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Poly(Lactic Acid) as a Biopolymer-Based Nano-Composite

Emad A. Jaffar Al-Mulla^{1,2} and Nor Azowa Bt Ibrahim¹

¹*Department of Chemistry, Faculty of Science,
Universiti Putra Malaysia, Serdang, Selangor*

²*Department of Chemistry, College of Science,
University of Kufa, An-Najaf,*

¹*Malaysia*

²*Iraq*

1. Introduction

Petrochemical-based polymer technology has created a lot of benefits to society. One of these benefits is the use of plastics in packaging. The most important factors determining rapid growth in the use of plastics in packaging industries are convenience, safety, low price and good aesthetic qualities. However, petrochemical-based polymers are produced from fossil fuel, consumed and discarded into the environment, ending up as undegradable waste. Increasing undegradable wastes are significantly disturbing and damaging the environment. Environmental specialists do not have a clear answer about dealing with these undegradable wastes yet. Incineration of these wastes produces large amounts of carbon dioxide that will contribute to global warming.

These environmental issues, created a dire need for the development of green polymeric materials, which would not involve the use of toxic and noxious component in their manufacture and could be degradable in nature. For these reasons, through the world today, the development of biodegradable materials with controlled properties has been a subject of great research challenge for the community of material scientists and engineers.

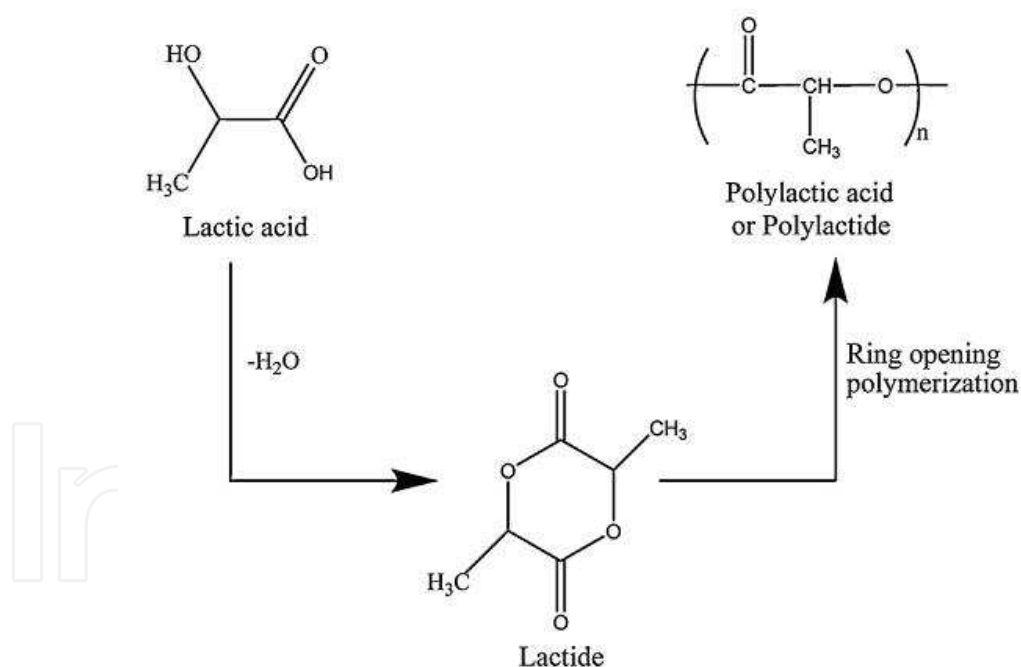
The importance of renewable products for industrial applications has become extremely clear in recent years with increasing emphasis on environmental issues such as waste disposal and depleting non-renewable resources. Renewable resources can create a platform to substitute petroleum-based polymers through innovative bio-based polymers which can compete with or even surpass existing petroleum-based materials on a cost performance basis with the added advantage of eco-friendliness. There is a growing urgency to develop and commercialize new bio based products and other innovative technologies that can reduce widespread dependence on fossil fuel and the same time would enhance national security, the environment and the economy (Miyagawa *et al.*, 2005).

