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MARIAPPAN CHIDAMBARAKUMAR

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DEVELOPMENT OF POLYLACTIC ACID (PLA) BASED BLENDS AND THEIR NANOCOMPOSITES FOR PACKAGING APPLICATIONS

By

Mariappan Chidambarakumar

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ABSTRACT

DEVELOPMENT OF POLYLACTIC ACID (PLA) BASED BLENDS AND THEIR NANOCOMPOSITES FOR PACKAGING APPLICATIONS

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Plastics packaging is one of the worst pollution menaces today. Therefore it is necessary that 'packaging should go green'. Polylactic acid (PLA), renewable resources based biodegradable polyester, is a viable alternative to many fossil-fuel based plastics. However, natural poly-l-lactic acid (PLLA) is a stiff plastic, and thus needs to be made tougher for many packaging applications. Toughening of PLLA can be achieved by blending PLLA with tough polymers. This research consists of two parts: (i) toughening of PLLA through blending with selected tough bio-polymer and (ii) fabrication of nanocomposites from selected blends and a specific organically modified montmorillonite (OMMT) clay to achieve the stiffness-toughness balance. 'Nanocomposite' is one of the best techniques to achieve the required material performances. Extrusion followed by injection molding was adopted in fabricating various samples from blends and nanocomposites. PLLA was melt compounded with several tough biodegradable polymers and a specific tough plastic (poly-(butylene adipate-co-terephthalate), PBAT) was selected for further studies. PLLA-PBAT blends of varying compositions were reinforced with OMMT clay. The blends and nanocomposites were characterized through thermo-physical and mechanical analyses. Environmental scanning electron microscopy (ESEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM) were used to study the morphology behaviors. Extrusion followed by compression molding was adopted in fabricating films for barrier property evaluations. Finally, experimental results were correlated with theoretical Halpin-Tsai model using pseudo-inclusion.

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Chapter 1 Introduction

Plastics are widely used in packaging and most of them are conventional petroleum based plastics that are very harmful to our environment. Due to their technological significance, packaging is totally dominated by these synthetic plastics like Polyethylene (PE), Polypropylene (PP), Poly (ethylene terephthalate) (PET), Polystyrene (PS), Poly (vinyl chloride) (PVC) etc. Despite their appreciable advantages over other types of packaging materials, they are made from the non-renewable resources, thus are not environmentally friendly. They are not degradable for years and even incineration emits excess of CO_2 to the atmosphere. This is also one of the reasons for the global warming. The packaging plastics wastes are growing drastically worldwide and shortage of landfills has led the plastics packaging to become one of the worst pollution menaces today. Therefore it is necessary that 'packaging should go green' and the obvious solution to this waste management of packaging would be the usage of biodegradable plastics in packaging. Biodegradable plastics are generally biodegradable from few months to 2 years under the given bioactive conditions. The growing need of the sustainable and green materials to substitute the conventional ecologically dangerous plastics led to the innovations and research works on the biodegradable plastics application in packaging. Biodegradable plastics are not new to the world or for research. They have been widely used in the biomedical applications. For example, polylactic acid (PLA) has been used in the biomedical application since 1970s. Due to their higher cost it was not considered into other applications where cheaper options were already available with conventional plastics. Now the growing awareness of protecting the environment is leading to the investment of skills and resources for the innovations & research on biodegradable plastic applications in various fields primarily in packaging [1.1-1.3].

Recently, there are many biodegradable plastics being used in the packaging applications but struggling to compete with the conventional petroleum based plastics due to their cost and performance factors. Of course, the volume of usage will definitely bring down the cost however the challenges of performances are still there from the conventional plastics. For this, there are many researches already initiated by the government as well as nongovernmental organizations worldwide to meet the performances and other application challenges from the conventional petroleum based plastics. Biodegradable plastics are derived from the renewable resources or from petroleum based nonrenewable resources or from both renewable as well as nonrenewable resources. Many of these biodegradable polymers such as, PLA, Polyhydroxy Butyrate (PHB), aliphatic-aromatic polyesters like Poly-(butylene adipate-co-terephthalate) (PBAT) & poly-(tetramethylene adipate-co-terephthalate) (PTAT), Poly (ε-caprolactone) (PCL), Polybutylene Succinate (PBS), Polyesteramide (PEA) and cellulose based polymers are making inroads into packaging. Among these, most promising biopolymer is PLA and it is widely applied in packaging applications in the forms of bottles, films, thermoform cups etc. Already many researches are underway to explore more on PLA and its applications.

PLA is made from the 100% renewable resources and it was the first bio polymer made from these resources. It requires very less energy to produce unlike the conventional polymers [1.1, 1.4]. Cargill Dow is the leading company who is pioneer in PLA technology and its applications. Thus, Cargill Dow has already started its way to prevent pollution, substitute the petroleum based feedstock with green polymers and to eliminate the use of solvents and hazardous materials. PLA is an intrinsically rigid and stiff bio-polymer whose properties depend on the % of D-Lactide contents presents in the polymer. It behaves like PET and PS in many ways and has better performances than PP and so has an ample scope of applications in packaging. Although PLA is the stiff and rigid polymer due to its high crystallinity and higher glass transition temperature (T_g) value, its brittle nature would reduce the scope of applications in packaging. So, it is very much necessary to make stiff PLA as tough just like making plasticized PVC or High impact polystyrene, and this will provide more chances for PLA to go for many applications including packaging. Toughening of PLLA can be achieved through plasticization, incorporation of its own isomers during polymerization, or blending PLA with tough polymers. Many researches are also underway in improving the toughness of Poly-l-lactic acid (PLLA) that is naturally produced in which almost 100% L-lactide monomers exists [1.1, 1.3, 1.4].

Based on these studies and researches to improve the toughness of the PLLA, it was decided to blend with a tough biodegradable polymer in optimum composition so as to improve it toughness to a required level. There are many tough biodegradable polymers like PBAT, PTAT, PBS, PCL, PEA etc already available in the market. A number of researches have already been done on these kinds of blends too. This leads us to select the suitable tough biodegradable polymer and blend in the right composition with PLLA to improve the toughness of PLLA with out adding any plasticizers.

Presently, ‘Nanotechnology’ is one of the hot research areas in which ‘Polymer Nanocomposite’ has plenty of scopes in many applications including packaging. Nanotechnology is defined as *“Technology development at the atomic, molecular, or macromolecular range of approximately 1-100 nanometers to create and use structures, devices, and systems that have novel properties”* [1.5]. Nanocor defined ‘Nanocomposite Technology’ as *“the materials and processes required to disperse nano-scale particles in plastics, metals, or ceramics”* and also defined ‘Polymer Nanocomposites’ as *“new class of plastics derived from a highly refined form of nanoclay that disperses in plastic matrix”.* So, polymer nanocomposites are the polymers that are reinforced with natural nano clay platelets (in the range of 2% to 5%) that are about 100 nm in length and 1 nm in thickness. Various natural nano scale clays are available for this nanocomposite purpose and montmorillonite is one of the most widely used ones among all.

Three kinds of polymer/clay nanocomposites can be achieved based on the clay structure and morphology in the polymer matrix and they are intercalated, intercalated and flocculated and exfoliated nanocomposites. In intercalated nanocomposites, the clay platelets got separated further each other within its agglomerate by the incorporation of polymer chains between the nano clay platelets (each single clay plate is about 1 nm in thickness) when compare to the natural or modified clay platelets. Where as, in the exfoliated nanocomposite, the nano clay platelets are well separated from each other and well dispersed across the polymer matrix uniformly in various angles. Here, surface area of clays due to the high aspect ratios will be more and so more interaction between the polymer and clay and so improvement in properties. Barrier properties are also improved due to the tortuousity created by these exfoliated clay particles across the polymer matrix. Nanocomposites can be prepared through many ways like melt compounding, in-situ polymerization, solvent casting method etc. However, melt compounding is claimed to be the better method to exfoliate the clay particles in the polymer matrix since the shear force helps in the separating the clay platelets effectively. Still, the exfoliation is not always possible to achieve and mostly intercalation of clays take place. It also depends on the hydrophilic and hydrophobic balance between the surface of the clay and that of the polymer. The nanocomposite gives better performances in terms of thermo-physical properties, mechanical properties, barrier properties etc [1.6]. Due to the exfoliation of the clay particles within the polymer matrix, it tends to increase the heat defection temperature (HDT) and coefficient of linear thermal expansion (CLTE) and also creates the tortuous path for gas / vapor molecules to pass through the polymer matrix across its thickness and so giving better barrier performances. Barrier is one of the important parameters in food and medical packaging applications. Nylon-6 was the first plastic to be used for its nanocomposites that leads the way to other plastic and various other polymers were tried for the nanocomposites [1.7]. However, few biodegradable polymers were prepared for their nanocomposites and many researches were already done with PLA based nanocomposites. Mohanty et al has already provisionally applied for a US patent on "Biodegradable Polymeric Nanocomposite Packaging Materials and Production Methods" [1.8].

PLLA is yet to compete with the conventional plastic due to its higher cost and its moderate performance. PLLA is blended with a tough biopolymer to improve its toughness while there may be some reduction in the strength and modulus. However, to maintain the stiffness-toughness balance, nanocomposite method is used; since incorporation of nano-clay will improve the strength and modulus while improving the barrier properties provided the right exfoliation takes place in the polymer matrix. To achieve this, we decided to use specific organically modified montmorillonite (OMMT) nano-clay with more hydrophobicity since PLLA resins are hydrophilic in nature and also that will maintain the hydrophilic-hydrophobic balance in the polymer blended matrix. This OMMT clay is organophilic and so better chances of mixing with the polymer like PLLA that is also organophilic in nature. Not many researches are done with any biopolymer blend based nanocomposite. Hence, from the above finalized right blend composition, the nanocomposite for the same would be prepared through the melt compounding process to achieve the required performances.

Thus, the objectives are derived as:

"To develop a passive bio-degradable packaging material by utilizing nano composite technology with optimized Poly L- Lactic Acid (PLLA) based blend with a suitable flexible/tough biodegradable polymer without using any compatibilizer."

This objective will be achieved in the three phases of activities. In the first phase, PLLA will be melt compounded with the tough biodegradable polymers such as, PBAT, PTAT, PBS, PCL and PEA in 50:50 (wt %) compositions and will be evaluated for their thermo-physical and mechanical behaviors to choose the suitable tough biodegradable polymer.

In the second phase, with the above selected tough biodegradable polymer blend partner, different blend compositions would be melt compounded and optimized for the right compositions based on their mechanical and thermo-physical properties. Hence the significance of the blending here is to improve the toughness of the stiff biopolymer that is PLLA.

In this third phase, from the above selected blend compositions, nanocomposites of the same will be prepared with specific OMMT clay and evaluated for the mechanical, thermo-physical and barrier properties. Then the optimized nanocomposite formulation will be evaluated for the structural and morphology analyses. Hence, the significance of the nanocomposite here is to maintain the stiffness-toughness balance as well as to improve the barrier properties.

Chapter 2 Background and Literature Review

Plastics are widely used in many different applications including in medicines due to their versatile properties. Today it's almost impossible to live without plastics in our daily life in this modern society. It is not surprising to see that plastics are dominant materials for packaging. However, most of them are conventional petroleum based plastics that may have many advantages but at the cost of environment and landfill spaces. These conventional nonrenewable plastics do not degrade for years and also not all the plastics are recyclable either due to their nature or their applications. Incineration also emits hazardous gases and CO_2. In contrast, the biodegradable plastics can be collected and disposed in

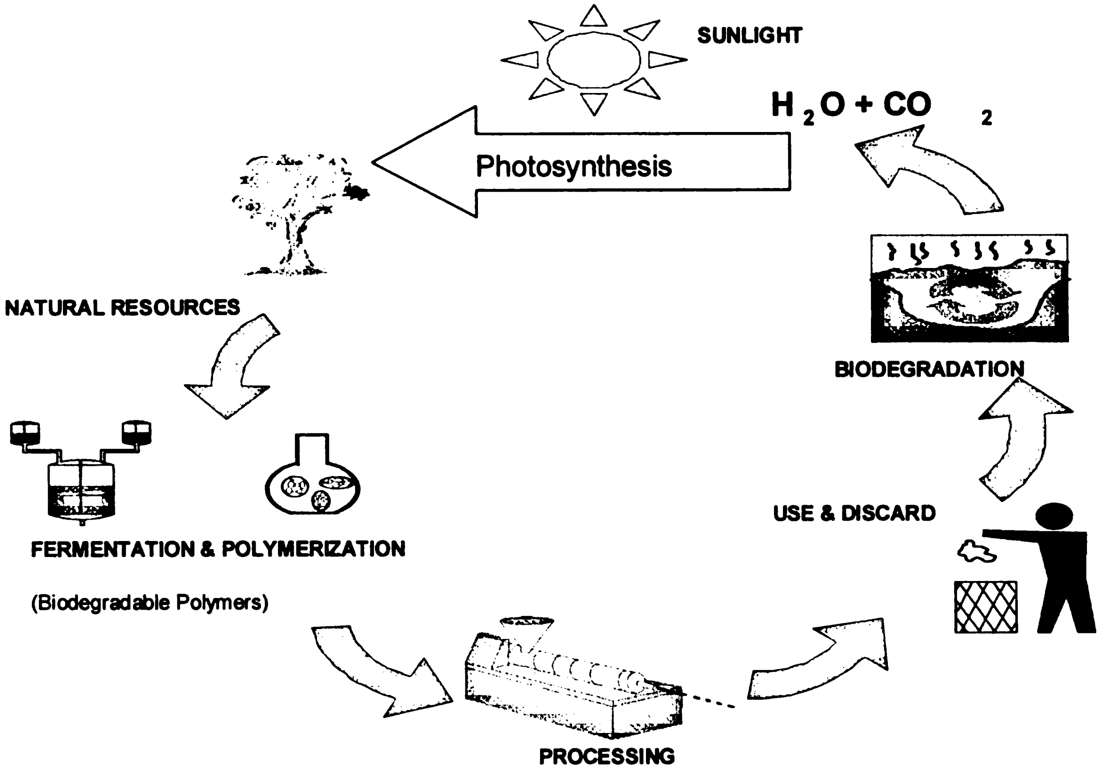

Figure 2.1 Life cycle of biobased biodegradable polymers - CO_2 balance in the environment [2.2]

bioactive environments and can be either degraded by microorganisms like bacteria, fungi and algae through enzymatic actions or by nonenzymatic process through chemical synthesis. Then biodegradable polymers will be degraded into CO_2, methane, water, biomass, humic matter, and other natural substances and thus these biodegradable polymers are naturally recycled by biological processes (Figure 2.1). [2.1, 2.2]

Hence, a feasible solution to protect the environment will be to substitute the conventional plastics with the degradable plastics. In this turn of 21st century, recent developments and innovations leads to the naturally derived resources based materials that will dominate and contribute in many applications. Also present researches efficiently bringing the success to the developments and technologies to cut down the costs and to match the performances of the biodegradable plastics to the conventional plastics. This research project also has the similar kinds of objectives. There is difference between the terms 'biobased' and 'biodegradable' which are often wrongly used. In simple terms, biobased can be biodegradable where as not necessarily the other way. There are biodegradable materials that are actually derived from the nonrenewable resources like petroleum. So we can say the materials (plastics) derived from renewable resources such as corn (e.g. PLA), are biobased materials that can be degradable in the above said manners. [2.3]

Biodegradable polymers can be classified in three ways as schematically explained in the Figure 2.2 [2.4].

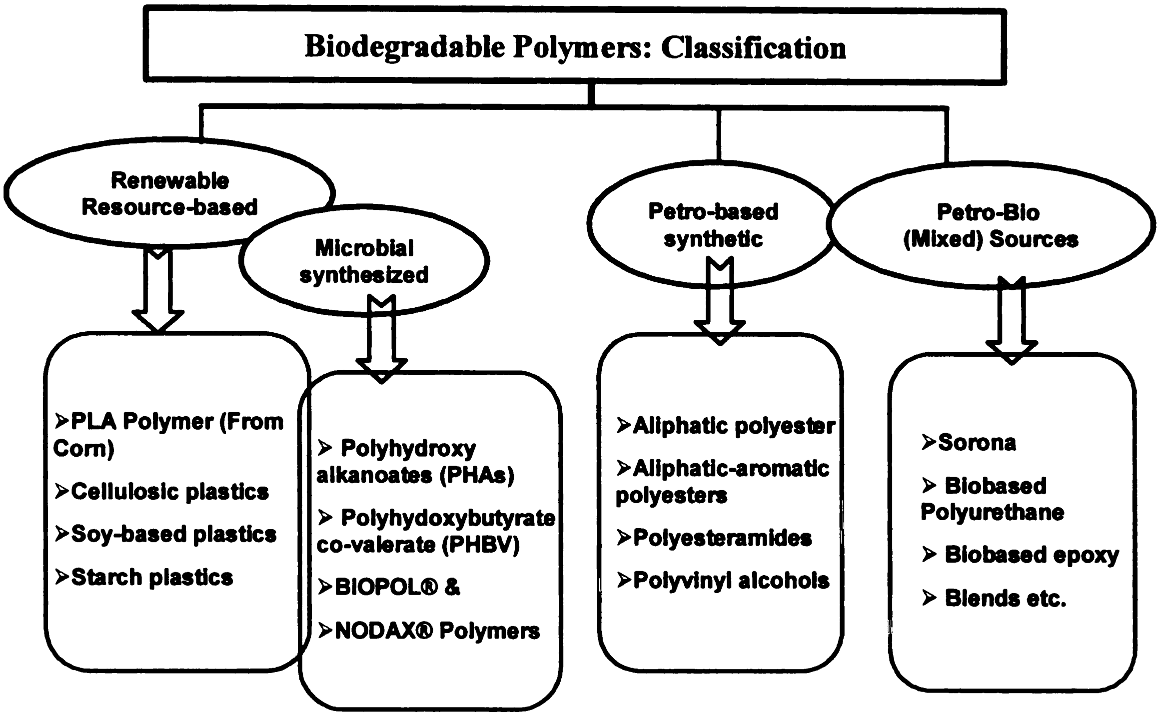

***Figure 2.2** Classification of biodegradable polymers [2.4]*

We can classify three major kinds of biodegradable polymers based on the way they were derived viz., from renewable resources, from nonrenewable resources and from both renewable and nonrenewable resources (mix). Various kinds of biodegradable polymers such as starch and cellulose based, polyesters based are available and some are water soluble too. However, the focus would be more on the polyesters based ones here. This polyesters family contains both renewable-resource based ones like PLA, PHB etc, as well as nonrenewable-resource based biodegradable plastics like, PBAT, PTAT, PBS, PCL, PEA etc.

The physical properties for few of the biodegradable polyesters have been reported as shown in the following Table 2.1 [2.1].

Table 2.1 Physical properties of biodegradable polymers [2.1]

Property	Melting Point (°C)	Tensile Stress at break (MPa)	Elongation at break (%)	Tensile Modulus (MPa)	Density (g/cc)
PHB (Biopol)	177	40	6	4000	1.25
PHB-V (Biopol)	135	25	25	1000	1.25
PCL (Tone 787)	60	4	800–1000	386	1.145
PLA (Ecopia)	177–180	45	3	2800	1.21
PAS (Bionolle)	114	60	800	500	1.2
PEA (BAK 1095)	125	25	400	180	1.07
Ecoflex	110–115	36	820	80	1.25
Eastar Bio	108	22	700	100	1.22

Among these biopolymers, some are stiff and some are tough in nature. For example, PLA, PHB are the examples of the stiff bio polyesters where as PBAT, PEA, PBS, PCL are few of the tough biodegradable polyesters. There are different kinds of polyesters viz., aliphatic polyesters (eg: PLA, PCL), aromatic polyesters and aliphatic-aromatic polyesters (eg: PBAT). Most of these polymers are similar in performance and behaviors to some conventional polymers such as LDPE, PS, PP and PET. Among all, PLA is the most widely used bioplastic commercially even in packaging and the behaviors of PLA are comparable with that of PS, PP and PET [2.1, 2.2, 2.5]. The focus here would be mainly on the PLA, stiff biodegradable aliphatic polyester made from the renewable resources like corn. Few of the tough biodegradable polymers such as PBAT, PTAT, PCL, PBS and PEA would also be discussed.

