ➢ Production of low MW PLA compared to other methods leads to poor mechanical performance
  - ➢ Output of the process is low

- ➢ Reaction is uncontrollable and discolouration can happen
- ➢ Impurities from solvent may deteriorate the polymer matrix
- ➢ Induces side chain reactions like trans-esterification, racemization
- ➢ Solvent consumed during the process is an environmental threat

- **Melt Polycondensation:**This process produces polymers in the absence of solvent and so less waste generation to the environment. The polymerization is single step, economic process and requires high reaction temperature which can lead to decomposition of product. PLA produced by this process has less MW as compared to ROP produced PLA. Even though simple procedure and low synthesis cost with short reaction time, the sensitiveness to reaction conditions limits its industrial application (Gao et al., 2002).

2. **Ring-Opening Polymerization:** Disadvantages of low molecular weight PLA production by direct polymerization method can be counteracted using ROP which can yield high MW PLA. Monomer is reacted in presence of catalyst and under vacuum conditions to yield PLA. By controlling factors such as type and concentration of catalyst, temperature, time, the ratio of L and D isomer in the final product can be controlled (Auras et al. 2011). Catalysts used in the process are toxic in nature and so PLA produced by ROP is restricted for use in medical field. Purity of lactide monomer is essential to achieve a desired final product which can increase the cost. ROP reaction is given in Figure 5.

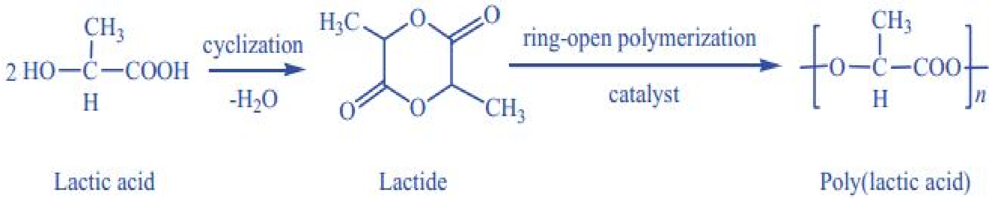


Figure 5: PLA synthesis using ROP
(Source: Xiao et al. 2012)

3. **New Solutions (Variations in Polymerization Conditions and use of New Catalysts):** Various new techniques are under development to tackle the environmental pollution that may occur due to use of heavy metal catalysts. Replacement with catalysts derived of Mg, Al, Zn, alkali metals which are non-toxic can produce high MW PLA with less pollution. Supercritical carbon dioxide (SC-CO_2) as a replacement for traditional solvent is gaining attention due to inertness, non-toxicity, non-flammability and eco friendliness of the same (Nalawade et al., 2006).

4. **Biosynthesis/Bioprocess:** The chains of PLA obtained with -COOH and -OH terminal groups are extended using a suitable complex compound HDI (Hexamethylene diisocyanate) having highly reactive functional groups (Lasparilla *et al.* 2012). Another novel technology employed is the replacement of metal catalysts with lactic acid polymerizing enzymes which can directly enable PLA biosynthesis. Implementation into industry is difficult and challenging which can be counteracted by development of microbial strains that can produce PLA. Process of biosynthesis is efficient, non-toxic,

cheaper and one step process and is explained in Fig.6. Process is slow and is in development stage. Lot of research is yet to be done to commercialise this technology.

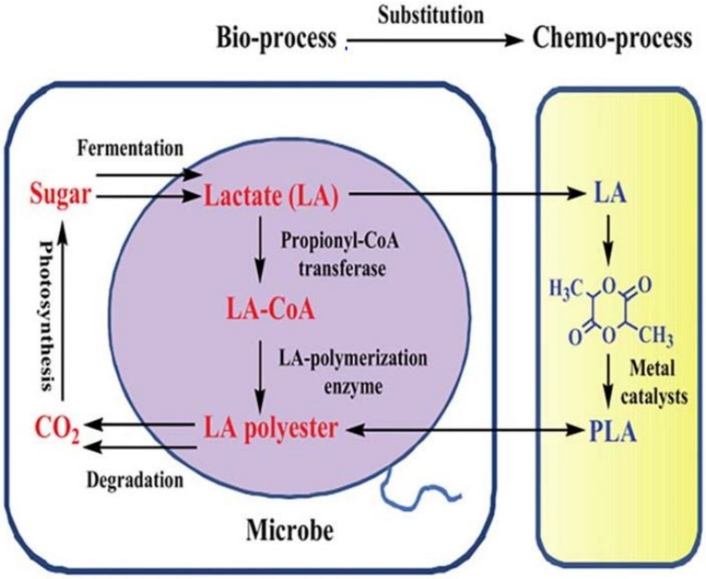


Figure 6: Biosynthesis of PLA
(Source: Siakeng et al., 2018)

V. ADVANTAGES AND DISADVANTAGES OF PLA

1. Advantages

- **Biocompatibility**: The lactic acid, which is the degradation product of PLA, is non-toxic in nature and can be completely metabolized by microorganism itself

- **Energy Savings**: The energy requirement is 25-55% lesser than that for petroleum-based polymers