Biodegradable polymers are polymers that undergo microbially induced chain scission leading to mineralization. Biodegradable polymers may not be produced from bio-source only, but it can be derived from the petroleum source (Ray and Bousmina, 2005). Efforts

have been made to improve mechanical properties by the addition of reinforcement particles or fibres to polymer matrices optimising them for engineering applications (Kulinski and Piorkowska, 2005). Flax has been considered as cost-effective alternative to glass in composites, since new technology and separation techniques have lower the cost to produce fibres that are more uniform in colour, strength, length and fineness and thus better suited to composites (Foulk *et al.*, 2004). Clay is an abundant natural mineral so it has been used as filler for rubber and plastics for many years, but its reinforcing ability is poor so it can only be used for conventional micro-composites. A new way has been found to improve the reinforcing ability of clay; clay can be chemically modified to produce clay complexes with organic monomers and polymers (Usuki *et al.*, 1993).

2. Poly(lactic acid) (PLA)

PLA is a thermoplastic aliphatic polyester, biodegradable and derived from renewable resources by means of a fermentation process using sugar from corn, followed by either ring-opening polymerization or by condensation polymerization of lactic acid (Scheme 1). It is one of the most important biocompatible and biodegradable polymers in a group of degradable plastics. In addition to its application in textile industries, automotive and clinical uses, PLA represents a good candidate to produce disposable packaging due to its good mechanical properties and processability (Murariu *et al.*, 2008).



Scheme 1. Reaction scheme to produce PLA (Linnemann *et al.*, 2003)

3. Composites

Composites are combinations of two or more materials with the properties shown by individual components. They are made to perform as a single material. Nature made the first composite in living things. Wood is a composite of cellulose fibers held together with a matrix of lignin. Most sedimentary rocks are composites of particles bonded together by

nature cement and many metallic alloys are composites of several quite different constituents. Steel reinforced concrete and medical pills are composite materials that are homogenous on a macro scale. The term composite was used in the reinforced plastic industry during the 1940s (Donald and Dominick, 1994).

4. Addition of fillers

Some polymers ignite quite easily when exposed to a flame. In particular acrylates, which are commonly used for extruded sheets or molded, paints and shellacs, are highly combustible and very difficult to render flame retardant, even with the addition of large amounts of conventional flame retardant (FR) agents, such as halogenated compounds, phosphorus and inorganic materials. Recently several groups have reported that addition of a small amount of organo-clay can significantly decrease the heat release and mass loss rate, as measured by cone calorimetry (Zanetti *et al.*, 2001; Alexandre and Dubois, 2000; Gilman *et al.*, 2000).

Clays have long been used as fillers in polymer systems because of low cost and the improved mechanical properties of the resulting polymer composites. If all other parameters are equal, the efficiency of a filler to improve the physical and mechanical properties of a polymer system is sensitive to its degree of dispersion in the polymer matrix (Krishnamoorti *et al.*, 1996). In the early 1990s, Toyota researchers (Okada *et al.*, 1990) discovered that treatment of montmorillonite (MMT) with amino acids allowed dispersion of the individual 1 nm thick silicate layers of the clay scale in polyamide on a molecular. Their hybrid material showed major improvements in physical and mechanical properties even at very low clay content (1.6 vol %). Since then, many researchers have performed investigations in the new field of polymer nano-composites. This has lead to further developments in the range of materials and synthesizing methods available.

5. Structure of clay

Natural clays such as MMT belong to the 2:1 layered silicate group (Figure 1). Their crystal lattice consists of two tetrahedral silica sheets sandwiching an edge shared octahedral sheet of either aluminium or magnesium hydroxyl. A regular Van der Waal's space between the layers, called an interlayer or gallery arises due to stacking of the layers (Alexandre and Dubois, 2000). The gallery is normally occupied by cations such as Na^+ , Ca^{2+} and Mg^{2+} . The starting clay materials are easily available and cheap. MMT is chosen as the filler due to its suitable layer charge density, high cation exchange capacity (70-150 meq/100g) and its ability to show extensive interlayer expansion.

Due to the relatively weak forces between the layers of MMT, water and other polar molecules can enter between the unit layers, causing the lattice to expand in the thickness direction. The charge deficiency on the sheet surface is typically balanced by exchangeable cations adsorbed between the unit layers and around their edges because of the substitution of ions of different valence.