PLA comes under the biobased plastics and is made from 100% annually renewable resources like corn & sugar beets and has highest potential for the commercial large-scale production and applications in packaging materials. It is stiff, rigid thermoplastic and can have totally amorphous or semi crystalline nature depends on the stereochemistry of the polymer backbone, however, Poly L-lactic acid (2-hydroxy propionic acid) is the common form of this polymer. D-lactic acid monomers are incorporated to modify the crystallization behavior to have certain properties and applications. These modified flexible PLA can be used to make sheets, films, blow molded articles and thermoformed articles. PLA can be used in the conventional processing machines and equipments to make required articles or finished products. PLA is not a new material, because it was produced from lactic acid in 1932 by Carothers and then later on further developments done by Dupont and Ethicon. However, it has been used only in the bio-medical applications in commercial form and has not been used in other applications due to their high cost until late 1980s. Technological innovations and cost reduction made PLA available for the non-medical applications in larger scale. Still, it achieved little success and was yet to compete and replace the conventional plastics, due the higher cost and relatively lower performances so far. Cargill Dow LLC took appreciable efforts to reduce its cost of production and made PLA as large scale produced plastic by innovations and business mergers of 2 larger companies and thus Cargill Dow LLC is the largest producer and supplier of PLA based polymers in the world now. Unique thing about PLA is that it is degraded primarily by the simple hydrolysis and does not require the microbial attacks to do the hydrolysis [2.1, 2.2, 2.6, 2.7].

PLA can be produced with high molecular weight ranges with different techniques. For example, Cargill Dow uses the solvent free continuous process followed by the novel distillation method where as Mitsui Toatsu uses the solvent based process with azeotropic distillation to convert the lactic acid into high molecular weight PLA [2.1]. It has been reported that PLA is prepared with two kinds of methods viz., direct condensation of lactic acid and ring opening polymerization of the cyclic lactide dimer (Figure 2.3) [2.7]

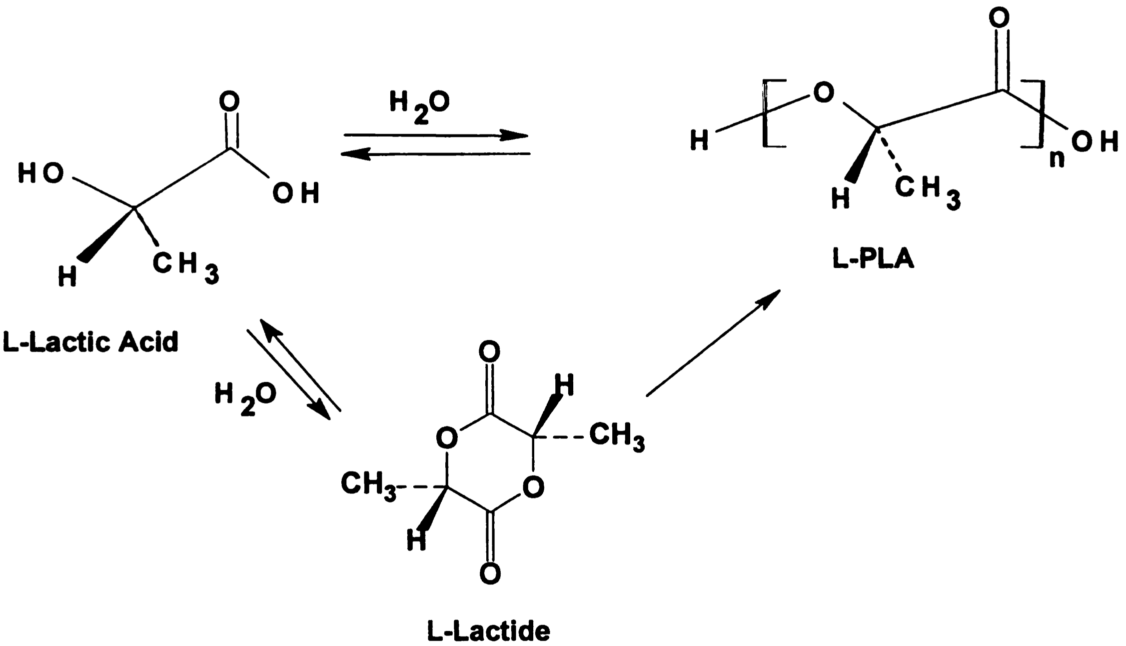

Figure 2.3 Polymerization routes to polylactic acid [2.7]

However, most of the productions are based on the later method ie., ring opening polymerization, although as Mitsui Toatsu patented the solvent based process with azeotropic distillation to remove the water in the direct etherification process. Cargill Dow developed and patented the low-cost continuous process that is based on the melt method rather than the solution one and so solvent free with

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substantial economic and environmental benefits. In this process, prepolymer of low molecular weight PLA is produced first by the continuous condensation process of aqueous lactic acid. Then to increase the rate and selectivity of the intramolecular crystallization reaction, using the tin catalyst, that prepolymer is depolymerized into a mixture of lactide stereo isomers which is then purified by the vacuum distillation. At last, the high molecular weight PLA is produced through the ring opening polymerization of those lactides in the melt form using the tin catalyst again and thus avoiding the use of the costly and non-eco-friendly solvents. The unreacted monomers will be removed under vacuum and recycled back to the beginning of this process (Figure 2.4) [2.7]

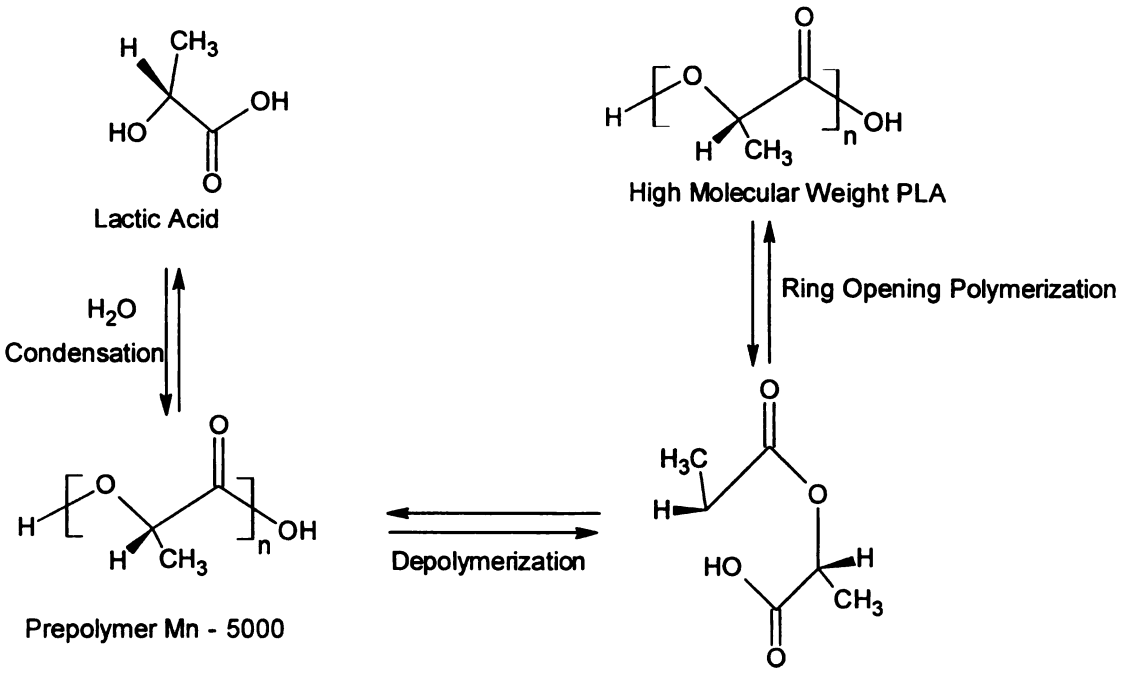


Figure 2.4 *Schematic of PLA production via prepolymer and lactide [2.7]*

There are many other ways to polymerize the lactide monomers though tin catalyst based one is the predominant in practice. Other catalysts systems used are complexes of aluminum, lanthanides, zinc and some strong bases like metal alkoxides. Stereochemistry of PLA is also an important part that results in the final polymer's thermal behaviors and so their mechanical and thermo mechanical performances. It has 3 kinds of stereo isomers viz., L-lactide, D-lactide and meso-lactide. PLA has its highest melting point (T_m) of 180°C with an enthalpy of 40-50 J/g, however for the semi crystalline PLA, depending on the structure, the range would be from 130 – 230°C and would have glass transition point (T_g) of about 58°C. An enthalpy of fusion of about 93.1 J/g (ie., $\Delta H^{\circ}_m = 93.1$ *J/g)* can be used for the 100% crystalline PLLA or PDLLA homopolymers that would have infinite crystal thickness and the following equation–2.1 can be used to calculate the % crystallinity:

$$\% \text{ of crystallinity} = [\Delta H_m - \Delta H_c]*100 / 93.1 \qquad (2.1)$$

Where, ΔH_m is the heat of fusion measured and ΔH_c is the heat of crystallization. The pure crystalline PLLA has estimated density range of 1.37 – 1.49 g/cc however, the solid amorphous PLA has the density of about 1.25 g/cc. The incorporation of other monomers in this predominantly produced natural P(L)LA will affect its stereo chemistry, crystallization and so their properties although T_g will have little effects. It is also possible to derive the purely amorphous PLA by incorporating about 15% of meso-lactide monomers. It's been reported that the optimized crystallization temperature (T_c) in the range of 105 – 115°C [2.1, 2.7].

Based on the above PLA behaviors it is possible to make various kinds of PLA resins (Nature works PLA) that can be made into blown films, cast films, biaxially oriented films, injection molded and blow molded articles, fiber spinning etc by controlling the certain process parameters at the molecular levels like, branching, MWD, D-isomer contents and branching introduction and also by incorporating the L-, D- and meso lactide isomers at various levels in the PLA back bone allows PLA for specific applications [2.8]. PLA has some distinct properties even compare to the regular plastics. It has excellent oil & grease barrier, very good barrier for aroma and flavor, low temperature sealability, good crease retention and crimp properties and these all make an excellent choice for many applications especially in packaging. PLA has very good modulus, even the solid state amorphous PLA has the modulus in the range of 2 – 3 GPa where as the semi crystalline PLA has the modulus in the range of 3 – 4 GPa. A review paper has reported mechanical properties of oriented PLA as well as of non oriented PLA as shown in the following Table 2.2 [2.1, 2.6, 2.7].

Table 2.2 Comparison of Physical Properties of High molecular weight PLA [2.6]

Property	**Unoriented**	**Oriented#**
Ultimate Tensile Strength (psi x 10^3,MPa)	6.9–7.7, 47.6–53.1	6.9–24, 47.6–166
Tensile Yield Strength (psi x 10^3,MPa)	6.6–8.9, 45.5–61.4	N/A
Tensile Modulus (psi x 10^3,MPa)	500–580, 3447–4000	564–600, 3889–4137
Notched Izod Impact (ft-lb/in)	0.3–0.4	N/A
Elongation at break (%)	3.1–5.8	15–160
Rockwell hardness	82–88	82–88
Specific Gravity (g/cc)	1.25	1.25
Glass Transition temperature (°C)	57–60	57–60
# *Results depend on the degree of orientation and isomer content*		

PLA possesses good water vapor barrier and relatively good oxygen barrier and this makes PLA as one of the favorable food packaging materials among the biodegradable plastics. The physical and barrier properties for the biobased materials such as Polylactate, PLA, polyhydroxybutyrate, PHB, wheat starch and corn starch were investigated. PLA and PHB have the O_2:CO_2 permeability ratio in the range of 1:7 to 1:12 that makes these materials suitable for packaging of food with high respiration. The mechanical properties were comparable to the conventional polymers like PE and PS and they had relatively good barrier properties, however the starch based materials required many improvements to be used as food packaging materials [2.9]. Comparison of barrier and physical properties between the PLA, PS and PET has been reported. PLA showed better barrier performances than PS but little lower than the PET where as PLA showed similar physical behaviors with that of PS but much less than that of PET. PLA has very good aroma barrier that makes it to be co extruded with conventional polymers like LDPE according to the requirement in the multiplayer packaging materials [2.3, 2.5].

Properties of Plasticized PLA were investigated in which tributyl citrate and other plasticizers were used to improve the flexibility of PLA to overcome its brittleness however, it reduces the T_g and resulted in the unstable system due to the morphological changes that was caused by the cold crystallization. So there was a requirement of optimum PLA-Plasticizer composition prior to achieve the balance of required properties while maintaining the minimum required flexibility and morphological behaviors [2.10]. This discussion so far has been on the toughening of PLA either by the incorporation of other isomers of PLA or by some other plasticizers.

There is another possibility of improving the flexibility and toughness for the stiff polymers like PLA through blending technique with some other tough polymers just like toughening the conventional plastics (e.g. High Impact Poly Styrene (HIPS) – by blending and co polymerization). Its been reported that PCL improved the plasticity of the PHB biopolymer through a reactive blending method and showed improved toughness compare to PHB and improved strength compare to PCL and could achieve optimized properties [2.11]. Another study reported that blending of PLLA-CL with PLLA and PCL was miscible and improves the tensile modulus and break elongation of the blended films [2.12]. Thermal and physical properties of PLLA-PEO blends have been reported. In the amorphous phase, one T_g was found that indicates the miscibility of the blend in this phase however, T_m of PLLA decreases with increasing the PEO. It was reported that less than 10% of PEO in the blend does not affect the mechanical properties significantly and it is improving the flexibility while maintaining the required expected strength however more the quantity of PEO better will be the elongation. Also, PEO presence increases the crystallinity of the blend than the neat PLLA at high undercooling where as other way at low undercooling [2.13].

Another interesting research reported on the PLA polymeric blends with PDLLA and PCL with and without surfactants in which the purpose of the study was to improve the toughness of the hard and brittle PLLA without sacrificing much with the original strengths. This study followed the solution blending method to prepare the blending samples and blending proportions from 20 wt% to 80 wt% were followed and it was found that PCL and PDLLA improved the toughness at the cost of its strength. However, PDLLA with 2 wt% surfactant improved the toughness while keeping the strength especially 40PLLA/60PDLLA provide better toughness and hardness than the neat PLLA [2.14].

PLLA, one of the stiff and rigid thermoplastic polyesters in the biodegradable polymers like PHA & PHB, has been discussed so far. There are flexible biodegradable polymers like PBAT, PTAT, PBS, PCL, PEA etc also being used and these are thermoplastic polyesters or co-polyesters category. Since these are also used for providing the flexibility and toughening the stiff polymers and act like a plasticizers as we just discussed above. Many researches and investigations have also been carried out on these tough biodegradable polymers and their blends with any stiff polymers.

Poly-(butylene adipate-co-terephthalate) (PBAT), is a thermoplastic aliphatic-aromatic co-polyester, produced by condensing the 1,4-butanediol with 1,4-benzenedicarboxylic acid (terephthalic acid) and hexanedioic acid (adipic acid). It is an important biodegradable flexible polymer, which has also been used in established blown-film applications [2.15].

PBAT has the properties similar to the LDPE due to their long chain branched molecular structure. BASF is the leading supplier for this polymer under the brand name of 'Ecoflex'. It can be biodegraded by the microorganisms and the process of biodegradation depends on the specific environment includes soil quality, population of microorganisms and the climate. It has very good compatibility with other biopolymers like PLA (dry blend), other bio polyesters and starch. As per BASF, this material can replace many conventional film applications as well as in packaging applications. It is very much biodegradable however made from non-renewable resources. It is hydrophobic and relatively has good water vapor barrier that make this used for hydrophobic applications and it is approved for the food contact applications that make an opportunity for this to be used as very good packaging material. Blown films can be made in conventional equipments and typical applications include packaging, agricultural films and compost bags. This can be transparent to translucent in nature, and has semi-crystalline structure with melting point in the range 110 – 120 °C with the density range of 1.25–1.27 g/cc.

Table 2.3 Material Properties of Ecoflex® F BX 7011 [2.16]

Property	**Unit**	**Test Method**	**Ecoflex® F BX 7011**	**Lupolen 2420 F**
Mass density	g/cc	ISO 1183	1.25 – 1.27	0.922 – 0.925
Melt flow rate MFR 190°C, 2.16 kg	g/10min	ISO 1133	2.7 – 4.9	0.6 – 0.9
Melting point	°C	DSC	110 – 120	111
Viscat VST A/50	°C	ISO 306	80	96
For the blown film, 50µm				
Transparency	%	ASTM D1003	82	89
Tensile Strength	N/mm^2	ISO 527	35 / 44	26 / 20
Ultimate Elongation	%	ISO 527	560 / 710	300 / 600
Failure Energy (Dyna-Test)	J/mm	DIN 53373	24	5.5
Oxygen Permeation rate	cc / $(m^2.d.bar)$	DIN 53380	1400	2900
Water vapor Permeation rate	g / $(m^2.d)$	DIN 53122	170	1.7

PBAT possesses high ultimate break elongation (560 % to 710%) and high failure energy (24J/mm). It has good thermostablity up to 230°C and can blown film processed in the conventional blown lines. The film can be down gauged up to 10 μm and it can be heat sealable and printable. The BASF has reported a comparison chart of PBAT with LDPE as shown in the following the Table 2.3 [2.16]. PBAT is also widely used in polymer blending for various purposes. It has been reported that PBAT was used as a plasticizer for making the starch foams. This study discussed about the maleated PBAT (MA-g-PBAT) used as a compatibilizer between starch and PBAT prior to improve the resilience and hydrophobic nature of the Starch and so lower weight gains and better dimensional stability on the moisture sorption with reduction in the density that give more yield of the finished products. It also reported that maleated PBAT (MA-g-PBAT) is acting better as a compatibilizer between the Starch and PBAT than as a blending component with starch [2.15].

Aliphatic-aromatic polyester was investigated for their degradation behaviors and ecotoxicological impacts of the degradation intermediates by U. Witt et al. The chemical structure was analyzed for the monomers and branching chains and their effects in the degradations (Figure 2.5) [2.17]. The C-NMR analysis of the

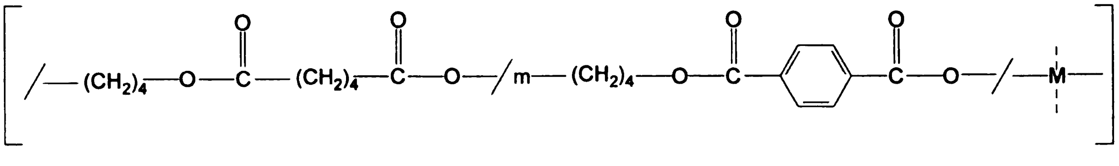


***Figure 2.5** Chemical structure of the aliphatic-aromatic copolyester (M = modular components, e.g. monomers with a branching or chain extension effect) [2.17]*

neat polymer composition reported for the content of the diol and diacids (butanediol–50 mol%, adipic acid–27.8 mol%, terephthalic acid–22.2 mol%). It was reported that almost 99.9 % of the polymer has been depolymerized after the 22 days of degradation and no significant toxicological effect was observed neither from the intermediates of the monomers nor from that of the oligomers and so concluded that no environmental risk and can be fully biodegradable [2.17].

US Patent (US 6573340 B) reported the investigation on the blending of hard polymers with tough polymers to achieve the optimized properties and performances. The polymer blends were targeted for the applications of laminates, a wraps and coatings and other packaging materials made from the at least one hard biopolymer having T_g>10°C and at least one soft biopolymer having T_g<0°C. The biodegradable polymers involved in the study were thermoplastics of polyesters, polyesteramides and starch based ones. Certain blends of hard and soft polymers possessed synergistic properties that are superior to those concerned neat hard or soft polymers by themselves. Water Vapor Permeability Coefficient was also analyzed for the laminated films [2.18].