- **Eco-Friendliness**: The raw materials used for production are mostly from renewable resources such as starches of corn, rice or wheat. Moreover, the PLA is compostable, biodegradable and even recyclable. Consumption of CO_2 during its production has a positive impact on environment

- **Processability**: Various processing methods such as blow molding, extrusion process, injection molding, spinning of fibres, film formation process etc. are compatible with PLA production process. PLA has higher thermal processability in comparison to other biopolymers and so has good compatibility with the process

2. Disadvantages

- **Hydrophobic Nature:** Due to its inherent hydrophobic nature (Contact angle= 80^o), polymers may swell in presence of biological fluids which is not advisable

- **Slow Degradation Rate:** Major degradation is by means of biotic (microbes) and abiotic (enzymes and hydrolysis) factors, but the reaction rate is slow, leading to a more residence time in the *in vivo* environment

- **Low Toughness:** PLA is highly brittle in nature and breaks even for an elongation <10% and so are not suitable for applications in adverse environments of high stress

- **Poor Resistance:** PLA has poor resistance towards alcohols, aromatic hydrocarbons, esters, greases and oil, halogenated hydrocarbons and ketones.

- **Lack of Side Chain Groups:** Groups associated with PLA are inert in nature and so less scope for surface modification and functionalization

VI. BIODEGRADATION OF PLA

PLA polymer is completely biodegradable in nature and it usually occurs in multiple stages. Initial degradation state consists of the conversion of PLA into LA monomers by hydrolysis through cleavage of ester bonds which is the polymer backbone. Hydrolytic cleavage reaction is given in Eqn. 1, where n, m and n+m are the number of monomer units and this reaction normally occurs in acidic conditions

$$P_{n+m} + H_2O + H^+ \leftrightarrow P_n + P_m + H^+ \tag{1}$$

This degradation is completely an abiotic process and is the major rate limiting step of the entire process. PLA solubilises in water when its MW falls below 20,000 g/mol (Gorassi and Pantani, 2013). Final degradation state is purely a biotic process which involves the action of microorganisms. Extracellular enzymes released by them directly cleaves the PLA chains and convert them into metabolic end products: Carbon dioxide, Water and some amount of biomass (Husarova et al., 2014)

Degradation of PLA starts within two weeks of composting with soil and other biomass and entire material will degrade in 3-4 weeks' time. Various factors that contribute to the rate of the reaction include MW, concentration of catalyst, temperature, pH, crystallinity and mechanical stress. Catalysts enhances the degradation rate by reduction of degradation temperature. Enzymes such as Trypsin, Lipases, Proteinase-K, PCL depolymerase, Serine proteases etc. which can cleave the ester bonds also contributes to PLA degradation in *in vivo* environment. These interactions mostly happen in the surface level leading to surface erosion as enzymes can't diffuse through the polymer matrix (Armentano et al. 2018).

VII. PLA CHALLENGES

Major challenge for PLA on industrial scale is its cost, which is high compared to other polymers with similar properties. The mechanical and barrier properties of the bio-based materials are low in comparison to the synthetic polymer alternatives. Moisture penetration is a major drawback and it can also lead to degradation of PLA by hydrolysis. Efficient barrier material needs to be included with the polymer to prevent moisture migration (Cairncross et al. 2006). PLA is found to be tougher than PS but is less compared to other common polymers such as PC and PET (Hamad et al., 2018). Brittleness of PLA mainly limits its industrial applications and the toughness can be improved by various methods including blending with tough polymers, incorporation of rubber crosslinking, plasticization block polymerization. These modifications can improve toughness but on the other hand sacrifices the strength and modulus. Comparative to other polymers, PLA has a lower thermal resistance and poor gas barrier which are drawbacks in application as a packaging material (Sinha et al., 2003).

VIII. MODIFICATIONS OF PLA

Modifications of PLA are essential to eliminate the inherent limitations of PLA such as brittleness, low impact strength, low decomposition temperature and high hydrophobicity. Modifications are mainly of two types: Bulk modification and Surface modification.

1. **Bulk Modification-** It involves modifications of bulk properties of the polymer by incorporation of additives, fillers, alteration of composition and modification of structure. Physical and chemical processes are used to achieve bulk modification.

2. **Physical Modification-** Physical modification mainly consists of three processes: Composition, Blending, Plasticization. In Composition, natural fibres or cellulosic materials are incorporated as reinforcement materials to improve or modify thermal stability and mechanical properties. Blending is a cheap, versatile method to produce new materials by combining different polymers in different proportions to achieve the desired features. Plasticization is also a bulk modification treatment with the use of low MW and volatility, high BP plasticizers such as Glycerol, PEG, etc. They have the ability to reduce T_g thereby improving softness and ductility of PLA.

3. **Chemical Modification-** Chemical modification mainly occurs by two processes: Copolymerization and Crosslinking. Copolymerization involves condensation reaction with other monomers due to the presence of functional groups such as -OH and -COOH groups. It can follow direct polymerization or ROP depending on the conditions. Crosslinking occurs in presence of additives that can act as initiators for crosslinking through chemical reactions or through irradiation technique (gamma and electron beam radiations).