X-ray was discovered in 1895 by W.K. Rontgen. After its discovery, studies of this radiation were expanded when in 1912 Laue and Friedrich found that the atoms in crystals diffracted

X-rays. This was followed by the mathematical solution of crystal structure from X-ray diffraction data in 1913 by Bragg. Since that, many applications of X-ray were found including structure determination of fine-grained materials, like soils and clays, which had been previously thought to be amorphous. Since then, crystals structures of the clay minerals were well studied (Ray and Okamoto, 2003).

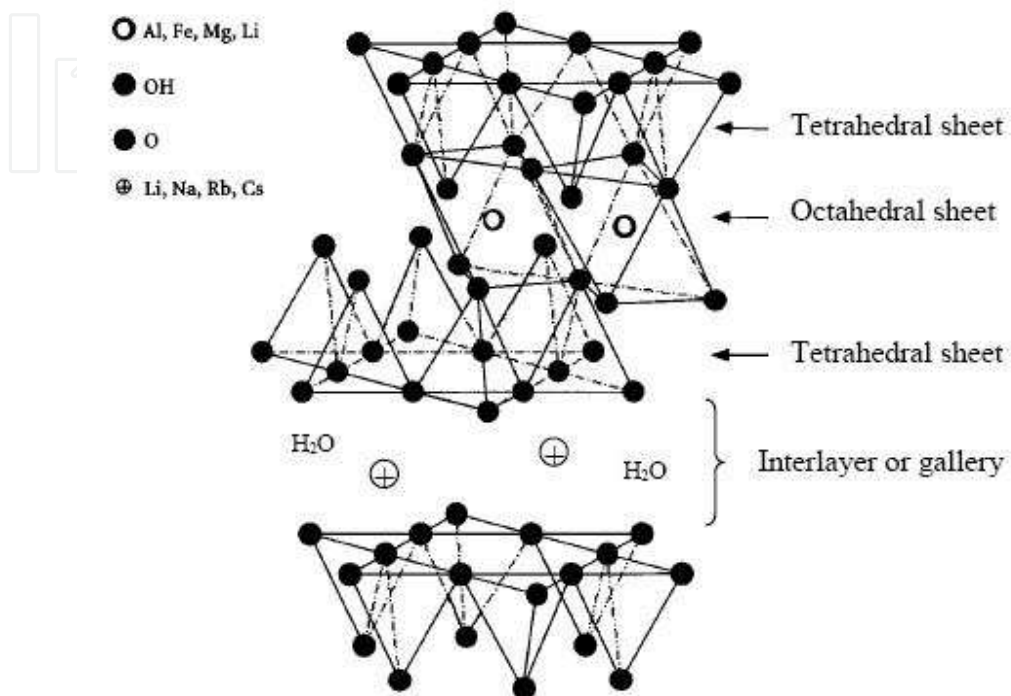


Fig. 1. Structure of 2:1 phyllosilicates (Giannelis *et al.*, 1999).

MMT, saponite and hectorite are the most commonly used layered silicates (LSs). LSs have two types of structures; tetrahedral and octahedral substituted. In the case of tetrahedrally substituted LSs, the negative charge is located on the surface of silicate layers, and hence, the polymer matrices can interact more readily with these than with octahedrally substituted material. Two particular characteristics of LSs are generally considered. The first is the silicate particles ability to disperse into individual layers. The second characteristic is modification ability for their surface chemistry through ion exchange reactions with organic and inorganic cations. These two characteristics of LSs are interrelated since the degree of dispersion of a layered silicate in a particular polymer matrix depends on the interlayer cation (Ray and Okamoto, 2003).

6. Modification of clay

MMT, and other layered silicate clays, are naturally hydrophilic. This property makes them poorly suited for mixing and interacting with most polymer matrices. Moreover, electrostatic forces hold tightly the stacks of clay platelets together. The counter ions can be shared by two platelets, resulting in stacks of platelets that are tightly held together (Giannelis, 1996).

Therefore, the clay should be modified before it can be used to make a nano-composite. After all, these stacks of clay platelets are larger than one nanometer in every dimension.

Making a composite using unmodified clay would not be a very effective use of material, because most of the clay is unable to interact with the matrix and would be stuck inside. A popular and relatively easy method of clay modification, making it compatible with an organic matrix, is ion exchange. The cations are not strongly restricted to the clay surface, so small organic cations can replace the cations present on clay (Giannelis, 1996).