There is another kind of useful flexible (soft) tough biodegradable aliphatic-aromatic thermoplastics co-polyester, Poly-(tetramethylene adipate-co-terephthalate), (PTAT), having linear structure unlike the above PBAT. It is marketed in the name of “Eastarbio” by Eastman Chemical Co. The chemical composition of this polymer is 1,4-benzenedicarboxylic acid polymer with 1,4-

butanediol and hexanedioic acid. It is a co-polyester of buthylene glycol and adipic and terephthalic acids. It has density of 1.22 g/cc and the melting temperature in the range of (T_m) of 109°C - 111°C with glass transition temperature (T_g) of about –30°C. As per this company, these co-polyesters are completely biodegradable and tough, resilient, liquid impermeable, fully compostable and ecologically safe while meeting the FDA and EU requirements for the food contact and so for the food packaging applications. It can be used in various applications including packaging, agricultural films, fabrics, nonwovens, medical disposals, fast food service wares. Its unique chemistry was designed to provide the combined effect of physical strength, extended shelf life and processability with complete biodegradable in nature. It has tensile properties similar to that of LDPE and its structure is highly linear in nature. It can be processed in the conventional processing equipments. It becomes invisible to the unaided eyes within 12 weeks and is completely biodegradable within 6 months under the active microbial environment like in a commercial composting site. It was found in a study that it has a crystallization temperature (T_c) of 29°C and the decomposition starts at 354°C [2.19, 2.20].

Polybutylene Succinate (PBS) is another one of the flexible biodegradable plastics available today. This is marketed by few companies and Show Highpolymer Co. Ltd., Tokyo, Japan, sells this under the trade name of 'bionolle'. It is a synthetic aliphatic polyester of buthylene glycol and succinic acid. It has density of 1.26 g/cc and the melting temperature (Tm) of 114°C with glass transition temperature (Tg) of –32°C. It has melt flow index (MFI) of 3 – 10 (g/10min) was reported on the crystallization temperature (Tc) in the range of 80 – 100°C [2.20]. PBS is commercially available, aliphatic thermoplastic polyester that has many interesting properties including melt processability, thermal and chemical resistance and biodegradability. Due to its excellent processability, it can be processed into melt blow, multifilament, monofilament, nonwoven, flat, and split yarn in the field of textiles and also into injection-molded plastics products and thus being a promising polymer for various potential applications including packaging. However, certain other properties of PBS, such as barrier properties, softness, and melt viscosity for further processing etc. are often not sufficient for various end-use applications [2.21].

Park et al investigated the morphological changes during heating PLLA/PBS blend systems as studied by differential scanning calorimetry (DSC) and synchrotron wide-angle (WAXS) and small-angle (SAXS) X-ray scattering techniques at a heating rate of 10 °C/min. Two distinct melting peaks from DSC analysis indicated the semicrystalline-semicrystalline blends over entire composition range of these blends systems. Depression of the melting point of the PLA component via blending was also observed. WAXS results revealed that there was no co-crystallization or crystal modification via blending. The SAXS data showed that well-defined double-scattering peaks during crystallization, indicating that this system possessed dual lamellar stacks [2.22].

Poly (ε-caprolactone) (PCL) is another example of tough/flexible biodegradable polymer. PCL is commercially sold under the trade name of 'TONE' by Union

Carbide Corporation. It is a homopolymer made by ring opening polymerization of ε-Caprolactone, a seven member ring compound. It has density of 1.145 g/cc. It is a semi crystalline polymer with low sharp melting temperature (T_m) of 60°C and has the glass transition temperature (T_g) range of –65 to –60°C. It has melt flow index (MFI) of 0.5 – 4 (g/10min) and has structure similar to that of PE. PCL has desirable thermogravimetric and electrical properties and also has the strong light stability unlike many conventional plastics. It can be processed in the conventional processing equipments. Various grades of PCL are available to make sheet extrusions, fibers, blown films, cast films as well as injection molded articles. It is nontoxic and truly biodegradable in nature when composted. It has better miscibility and mechanical compatibility with many polymers and also gives excellent adhesion to many substrates. It has FDA clearances for food contact [2.11, 2.23].

Polyesteramide (PEA) is also one of the tough/flexible biodegradable polymers commercially available. PEA is sold under the trade name of 'BAK' by Bayer AG, Germany. It is a thermoplastic with semi crystalline in nature. It is a co-polymer of poly amide and aliphatic polyester and in specific it is based on butanediol, caprolactam and adipic acid. It has density of 1.14 g/cc and the melting temperature (T_m) of 137°C with molecular weight (M_w) of 37,000 g/mol. It has melt volume rate (MVR) of 8.8 (cc/10min) at 2.16 Kg & 200°C. It is claimed to be biodegradable according to the DIN V 54900 and ecofriendly since it is free from halogens, solvents and heavy metals etc. It is also easy to process and recyclable and mechanical properties and thermal properties of PEA are similar to that of polyethylene [2.24-2.26].

Polymer blends are one of the rapidly expanding research areas to achieve the required properties and take advantage of the cost reductions. The resultant physico-mehanical behaviors depend on the ability to control the interfacial tension that produce a small phase size and strong interfacial adhesion to transmit applied force effectively between the component phases [2.27]. There are three types of polymers blends can be found based on their miscible behaviors and they are completely miscible, partially miscible and completely immiscible. However, based on the crystalline/amorphous nature these blend can also be divided as amorphous/amorphous, amorphous/crystalline and crystalline/crystalline polymer blends though, the later one is rarely found unless the specific requirement and technological interests. Otherwise the former two types of blends viz., amorphous/amorphous, amorphous/crystalline are found in general in most of the polymer blends [2.28].

Making new polymer by mixing 2 or more polymer together called blending. Polymer blends are mixtures of at least two macromolecular species, polymers and/or copolymers. Depending on the sign of the free energy of mixing, blends are either miscible or immiscible. Total polymer/polymer miscibility does not exist - observed miscibility is always limited to a "miscibility window," a range of independent variables, viz., composition, molecular parameters (viz., molecular conformation and configuration, molecular weight, molecular weight distribution, etc.), temperature, pressure, and others. In spite of a vast number of such "windows" being identified, immiscibility is dominant in polymer blend technology. However, it is not necessary that those polymers are miscible or compatible in nature. If it is so, we may get a behavior which is similar to a homopolymer's such as single melting point and glass transition point. They are called miscible blends. For examples, polystyrene (PS) with poly(phenylene oxide) gives miscible blend though PS generally don't mix with most of the polymers. Likewise other examples are PET with PBT and PMMA with PVDF give miscible blends. When polymer-A mixes with polymer-B in miscible nature then we can observe the two kinds of behaviors in the glass transition temperatures (Figure 2.6) of the resulting polymer depend on the nature and proportions of each polymer in the blend [2.29].

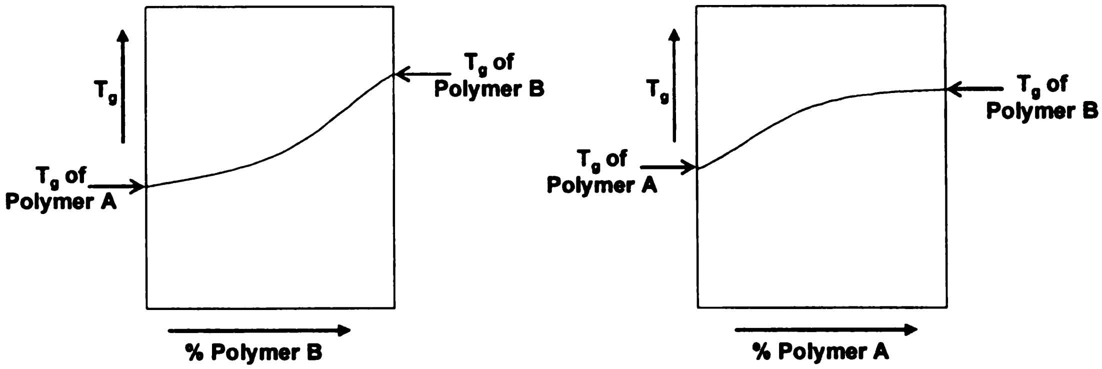


Figure 2.6 Glass transition temperature behaviors for the miscible blends [2.29]

Otherwise we get a phase separated or immiscible or incompatible blends. Often these immiscible blends do give the useful required properties. The best example for this, PS can be blended with small amount of poly butadiene (PBD) and gives required properties like toughness and flexibility to the stiff and brittle polystyrene. If we look at the following morphology (Figure 2.7), the small PBD spheres are dispersed in the PS matrix and the stress is applied these spheres provide the rubbery nature and absorb the energy and so giving better toughness to the blended polymer [2.29].

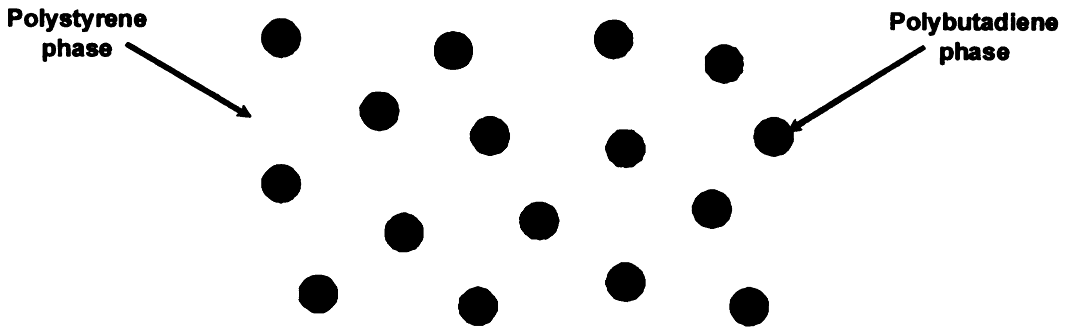


Figure 2.7 *The phase morphology of HIPS [2.29]*

This blend is also called High Impact Polystyrene (HIPS) which is already commercially available. These blend morphology plays an important role in deciding the properties especially in the immiscible blends [2.29]. There was a study on PLLA-PHB blend in which miscibility, crystallization and melting behaviors were investigated. It was found that low molecular weight PLLA/PHB blend showed better miscible over all the composition where as high molecular weight PLLA-PHB blend did not show any miscibility as expected on the basis of thermodynamics and the investigation was based on their spherulitic structure, growth rates and melting behaviors [2.30]. In another study on miscibility, crystallization and morphology behaviors of the PHB-PLA blends showed that both are immiscible when the blend was prepared by solvent casting method where as it showed few evidences of better miscibility when it was made from high temperature melt process. The crystallinity of PHB was affected by the presence of PLA contents and vice versa. However, the blend showed certain improved propertied when compared to plain PHB [2.31].

In any immiscible blend, the sphere size of the polymer which is less in proportions, does affect the properties. For constant volume, smaller the sphere, then more number of spheres and larger the total surface areas and vice versa for these immiscible blends. It is interesting to note that when stretching applied on these blends like in blown film or blow molding process where stretching is applied either uni-axially or bi-axially. During this, the spheres are stretched in plate or rod shaped phases that give another advantage in deciding their physico-mechanical properties. Sometimes these rods acts like reinforced fibers in composites. We can also make these immiscible blends to give stronger properties by using a suitable compatibilizer often a block copolymer, in case of conventional polymers. For example, copolymer of PS and PBD can be used successfully as a compatibilizer for this immiscible blend to enhance its properties further. Only few polymers can be blended effectively irrespective of their similarity in natures. For example, PE can not be blended effectively with PP even though both belong to polyolefin family and hydrophobic in nature. Apart from "like dissolves like" concept, the effective blending is also depending on the 'Entropy'. When polymer is blended, the polymer blend gets more disorder than that of the individual polymer. So, when the polymer is blended, its amorphous state already has more disorder and will not gain any more entropy due to the disorder gained from the blend and so they do not give the effective blends. However, few polymers behave in a different manner. In certain compositions two polymers may give a miscible blend where as in the rest of the compositions they may give immiscible blends and it also depends on the process parameters too. [2.29].

The purposes behind the blending of different polymers in different proportions have been discussed so far. Many studies have been done on the stiff/tough biodegradable polymer blends and their significances. Biodegradable polymers including PHB, PHBV, PBS, PES and PCL were investigated for their structure and properties that were significantly influenced by the miscibility, morphology, crystallization and melting behaviors. This study found different blend behaviors including the miscible crystalline/crystalline, immiscible crystalline/crystalline and miscible amorphous/crystalline blends for various polymer blends. It reported that binary blends of crystalline polymers including PES with PEO and PBS with PEO showed the miscible crystalline/crystalline behavior. It was also studied that the binary immiscible blends of crystalline polymers including PHB/PBS, PEO/PCL, PHBV/PCL and PBS/PCL and the crystallinity of one polymer had effective significant on that of the other polymer. PBS/PVPh binary blend was reported for their miscible amorphous/crystalline behavior based on their thermal, crystallization and morphological behaviors [2.28].

Takagi et al investigated and reported the morphologies and mechanical properties of the blends of PLA/ medium chain length PHA and PLA/chemically modified PHA (ePHA). It was found that both kinds of PHA improved the impact toughness of the PLA blends while decrease in the tensile strength and maintaining their biodegradability with more accessible to hydrolysis and microbial attack resulting better weight losses when compare to the neat PLA [2.32]. Terada et al patented a biodegradable film developed based on the investigation of the melt compounded blend of PLA with aliphatic biodegradable polyester (here PBS) other than PLA in the weight ratio range from 70:30 to 20:80. The objective was to develop a bio degradable film having high flexibility and transparency while degrade in the natural environment. It was found that by blending the PLA with aliphatic tough bio polyester (PBS) providing the biodegradable film possessing the tensile modulus of maximum of about 2.5 GPa with at least 65% transparency [2.33].

In another US patent, PLA based blends (with aliphatic polyester like PBS, PBSA and PES) including a compatibilizer were investigated in the weight ratio ranges of 9:1 to 1:9. Various mechanical properties such as stress, strain & %elongation, modulus and toughness were analyzed and reported. It was found that the brittle PLA based blends showed improved toughness and elongation while maintaining the significant strength even after few days of aging and also had the better degradation rates in comparison to PLA [2.34]. Sheth et al investigated the biodegradable polymer blends of PLA and PEG in the ratios of 100/0, 90/10, 70/30, 50/50, 30/70. These melt blended compound was analyzed at DSC and

DMA resulting that some blends are miscible where as some are partially miscible depend on the composition. Until 50% of PEG in the blend PEG plasticize the PLA and reduce modulus while increase the % elongation where as above 50% of PEG resulting in higher crystallinity of PEG and yielding higher modulus with lower break elongation. However, tensile strength decrease in linear manner with increase in % PEG contents and all the blends showed better enzymatic degradation than the pure PLA especially for less than 30% PEG content in the blend for the rest dissolution of PEG predominated in the degradation process [2.35].

Bastioli et al patented a research study in which they investigated ternary mixture of biodegradable polyesters that includes aliphatic-aromatic polyester (PBAT), aliphatic polyester (PBS) and PLA in various weight ratios and targeting food packaging and other applications. Tear strength, tensile properties with modulus and transparency behaviors were evaluated and claimed for the blended and extruded films in both directions [2.36]. There was an interesting investigation on the blend of PLA with PHA based copolymers (Nodax) that has lower crystallinity and melting point due to the incorporation of the 3HA units with medium chain length side groups just like in the LLDPE. This reduced crystallinity provides ductility and better toughness for many plastics applications and so when they incorporated little amount (below 20%) of these co polyesters with better dispersion in the PLA matrix providing extra ordinary results due to lower interfacial energy between these highly compatible PLA and PHA copolymer. This blend improved the toughness without compromising the optical clarity of the brittle PLA until 20% of the PHA in the PLA matrix in a manner similar to HIPS. However rest of the blending proportions (more than 20% of PHA) did not give any appreciable results due to the crystallinity behavior of the PHA in the PLA matrix [2.37]. Averous et al investigated the blends of thermoplastic starch with polyesteramide (up to 40%) in the presence of a compatibilizer prior to develop a starch based to biodegradable plastics. The blended samples were analyzed and reported for mechanical and thermo mechanical properties with thermal behaviors. It was reported that certain compatibility in the blend systems and PEA presence in the Starch matrix improved the hydorphobicity and mechanical properties while restricting the shrinkage during the injection process even at 10% of PEA in the blend [2.38].

The biodegradable polymers, their blends with their significance have been discussed so far. Just like biodegradable polymers, there is relatively new technology called 'Nanocomposite Technology' which is, *"the materials and processes required to disperse nanoscale particles in plastics, metals, or ceramics"* defined by NANOCOR. The materials derived from this technology are also called 'Nanocomposites' that is defined again by NANOCOR as *"new class of plastics derived from a highly refined form of nanoclay that disperses in plastic matrix"* [2.39]. In recent years, the synergistic effect of this technology with polymer/its blends providing enhanced properties with cost effective when compare to the conventional micro composites. This gives an ample scope for this technology to many applications including packaging and automotive. 2 million lb of nanocomposites were nanoclay-based nylon products produced by

Unitika and Ube Industries in Japan for automotive and packaging applications, respectively, out of the total of 3 million lb market. The rest of the 1 million lb was carbon nanotube-filled PPO/nylon nanocomposites made in North America for automotive body parts applications. It is expected that there will be strong growth over the next 10 years and Principia Partners Estimated that more than 1 billion lb of nanocomposites will be in demand worldwide for Nanocomposites out of which 160 million lb is carbon nanotube-filled products by 2009 [2.40]. The biodegradable polymers are still struggling to compete with the conventional polymers in many applications due to their cost and the performances. Cost can be brought down by having the more volume however performances can only brought up using these kinds of innovations and technology. So the synergistic effects of this nanocomposite technology with biodegradable polymer/blends would give the required polymer properties and performances so as to replace the petroleum based conventional polymers in many applications primarily in packaging. To discuss this nanocomposite further, it is required to understand the nano particles especially nano clay chemistry and its properties.

Nanoclay is a naturally occurring inorganic raw material originated from the volcanic ash. These volcanic ashes were deposited in the earth or in the sea and/or sea beds during the volcanic eruption about 85 – 125 million years back. Over the years the ash beds deposited inside the sea become accessible in the land form now due to the geographical changes in the earth. There are many different kinds of clay minerals are available such as montmorillonite, hectorite, saponite, betonite, smectite based. However the montmorillonite based nano clays will be discussed here. An individual clay particle is plate like structure however these clay platelets exists in the agglomerate stacks form. Each clay platelet is about one nanometer in thickness with 50 to 600 nm ranges of surface dimensions that gives the high aspect ratio (ranges from 100 to 1000) for the clay particles. As for its structure and chemistry, silica is the dominant constituent which is tetrahedral while alumina exists in the octahedral form that is also essential too. Each clay particle has sheet structure consisting of 2 types of layers which are silica tetrahedral and alumina octahedral layers. The silica layer has SiO_4 groups that are bonded together to give a hexagonal network of the repeating units of composition Si_4O_{10}. Where as, in alumina layer the aluminum atoms that coordinates the octahedral structure, are embedded in between the two sheets of closely packed oxygens or hydroxyls in such a way that aluminum atoms are equidistant from six oxygens or hydroxyls. The cross section of the single clay sheet can be seen the sandwich structure meaning the alumina octahedral layer is sandwiched in between the 2 tetrahedral silica layers (Figure 2.8) which shares their apex oxygen with the octahedral alumina layer. Thus, they are also called layered silicates. In this kind of structure, the negative charge is located on the surface of the tetrahedral silica layers and thus can readily interact with the polymer matrices. However this single clay platelet is bonded (van der waal's bond) through the exchangeable cations like sodium, potassium etc., with other clay platelets in the agglomerate stack forms as shown in Figure 2.8 [2.39, 2.41, 2.42].