4. **Surface Modification-** Modification of the surface is essential in deciding the application of the materials. Surface properties includes roughness, hardness, hydrophobicity and hydrophilicity, topography, surface energy etc. Physical methods of modification include Surface coating, Entrapment and Plasma treatment. Surface modification materials are

applied as a thin coating on to the surface in case of surface coating. Entrapment is a novel technology in which the polymer surface (PLA) is reverse swelled to trap the modifying species. Polymer without having any functional groups can also be modified using this as molecules just remain on the surface without any modification on the bulk structure. Plasma treatment involves the incorporation of hydroxyl, amino or carboxyl reactive side chain groups on to PLA main chain (Favia et al., 1998). Uniform surface modification can be achieved by this treatment, since the process is applied in controlled fashion. Plasma commonly used for treatment are of He, N and O gases. Chemical modification is by introduction of reactive side chain groups through amino lysis or hydrolysis into PLA, which further used to entrap other biomolecules.

IX. PLA BLENDS

PLA blends are normally classified into two based on the source of the blending material; PLA/Biodegradable and PLA/Non-biodegradable blends.

1. **PLA/Biodegradable Blends:** Commonly used biodegradable blending materials are Starch, PCL (Poly-ε-caprolactone), PBAT, PEG, PHB, chitosan (Sheth et al., 1997). These blends are environmentally degradable. Polycaprolactone (PCL) which is a biodegradable, elastic, low T_g polyester is one of the most widely used material to toughen PLA. Takayama and Todo (2011) reported that the addition of lysine triisocyanate (LTI) improved the impact strength of PLA/PCL blend due to crosslinking of -OH groups of PLA/PCL with isocyanate of TCI and annealing induced crystallization. Dicumyl peroxide (DCP) which can induce crosslinking in the polymer and also improves the properties of PLA/PCL blend (Semba et al., 2006).

   PLA/Starch blend is a completely biodegradable blend since both are derived out of natural resources. Major difficulty of blending PLA, which is hydrophobic, with starch is the hydrophilic nature of the latter. Pressure-induced flow processing can suitably blend the both, yielding an enhanced impact and tensile strength with formation of a layered microstructure (Zhang et al., 2013). PLA blending with thermoplastic starch blends (TPS) has been conducted by Wootthikamokkhan et al. (2012) to produce PLA-g-MTPS by two stage reaction process. Maleated thermoplastic starch (MTPS) is first developed by reaction of cassava starch in presence of maleic anhydride and glycerol, followed by grafting it into PLA by using initiator as peroxide molecule. The mechanical properties are decided by amount of starch and type. Larger peroxide content induces better grafting between PLA and MTPS thereby resulting in improvement of properties.

   PLA modified with small quantity of Methacryloylocyethyl isocyanate (MOI) was found to have dramatic improvement in the impact strength with slight reduction in Tensile strength and Young’s modulus (Chen et al., 2010). Biodegradable Polyurethane (PU) on addition at the rate of 10% to PLA improved impact strength by 75% and also elongation at break with no effect on the biocompatibility/biodegradability of PLA. Improvement in the mechanical properties of the PLA can also be achieved using additives such as polybutylene adipate-co-terephthalate (PBAT) (Jiang et al., 2006) and (Poly tetra methylene adipate-co-terephthalate (PTAT) (Liu et al., 2005). Xu et al. (2009) recently developed a blend of PLA with Thermoplastic Konjac Glucomannan (TKGM).

Due to strong interactions, for a PLA/ TKGM (20/80) blend, impact strength increased to 26.7 kJ/m^2 from 11.9 kJ/m^2 and elongation for break from 14% to 520% in comparison to plain PLA.

2. **PLA/Non-Biodegradable Blends:** A few studies are only being conducted in comparison to biodegradable blends. Even though these blends can improve the impact strength of PLA, the biodegradability of the final polymer needs to be sacrificed. Non-biodegradable blends commonly used with PLA are PVA, LDPE and PP. LLDPE which is a soft, tough plastic and has been used as a blending material to improve toughness with no effect the polymer stiffness. PLA/LLDPE polymer made by melt blending, with compatibilizer such as PLA-b-PE copolymer has higher impact resistance and strength compared to PLA polymer (Anderson et al., 2003).

PLA/PP blend has higher resistance against hydrolytic and biological degradation, improving the material properties. Various rubber components have been tried with PLA and Acrylonitrile-butadiene rubber (NBR)/PLA blend was found to have improved toughness due to its crosslinking nature. Smaller the NBR particles, larger the impact strength attained by the final product (Ishada et al., 2009).

X. PLA COMPOSITES

1. **Natural Fibre/PLA Composites:** They are eco-friendly materials derived by incorporation of naturally available fibres as reinforcement material. Even though the biodegradability of the composite is very high since reinforcement and matrix material are derived out of renewable resources, a few factors that restrict the application include:
Low degradation temperature (<200 ^{o}C)
Hydrophilic nature of fibres may attract moisture, which can degrade PLA and swelling of the composite, may distort the structure
Microbial resistance is low and so is not suitable for long storage period

Complete degradability enhanced the application of this material in the automobile industry. Major constituents of most of fibres are lignin, hemicellulose, cellulose and pectin. Most commonly used natural fibres are Kenaf, Jute, Sisal, Flax, hemp, bamboo fibres etc. (Zuza et al., 2016).