If the cations were quaternary alkylammonium ions with long chains, clay would be much more compatible with an organic matrix. By exchanging sodium ions with various organic cations, MMT can be compatibilized with several different matrix polymers. They can be more easily intercalated and exfoliated because this process helps to separate the clay platelets. Nano-composites can then be formed by incorporating the intercalated or exfoliated clay in a matrix. The first commercial clay nano-composite was prepared via an ion exchanging process (Ray and Okamoto, 2003; Giannelis, 1996). Recently, many studies were reported for MMT modification using alkylammonium ions produced from vegetable oils (Al-Mulla *et al.*, 2009; Al-Mulla *et al.*, 2010a; Hoidy *et al.*, 2010a; Hoidy *et al.*, 2010b).

7. Nano-composites

Performance of polymers during use is a key feature of any composite material, which decides the real fate of products in outdoor applications. Whatever the application, there is concern regarding the durability of polymers, partly because of their useful lifetime, maintenance and replacement. The deterioration of these materials depends on the duration and extent of interaction with the environment (Homminga *et al.*, 2005).

Nano-composites (NCs) are materials that comprise a dispersion of particles of at least one of their dimensions is 100 nm or less in a matrix. The matrix may be single or multicomponent. It may include additional materials that add other functionalities to the system such as reinforcement, conductivity and toughness (Alexandre and Dubois, 2000). Depending on the matrix, NCs may be metallic (MNC), ceramic (CNC) or polymeric (PNC) materials. Since many important chemical and physical interactions are governed by surface properties, a nanostructured material could have substantially different properties from large dimensional material of the same composition (Hussain *et al.*, 2007).

8. Polymer layered-silicate nano-composites

Polymer layered-silicate clay nano-composites (PLCN) attracted lately major interests into the industry and academic fields, since they usually show improved properties with comparison by virgin polymers or their conventional micro and macro-composites. Improvements included increase in strength, heat resistance (Giannelis, 1998), flammability (Gilman, 2000) and a decrease in gas permeability (Xu *et al.*, 2001) as well as an increase in biodegradability (Sinha *et al.*, 2002).

However, the field of polymer clay silicate has only started to speed up recently, mixing the appropriate modified layered silicate with synthetic layered silicates has long been known (Theng, 1979). The interest in these materials came from two important findings, first has been reported by Toyota research group of a Nylon-6 (N6)/Na-MMT nano-composites (Okada *et al.*, 1990) where very small amounts of layered silicate loadings resulted in the improvements of thermal and mechanical properties and second the findings of Vaia *et al.* (1993) about the

possibility to melt-mix polymers with layered silicates without using organic solvents. Worldwide effort in applying this technology, as evident from using several polymer matrices such as PLA (Ljungberg *et al.*, 2005), ethylene vinyl acetate copolymer (Zanetti *et al.*, 2001), polypropylene (Kato *et al.*, 1997), polycaprolactone (Zhenyang *et al.*, 2007), ethylene propylene diene methylene (Usuki *et al.*, 2002), polymethyl methacrylate (Okamoto *et al.*, 2001), polystyrene (Meneghetti and Qutubuddin, 2006) and others.

9. Type of polymer /clay nanocomposites

Three main types of composites can be formed when the layered clay is incorporated with a polymer, as shown in Figure 2 (Alexandre and Dubois, 2000). Types of composites formed mostly depend on the nature of the components used (layered silicate, organic cation and polymer matrix) and the method of preparation.

Micro-composites are formed when the polymer chain is unable to intercalate into the silicate layer and therefore phase separated polymer/clay composites are formed. Their properties remain the same as the conventional micro-composites as shown in Figure 2(a). Intercalated nano-composite is obtained when the polymer chain is inserted between clay layers such that the interlayer spacing is expanded, but the layers still bear a well-defined spatial relationship to each other as shown in Figure 2(b). Exfoliated nano-composites are formed when the layers of the clay have been completely separated and the individual layers are distributed throughout the organic matrix as shown in Figure 2(c).