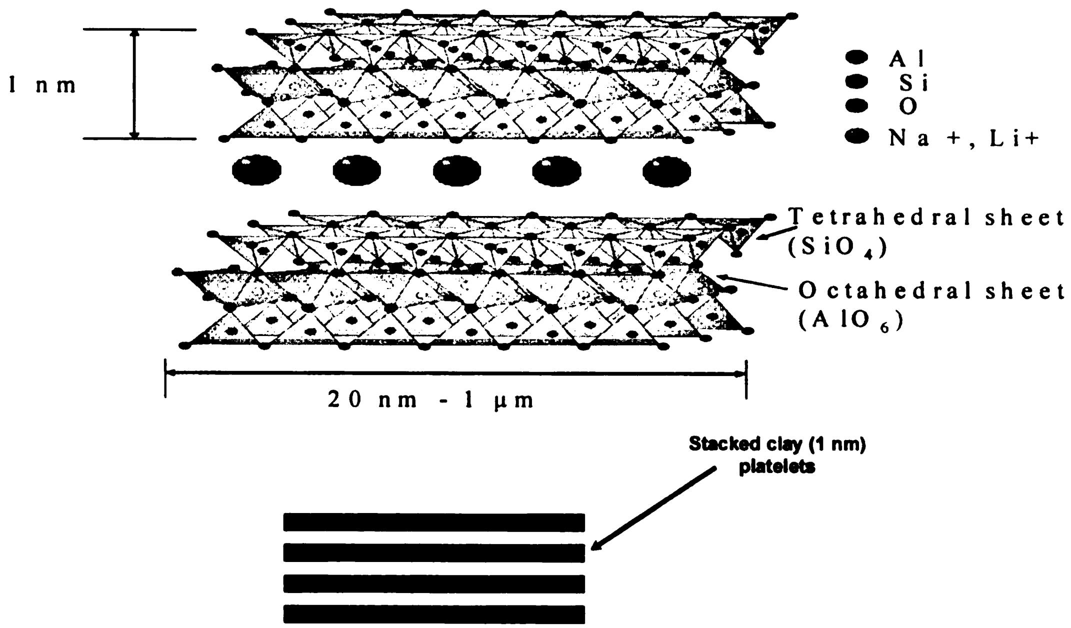


Figure 2.8 *The crystal structure of single nano clay platelet (2:1 layered silicates)*
Source: Modified by Dr. AKM's group after referred from NANOCOR [2.39]

It is also important to understand how this clay (montmorillonite based) is going to be effectively used in the polymer nanocomposite especially. The agglomerated clay platelets need to be separated prior to disperse in the polymer matrix and so giving the better properties and performances. This natural montmorillonite (MMT) clay is hydrophilic in nature due to the hydroxyl groups in the structure, where as the most of the polymers are organophilic in nature and so these clays can not be dispersed in the polymer matrix effectively. For this purpose, the MMT is organically modified prior to be more compatible and can disperse easily in the polymer matrix. Generally the platelets or silicate layers are agglomerated within a distance between the adjoining layers of 0.35 nm and so surface treatment reduces the particle-particle attractions and increase the space between layers more than 2 nm (Figure 2.9). Various modifications techniques are in practice. In general, this is done by the ion-exchange reactions with cationic surfactants including the primary, secondary, tertiary and quaternary alkyl ammonium or alkyl phosponium cations which lowers the surface energy and improves the wetting ability of the clay in the polymer matrix and results in the larger interlayer spacing of the platelets. This surface modified MMT is also called organically modified montmorillonite (OMMT). Spacing varies depend on the packing mode and the chain length of the polymer inserted [2.39, 2.42].

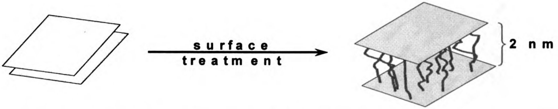


Figure 2.9 *The surface treatment of the agglomerated nano clay platelets (silicate layers) [2.39]*

In general up to 5% of clay (OMMT) would be dispersed in the polymer matrix prior to achieve the effective nanocomposites. It can be done through various ways of polymerization or polymer processing such as in-situ polymerization, solvent casting and also though melt process. However the focus here would be mainly on the melt process. It is expected that melt process gives better results since the shear rate plays an important role in separating the clays further within the polymer matrix so as to get the exfoliation of the clay in the polymer matrix. When there is a complete dispersion of the clay platelets or the layered silicates with in the polymer matrix after the compounding operation then it is called exfoliated clay in the polymer (Figure 2.10) [2.39].

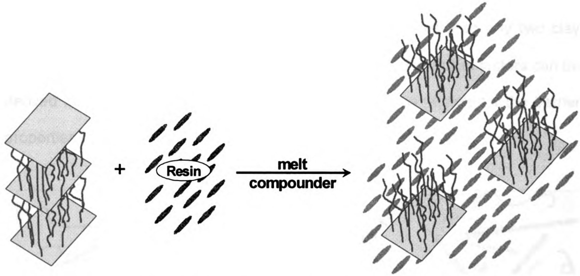
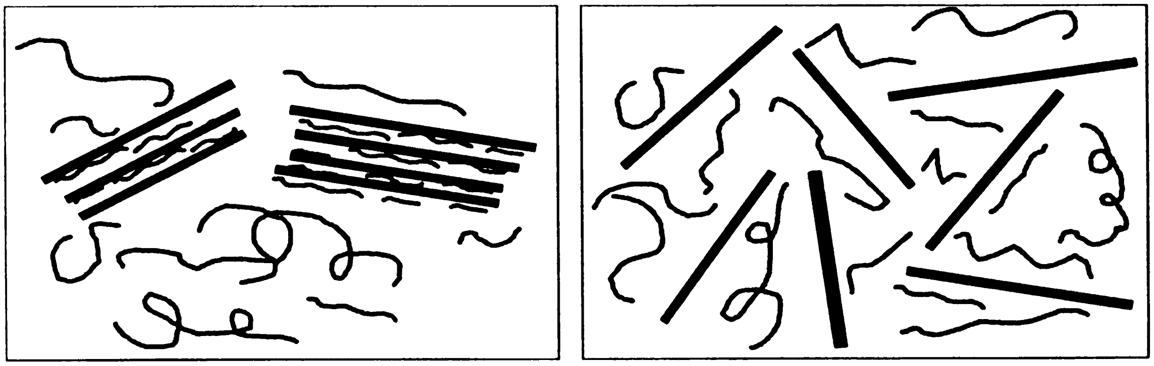
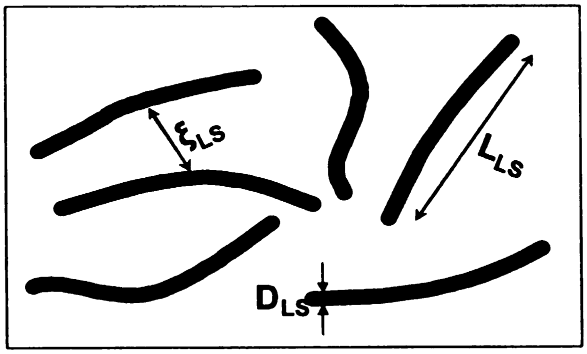


Figure 2.10 *The complete dispersion (exfoliation) of the clay platelets (silicate layers) during the compounding operation [2.39]*

Depending on the interaction between the polymer and the clay surfaces, three different kinds of nanocomposites can be formed viz., intercalated, flocculated and exfoliated nanocomposites. Intercalated nanocomposites are commonly found in which, insertion of polymer chains between the clay platelets to provide more spacing in a crystallographically regular fashion, regardless of polymer to OMMT ratio, with a repeat distance of few nanometers. Flocculated is conceptually same as above however silicate layers are flocculated sometimes due to the hydroxylated edge-edge interaction of the silicate layers. Exfoliated is usually very difficult to achieve in which each clay platelets are separated and dispersed in an average distance with in the polymer matrix. Usually, it is possible to achieve the mixed behaviors of the nanocomposites discussed above. In the exfoliated nanocomposites, we can see three kinds of form factors that are L_{LS}, D_{LS} and ξ_{LS} where, L_{LS} and D_{LS} are the length and thickness of the exfoliated clay platelet and ξ_{LS} is the average distance between any two clay platelets in the polymer matrix of exfoliated nanocomposite. These factors can be derived from the TEM images and can be used to derive models for the barrier properties correlations (Figure 2.11) [2.43].



Intercalated and flocculted **Exfoliated**



Form factors of dispersed layered silicates

Figure 2.11 The schematic illustration of thermodynamically achievable polymer / layered silicate nanocomposite [2.43]

These clay behavior and morphology in the nanocomposite can be analyzed through transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis and can be found what kind of nanocomposite is achieved. All the polymers are not compatible with all the clays. It also depends on the hydrophilic-hydrophobic balance of the Clay-Polymer matrix. These nanocomposites results in better barrier, flame resistance, structural, dimensional stability, and thermal properties with improved mechanical and thermo mechanical properties yet without significant loss in impact or clarity. These exfoliated clay that is one nm in size generally does not affect the transparency and also creates the tortuous path for the movement of the molecules that pass through the polymer system and so providing better barrier properties. These leads to the applications such as food packaging, non food films and rigid containers. These light weight plastic nanocomposite having better impact and scratch resistant with higher HDT performances makes it possible to apply in many automotive applications as well [2.39, 2.42].

Nylon-6 was the first polymer made into nanocomposite through in-situ polymerization. After that, various conventional polymers have been tried to be made into nanocomposites. It has been reported in a NANOCOR technical paper that up to 8 wt% of nanoclay incorporation through in-situ process in the Nylon6, improved the Nylon6 properties viz., 110% improvement in flexural and tensile moduli and 175% improvement in HDT (Table 2.4). Normalized Oxygen transmission rate evaluated at 65% RH, is reduced to one fifth (ie., from 35 to about 7 cc.mil/m^2.d) after 8wt% of nanoclay incorporation in the nylon 6 polymer matrix. This makes an appropriate choice for many packaging applications [2.44].

Table 2.4 Mechanical properties of Nylon 6 Nanocomposites [2.44]

Nanoclay ADA-MONT (wt. %)	Flexural Modulus (MPa)	Tensile Modulus (MPa)	HDT (°C)
0%	2836	2961	56
2%	4326	4403	125
4%	4578	4897	131
6%	5388	5875	136
8%	6127	6370	154

The synthetic roots and materials properties of the PP-MMT nanocomposites were reviewed in a review paper. It discussed about the 2 ways of making nanocomposites viz., functionalized PP with OMMT and neat PP with semi fluorinated OMMT and the resulted polymer nanocomposites made through melt process were characterized and found to be having bother intercalated and exfoliated behaviors. Also it has been reported about the improvement in the tensile properties, HDT, barrier, scratch resistant and flame resistant while retaining the optical clarity for the nanocomposites containing up to 6% of clay [2.45]. In another study, Ethylene co-vinyl alcohol (EVOH) nanocomposites with 3% OMMT were examined. Nanocomposites were prepared through melt compounding and later extruded into blown film. It has reported the morphology, mechanical and thermal properties. Intercalation was evident from the morphology analysis with a higher degree of dispersion and alignment in the blown film in contrast to compounded material. There was an improvement in the thermal stability with the addition of MMT and also found improved modulus in the nanocomposite film [2.46]. So far, the polymer nanocomposite in a single polymer matrix has been discussed. There were some nanocomposites prepared from the polymer blends and nano-clay. There was a study on a polymer blend nanocomposite in which PP/EPDM blends based nanocomposites with OMMT were prepared by direct melt intercalation in an internal mixer. The nanoreiforcement is constrained to exist either in continuous matrix or in the dispersed phase or in both phases of this thermoplastic and thus not only affected the interaction like in the single polymer system but also the degree of blending that in turn will affect the micro scale morphology and nanoscale dispersion. This kind of selective reinforcement strongly affected the morphology and mechanical properties of the blended nanocomposite. However mechanical properties strongly further dependent on the blend composition as well. XRD and TEM were used to analyze the morphology behavior of both blending and nanocomposites [2.47].

The nanocomposites of the conventional polymers have been discussed. Many researches have been reported on the polymer-clay nanocomposites [2.48-2.68]. Recently, many studies have been done with biodegradable polymers based nanocomposites especially with PLA based nanocomposites [2.21, 2.24, 2.25, 2.58-2.68]. Few researches have also been done on the polymer blends based nanocomposite [2.47]. However almost no study on the nanocomposites of PLA based blends.

Polymer blends including the biopolymer blends and nanocomposites in a single polymer phase as well as blended phase have been discussed. PLLA is a very stiff thermoplastic aliphatic polyester which can have more opportunity to be used in many applications if we can overcome few of its draw backs such as barrier, its brittleness but not at the cost of its existing properties like modulus and strength. So, by combining all the above discussed techniques, we can come up with a need for the development of the sustainable green polymer which can equally compete with conventional polymers. Being a widely used biopolymer today, PLA has the ample scope of applications; we can apply the above said convergence that gives the synergistic effects to achieve the target. Thus, PLA can be blended with one of the best suitable tough/flexible biodegradable polymers and then nanocomposites can be prepared with the specific OMMT with out using any compatibilizer. PLA would tend to have lower strength while improving the toughness after the blending with that tough biodegradable polymer. However that will be either compensated or improved by maintaining the stiffness-toughness balance after the effective nano-clay reinforcement. Thus we reached our objective to develop the PLA based blends and nanocomposites that can go for packaging applications.

Chapter 3 Materials and Methods

3.1 Materials

3.1.1 Poly-L-lacticacid (PLLA), Aliphatic Polyester

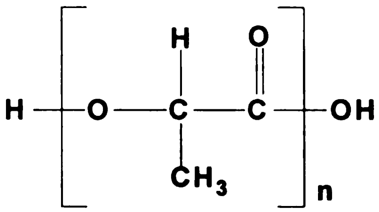


Figure 3.1 *Structure of Polylactic Acid (PLA)*

Poly-L-lacticacid, PLLA pellets were supplied by Biomer, Germany under the trade name of Biomer® L9000. PLLA has a density of 1.25 g/cc with the melting temperature (T_m) range of 168 – 172°C and the glass transition temperature (T_g) range of 50 – 60°C. It has melt flow index (MFI) of 3 – 6 (g/10min). It is transparent, odorless, and an inert solid that can thermal decompose at about 250°C. It is biodegradable and can be disposed off by composting, incinerating or depositing in landfills. The pellets were dried in the vacuum oven at 40°C for 4 hours prior to process and then packed in air tight zipper bags since it is sensitive to humidity. It does not contain any additives like plasticizer and it is catalyst free. PLA is one of the leading biopolymers used in many applications especially in packaging.

3.1.2 Poly-(butylene adipate-co-terephthalate), (PBAT), Aliphatic-Aromatic Co polyester

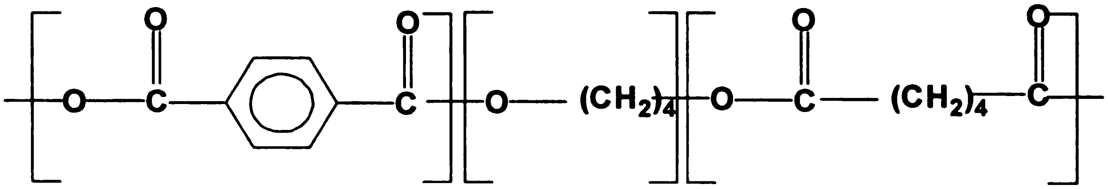


***Figure 3.2** Structure of Poly-(butylene adipate-co-terephthalate) (PBAT)*

Poly-(butylene adipate-co-terephthalate) (PBAT), film grade pellets were supplied by BASF AG, Germany under the trade name of Ecoflex® F (BX7011). PBAT is made by the condensation reaction of 1,4-butanediol with 1,4-benzenedicarboxylic acid (terephthalic acid) and hexanedioic acid (adipic acid). It has density range of 1.25 – 1.27 g/cc with the melting temperature range (T_m) of 110 – 120°C with good thermal stability up to 230°C. It has melt flow index (MFI) of 2.7 – 4.9 (g/10min). It is transparent to translucent with semi crystalline structure. It is compostable and biodegradable with non-hazardous in nature since it can be degraded by microorganisms. As pre the supplier's recommendation, no need of predrying the pellets prior to process. It has properties similar to LDPE due to its higher molecular weight and longer chain branched molecular structure. It complies with the European food stuff legislation for food contact. It has wide opportunity for the flexible packaging applications through blown films.

3.1.3 Poly-(tetramethylene adipate-co-terephthalate), (PTAT), Aliphatic-Aromatic Co polyester

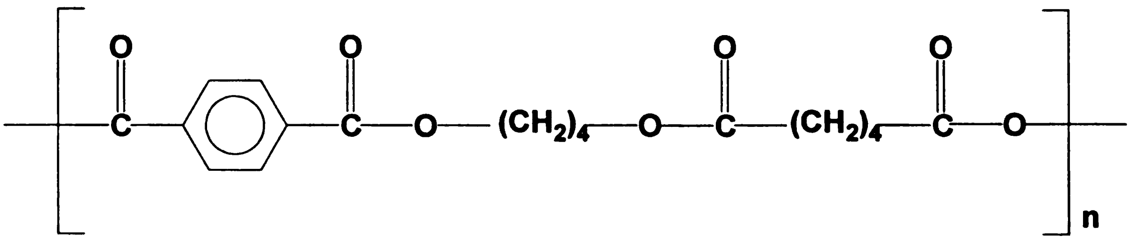


Figure 3.3 *Structure of Poly-(tetramethylene adipate-co-terephthalate), (PTAT) [3.1]*

[1,4-benzenedicarboxylic acid, polymer with 1,4-butanediol and hexanedioic acid]

Poly-(tetramethylene adipate-co-terephthalate), (PTAT), general purpose grade pellets were supplied by Eastman Chemical Co., TN, USA, under the trade name of 'Eastarbio' GP co polyester. It is a copolymer of terephthalic and adipic acid and butanediol. It has density of 1.22 g/cc and the melting temperature (T_m) of 108°C with glass transition temperature (T_g) of –30°C. It has melt flow index (MFI) of 28 (g/10min). The pellets were dried in the vacuum oven at 65°C for 6 hours prior to process.

3.1.4 Polybutylene Succinate (PBS), Aliphatic polyester

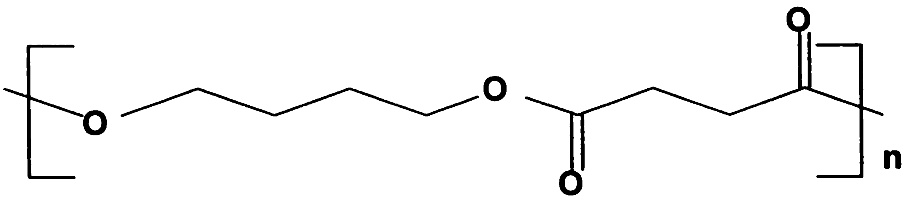


Figure 3.4 *Structure of Polybutylene Succinate (PBS)*

Polybutylene Succinate (PBS), pellets were supplied by Show Highpolymer Co. Ltd., Tokyo, Japan, under the trade name of bionolle(1020). It is aliphatic thermoplastic polyester that is chemically synthesized by polycondensation of 1,4-butanediol with succinic acid. It has density of 1.26 g/cc and the melting temperature (T_m) of 114°C with glass transition temperature (T_g) of –32°C. It has melt flow index (MFI) of 3 – 10 (g/10min). The pellets were dried in the vacuum oven at 70°C for 2 hours prior to process.

3.1.5 Poly (ε-caprolactone), (PCL), Aliphatic polyester

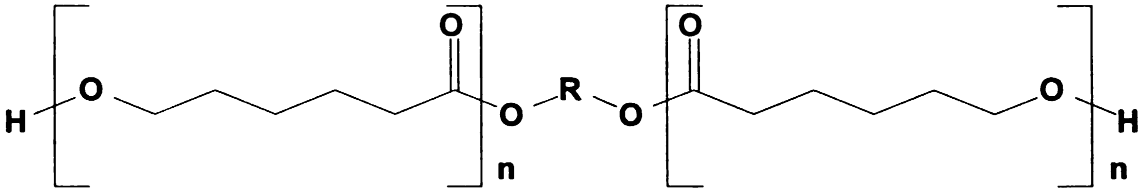


Figure 3.5 *Structure of Poly (ε-caprolactone) (PCL)*

Poly (ε-caprolactone) (PCL), pellets were supplied by Union Carbide corporation, under the trade name of TONE (P-787). It is a homopolymer made by ring opening polymerization of ε-Caprolactone, a seven member ring compound. It has density of 1.145 g/cc. It is a semi crystalline polymer with low sharp melting temperature (T_m) of 60°C and has the glass transition temperature (T_g) range of –65 to –60°C. It has melt flow index (MFI) of 0.5 – 4 (g/10min). The pellets were sufficiently dried in the vacuum oven prior to process. It is nontoxic and biodegradable in nature when composted. It has FDA clearances for food contact.