- **PLA/Kenaf:** It is one of the extensively used natural fibre. Kenaf is widely accepted as a suitable reinforcement material for polymer composites. Composite boards, Pulps for paper industry, textiles can be made out of these fibres. Pan et al. (2007) reported that incorporation of Kenaf fibres improved the storage modulus, tensile strength and even the crystallization rate. Incorporation of silane coupling agent reduced swelling of polymer in presence of water and improved heat deflection temperature and modulus (Lee et al., 2009). An optimum formulation has been identified for automobile headliners with PLA and Kenaf (50:50) with silane (3 parts). Studies conducted by Taib et al. (2012) revealed that a linear increament in tensile modulus on increase of fiber content, due to the induced reinforcement by Kenaf.

- **PLA/Jute:** Jute is considered as a cheapest bast fiber, belonging to Tiliaceae family, which is an eco-friendly substitute for synthetic fibres. As the jute fiber fraction is increased in PLA composite, an increase in modulus and tensile strength has also been found (Khondker et al., 2006). Thermal stability of these composites is improved on treatment with silane as compared to untreated ones. Due to the better interactions between the components, the abrasion resistance is improved. Trimethoxy methyl silane treatment improved the tensile strength and modulus. Fibre incorporation reduced the mobility of the polymer chain which finally resulted in increase of T_g.

- **PLA/Sisal:** Fibres extracted from sisal plant (Agave sisalana) are hard fibres, obtained by crushing of sisal leaves. These fibres inherently are durable, having good strength and less susceptible to saltwater induced deterioration. Improvements in strength and modulus of these PLA/Sisal composites are made by treatment with Caustic soda, which increased the interfacial stress transfer effectively (Bodros et al., 2007).

- **PLA/ Flax:** Composite strength has increased by about 50% on addition of Flax to PLA in comparison to composites of PP/Flax (Oksman et al., 2003). Modulus and tensile strength values are close to that of composites of Glass fiber/polyester.

- **PLA/Bamboo:** Bamboo is a cheaply available natural fibre which has low density and high mechanical strength making it suitable for flooring and building construction purposes. Fibres are extracted from evergreen woody plant. Enhancement in thermal properties and bending strength are achieved by incorporation into PLA matrix (Tokoro et al., 2008). Coupling agent commonly used is LDI (Lysine diisocyanate), which can improve the tensile strength and modulus. Elongation at break was less influenced by LDI addition. Moisture absorption of polymers was found to increase with increase in fibre content and it also reduced the degradation temperature (Lee et al., 2007). Fazita et al. (2015) reported that biodegradability of the composite is mainly depended on the conditions of composting and amount of bamboo fibre. The degradation time taken by the composite was more than pure PLA. Researchers also founded out that the recycled bio-composites from PLA/Bamboo fiber have more brittleness and decreased impact strength (Goriparthi et al., 2012).

- **PLA/Acetylated Bacterial Cellulose:** Cellulose synthesized by bacteria is modified using acetylation to prepare a stabilized cellulose. Tome et al. (2011) used mechanical compounding method to incorporate this modified cellulose into PLA matrix and found that large increments in tensile strength. Higher values of Young’s modulus and elastic modulus can be obtained by this process.

- **PLA/CMF:** Cellulose microfibrils (CMF) derived from Sisal fibres are modified using silane and incorporated with PLA which improved its impact strength by 24% (Johari et al. 2016). Iwatake et al. (2008) incorporated CMF to produce PLA based bio composites. PLA is properly mixed with CMF using a chemical solvent followed by kneading for attainment of uniform dispersibility. CMF inclusion reinforced the PLA matrix and improved both the Tensile strength and Young’s modulus. Solvent casting was used by Bulota et al. (2012) for the preparation of PLA/acetylated CMF composite. Young’s modulus remains unaffected up to 10% of CMF addition, beyond which a greater modulus and toughness has been achieved.

- **PLA/CNF**: CNF can also improve the properties of PLA if it is suitably dispersed in the matrix. Carbon nanofibrils (CNF) is hydrophilic and so is difficult to properly disperse into hydrophobic matrix. Wang et al. (2012) successfully incorporated CNF into the matrix, which improved the strength by 210% and modulus by 58%; improved the ability of polymer to withstand heavy loading.

- **PLA/CNC:** PLA composites with Cellulose Nanocrystals (CNC) has almost similar degree of crystallinity as that of the base PLA polymer. A significant increase in the rate of crystallization is achieved in presence of CNC, due to its nucleation action in the process.

2. **PLA Nanocomposites:** Nanocomposites are gaining a huge recognition in the present world due to its applicability in wide range of products. They are produced by incorporating or dispersing nanoparticles into the polymer matrix. Superior mechanical properties can be obtained with very low amount of filler compound because of its small size and higher aspect ratio. Interest of researchers and scientists is towards the production of PLA based nanocomposites and development of suitable nano fillers depending on the requirement. Usually melt processing and solvent casting techniques are commonly employed for the development of PLA based nanocomposites. Preparation of films based on the nanocomposites require extrusion process. These materials will undergo nanoscale distribution and improvements in the material properties achieved is high compared to micro and macro composites.