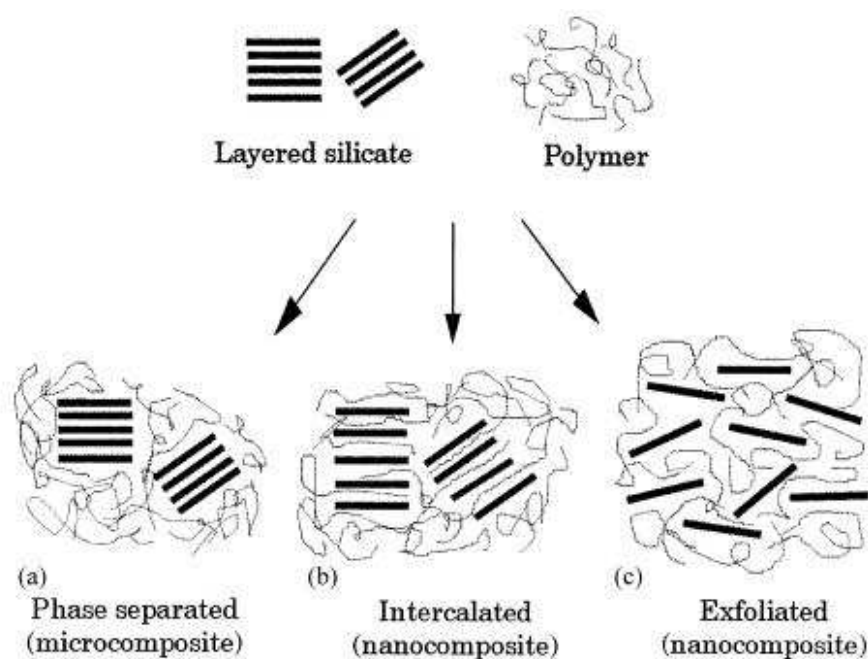


Fig. 2. Three types of composites when layered clays are incorporated with the polymer (Alexandre and Dubois, 2000)

The nano-scale structures in polymer layered-silicate nano-composites can be thoroughly characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD is used to identify intercalated structures. XRD allows quantification of changes in layer spacing and the most commonly used to probe the nano-composite structure and

occasionally to study the kinetics of the polymer melt intercalation (Ray and Bousmina, 2005). The intercalation of the polymer chains usually increases the spacing of interlayer, in comparison with the spacing of the organo-clay used and can be observed as a shift of the diffraction peak towards lower angles. The values of angle and layer spacing are being related through the Bragg's relation $\lambda = 2d \sin \theta$, where λ corresponds to the wavelength of the X-rays radiation used in the diffraction experiment, d is the spacing between diffraction planes and θ is the measured diffraction angle (Alexandre and Dubois, 2000).

On the other hand, TEM shows a qualitative understanding of the internal structure, spatial distribution of the various phases, and views of the defect structure through direct visualization (Ray and Bousmina, 2005).

10. PLA modifications

Although PLA is an eco-friendly bioplastic with good biocompatibility, poor hardness, slow degradation, hydrophobicity, and lack of reactive side-chain groups limit its application (Rasal *et al.*, 2010). Therefore, the tailoring of its properties to reach end-users demands is required. In addition, mechanical properties being better than or comparable to conventional plastics, controlled surface properties such as hydrophilicity, roughness, and reactive functionalities are the successful implementation of PLA in consumer and biomedical applications.

In recent times, blending was the main approach to improve the mechanical properties of PLA by using different plasticizers and polymers to reach desired mechanical properties. PLA, which is a glassy polymer at room temperature, has a poor elongation at break (Rasal *et al.*, 2008). Various biodegradable and non-biodegradable plasticizers were used to lower the glass transition temperature (T_g), improve processibility, and increase flexibility (Mascia *et al.*, 1992). These aspects were carried out by modification some of the plasticizer properties: polarity, molecular weight, and end groups.

Lactide is a natural choice to plasticize PLA and showed a significant increase in elongation at break (Sinclair, 1996) but undergo stiffening with time due to migration of low molecular mass lactide toward the surface (Jacobsen *et al.*, 1999). Oligomeric plasticizers that would not migrate toward the surface due to their relatively higher molecular mass were also used. Glycerol, citrate ester, polyethylene glycol, and oligomeric lactic acid were used to plasticize PLA and found that oligomeric lactic acid and low molecular mass polyethylene glycol gave finest results while glycerol was found to be the least competent plasticizer (Martin and Avérous, 2001). Citrate esters were found to be miscible with PLA at all compositions. Elongation at break was significantly improved accompanied with considerable loss of tensile yield strength (Labrecque *et al.*, 1997).