3.1.6 Polyesteramide (PEA)

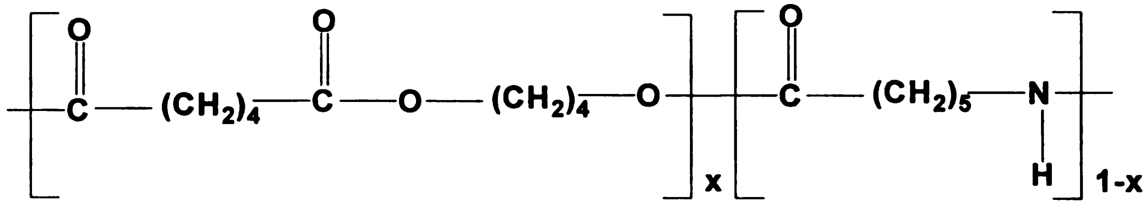


***Figure 3.6** Structure of Polyesteramide (PEA) [3.3, 3.4]*

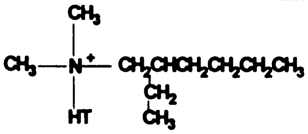
Polyesteramide (PEA), pellets were supplied by Bayer AG, Germany, under the trade name of LP BAK 404 004. It is a co-polymer of poly amide and aliphatic polyester and in specific it is copolymer of butanediol, caprolactam and adipic acid. It has density of 1.14 g/cc and the melting temperature (T_m) of 137°C with molecular weight (M_w) of 37,000 g/mol. It has melt volume rate (MVR) of 8.8 (cc/10min) at 2.16 Kg & 200°C. It is claimed to be biodegradable according to the DIN V 54900 and ecofriendly since it is free from halogens, solvents and heavy metals etc. It is also easy to process and recyclable and mechanical properties and thermal properties of PEA are similar to polyethylene. The pellets were dried in the vacuum oven at 80°C for 3 hours prior to process [3.2-3.4].

3.1.7 Organically Modified Montmorillonite (OMMT) Clay

Organically modified montmorillonite (OMMT) clay in the powder form was supplied by Southern Clay Products Inc., under the trade name of Cloisite®25A. This clay is natural montmorillonite clay modified with (Dimethyl, hydrogenated tallow, 2-ethylhexyl quaternary ammonium), a quaternary ammonium salt. Table

3.1 shows the relative structure information, XRD patterns and specific gravity for this clay. Clay was predried at 60°C for about 4-6 hours in oven prior to process.

Table 3.1 Structural information for the organically modified montmorillonite clay [3.5]

OMMT clay	**Structure**	**XRD – Bascal spacing (001) – d001 (nm)**	**Extent of Modification [meq/100g clay]**	**Specific Gravity (g/cc)**
Cloisite® 25A		1.86	95	1.87

Where 'HT' is Hydrogenated Tallow (~65% C18; ~30% C16; ~5% C14) with methyl sulfate anion [3.5]

3.2 Methods

This research project methodology is given the following schematic (Figure 3.7). This has got three phases. In the first phase, stiff biopolymer (PLLA) was melt compounded with tough bio polymers such as PBAT, PTAT, PBS, PCL and PEA in certain (50/50 in wt%) composition. Based on their mechanical and thermo-physical properties, suitable tough bio polymer was selected. In the second phase, PLLA was melt compounded with that selected tough biopolymer (PBAT) in various compositions. These samples were evaluated for their mechanical and thermo-physical properties based on which the optimized compositions were selected for making nanocomposites. Thus far, the significance of the blending is to improve the toughness. In the third phase, above selected compositions of PLLA-PBAT blends were reinforced with the specific OMMT of 5 wt%. These samples were then analyzed for their mechanical, thermo-physical and barrier properties. Based on these properties, the suitable nanocomposite composition was chosen for further studies such as morphological studies to understand the structural-property correlation in order to understand the chemistry behind the nanocomposite and their behaviors. Here the significance of the nanocomposite is to maintain the stiffness-toughness balance and to improve the barrier.

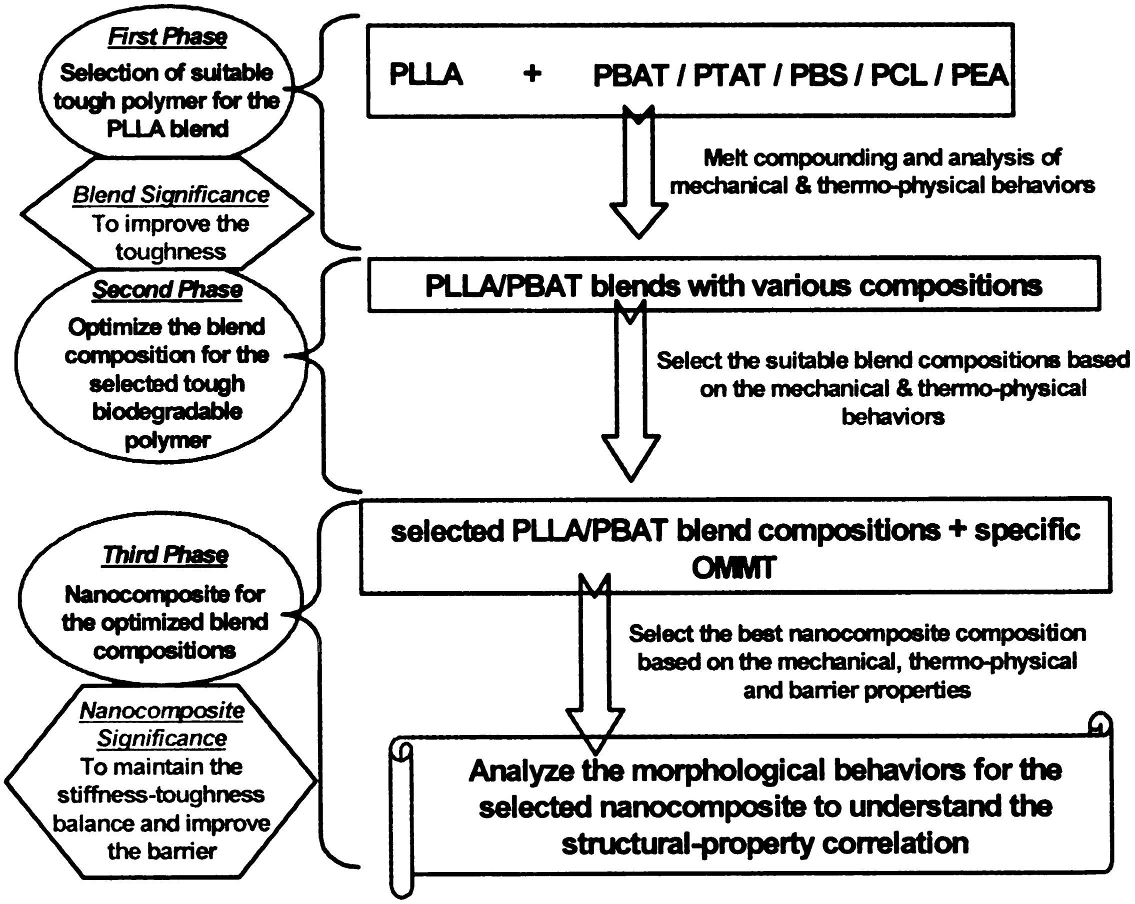


Figure 3.7 *Schematic representation of this research project methodology*

3.3. Equipments and Preparation

3.3.1 DSM Microcompounder

The polymers with or without clay were melt compounded at the DSM Micro 15cc extruder-compounder (DSM Research, The Netherlands) having vertical conical co-rotating twin screw extruding unit with screw length of 150 mm, L/D of 18 and barrel volume of 15 cc. The schematic diagram of the microcompounder is shown in the following figure 3.8. From the melt compounds of the extruder,

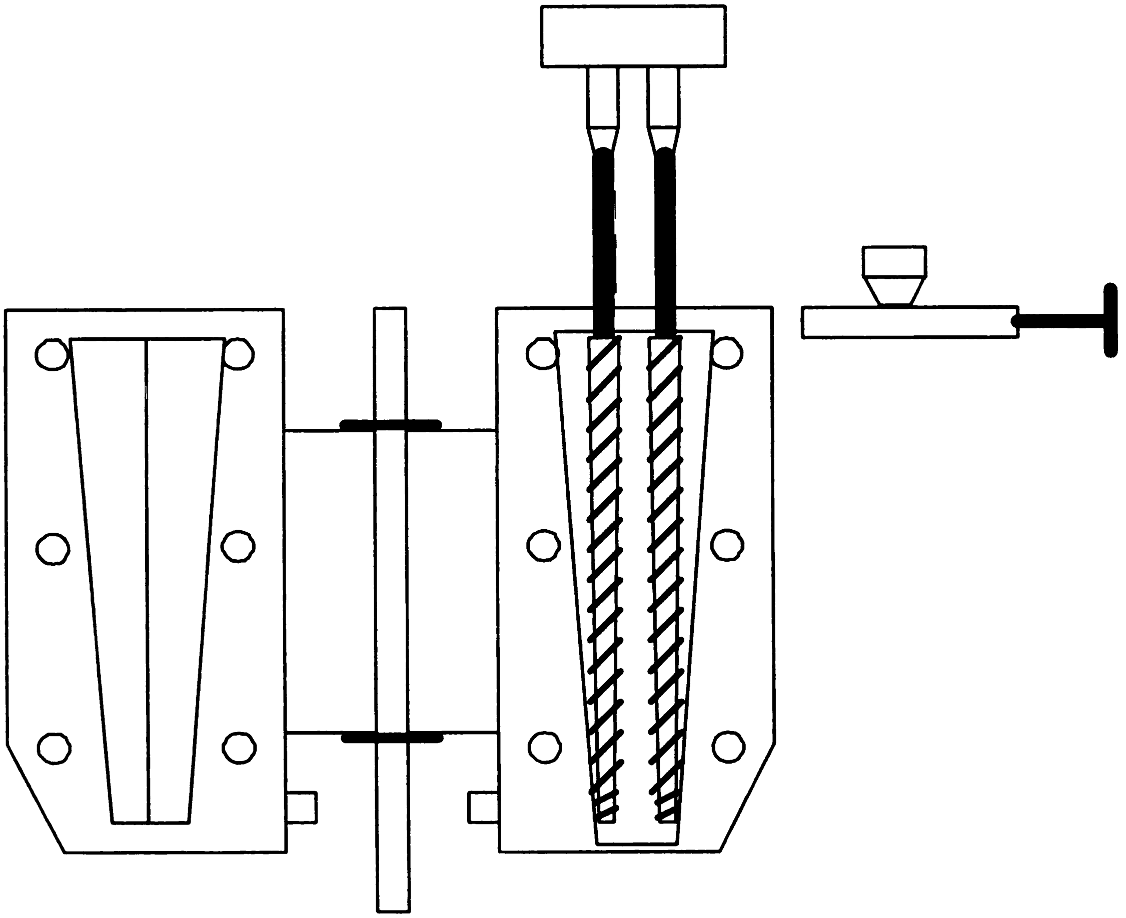


Figure 3.8 Schematic of Microcompounder Extruder unit [3.6]

strands were extruded out from this pellets were prepared using a palletizer prior to make master batches as well as to make compression molded films. The various kinds of samples such as DMA bars, izod bars, tensile and flexural specimens and discs, were also prepared by taking molten polymers in a preheated cylinder from the extruder and then injected into a preheated mold that is placed in an injection molding unit where we can us maximum injection pressure of 160 psi.

In this research experiments, all the blend compositions or nanocomposite compositions are taken in weight percentages (wt %). PLLA was melt compounded with different tough polymers in the 50/50 (in wt%) composition to find the suitable tough polymer that would give the required optimized properties so as to prepare the nanocomposite for the same. For this purpose, PLLA was blended with Poly-(butylene adipate-co-terephthalate) (PBAT), Poly-(tetramethylene adipate-co-terephthalate), (PTAT), Polybutylene Succinate (PBS), Poly (ε-caprolactone) (PCL) and Polyesteramide (PEA) in the 50/50 (in wt%) composition and the parameters used in the DSM are given in the Table 3.2.

Table 3.2 Blending compositions and process parameters used in DSM Microcompounder for PLLA with various tough biopolymers

Blend Composition (in wt %)	Screw Speed (rpm)	Cycle Time (min)	Temperature (Top–Center–Bottom) (°C)	Mold Temperature (°C)	Injection Pressure (psi)
100PLLA	100	5	185 – 185 – 185	55	120
50PLLA / 50PBAT	100	5	185 – 185 – 185	53	120
100PBAT	100	5	150 – 150 – 150	50	90
50PLLA / 50PTAT	100	5	185 – 185 – 185	53	100
100PTAT	100	5	150 – 150 – 150	50	80
100PBS	100	5	150 – 150 – 150	50	80
50PLLA / 50PBS	100	5	185 – 185 – 185	53	90
100PCL	100	4	150 – 150 – 150	45	80
50PLLA / 50PCL	100	5	185 – 185 – 185	52	120
100PEA	100	4	160 – 160 – 160	50	90
50PLLA / 50PEA	100	5	185 – 185 – 185	52	100

From the above blended combinations, the PLLA/PBAT blend combination was finalized for further studies and their nanocomposites based on their mechanical and thermo-physical behaviors. The four different PLLA/PBAT (in wt%) blending compositions were prepared for the characterizations with the neat polymers viz., 100/0, 70/30, 60/40, 50/50, 30/70, 0/100 From these, nanocomposites of 100/0, 70/30, 60/40, 50/50 and 0/100 blends with 5 wt% of OMMT were also prepared.

The different parameters are used for different blend compositions and materials as given in the Table 3.3.

Table 3.3 Blending compositions and process parameters used in DSM Microcompounder for PLLA/PBAT/Clay blends

PLLA/PBAT/clay (in wt %)	**Screw Speed (rpm)**	**Cycle Time (min)**	**Temperature (Top–Center–Bottom) (°C)**	**Mold Temperature (°C)**	**Injection Pressure (psi)**
100 / 0 / 0	100	5	185 – 185 – 185	55	120
70 / 30 / 0	100	5	185 – 185 – 185	54	120
60 / 40 / 0	100	5	185 – 185 – 185	53	120
50 / 50 / 0	100	5	185 – 185 – 185	53	120
30 / 70 / 0	100	5	185 – 185 – 185	52	100
0 / 100 / 0	100	5	150 – 150 – 150	50	90
95 / 0 / 5	150	8	185 – 185 – 185	55	120
0 / 95 / 5	100	6	150 – 150 – 150	50	120
47.5 / 47.5 / 5 #	150	8	185 – 185 – 185	55	120
0 / 80 / 20 ##	150	4	150 – 150 – 150	----	----
66.5 / 28.5 / 5 ###	150	6	185 – 185 – 185	54	120
57 / 38 / 5 ###	150	6	185 – 185 – 185	53	120
47.5 / 47.5 / 5 ###	150	6	185 – 185 – 185	52	120

directly blend in one shot

for the master batch preparation

from the master batch

Note: *Processing parameters were followed and fine tuned based on their thermal behaviors (derived by DSC & TGA) and their suppliers' guidelines.*

Direct as well as master batch methods were used in order to choose the efficient process engineering for the nanocomposites preparation. This would be discussed in detail in the following chapter. Master batch method was giving better results in terms of mechanical and thermo-physical properties and so decided to carry only master batch method for the rest of the nanocomposite preparations. In direct way, we blend all the materials such as, polymers and clay melt compounded in one shot where as in the master batch method, we prepared the melt compound of 80% PBAT with 20% of the Clay, as a master batch pellets using the micro compounder as well as the pelletizer. Then these pellets were again melt compounded with appropriate proportions of neat polymers viz., PLLA and PBAT so as to get the required blend combination like the 5% nanocomposites of 50/50, 60/40 and 70/30 blends.

3.3.2 Compression Molding Machine

Compression molding machine (Model – M, Carver Laboratory Press, USA) was used to prepare films from pre-blended pellets that was in turn prepared from the above said microcompounder twin screw extruder. These films were prepared for the barrier properties measurements. This is one of the simple processes to make the films by just compressing the pellets in between the two hot platens. The blending compositions and the process parameters followed to prepare the films as shown in the following Table 3.4. Teflon sheets were used for the preparation of the films prior to avoid the stickiness of the molten plastic to the metal plates or molds.

Table 3.4 Blending compositions and process parameters followed in Compression molding machine for making PLLA/PBAT/Clay blends/nanocomposites based films

PLLA/PBAT/clay (in wt %)	Samples Size (g)	Residence Time (minutes) (x + y) ##	Mold Temperature (°C)	Compression Pressure (psi)
100 / 0 / 0	4	2 + 3	190	185 – 210
70 / 30 / 0	4	1 + 3	190	185 – 210
60 / 40 / 0	4	1 + 3	190	185 – 210
0 / 100 / 0	4	0 + 3	150	185 – 210
66.5 / 28.5 / 5 #	3.5	1 + 3	190	148 – 173
57 / 38 / 5 #	3.5	1 + 3	190	148 – 173

 # these pellets were prepared through the master batch method using DSM

Residence time includes the time involved in softening (x = preheating with out any pressure in between the molds) and the compression time (y) i.e., (x + y) minutes.

3.4. Characterization

3.4.1 Dynamic Mechanical Analyzer (DMA)

Dynamic Mechanical Analyzer (DMA Q800 – TA Instruments, USA) was used to measure the thermo-physical behaviors such as storage modulus, tan delta, loss modulus and HDT. DSM molded rectangular specimens were used for the experiments. Dual cantilever bending mode was used at an oscillating frequency of 1.0 Hz to measure the behaviors except for Heat Deflection Temperature (HDT) for which 3-point bending mode was used. Testing was carried out at dual cantilever using multi frequency strain mode at amplitude of 15 µm while heating from 29°C to 100°C at the scanning rate of 3°C/min. In the 3-point bending, using controlled force mode according to ASTM D648 standard, HDT was measured at 0.195% strain and amplitude of 20 μm while heating from ambient temperature to 80°C at the scanning rate of 2°C/min under constant load of 'P' where $P = [2\sigma t2w / 3l]$ in which, stress (σ) is 66 psi (455 KN/m^2), t = thickness, w = width, l = length (50mm). At least 3 specimens were tested for any of the above experiments.

3.4.2 Universal Testing Machine (UTM)

Universal Testing Machine (UTS, USA, model: SFM-20) was used to measure the tensile properties as well as flexural properties such as, % Elongation at break, tensile strength, flexural strength and their relative modulus. The tensile testing was done as per the ASTM D638 standard except the sample size and the gauge length, since the DSM made tensile samples are smaller in size unlike the standard size. So the gauge length of 1 inch was followed instead of the standard 2 inch gauge length. Grip separation speed of 1 in/min was used for almost all the samples except for neat PBAT samples for which the speed of 10 in/min was used. At least five specimens were used for each sample and a load cell of 1000 lb was used for all the experiments.

3.4.3 Izod Impact Tester

Monitor Izod Impact tester (Testing Machines Inc., USA, Model TMI® 43-02-01) was used with 5-lb pendulum to measure the notched Izod Impact strength of samples at ambient conditions according to the ASTM D256 standard. TMI notching cutter (model-22-05) was used to notch the samples as per that standard. The notched samples were conditioned for at least 48 hours at 23°C and 50% RH. At least five specimens were used for any sample.

3.4.4 Thermal Behaviors (DSC & TGA)

Thermal properties of the polymers, clay and their blends & nanocomposites were analyzed using Differential Scanning Calorimetry (DSC – TA Q100, TA Instruments, USA) and Thermo Gravimetric Analysis (TGA – moel-2950, TA Instruments, USA). In DSC, experiment was carried out at scanning rate of 10°C/min in the temperature range of – 50°C to 200°C with Heat-Cool-Heat cycle prior to measure the thermal properties such as melting temperature (T_m), glass transition temperature (T_g), crystallization temperature (T_c) etc. In TGA, the experiment was done at the scanning rate of 25°C/min in the presence of inert nitrogen atmosphere prior to process the pellets and also to analyze the degradation behavior of the biopolymers and their nano composites.

3.4.5 Barrier Properties (OP & WVP testers)

Oxygen Permeability was measured by the Oxygen Permeation tester (MOCON OX-TRAN® 2/21). At least 5 cm^2 area exposures of samples with aluminum mask were used for testing any specimen. The film samples were tested at 23°C, 0% R.H. and 740 mmHg. Water Vapor Permeability was measured by the Water Vapor Permeation tester (MOCON PERMATRAN-W® 3/33) and the samples were tested at 37.8°C, 85% R.H. and 740 mmHg.