   - **PLA/MMT Nanocomposites:** Nanocomposites based on clay has been widely studied due to the ease of availability, cheap and reduced impact on the environment. Most widely used clay-based nano-filler is Montmorillonite (MMT) which has a higher affinity towards PLA and imparts barrier properties to the polymer. Addition of MMT as filler material under hot conditions (>60 ^{o}C), improved the elastic properties as well as thermomechanical stability which can be attributed to the interactive reactions between the -OH groups of filler and carbonyl part of PLA leading to formation of hydrogen bonds (Fukushima et al., 2012). Water absorption was also reduced due to the incorporation of Nano clay into the composite. These composites form a highly ordered and layered structure. Studies conducted by Di et al. (2005) revealed that addition of MMT to PLA reduced the recrystallization temperature (T_c) of the nanocomposite by producing large surface area and effective nucleation site, which facilitates the process of crystallization. Strong interactions between the two resulted in exfoliation of MMT which increased the sites for nucleation and improved the rate of crystallization. Large surface area and layered structure offered by MMT prevented mobility of PLA (Pluta et al., 2006). Increased addition of nano clay and its proper dispersion improved both the storage and loss modulus (Pluta et al., 2007). Incorporation of MMT modified using chitosan and CTAB cations improved compatibility with PLA and improved temperature stability and mechanical properties compared to plain PLA.

- **PLA/CNT nanocomposites:** Medical and industrial field are towards the use of Carbon Nanotube based PLA composites due to its high thermal, mechanical and electrical properties (Kaseem et al., 2017). CNT can enhance both thermal and mechanical properties significantly (Wu and Liao, 2007). Addition of even a small amount of CNT can improve the conductivity of the PLA polymer matrix which is attributed to the conductivity of Carbon nanotubes. Crystallinity can be directly influenced by addition of CNT, which improved the orderings in the structure and increased the melting temperature. CNT influences the thermal degradation (Lizundia et al., 2011) and physical aging (Lizundia et al., 2012) of PLA. The interactions between PLA and CNT can be improved using Pyrene-end-polylactide as stabilizer. Stereo complex structured PLA can be developed by incorporation of MWCNTs in small amounts into PLA in presence of heat treatment (Martinez et al., 2015).

- **PLA/CNF composites:** Cellulose nanofibrils are incorporated into PLA using chemo-mechanical treatment to form nanocomposites with PEG as compatibilizer. PEG acted as a reinforcement material, improved miscibility and interaction between PLA (hydrophobic) and CNF (hydrophilic). This improved the elongation and tensile strength by 60 % and 57% respectively (Qu et al., 2010).

- **PLA/MCC Nanocomposites:** Microcrystalline cellulose is abundant in nature and can be extracted from various renewable sources such as wood pulp (WP), wood flour (WF), biomass of oil palm. Hafiz et al. (2013) reported that incorporation of MCC into PLA did not alter the inherent chemical structure of PLA while improved thermal stability (improvement in thermal stability) and Young’s modulus. Addition also resulted in decrease in percent elongation at break and tensile strength. WP and WF were found to better MCC in terms of toughness, tensile strength and elongation at break due to the low aspect ratio of latter (Mathew et al., 2005).

- **PLA/Nanocellulose composites:** This composite material is highly suitable for the present environment since both the materials are renewable and biodegradable and are known as “Green composites”.

- **PLA/CNW Nanocomposites:** Wide gain of attraction towards these composites since the last decade due to the large availability of cellulose in nature. Cellulose is abundant in plants and can also be produced by bacterial action. Due to the strong interactive forces between the neighbouring atoms, Cellulose nanowhiskers (CNW) inherently possess better mechanical properties than other reinforcing materials. Normally CNW are incorporated into PLA matrix by solution casting method (Petersson et al., 2007). In presence of surfactant, the dispersibility of CNW in PLA is found to be high. CNW can reinforce PLA improving its tensile strength.

XI. APPLICATIONS OF PLA BASED BLENDS AND COMPOSITES

There is a huge demand across the world for replacing non-degradable plastics with degradable ones. Light weight and biocompatibility of PLA makes it suitable degradable alternative for various applications. Addition of fillers and fibres as reinforcement material improved the mechanical strength of PLA. Composites of PLA with good thermal stability are used for medical equipment manufacture such as dialysis media, stents, plates, screws, drug delivery systems, sutures and scaffolds. Biodegradability of PLA is utilized to produce disposable packaging materials for food products, single use polymers, disposable plates and loose-fill packaging. This feature is also utilized for tissue engineering which involves the regeneration of damaged cells by incorporating cells with biomaterials which can be an alternative for organ or tissue replacement. Regeneration of damaged bone can be achieved by electro spun 3D scaffolds. PLA nanocomposites can be used for delivery of drug to desired sites with less side-effects. Dosage of drug can be in the form of micro or nano particles, pellets, capsules etc. Drug release occurs by degradation of the polymer. Immobilization of drugs can be achieved by electrospinning it within the nanofibers. Lower production cost due to the introduction of modern technologies increased the applicability of PLA in various fields. Automobile industries are presently replacing plastics with PLA based green composites. Automobile parts, Electronic and electrical equipments which requires flame retardant properties, mechanically and thermally stable materials can be derived out of PLA composites. Various textile products such as disposable garments, hygiene female products, upholstery can be manufactured out of PLA. Techniques such as blending, copolymerization and plasticization can be done to improve the properties according to the requirement (Sangeetha et al., 2018).