Ljungberg and Wesslén (2002) plasticized PLA using triacetin and tributyl citrate, and succeeded in lowering T_g to around 10°C at 25 wt%, after which phase separation occurred. Triacetin- or tributyl-citrate-plasticized PLA films underwent crystallization, and plasticizer molecules migrated toward the surface with storage time due to their low molecular mass (Ljungberg *et al.*, 2003). To overcome the aging problem, tributyl citrate oligomers (Scheme 2a) were synthesized by trans-esterification of tributyl citrate and diethylene glycol. However, these oligomeric tributyl citrate plasticizers also underwent

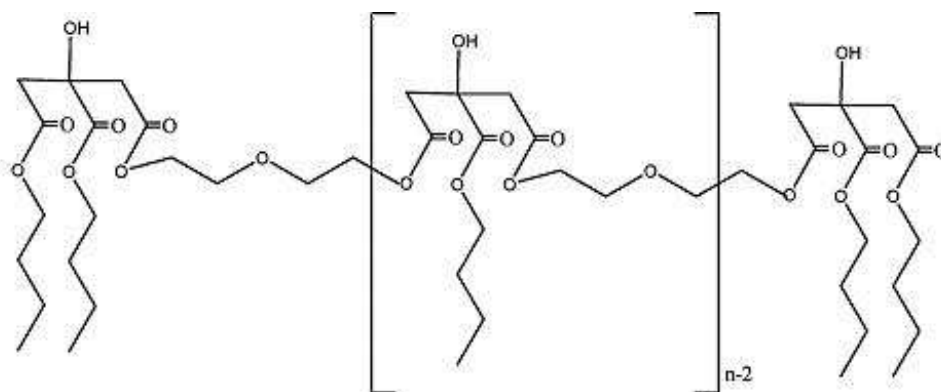
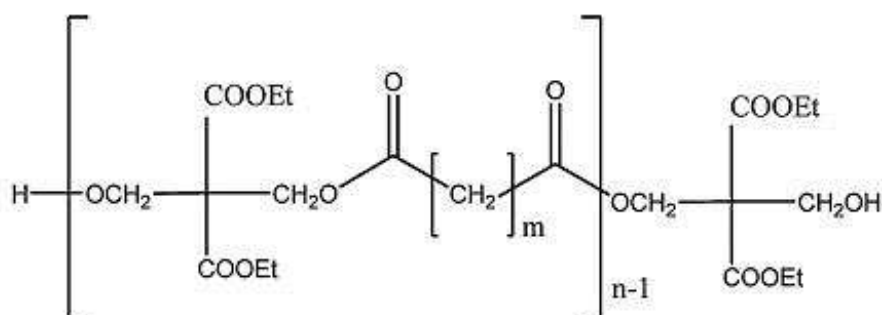
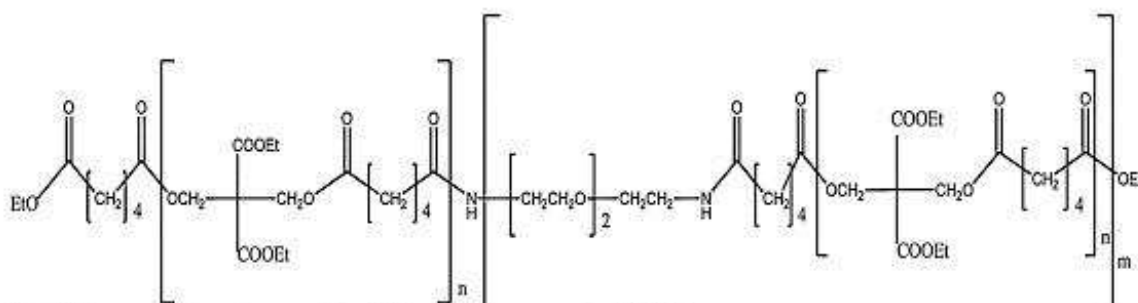
phase separation over time (Ljungberg and Wesslén, 2003). To obtain better stability, these researchers used diethyl bishydroxymethyl malonate (DBM) and its oligomer (Scheme 2b), synthesized through an esterification reaction between DBM and dichloride. When DBM alone was used as a plasticizer, it showed a tendency to phase separate and migrate toward the surface. DBM-oligomer plasticized PLA demonstrated morphological stability with storage time (Ljungberg *et al.*, 2004). Oligomeric polyesters and esteramides (Scheme 2c) have also been used to plasticize PLA, showing better plasticizing properties due to an increased number of polar amide groups (Ljungberg *et al.*, 2005).