3.4.6 X-ray Diffractometer (XRD)

X-ray diffraction (Rigaku 200B XRD diffractometer with 45kV, 100mA) studies were carried out for the nanocomposites of neat PLA and 60PLLA/40PBAT blended injection molded samples. XRD studies were done with CuKα radiation (=0.1516 nm) and a curved graphic crystal monochromator at a scanning rate of 0.5 °/min. Wide angle measurements and d-spacing in the nanocomposites were derived prior to analyze the intercalation and/or exfoliation behaviors of the clay in the bio polymer matrix and correlate with the mechanical, thermo-physical and morphological behaviors.

3.4.7 Environmental Scanning Electron Microscope (ESEM)

ESEM was used to analyze the morphology of the both neat polymer blends as well as the blend based nanocomposites. The fractured surfaces of the samples were analyzed for this purpose using ESEM (Phillips Electroscan 2020) with 4.0 torr water vapor and field emission filament (current set at 1.83A). An accelerating voltage of 15 kV was used to collect the ESEM images for these samples which were angled perpendicular to the fractured surface prior to view and record the images. Prior to view the same, a gold and platinum coating was applied on those fractured surfaces by Denton Desk II XLS sputter coater.

3.4.8 Transmission Electron Microscope (TEM)

The morphological behaviors of the nanoclay platelets in the nanocomposites of the 60PLLA/40PBAT blended polymer matrix were observed in the Transmission Electron Microscopy (TEM). Cryogenically microtomed ultra thin film specimens of the nanocomposites with the thickness of about 100 nm were used for the TEM observations. The microtoming was carried out at –120°C using the ultramicrotomy with a cryogenic attachment and diamond knife having an included angle of 4 deg. A Joel 100 CX TEM with LaB6 filament in 100kV accelerating voltage was used to collect bright field TEM images of these nanocomposites.

Chapter 4 Results and Discussion

4.1 PLLA based blends with tough biodegradable polymers

Stiffness and toughness are the critical properties that will decide the performance of the plastics and their applications. Storage modulus and notched izod impact strength were evaluated to finalize the suitable tough biopolymer that would give the required performances once blended with PLLA. Storage modulus and notched izod impact strength are related to the stiffness and toughness respectively. So, thermo-physical properties like storage modulus and mechanical properties like notched izod impact strength were used to choose the suitable tough polymer to blend with PLLA. In the first phase, PLLA was blended with selected biodegradable tough polymers such as PBAT, PTAT, PBS, PCL and PEA in the 50/50 (in wt%) composition to finalize the tough polymer.

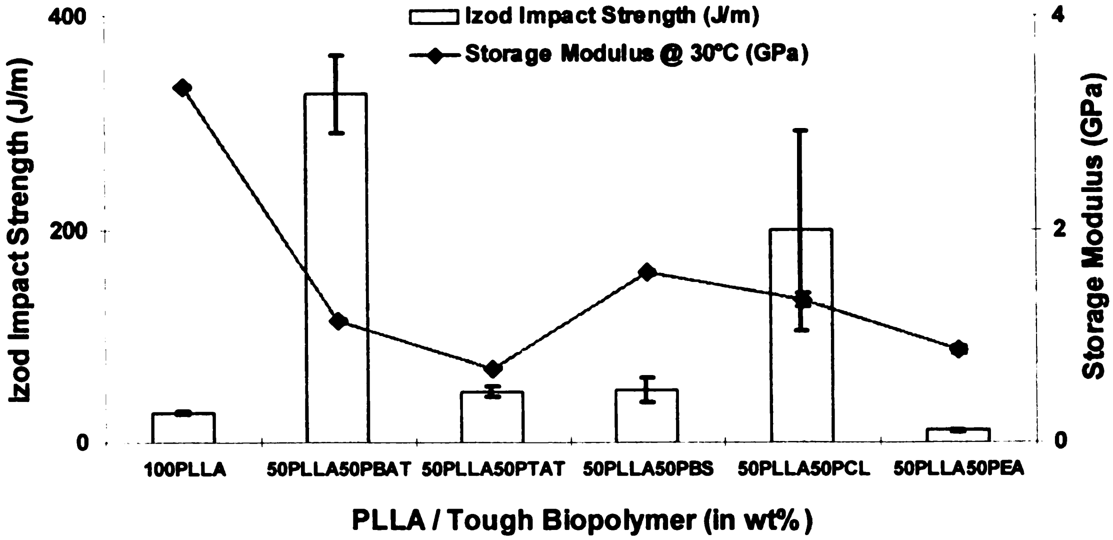


Figure 4.1 Storage modulus and notched izod impact strength of 50PLLA-50Tough biopolymer (PBAT, PTAT, PBS, PCL or PEA) blends

Injection molded samples were prepared from the DSM and then they were tested and evaluated at DMA and Izod impact tester to derive the above mentioned properties. Storage modulus data as well as notched izod impact data for the above said compositions are given the following Table 4.1 and Figure 4.1.

Table 4.1 Storage modulus and notched izod impact strength of 50PLLA-50Tough biopolymer (PBAT, PTAT, PBS, PCL or PEA) blends (in wt%)

PLLA-Tough Biopolymer (in wt. %)	Izod Impact Strength (J/m)	Std. Dev.	Storage Modulus @ 30°C (MPa)	Std. Dev.
100PLLA	28	2	3331	22
50PLLA / 50PBAT	327	36	1139	14
50PLLA / 50PTAT	47	5	692	2
50PLLA / 50PBS	49	12	1592	32
50PLLA / 50PCL	199	94	1343	64
50PLLA / 50PEA	11	1	867	39

From the above results, it was evident that 50PLLA/50PBAT blend was having better properties (storage modulus=1.139 GPa and izod impact strength = 327 J/m) although PLLA-PBS blend showed better storage modulus at the cost of the impact strength that is very poor. PLLA/PBAT blend has got required modulus and izod impact strength is much better than any other tough plastics based blends here. It can be seen that more than 1000% improvement in the toughness when compare to the neat PLLA while maintaining about one third of its modulus. Still this modulus is comparable to that of conventional PP. As the objective is to improve the toughness of this PLLA while maintaining the required the modulus, it was decided to go for further studies for the optimization of the best blend compositions for PLLA with PBAT from this reference blend proportion ie., 50PLLA/50PBAT.

4.2 PLLA – PBAT based blends

In the second phase, PLLA:PBAT blend ratios (in wt%) of 100:0, 70:30, 60:40, 50:50, 30:70 blend compositions were melt compounded and injection molded samples were prepared. Samples were evaluated at DMA, izod impact tester and universal testing machine for the thermo-physical properties like heat deflection temperature (HDT) and storage modulus and the mechanical properties like notched izod impact strength, % of elongation at break and tensile strength. The thermo physical properties for the above compositions are reported in the Table 4.2 and Figure 4.2

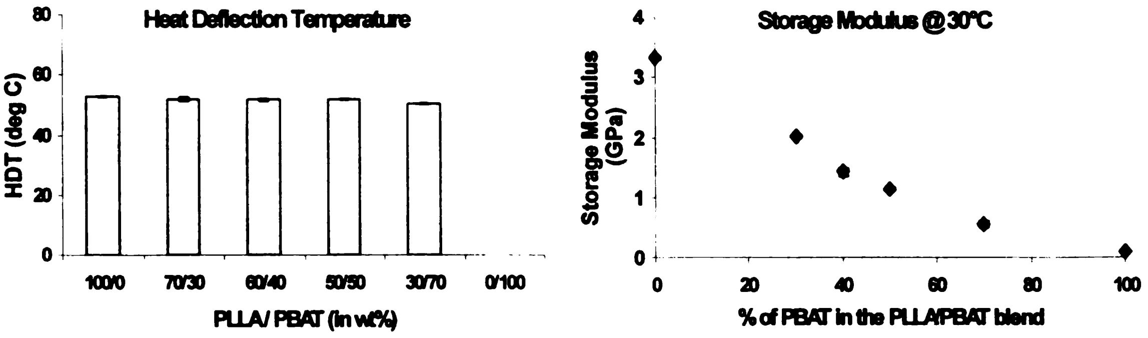


Figure 4.2 Thermo-physical properties viz., heat deflection temperature (HDT) and storage modulus for various PLLA-PBAT blends

It was clear from the above results that the storage modulus was quite coherent with the blend compositions ie., the storage modulus is decreasing with increasing in the % of PBAT in the PLLA blend matrix in a coherent manner. So, the blend worked well in better manner without any compatibilizer however, there might not be any miscibility or compatibility in these blends that was derived from the DSC results. HDT was not much affected by the PBAT presence in the PLLA matrix irrespective of the various weight % of PLLA or PBAT. Even at the 70% of PBAT had the HDT of 50.44°C in comparison to neat PLLA that had the HDT of 52.84°C. PLLA:PBAT blends of 50:50, 60:40 and 70:30 having the moderate storage modulus viz., 1139 MPa, 1423 MPa and 2009 MPa when compared to 100PLLA that had about 3331 MPa.

The injection molded samples were also evaluated for the mechanical properties such as notched izod impact strength, tensile strength and % break elongation. These mechanical properties are also important properties that decide the polymer selection for many applications especially in packaging. The mechanical properties such as notched izod Impact strength and tensile properties are reported in the Figure 4.3 and Table 4.3.

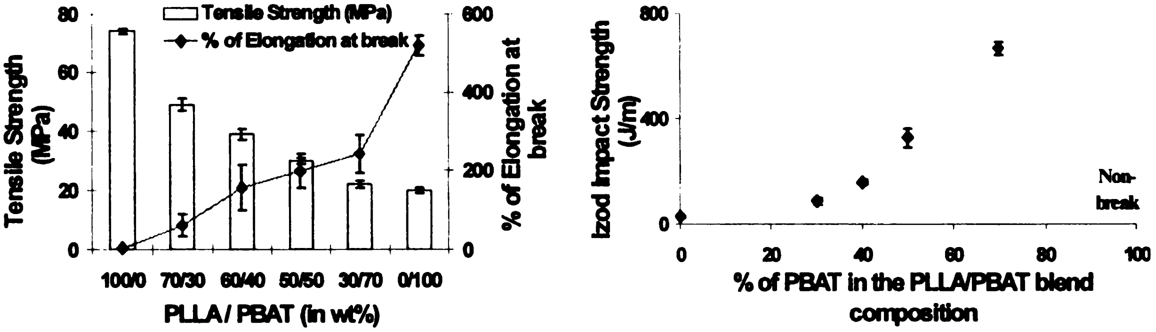


Figure 4.3 *Mechanical properties viz., tensile properties and notched izod impact strength for various PLLA-PBAT blends*

It was evident from the above data figure that the diversified performance of the various blends of PLLA/PBAT. Neat PBAT was highly flexible that it was not breakable in the notched izod impact strength. There was an increase in the impact strength of PLLA blends with increase in this tough polymer (PBAT) % in the blend matrix. The notched izod impact strengths improved for the PLLA/PBAT blends about 210%, 460% and 1070% for the blends of 70/30, 60/40 and 50/50 respectively when compared to neat PLLA. Also the % of elongation at break had improved from 2 % for neat PLLLA to 61% (30 times), 157% (78 times) and 199% (100 times) for the blends of 70/30, 60/40 and 50/50 respectively. However, tensile strength had come down from 74 MPa for the neat PLLA to 49 MPa, 39 MPa and 30 MPa for the blends of 70/30, 60/40 and 50/50 respectively. It was still found that larger standard deviations especially in elongation and that showed the incompatibility and immiscibility of the blends. The tough polymer PBAT was contributing its elongation behavior to the stiff polymer PLLA and improves the toughness that could be seen from the elongation and impact improvements for the blends in comparison to the neat PLLA. This indicated that they are very much comparable with the conventional plastics and it was decided to carry out the nanocomposite works on these compositions viz., PLLA:PBAT = 70:30, 60:40 and 50:50 (in wt%) based on the above performances.

4.3 PLLA – PBAT based blends and their Nanocomposites

In the third phase, PLLA:PBAT blend ratios (in wt%) of 70:30, 60:40 and 50:50 blend compositions were melt compounded with 5wt% of OMMT clay and injection molded samples were prepared from the same. In this research experiments, all the nanocomposites were prepared with 5wt% of OMMT. Now onwards, the phrase 'nanocomposite' would imply that it contains 5 wt% of OMMT in the polymer/polymer blend matrix.

4.3.1 Direct Method Vs Master batch Method

There were 2 methods of nanocomposite preparation were followed viz., direct blending and master batch based blending for one composition ie., 50/50 that was taken to choose the best method. The schematic diagram is shown in the figure about the both methods (Figure 4.4). In the direct blending method, we mix required ratios of the polymers and OMMT manually in a container and then this mixer was fed into the extruder through feeder to prepare the nanocomposite melt compounding. Where as in the other method, we prepared the master batch in which 80 wt% of PBAT and 20 wt% of OMMT were mixed and fed into the extruder to prepare the melt compounded strands from which the pellets were made using a pelletizer. This master batch was mixed with PLLA and PBAT in the required ratios and then this mix again fed into the extruder to get the final nanocomposite melt compounding. Here we took PBAT for the master batch preparations since it has better thermal stability than the PLLA. Both methods were used to prepare the samples and then were evaluated for their mechanical and thermo-physical properties in order to find the better method for the nanocomposite preparations.

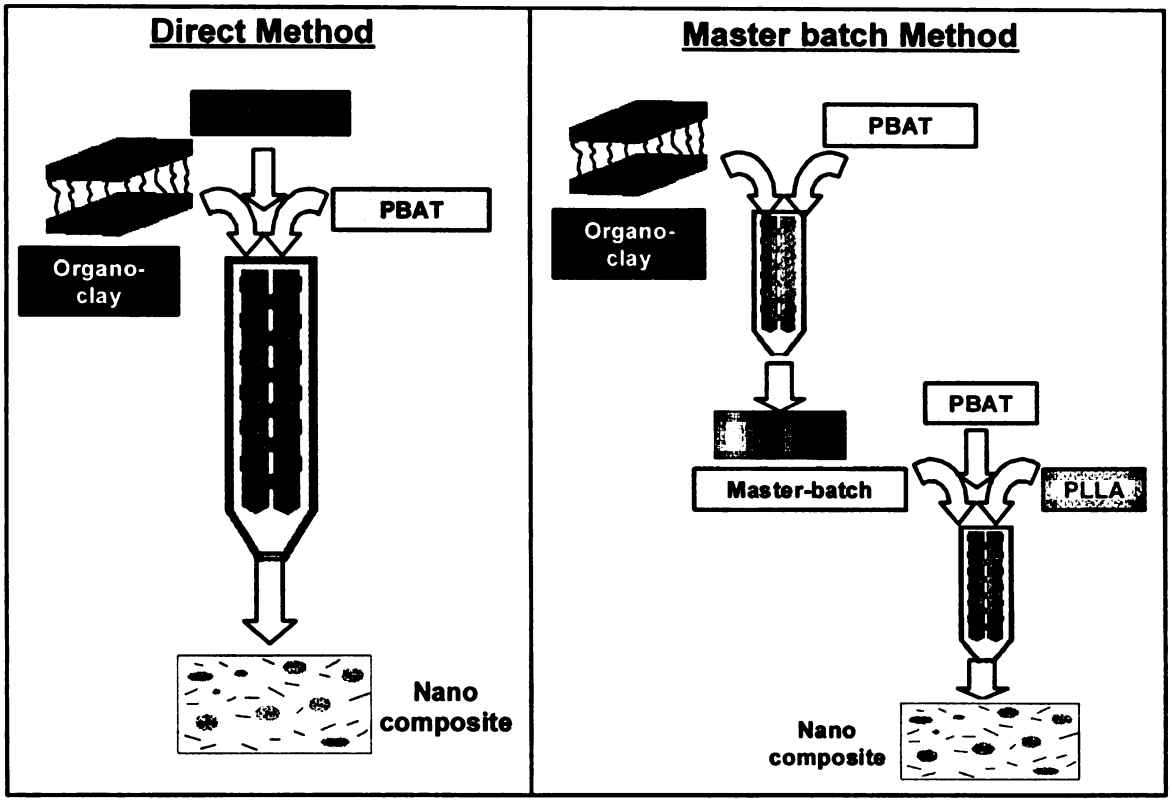


***Figure 4.4** Effective Process engineering for the nanocomposite preparations: Direct Method Vs Master batch Method*

The samples of master batch method showed better properties than that of direct method (Figure 4.5). This was decided based on the thermo-mechanical and mechanical behaviors. Although both methods show similar behaviors except in the tensile strength where master batch method exhibited better results. Then for the rest of the blends such as 60/40 and 70/30 of PLLA/PBAT, the master batch method was followed to prepare the nanocomposite samples. Nanocomposites of neat polymers viz., PLLA and PBAT were also prepared and evaluated for their mechanical and thermo-physical properties so as to give the comparison with their blends and nanocomposites.

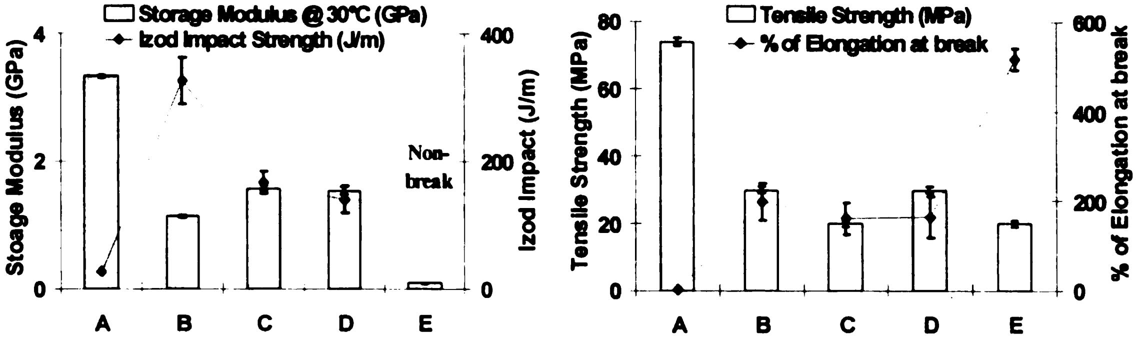


__Figure 4.5__ Optimization of effective process engineering between <u>direct method and master batch method</u> for the nanocomposites preparations. A=100PLLA; B=50PLLA50PBAT; C=47.5PLLA/47.5PBAT/5OMMT-Direct; D=47.5PLLA/47.5PBAT/5OMMT-Master batch; E=100PBAT (all are in wt %)

4.3.2 Thermo-physical and Mechanical Properties:

From the above, the selected compositions of PLLA:PBAT blends in the ratios of 70:30, 60:40 and 50:50 were fabricated into nanocomposites with 5wt% of OMMT through master batch method by melt blending technique. Blends showed

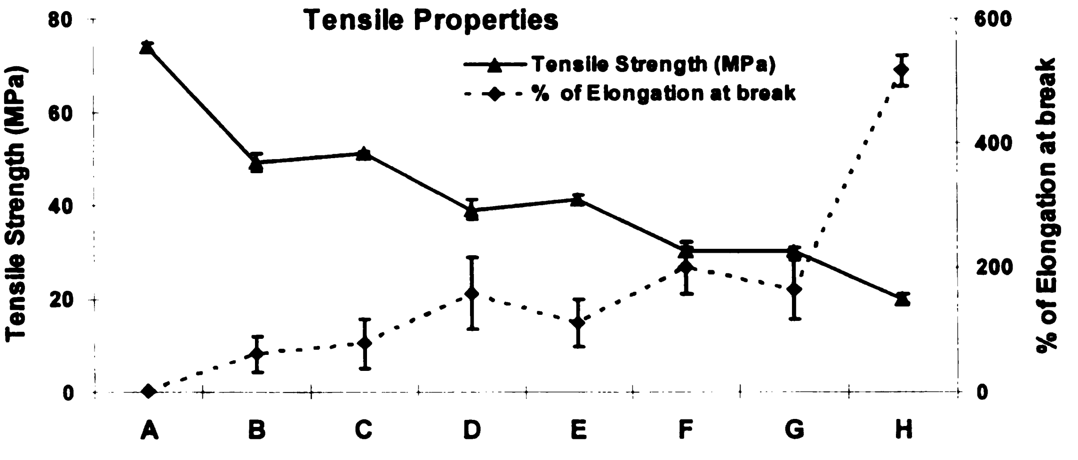


__Figure 4.6__ Tensile properties of the nanocomposites of various PLLA/PBAT blend compositions along with the respective neat blends. A=100PLLA; B=70PLLA30PBAT; C=66.5PLLA/28.5PBAT/5OMMT; D=60PLLA/40PBAT; E=57PLLA/38PBAT/5OMMT; F=50PLLA/50PBAT; G=47.5PLLA/47.5PBAT/5OMMT; H=100PBAT (all are in wt %)

coherent results again. Storage modulus had improved about 33%, 47% and 36% for the nanocomposites of PLLA:PBAT blends of 70:30, 60:40 and 50:50 respectively when compared to the respective neat blends. However, notched izod impact strength results were decreased viz., 35, 55, 140 J/m for the same