1. **Applications of Pla in Dairy Industry:** PLA based packaging is now gaining popularity as a biodegradable polymer. These can be either blow molded into cups or can be blown into thin films. This feature enhanced the applicability of the PLA into various food industries Commercial applications have been started in the field of dairy industry. Dannon™ has developed PLA based packaging material for various dairy products. For milk and cheese, the developed packaging material was able to provide good moisture, light and gas barrier. The cups formed from the PLA were used for yoghurt packaging which were found to have good mechanical strength with barrier to gases, moisture and grease (Whiteman, 2002; Haugaard et al., 2002). Activia® by Danone, Germany has developed thermoformed cups from PLA for packaging of yoghurt since 2010. The company has claimed that the introduction of this package reduced 25% carbon foot print. Moreover, it reduced the fossil fuel usage by about 43% in comparison to the traditional package. Organic yoghurt multipack cups were developed by Stonyfield Farm® USA in 2010-11, which is found to be efficient is packaging of yoghurt. The composite packaging was composed of 93 wt% PLA, Titanium dioxide (4% wt) and additives (3% wt). This package was able to reduce about 48% if the emissions by greenhouse gases (Aguirre et al., 2016). Shrink labels has been made for cream from recycled PLA by REddi-Wip®, PAM®; ConAgra Foods, USA in 2009 (Mochal, 2009). Rigid thermoformed containers were developed by Ingeo™ fibres (PLA NatureWorks®) which was found to a suitable biodegradable container for storage of Yoghurt. They also developed rigid bottles for the packaging of short shelf-life milk (Vink et al., 2004). Yoghut cups with PLA forming the major component were developed by Cristallina/Cargill Dow® which is commercially available (Platt, 2006). PLA films incorporated with nanoclay were used for packaging of cheese and found that the incorporation of nanoclay enhanced the barrier properties of the package. The authors also suggested that crystalline PLA films will be preferable for control of moisture absorption (Plackett et al., 2006). PLA is being used as an active packaging material for release of antioxidants to the fat rich dairy products to extend the

shelf life. It is suitable for fat rich products like ice cream, butter etc. Van Aardt et al. (2007) developed BHT/BHA/α-tocopherol loaded PLA films for use in dairy products for controlled release of the antioxidants and found that the polymers did not undergo degradation on storage. The researchers found it to be suitable for use in dry milk powders, oil and fat rich products. PLA containers are suitable for milk containers as the medium pH of milk has less effect on the degradability of the PLA chains in comparison to acidic and basic pH.

2. **PLA and Antimicrobial Packaging:** Incorporation of antimicrobials into packaging materials have gained popularity as it can preserve and improve the shelf life of the food products contained. It will provide a safe and wholesome product to the consumers. Commonly incorporated antimicrobial agents in antimicrobial packaging are chelators like EDTA, lysozyme, organic acids and its salts, lactoferrin, nisin and pediocins and silver-substituted zeolites. Nisin is most widely used antimicrobial among them and also it also possesses FDA GRAS status (Joerger, 2007).

   It is essential to have controlled release of the antimicrobials into the food, which is mainly by diffusion and migration process. The process of diffusion is mainly controlled by interactions between the package and the antimicrobial substances. Direct incorporation into the polymer matrix can result in dilution of the components and loss of activity. Researchers have found that incorporation in PLA materials reduced the release of these compounds and the antimicrobials were able to maintain higher concentrations. *Listeria monocytogenes* which is a common pathogen in food, was found to be less effective in presence of the high concentration of the antimicrobial agents (Jin e al., 2009). Antimicrobial packaging developed based on PLA were using Chitosan (Torres-Ginner et al., 2006), Lysozyme (Del Nobile et al., 2009), Lactic acid and Nisin (Jin et al., 2009; Ariyapitipun et al., 1999).

3. **Stability of PLA:** PLA is solely composed of oligomers, dimers or monomers of lactic acid and so lactic acid will only be the migrant from the pure PLA blend. Various studies have been conducted by researchers on the safety of PLA in food packaging applications and have reported that it is safe in food applications. FDA has provided GRAS status for the use of PLA in food packaging (Con et al., 1995). Migration of the components can be expected during storage when packaging materials come in contact with the food. In presence of water containing environments, there are chances of decomposition of the PLA, which results in the migration of the component molecules such as oligomers, lactides and lactic acid. Studies conducted by researchers revealed that the PLA remained stable over 6 months without significant amount of migration at 40^{o}C. The migration level was found to increase, when the exposure temperature was raised to a temperature above 60^{o}C, which is its glass transition temperature (Colomines et al., 2008). Expert committee of joint FAO/WHO suggested that PLA packaging materials should be avoided in infant products (Mutsuga et al., 2008).