Epoxidized oils were also used to modify PLA; Ali *et al.* (2009) reported that its use as a plasticizer to improve flexibility. Thermal and scanning electron microscope analysis revealed that epoxidized soybean oil is partially miscible with PLA. Rheological and mechanical properties of PLA/epoxidized soybean oil blends were studied by Xu and Qu (2009). Epoxidized soybean oil exhibited a positive effect on both the elongation at break and melt rheology. Al-Mulla *et al.* (2010b) also reported that plasticization of PLA (epoxidized palm oil) was carried out via solution casting process using chloroform as a solvent. The results indicated that improved flexibility could be achieved by incorporation of epoxidized palm oil.

PLA-biodegradable polymer blends were studied and extensively investigated more than PLA-non-biodegradable polymer blends due to their property improvements without compromising biodegradability. For instance, polyhydroxyalkanoates (PHA) produced by bacteria from biodegradable aliphatic homo or copolyesters with over 150 unlike kinds composed of dissimilar monomers (Steinbüchel and Lütke-Eversloh, 2003). Poly(3-hydroxy butyrate) (PHB) and its copolymers with 3-hydroxyvalerate (PHBHV), 3-hydroxyoctanoate (PHBHO), and 3-hydroxyhexanoate (PHBHHx) units are among the largely employed PHAs (Bluhm *et al.*, 1986; Doi *et al.*, 1988; Noda *et al.*, 2004). The high crystallinity of PHB homopolymer results in a hard and brittle material, inconvenient to blend with PLA.

PLA/PHBHV solvent cast blends were incompatible and showed minimal improvement in elongation at break (Iannace *et al.*, 1994). Although Takagi *et al.* (2004) found PLA/ poly(3-hydroxyoctanoate) (PHO) blends to be immiscible, they exhibited better impact toughness. PLA phase in PLA-PHBHHx blends (90%wt PLA) undergo when stored quick physical aging comes out with major toughness loss (Rasal *et al.*, 2008). A similar observation was reported for PLA/starch blends, where blends lost their toughness with physical properties (Drumright *et al.*, 2000).

PLA/polycaprolactone (PCL) is another extensively studied biodegradable PLA blend system. PCL as a rubbery polymer, has a low T_g and degrades by hydrolytic or enzymatic pathways. Broz *et al.* (2003) observed changes in modulus, elongation at break and tensile strength by blending PCL with PLA. Elongation at break increased only above 60 wt% PCL. However, the elongation at break improvement was not significant and resulted in a large modulus and tensile strength loss. The addition of a small quantity of surfactant (copolymer of ethylene oxide and propylene oxide) did not lead to any significant elongation at break improvement for PLA/PCL blends (Chen *et al.*, 2003). However, addition of a small amount of PLA-PCL-PLA tri-block copolymer (4%wt) to PLA/PCL (70/30, w/w) blends enhanced the dispersion of PCL in PLA and improved the flexibility of the resultant blend.

(a) Oligomeric tributyl citrate (Ljungberg *et al.*, 2003)(b) Oligomeric diethyl bishydroxymethyl malonate (DBM) (Ljungberg *et al.*, 2004)(c) Oligomeric ester amide (Ljungberg *et al.*, 2005)

Scheme 2. Chemical structures of oligomeric plasticizers

11. PLA/clay nano-composites

The incorporation of organo-clays in the PLA to produce a nano-composite is a means to improve PLA's mechanical properties and to accelerate its degradation rate. Different PLA/silicate nano-composites have been explored: montmorillonites and fluorohectorites clays or organo-clays, were blended with the PLA (Oliva *et al.*, 2007; Aguzzi *et al.*, 2007). Properties and the behaviour of the PLA/clays composites in aqueous environment were studied. The combination of PLA and clays, at the nano-scale, often results in remarkably improved mechanical and functional properties compared with pure PLA or conventional composites (Okamoto *et al.*, 2001). Higher modulus, increased strength and increased degradation rate in the case of biodegradable PLA have been reported.