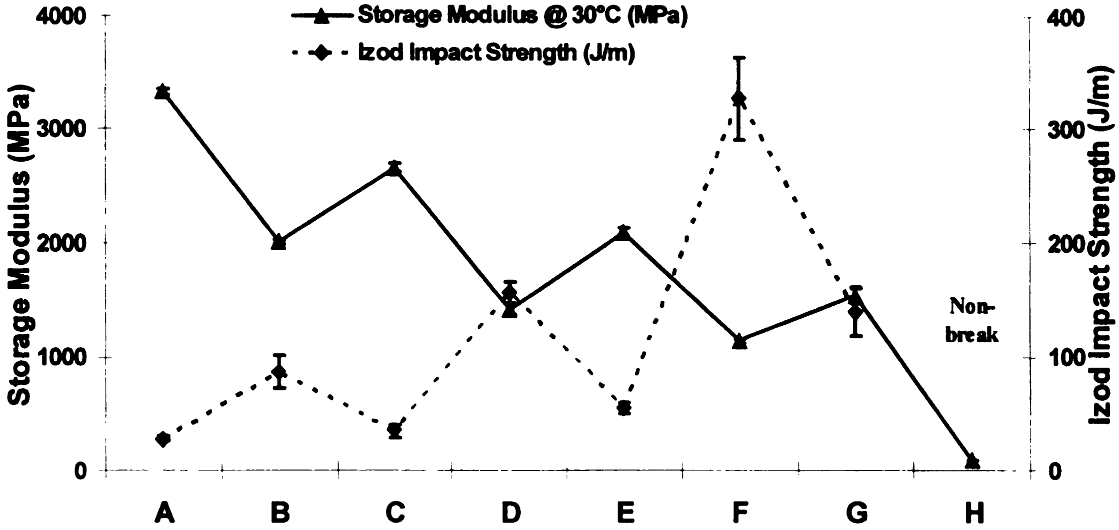


Figure 4.7 Thermo-physical and mechanical properties of the nanocomposites of various PLLA/PBAT blend compositions along with the respective neat blends. A=100PLLA; B=70PLLA30PBAT; C=66.5PLLA/28.5PBAT/5OMMT; D=60PLLA/40PBAT; E=57PLLA/38PBAT/5OMMT; F=50PLLA/50PBAT; G=47.5PLLA/47.5PBAT/5OMMT; H=100PBAT (all are in wt %)

nanocomposites when compared to the respective neat blends that had 87, 157 and 327 J/m respectively for 70/30, 60/40 and 50/50 based blends (Table 4.2, Table 4.3 and Figure 4.7). Still tensile strength and elongation results are retained near to that of neat blends (Table 4.3 and Figure 4.6). The mechanical and thermo-physical properties of these nanocomposites along with neat blends' are given in the Tables 4.2 & 4.3 and Figures 4.6 & 4.7.

Table 4.2 Thermo-physical properties viz., heat deflection temperature (HDT) and storage modulus of PLLA-PBAT-OMMT blends/nanocomposites based injection molded samples

PLLA/PBAT/OMMT (in wt %)	Heat Deflection Temperature (°C)	Std. Dev.	Storage Modulus @ 30°C (MPa)	Std. Dev.
100 / 0 / 0	52.84	0.15	3331	22
70 / 30 / 0	51.96	0.47	2009	22
60 / 40 / 0	51.80	0.22	1423	55
50 / 50 / 0	51.89	0.16	1139	14
30 / 70 / 0	50.44	0.06	565	45
0 / 100 / 0	---	---	92	6
95 / 0 / 5	57.17	0.10	4261	93
0 / 95 / 5	42.10	1.65	188	2
47.5 / 47.5 / 5 #	55.91	0.48	1574	45
66.5 / 28.5 / 5 ##	54.76	0.14	2663	30
57 / 38 / 5 ##	54.72	0.32	2086	41
47.5 / 47.5 / 5 ##	54.80	0.35	1544	66

directly blend in one shot

from the Master batch

Table 4.3 Mechanical properties viz., notched izod impact strength and tensile properties of PLLA-PBAT-OMMT blends/nanocomposites based injection molded samples

PLLA/PBAT/ OMMT (in wt%)	Izod Impact Strength (J/m)	Std. Dev.	Tensile Strength (MPa)	Std. Dev.	% of Elongation at break (%)	Std. Dev.
100 / 0 / 0	28	2	74	1	2	1
70 / 30 / 0	87	14	49	2	61	29
60 / 40 / 0	157	9	39	2	157	57
50 / 50 / 0	327	36	30	1	199	42
30 / 70 / 0	665	26	22	1	243	47
0 / 100 / 0	Non-break	---	20	1	516	25
95 / 0 / 5	28	1	73	1	7	2
0 / 95 / 5	Non-break	---	18	2	285	16
47.5 / 47.5 / 5 #	167	17	20	1	161	36
66.5 / 28.5 / 5 ##	35	6	51	0.33	78	39
57 / 38 / 5 ##	55	5	41	1	111	38
47.5 / 47.5 / 5 ##	140	22	30	1	164	46

[#] *directly blend in one shot*

[##] *from the Master batch*

It was evident from the storage modulus curve analysis that storage modulus was improved due to the nanoclay reinforcement even better than neat PLLA above the T_g of PLLA (Figure 4.8).

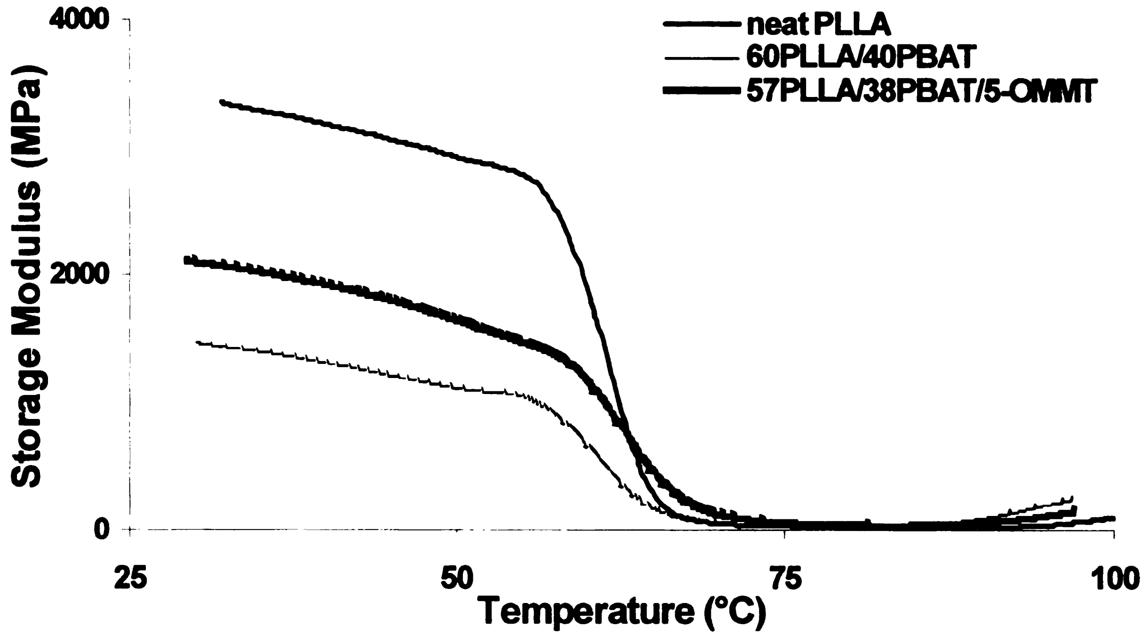


Figure 4.8 *Storage modulus curve analysis for the neat PLLA, 60PLLA/40PBAT blend and its nanocomposite (all are in wt%)*

Also the stress-strain curved analysis showed that area under the curve for the nanocomposite was larger than that of the respective neat blend and this implied that energy absorption would be more for the nanocomposite samples than that of the respective neat blend (Figure 4.9).

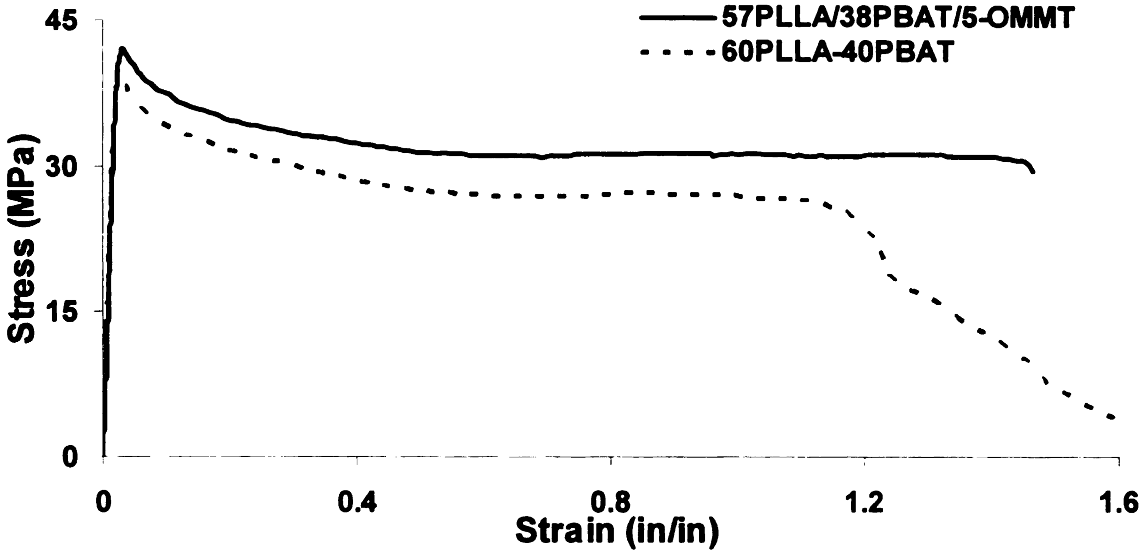


Figure 4.9 Stress-strain curve analysis for 60PLLA/40PBAT blend and its nanocomposite (all are in wt%)

4.3.3 Thermal Properties:

Thermal properties were evaluated using DSC and TGA. The glass transition temperature (T_g) and melting point (T_m) of PLLA were not affected by the presence of nanoclay reinforcement when compared to the neat PLLA. This was also evident from the storage modulus curves discussed earlier. HDT showed the similar behavior that was discussed earlier in the thermo-physical properties. However, the DSC curves showed that the crystallization temperature (T_c) of the nanocomposite lied in between that of the neat PLLA and that of the respective neat blend (Figure 4.10). This implied that crystallization was affected by the presence of the nanoclay particles in the polymer blend matrix and improved the crystallization of the nanocomposite when compared to the respective neat blend. TGA curves showed that nanocomposite improved the thermal degradation temperatures when compared to the neat blend (Figure 4.11).

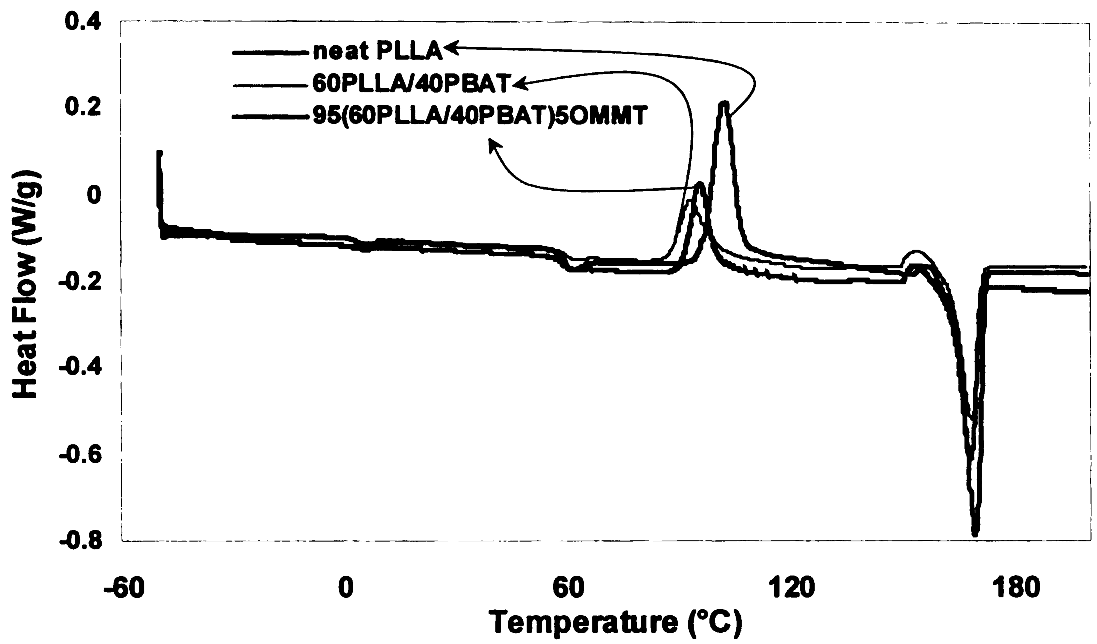


Figure 4.10 *DSC curve analysis for the neat PLLA, 60PLLA/40PBAT blend and its nanocomposite (all are in wt%)*

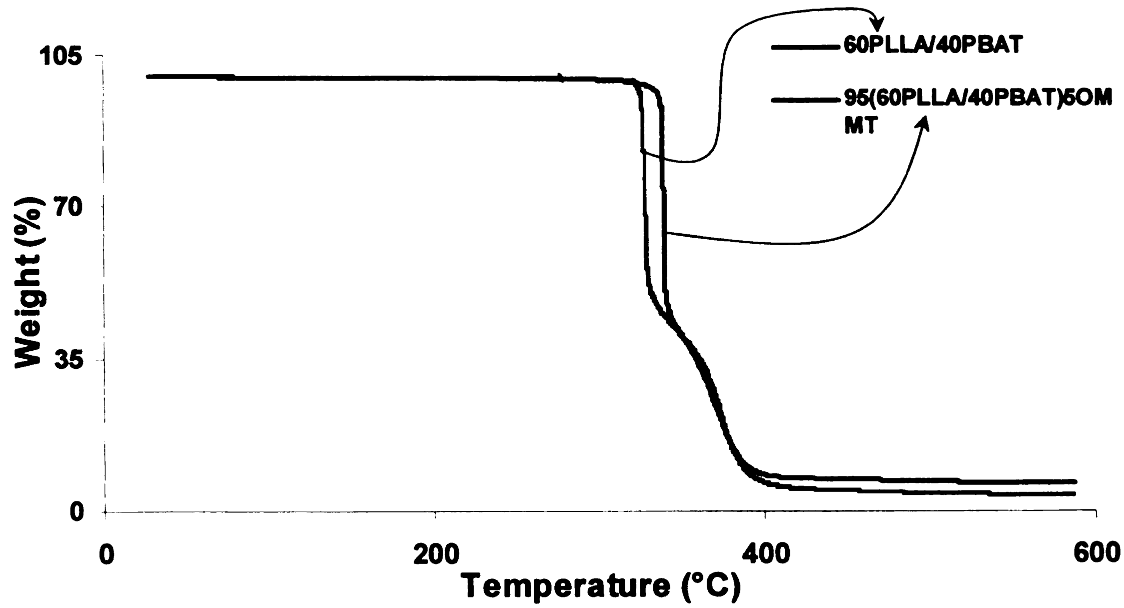


Figure 4.11 *TGA curve analysis for 60PLLA/40PBAT blend and its nanocomposite (all are in wt%)*

4.3.4 Barrier Properties:

Based on the above mechanical properties only selected combinations like 60/40 and 70/30 blends and their nanocomposites along with neat PLLA and neat PBAT were evaluated for the barrier properties. We used the compression molded films and for blends, strands were extruded from the DSM micro compounder and then they were pelletized prior to use in compression molding. Barrier properties such as Oxygen Permeability and Water Vapor Permeability data are reported in two different units in the following Tables 4.4 & 4.5. Also barrier properties also reported (Table 4.6) for some of the conventional plastics like PE, PP, PS, PET and Nylon that are widely used in packaging.

Table 4.4 Barrier properties viz., Oxygen Permeability and Water Vapor Permeability of PLLA-PBAT-OMMT blends/nanocomposites based compression molded films (in SI units)

PLLA / PBAT / OMMT (in wt %)	Oxygen Permeability (Kg.m/m^2.s.Pa) (10^{-21}) @ 23°C & 0% RH	Std. Dev.	Water Vapor Permeability (Kg.m/m^2.s.Pa) (10^{-14}) @ 37.8°C & 85% RH	Std. Dev.
100 / 0 / 0	9.2026797632	0.133520554	1.811337475	0.21827045
70 / 30 / 0	---	---	3.043114272	0.444018386
60 / 40 / 0	9.560034810	1.387556138	3.508807439	0.596093638
0 / 100 / 0	23.181543925	1.277135773	6.274510735	0.016147332
66.5 / 28.5 / 5 #	---	---	2.325265472	0.137291689
57 / 38 / 5 #	**8.323919854**	1.702471714	2.755923089	0.290641885

 # from the Master batch

Table 4.5 Barrier properties viz., Oxygen Permeability and Water Vapor Permeability of PLLA-PBAT-OMMT blends/nanocomposites based compression molded films (in USA standard industry units)

PLLA / PBAT / OMMT (in wt %)	Oxygen Permeability (cc.mil/100in^2.d.atm) @ 23°C & 0% RH	Std. Dev.	Water Vapor Permeability (g.mil/100in^2.d.mmHg) @ 37.8°C & 85% RH	Std. Dev.
100 / 0 / 0	155.40	2.26	0.53	0.064
70 / 30 / 0	---	---	0.89	0.130
60 / 40 / 0	161.43	23.43	1.03	0.174
0 / 100 / 0	391.45	21.57	1.84	0.005
66.5 / 28.5 / 5 #	---	---	0.68	0.040
57 / 38 / 5 #	**140.56**	28.75	0.81	0.085

from the Master batch

Table 4.6 Barrier properties of conventional plastics such as LDPE, HDPE, OPP, PS, OPET, and Oriented Nylon6 (in USA standard industry units)

Literature Data [4.1]		
	Oxygen Permeability (cc.mil/100in^2.d.atm) @ 23°C & 0% RH	Water Vapor Permeability (g.mil/100in^2.d.mmHg) 40°C & 90% RH
LDPE	554	0.02289543
HDPE	150	0.00763181
OPP	163	0.00763181
PS	260	0.17071153
OPET	2.3	0.02410045
Oriented Nylon6	1.78	0.20485383

It was found out to be about 13% improvement of oxygen barrier and was about 22-24 % improvement of the water vapor barrier for the nanocomposite when compared to the concerned neat blends. This implied that clay might not be fully exfoliated and the tortuousity across the polymer matrix might not be achieved successfully. However the tortuousity due to the intercalated and flocculated platelets contributed certain improvements in the barrier properties of the nanocomposites. It was also evident from the compression molded films that have transparent spots formed due the agglomerates and this was also evident from the morphology analysis that would be discussed later here. Oxygen barrier of the nanocomposite was better than that of the oriented polypropylene and polystyrene where as the oxygen barrier of neat blend molded film was comparable to that of polyolefins. Here we didn't consider the orientation effects since we were using the compression molded film that doesn't give any orientation effects. Still they are good enough to compete with those oriented conventional polymers. This gives a scope of replacing few of the conventional polymers at this stage it self.