XII. LIMITATIONS OF PLA BASED BLENDS AND COMPOSITES

Even though PLA has been accepted as a suitable alternative for plastic as a degradable polymer in medical, packaging and automobile fields, price variations limits its applications. Cost vary depending on the source and the process used for manufacture. There is a disadvantage associated with the fillers used for fabrication due to its dispersibility and self-aggregation. Some of the fillers may undergo migration into the product when these composites are used as packaging materials. Inherent brittleness, low rigidity and tensile strength prevents the applications of PLA in harsh environments of high stresses. Incorporation of fillers can improve the impact strength but the elasticity and tensile strength may be sacrificed. Moreover, PLA blends are highly biodegradable both by abiotic (enzymes, hydrolysis) as well as biotic (microorganisms) agents which restricts its application for long term products. The production mechanisms used are slow and produces only low yield which may not suitable on industrial basis. PLA may undergo degradation on repeated usage and exposure to environment by three means: Hydrolysis, Photo degradation, Thermal degradation.

1. **Hydrolysis:** Hydrolytic reactions occur in presence of moisture, which will enhance degradation in the PLA polymer. As a result, there occurs the cleavage of the ester groups present in the main chain, which will finally release monomers and oligomers. Degradation products will catalyse the reaction further. Hydrolysis will also reduce the molecular weight of PLA, reducing its strength and other mechanical properties. Common hydrolytic reaction is given by Eqn. 2:

$$-COO + H_2O \xrightarrow{yields} - COOH + OH - \tag{2}$$

Hydrolytic degradation is one of the mechanism involved in the degradation of PLA in environment. Factors such as soil moisture, temperature and pH largely affects the degradation reaction occurring in soil.

In packaging applications, hydrolytic reactions can degrade the PLA packaging material properties. With the rise in the temperature under exposure, a faster rate of ester bond cleavage was detected (Lyu et al., 2007). Swelling problems were also found in PLA packaging used for alcoholic products. Ethanol will behave as a plasticizer and will enlarge the chain gap and increases the chain mobility. This will finally result in solvent induced crystallinity problems (Tsuji and Sumida, 2001; Sato et al., 2013; Gao et al., 2012). Packages exposed for higher and lower pH range are also critical to hydrolytic degradations as the pH will directly affect the rate of the reaction (Jung et al., 2006). These reactions are catalysed by the H_3O^+ and OH^- ions. Low pH exposure initiates the hydrolytic reaction to follow chain-end scission mechanism (Jong et al., 2001).

2. **Photo Degradation:** PLA based polymers will be exposed to various light sources such as sunlight during its application. PLA polymers are susceptible to exposure of high energy low wavelength radiations such as UV during the process of sterilization, irradiation, exposure to sunlight etc. Increased rate of degradability of PLA is due to the absorption of UV radiation at a wavelength of about 280 nm by the carbonyl groups present on the structure (Sakai and Tsutsumi, 2010). UV radiation also resulted in reduction of molecular weight of PLA. The molecular weight distribution is found to be affected by the same, which can finally result in degradation of mechanical properties,

making the material more brittle. The rate of degradation is directly related to the time of exposure (Tsuji et al., 2006; Santonja-Blasco et al., 2013).

Studies by Janokar et al. (2007) proposed two mechanisms of photo degradation that usually happens in PLA and the major degradation effects are found in the wavelengths ranging from 200 to 300 nm, mainly by UV radiation. Photolysis of the main chain occurs in one mechanism and second mechanism involves hydroperoxide formation and further induction of photo oxidation leading to release of degradation compounds including diketone end groups and carboxylic acid. UV exposure was found to reduce the glass transition temperature, crystallinity, molecular weight as well as the amount of elongation during break on exposure to different temperatures and RH (Copinet et al., 2004).

In addition to the UV exposure, the material may also be subjected to the γ-radiation on subjecting the packaging material to sterilization. Chain scission was induced by these radiations which reduced the strength of sample as well as molecular weight. These reactions are found to occur maximum in the amorphous region of the polymer (Collet et al., 1989). On exposure to the γ-radiation, scission of the ester bonds and the Hydrogen removal from the methane groups found in the main chain occurs resulting in release of free radicals which further induced degradations in the structure.

3. **Thermal Degradation:** PLA materials are susceptible to temperature induced degradations and the most of these degradations have a complex phenomenon. Major degradation products released include methyl ketone, CO_2, CO, lactide, cyclic and linear oligomers with different molecular weight and other low MW molecules (Kopinke et al., 1996). Most of the thermal induced degradations are found to be above 200°C. The reactions commonly involved are cis-elimination, non-radical and radical reactions, inter and intramolecular ester exchange (Kopinke et al., 1997). Other degradation reactions induced are intermolecular transesterification, unzipping depolymerisation and random scission (Abe et al., 2004). Degradation was detected in PLA exposed to a temperature of 270°C and acetaldehyde was formed as result of this, whose concentration increased with the rise in temperature. The thermal degradation was found to be influenced by the factors such as MW of the polymer, amount of moisture, catalysts used for polymerization, residence time within the extruder (Wachsen et al., 1997). Moreover, the presence of residual metals also enhanced the heat induced degradation of PLA. The thermal stability of the polymer can be improved by methods such as use of chain extenders and employment of end-protection. Acetylation process can provide end-protection as well and can remove the residual metals (Abe et al., 2004). Chain extenders commonly used for prevention of degradation are polycarbodiiamide (PCDI) and tris(nonylphenyl) phosphite (TNPP) (Aguirre et al., 2016).