Ogata *et al.* (1997) first prepared PLA/organoclay (OMMT) blends by dissolving the polymer in hot chloroform in the presence of dimethyl distearyl ammonium modified MMT (2C₁₈MMT). XRD results show that the silicate layers forming the clay could not be intercalated in the PLA/MMT blends, prepared by the solvent-cast method. Thus, the clay existed in the form of tactoids, consisting several stacked silicate monolayers.

These tactoids are responsible for the particular geometrical structures formation in the blends, which leads to the formation of superstructures in the thickness of the blended film. The Young's modulus of the hybrid is increased by this kind of structural feature. After that, the preparation of intercalated PLA/OMMT nano-composites with much improved mechanical and thermal properties was reported by Bandyopadhyay *et al.* (1999).

Sinha *et al.* (2002) used melt intercalation technique for the preparation of intercalated PLA/layered silicate nano-composites using octadecyl ammonium modified MMT (C₁₈MMT). Nano-composites loaded with a very small amount of PCL as a compatibilizer were also prepared in order to understand the effect of PCL on the morphology and properties of PLACNs. XRD patterns and TEM results clearly indicated that the silicate layers of the clay were intercalated, and randomly distributed in the PLA matrix. Incorporation of a very small amount of PCL as a compatibilizer in the nano-composites led to better parallel stacking of the silicate layers, and also to much stronger flocculation due to the hydroxylated edge-edge interaction of the silicate layers. Owing to the interaction between the PLA matrix and clay platelets in the presence of a very small amount of PCL, the strength of the disk-disk interaction plays an important role in determining the stability of the clay particles, and hence the enhancement of mechanical properties of such nano-composites.

In the matrix of PLA/polycaprilactone (PCL)/OMMT nano-composites, the silicate layers of the organoclay were intercalated and randomly distributed (Zhenyang *et al.*, 2007). The PLA/PCL blend significantly improved the tensile and other mechanical properties by addition of OMMT. Thermal stability of PLA/PCL blends was also explicitly improved when the OMMT content is less than 5%wt. Preparation of PLA/thermoplastic starch/MMT nano-composites have been investigated and the products have been characterized using X-Ray diffraction, transmission electron microscopy and tensile measurements. The results show improvement in the tensile and modulus, and reduction in fracture toughness (Arroyo *et al.*, 2010).

PLA/PCL-OMMT nano-composites were prepared effectively using fatty amides as clay modifier. The nano-composites shows increasing mechanical properties and thermal stability (Hoidy *et al.*, 2010c). New biopolymer nano-composites were prepared by treatment of epoxidized soybean oil and palm oil, respectively plasticized PLA modified MMT with fatty nitrogen compounds. The XRD and TEM results confirmed the production of nano-composites. The novelty of these studies is use of fatty nitrogen compounds which reduces the dependence on petroleum-based surfactants (Al-Mulla *et al.*, 2011; Al-Mulla *et al.*, 2011; Al-Mulla *et al.*, 2010c).

Plasticized PLA-based nano-composites were prepared and characterized with polyethylene glycol and MMT. It is reported that the organo-modified MMT-based composites show the possible competition between the polymer matrix and the plasticizer for the intercalation between the alumino-silicate layers (Paul *et al.*, 2002).

12. References

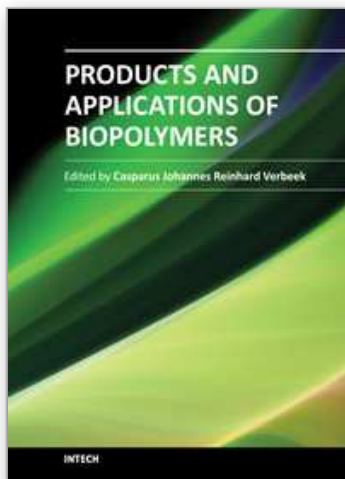
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It is interesting to consider that biopolymers are by no means new to this world. It is only because of our fascination with petrochemical products that these wonderful materials have been neglected for so long. Today we face a different challenge. Environmental pressure is pushing away from synthetic or petro-chemically derived products, while economic factors are pulling back from often more expensive "green" options. This book presents two aspects of biopolymers; potential products and some applications of biopolymers covering the current relevance of biopolymers.

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University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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