4.3.5 Structural Analysis:

XRD was used to analyze the clay behaviors in the polymer matrix as shown in the following Figure 4.12 and Table 4.7. As per the supplier's data, the neat treated clay (OMMT clay) has the d-spacing of 18.6 A^{o} where as, the nanocomposites of neat PLLA and the 60PLLA:40PBAT blended with 5wt% OMMT clay, was observed at $2\Theta=2.75^{o}$ and $2\Theta=2.65^{o}$ showed the d-spacing of

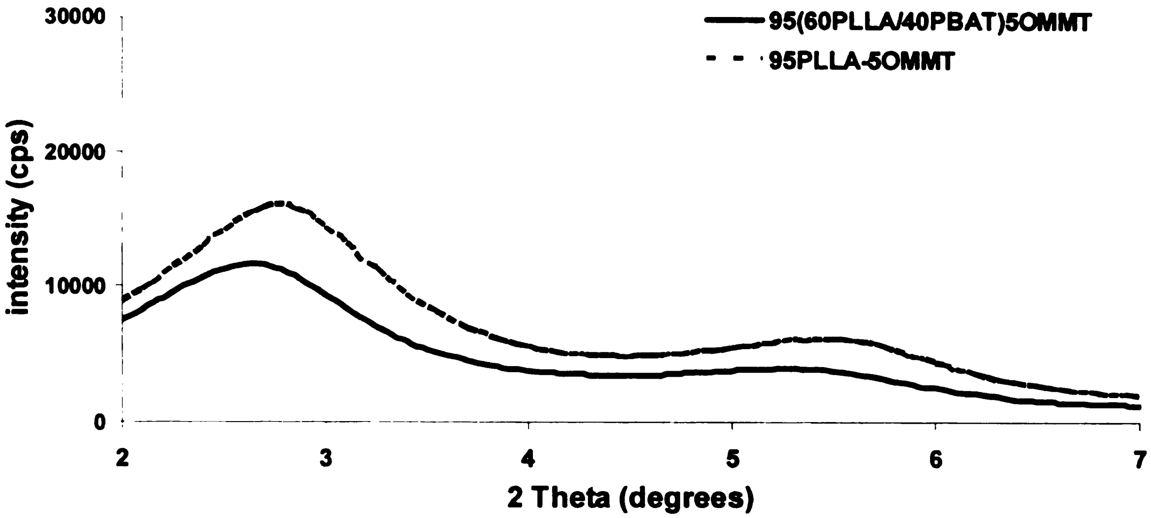


Figure 4.12 XRD patterns of nanocomposites of 100PLLA and 60PLLA/40PBAT with 5 wt% OMMT clay blended polymer matrix (all compositions are in wt%)

31.55 A° and 33.34 A° respectively. This implied that the interaction of clay platelets was existed in the nanocomposite polymer matrix. This was also evident from the following TEM image discussion. It was also found that the clay intercalation behavior is almost similar in both the neat PLLA nanocomposite and blended polymer nanocomposite though blended one has little higher value than the neat PLLA's d-spacing.

Table 4.7 XRD patterns of nanocomposites of 100PLLA and 60PLLA:40PBAT with 5wt% OMMT clay blended polymer matrix

	2Θ (°)	Θ (°)	SinΘ	d (A°)
OMMT (supplier's data)	---	---	---	18.6
100PLLA with 5%OMMT	2.8	0.024435	0.024432	31.55343
60PLLA40PBAT with 5%OMMT	2.65	0.023126	0.023124	33.33913

4.3.6 Morphology Analysis:

Morphological analyses were also done by the ESEM on the izod impact tested fracture surfaces of both the neat polymer blend and their nanocomposite especially for 60/40 and 70/30 blends and their nanocomposites. The ESEM images were taken in the magnification of 200µ scale bar to understand the morphology between the blend and the nanocomposite in the following figure (Figure 4.13). The phase separation is very much evident from all the blend images where as, the phase separation is reduced in the presence of OMMT cay. This implies that the clay acting as bridge between the 2 phases of PLLA and PBAT in the polymer matrix. However, the crystallization is affected by the presence of OMMT cay and its nucleation effects that can be seen in the nanocomposite based images where the spherulite sizes are reduced compare to the neat blend sample images. So it was expected to get the better impact and elongation based in the effect of the clay coupling between the phases however that was compensated by the crystallization behavior that again reduced the

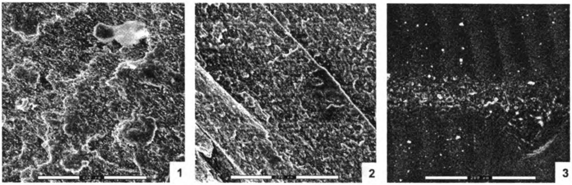


Figure 4.13 *ESEM micrographs on the fractured surfaces of 1. 60PLLA/40PBAT blend; 2. Nanocomposite of 60PLLA/40PBAT blend; 3. 70PLLA/30PBAT blend (all compositions are in wt%); <u>200 µm scale bar for all images</u>*

impact or elongation. This was evident from earlier discussed mechanical behaviors. Still this will give better barrier due to the crystallization as well as clay platelets presence, meaning more small no of spherulites with clay platelets give more tortuous path for the permeating molecules like oxygen or water vapor. It could be seen that 60/40 neat blend image showed the rougher surface than that of 70/30 neat blend and nanocomposite of 60/40 blend. This also indicated the fracture nature of the samples and more the PBAT present more the fracture resistance and also presence of clay particles reduce the same and so lesser resistance to fracture. These were coherent with the izod data derived earlier.

Morphological behaviors were analyzed by the TEM analysis for the nanocomposite of 60PLLA:40PBAT blend. The TEM images showed the phase separation in the blended polymer matrix as well as intercalated behaviors of the

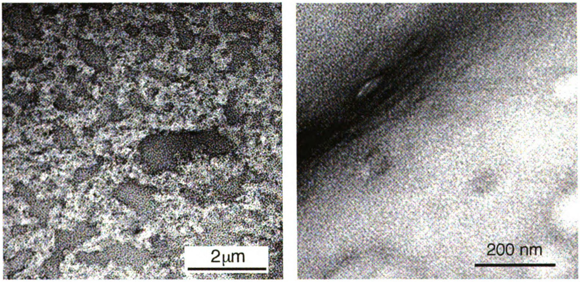


Figure 4.14 *TEM images for the phase separation (low & high magnifications) with the intercalated nano scale OMMT clay agglomerates (low magnification) views in the 5 wt% OMMT reinforced nanocomposite of 60PLLA:40PBAT polymer matrix (composition is in wt%)*

nanoscale OMMT agglomerates (Figure 4.14). The immiscible nature of the blend was evident from both low and high magnification TEM images in which it can be clearly seen that the white circular batches (high magnification) and whitish continuous batches (low magnification) indicated the PBAT component in the PLLA matrix. This immiscible nature was also evident from the DSC behaviors of these blends and nanocomposites. The Intercalation of the clay platelets was also evident from the agglomerates (darkish batches) in the high magnification TEM images. It was also supported from the transparent spots found in the compression molded films. It is assumed that due to the agglomeration of the intercalated clay platelets that stretch the near by the polymer chains and so created those transparent spots in the films that can be seen even by the plain eyes. Due to this intercalation behavior, the barrier properties improved for both nanocomposite films due to the tortuous bath created by these nano scale OMMT agglomerates in comparison to the neat blends and for oxygen barrier even compare to the neat PLLA. This could also evident for the improvement of storage modulus while retaining the tensile strengths for these nanocomposites.

4.3.7 Halpin-Tsai Model Correlation of Elastic Modulus through Pseudo-inclusion Model

The elastic modulus values were correlated with theoretical values calculated using the Halpin-Tsai equation through Pseudo-Inclusion model [4.2]. The models are explained in the Appendix 1. Since the TEM and XRD analyses showed the intercalated morphology, Halpin-Tsai was used through the Pseudo-Inclusion model. In the blend matrix, uniform dispersion of intercalated clay nanoplatelets was assumed. Additionally, it was also assumed that the PBAT secondary phase was uniformly dispersed in the PLLA primary matrix. Since the nanocomposite specimens were prepared by injection molding, the longitudinal property was taken for the calculation. It was found that the calculated elastic modulus curve of the nanocomposites was closely fit with values of the experimental nanocomposites (Figure 4.15).

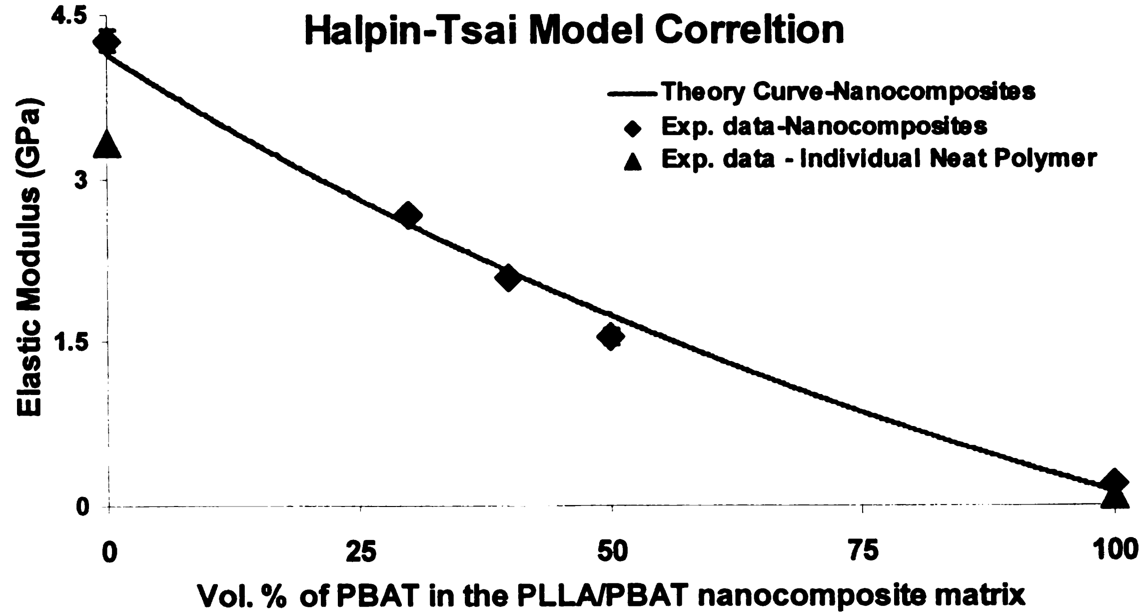


Figure 4.15 *Elastic modulus data correlation between the experimental data and theoretical calculated values of 5.0 wt.% (1.62 vol.%) clay nanocomposites using Halpin-Tsai model through Pseudo-inclusion model*

Chapter 5 Conclusions and Recommendations

We have discussed the melt compounding of PLLA based blends with various tough biodegradable polymers such as PBAT, PTAT, PBS, PCL and PEA in the absence of any compatibilizer in 50:50 (weight basis) ratio as the reference composition. Based on their mechanical and thermo mechanical properties, PBAT (impact – 327 J/m and modulus – 1.14 GPA) was finalized for further studies. In the second phase, PLLA:PBAT blend of 70:30, 60:40, 50:50, 30:70 melt compounded samples were prepared and evaluated for the mechanical and thermo mechanical behaviors. Based on the over all behaviors and performances of these blends, it was then decided to go for the preparation of nanocomposites for the 50:50, 60:40 and 70:30 blend of PLLA:PBAT composition since all these 3 showed the performances which are in the range of expected optimum scale while keeping at least 50 wt % of PLLA. In the third phase, the above finalized blends were made into nanocomposites prepared with 5 wt% of the specific commercially available OMMT (natural MMT clay modified with dimethyl, hydrogenated tallow, 2-ethylhexyl quaternary ammonium – a quaternary ammonium salt). These nanocomposite samples were further analyzed for their mechanical and thermo physical properties. It was found that PLLA:PBAT blend of 60:40 and 70:30 compositions showed optimum results in their mechanical and thermo-physical properties. These 2 nanocomposites were further studied for the barrier properties especially for water vapor barrier by using the compression molded films and compared with that of respective neat polymer blended films. However nanocomposite of the 60PLLA:40PBAT showed impressive optimum properties viz., tensile strength - 41 MPa, % break elongation – 111%, izod impact – 55 J/m and modulus – 2.01 GPa with improved barrier performances. These behaviors still are very much comparable to many conventional polymers like OPP. Here it was finalized to go for the 60PLLA:40PBAT based nanocomposite along with its neat polymer blends and individual polymer for further investigations like oxygen permeability, XRD, SEM and TEM analysis. In conclusion,

a. PLLA was giving required performances with PBAT with out any compatibilizer though it was an immiscible blend in comparison to other tough biodegradable polymers like, PTAT, PBS, PCL and PEA.

b. In the neat polymer blends, 60:40 and 70:30 blends of PLLA:PBAT providing the required optimum performances with improved toughness.

c. The nanocomposites of the above 2 blends were showing the expected behaviors. However, it was decided to go for 60PLLA:40PBAT blend since this has relatively better impact when compare to the nanocomposite of 70PLLA:30PBAT and rest of the properties like, tensile strength, % break elongation, modulus, barrier are as expected with linear coherency with the blend proportions in both nanocomposites. Thus the 60/40 nanocomposite provided the required stiffness-toughness balance with improved barrier properties

d. Improved thermal behaviors were observed for the nanocomposites when compared to the respective PLLA/PBAT blend

e. The nanocomposite of 60PLLA:40PBAT were analyzed for the Oxygen barrier, XRD, SEM and TEM. It showed both intercalated behavior in the morphological analysis. It was also visible in the compression molded films showing some transparent spots that indicates the agglomerations of the intercalated clays. These all also evident from the barrier results in which nanocomposites showed improved barrier in comparison to the neat blends. Oxygen barrier for this nanocomposite was better than its neat blend (60:40) that in turn was better than that of the neat PLA even. Otherwise the enhanced modulus was found in all the nanocomposites.

f. Another interesting finding was that nanocomposites retaining the tensile strength comparable to the concerned neat polymer blend while keeping the optimum impact as well as % break elongation.

g. However, most of the samples showed larger standard deviation especially in tensile properties and that also obvious that these blends are immiscible in nature that was already confirmed from the morphology analysis and DSC study.

h. Since one of the objectives for this present study was not to use any compatibilizer and examine the possibility of the blends, significant results have been achieved in improving the toughness for the PLLA while maintaining the stiffness-toughness balance without using any compatibilizer

i. These final results indicate that this nanocomposite still can compete with many conventional plastics being used today.

j. Based on the above conclusions, it would also be recommended for the future works that a well suited compatibilizer can be tried to achieve further requirements if any as a continuation this work.

k. While trying with any compatibilizer, it would also make sense to try for other combinations having lesser PBAT contents such as 90PLLA:10PBAT, 80PLLA:20PBAT etc.

l. Try another suitable nano-clay with effective process engineering in order to achieve the effective exfoliation in the PLLA

APPENDIX 1

The storage modulus can be calculated using the Halpin-Tsai (HT) equation [A.1]. HT equation is useful to predict the change of the elastic modulus of two-phase materials, such as composite materials. The following equations were used for the calculation of the elastic modulus in longitudinal direction [A.2]. :

$$E_L = E_m \frac{1 + \eta_L \xi V_c}{1 - \eta_L V_c} \tag{A.1}$$

where,

$$\eta_L = \frac{(E_c / E_m) - 1}{(E_c / E_m) + \xi} \tag{A.2}$$

E and V → the elastic modulus and volume fraction, respectively

L → the longitudinal property

m, c → matrix property, clay property,

ξ → $\xi = 2\,\alpha_c / 3 = 2\,l_c / 3\,t_c$ (A.3)

where,

α_c, l_c, and t_c → aspect ratio, length, and thickness of individual clay nano-platelets.

Since the TEM and XRD results showed the intercalated clay morphology in the nanocomposites, this HT equation was utilized with the pseudo-inclusion model. This pseudo-inclusion model [A.2] was used to analyze polymer-intercalated clay matrix assuming that intercalated clay nanoplatelets were dispersed uniformly in polymer (PLLA or PBAT) matrix. With the pseudo-inclusion model, it was considered that 'individual clay nanoplatelets' in the original HT equation were assumed to be 'the intercalated clay nanoplatelets'. As a result of the above assumptions, the modulus, aspect ratio, and the volume fractions of the pseudo-inclusion were calculated according to the rule of mixtures that lead to the following modified equations.

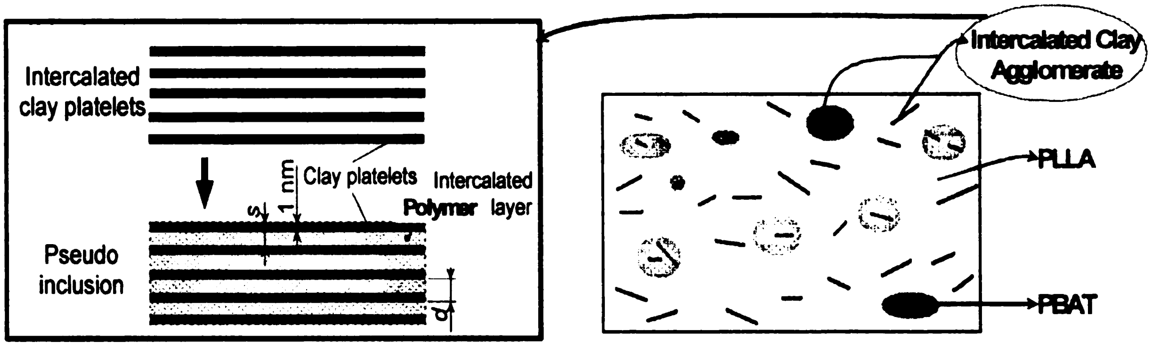


Figure A-1 A model of three phase nanocomposites with a pseudo-inclusion [A.1]

<u>Courtesy:</u> *Dr. A. K. Mohanty's Research group, 2005*

$$E_p = E_c \left\{ \frac{1}{1 + (1 - 1/N)s/t} \right\} + E_m \left\{ \frac{(1 - 1/N')\, s/t}{1 + (1 - 1/N)s/t} \right\} \qquad \text{(A.4)}$$

$$\alpha_p = \frac{\alpha_c}{N'[1 + (1 - 1/N')\, s/t_c]} \qquad \text{(A.5)}$$

where,

$$V_p = V_c [1 + (1 - 1/N') s/t_c] \tag{A.6}$$

$$N' = N + \{(1 - N)(s/t_c)(V_c/(1 - V_c))\} \tag{A.7}$$

where,

α → the aspect ratio

N → the number of intercalated clay platelets

N' → the modified number of intercalated clay platelets

s → the spacing between platelets

t_c → the thickness of clay platelets (1 nm)

V → the volume fraction

E → the elastic modulus

p, c, and m → pseudo-inclusion, clay platelet, and polymer matrix respectively.

The following values were used:

Elastic modulus of clay: E_{OMMT} = 170 GPa

Based on the TEM images:

Average length of the intercalated clay platelets: l_c = 500 nm

Average thickness of the intercalated clay (N=20 clay stacks) = 50 nm

Based on the experimental data:

Neat PLLA elastic modulus = 3.331 GPa

Neat PBAT elastic modulus = 0.092 GPa

It was also possible to predict the change of the elastic modulus with increasing the content of second rubbery phase using the HT equation. In other words, the change of the storage modulus of PLLA/PBAT blend could be predicted using HT equation, when the PBAT was separated from the main PLLA matrix as the second phase. It was also assumed that PBAT secondary phases were uniformly dispersed in the PLLA primary matrix. When clay/PLLA/PBAT nanocomposites were processed, the same phase separation was still observed by TEM as shown in Fig. 4.14. The aspect ratio of PBAT is considered to be 1, due to the circular shape.

Figure A-1 shows a model describing that the secondary PBAT rubbery phase is dispersed in the PLLA primary matrix, where intercalated clay nanoplatelets were dispersed in both PLLA and PBAT phases. For this nanocomposite study, it is necessary to separately calculate the elastic modulus of the PLLA primary phase including intercalated clay nanoplatelets and that of the second phase consisting of PBAT and intercalated clay nanocomposites using HT equation. In this calculation, it is assumed that clay content in vol. % is the same in both PLLA and PBAT phases. After obtaining the reinforced elastic modulus of both PLLA and PBAT phases after the addition of intercalated clay nanoplatelets, the elastic modulus of such three phase nanocomposites is finally calculated using HT equation. Since, the injection molded samples having tendency of longitudinally aligned dispersion of clay nanoplatelets were used for the experiments, elastic modulus of such nanocomposites was derived from longitudinal equation. The above pseudo-inclusion equations (A-4 to A-7) were used for the three-phase nanocomposites.

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