4. **Microbial Degradation:** PLA polymers are prone to degradation by microorganisms. These microorganisms are specific to L-PLA substrate. PLA when used in food packaging are more susceptible to these degradation reactions. Microorganisms such as *Geobacillus thermocatenulatus, Brevibacillus, Amycolatopsis sp.* are able to produce protease enzyme, which degrades polymer by weight loss and production of monomers.

Bacillus sinithii, Paenibacillus amylolyticus strain and *Cryptococcus sp. strain* produces Lipase enzyme which also initiates degradation reactions (Tokiwa and Calabia, 2006).

XIII. CURRENT AND FUTURE TRENDS

Even though recent attention is being received to the field of biodegradable polymers, it is essential to develop modern materials with better properties to enhance the applicability. The newer field of applications is to be assessed, which can help to replace the traditional polymers with the environmental friendly materials. Fields such as energy, aerospace and chemical industries need to be properly explored in the future. Research should be more focused on additive materials which are best suitable with PLA and can improve the properties. CNT composites are found to be one of the attractive polymer developed and need to be applied to a wider range of fields to utilize its benefits.

More exploration is to be conducted on the application of 3D printing in the field of PLA. Through the 3D printing technologies, it is possible to develop new structures that can be suitable for medical, structural and industrial applications. Major hindering factor of the PLA usage in printing is the maintenance of the viscosity during the entire process (Taboas et al., 2013). More flexible PLA blends are found to be better materials for 3D fabrication.

Porosity of the materials are one of the essential requirements in biomedical applications. Tissue scaffolding is one among them, where pores of sub-micrometer size can be used for cell differentiation and those pores having size above micrometer size for tissue ingrowth enhancement (George et al., 2010). Suitable material with continuous morphology are ideal for fabricating the same. PLA-PS blend is one such material and more such materials needs to be explored. The blending materials, solvent and the processing conditions should be properly controlled for the development of porous materials.

PLA materials are highly susceptible to biodegradation, while those materials which are blends of non-biodegradable polymers have reduced biodegradability. This can still pose problems to the environment. Even though these blends will improve the properties of the PLA, problems of the low biodegradability need to be addressed (Singh et al., 2012). Significant researches need to be developed to obtain PLA blends with very good mechanical properties as well as biodegradability. PLAs requires high cost of production, which hinders the applicability of the material in commercial scale. Cheaper alternatives need to be identified to obtain materials of low cost to replace the plastics.

XIV. CONCLUSION

PLA can be selected as a suitable alternative for petroleum-based polymers to counteract the problems due to White pollution. Even though many challenges are associated with PLA in application on industrial basis due to its low mechanical and thermal properties in comparison to its alternatives. With less CO_2 emission levels and completely compostable nature, PLA has got a huge market potential. More innovative materials with better properties can be synthesized through nanocomposite concepts. There is a huge potential for use of these materials as carriers of drugs, additives and antimicrobials whose release can be in controlled manner, making it an active packaging. Introduction of modern blending techniques and production of micro/nanocomposites of PLA can overcome most of the drawbacks associated with it. Low scale of production, high economics of production, property limitations in comparison to the alternate plastic polymers confine their applications on to a wider scale. More attention is to be given in the field of PLA composites to enhance and promote its production and usage. Researches should be focused on developing composites with better formulation, improved production practices, reduced requirement of fossil resources and easy of production and scalability to make a favourable environment for the wide scale usage of biodegradable polymers. The distinct features and properties of the PLA will the nourish the global growth of its market and will serve the mankind in future.

XV. ABBREVIATIONS

Al- Aluminium
BP- Boiling point
CMF-Cellulose microfibrils
CNF-Cellulose nanofibrils
CNT-Carbon Nanotube
CNW - Cellulose nanowhiskers
CTAB- n-hexadecyl trimethylammonium bromide
EDTA – ethylene diamine tetra acetic acid
He-Helium
LDPE- Low density polyethylene
LLDPE- Linear low-density polyethylene
MCC- Microcrystalline cellulose
Mg- Magnesium
MMT- Montmorillonite
MTPS- Maleated thermoplastic starch
MW- Molecular Weight
N-Nitrogen
O-Oxygen
PBAT- poly (butylene adipate-*co*-terephthalate)
PC – Polycarbonate
PEG- Poly ethylene glycol
PET – Polyethylene terephthalate
PLA- Poly Lactic acid
PP- polypropylene
PVA-Poly vinyl acetate
ROP- Ring Open Polymerization
T_g- Glass transition temperature
T_m- Melting temperature
Zn-Zinc

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